Synthesis of Organosilicon Macrocycles. Palladium-Catalyzed Ring-Enlargement Oligomerization of Cyclic Disilanes via Si−Si σ-Bond Metathesis

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Bis(*tert*-alkyl isocyanide)palladium(0) complexes catalyzed a ring-enlargement oligomerization of 1,1,2,2-tetramethyl-1,2-disilacyclopentane through Si−Si σ-bond metathesis to give cyclic oligomers up to the 40-membered octamer. The cyclic structure of the tetramer was established by the single-crystal X-ray diffraction method, which showed that the four Si−Si bonds of the tetramer were in a close to parallel arrangement. Reactivities of the dimer, trimer, and tetramer in the presence of bis(*tert*-butyl isocyanide)palladium(0) revealed that the present Si−Si σ-bond metathesis proceeded reversibly, in which the $-Me_2Si(CH_2)_3SiMe_2-$ unit of the disilacyclopentane was successively inserted into the Si−Si bond of the oligomer to give higher oligomers. The intermediary 6-membered bis(organosilyl)bis(*tert*-alkyl isocyanide)palladium complex, which arose from oxidative addition of the disilacyclopentane onto bis(*tert*-alkyl isocyanide)palladium(0), was isolated and characterized by the single-crystal X-ray method. The insertion of the $-Me_2Si(CH_2)_3SiMe_2-$ unit also occurred with linear disilanes and digermane to give linear oligomers. The cyclic trimer and tetramer reacted with 2,6-diisopropylphenyl isocyanide in the presence of $Pd(OAc)_2$ to afford an 18-membered-ring triimine and 24-membered-ring tetraimine, respectively, in which the isocyanides were inserted into all the Si−Si linkages. Oxidation of the cyclic oligomers with trimethylamine oxide gave the corresponding cyclic oligo(disiloxane) species in quantitative yields. Unexpected polymerization of the disilacyclopentane occurred in the presence of the (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) catalyst to give poly($Me_2Si(CH_2)_3SiMe_2$) compounds with high molecular weights.

Introduction

Much attention has been focused on the design and synthesis of organic macrocycles containing heteroatoms and functional groups as functional molecules.[1] Introduction of electropositive elements such as group 14 metals instead of electronegative elements into organic macrocycles with appropriate arrangement may lead to the development of new functional molecules. Especially, in view of the intriguing chemical and physical properties of Si−Si σ-bonds,[2] an efficient synthesis of macrocycles with regularly arranged Si−Si bonds may be desired. Palladium-catalyzed Si−Si σ-bond metathesis of cyclic disilanes seemed to provide a convenient method for preparation of macrocycles containing Si−Si bonds in the ring. However, palladium(0)−phosphine catalysts have been successfully applied only to cyclodimerization of cyclic four- and five-membered disilanes through the Si−Si σ-bond metathesis.[3−5]

We have reported that bis(*tert*-butyl isocyanide)-palladium(0) catalyzes a selective intramolecular Si−Si σ-bond metathesis of some bis(disilanyl)methanes.[6] The use of *tert*-alkyl isocyanide ligands on palladium was crucially important for the activation of the Si−Si bonds.[7] On the basis of this activation, we recently found that a catalytic amount of bis(*tert*-butyl isocyanide)-palladium(0) induced intermolecular Si−Si σ-bond metathesis of 1,1,2,2-tetramethyl-1,2-disilacyclopentane to lead to ring-enlargement oligomerization that gave macrocycles with regularly arranged Si−Si bonds.[8] Herein, we describe in full detail the oligomerization of the disilacyclopentane, in which a cyclic bis(organosilyl)-bis(*tert*-alkyl isocyanide)palladium(II) complex is involved as an intermediate. We also present the synthesis of linear oligo- and poly(disilanes) by palladium-catalyzed reactions of the five-membered cyclic disilane. The cyclic oligomers thus prepared were further elaborated by insertion reactions and oxidation of the Si−Si linkages to give new functionalized organosilicon macrocycles.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1996.

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(2) (a) West, R. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Chapter 19. (b) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359−1410. (c) Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 419−421 and references therein.

(3) For a five-membered cyclic disilane, see: Tamao, K.; Hayashi, T.; Kumada, M. *J. Organomet. Chem.* **1976**, *114*, C19−21.

(4) For four-membered cyclic disilanes, see: (a) Kusukawa, T.; Kabe, Y.; Ando, W. *Chem. Lett.* **1993**, 985−988. (b) Kusukawa, T.; Kabe, Y.; Nestler, B.; Ando, W. *Organometallics* **1995**, *14*, 2556−2564.

(5) For linear disilanes, see: Sakurai, H.; Kamiyama, Y.; Nakadaira, Y. *J. Organomet. Chem.* **1977**, *131*, 147−152.

(6) Suginome, M.; Oike, H.; Ito, Y. *Organometallics* **1994**, *13*, 4148−4150.

(7) For bis-silylation catalyzed by *tert*-alkyl isocyanide−palladium complexes: (a) Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948−1951. (b) Murakami, M.; Suginome, M.; Fujimoto, K.; Nakamura, H.; Andersson, P. G.; Ito, Y. *J. Am. Chem. Soc.* **1993**, *115*, 6487−6498. (c) Suginome, M.; Matsumoto, A.; Nagata, K.; Ito, Y. *J. Organomet. Chem.* **1995**, *499*, C1−C3. (d) Suginome, M.; Yamamoto, Y.; Fujii, K.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 9608−9609 and references therein.

(8) Preliminary communication: Suginome, M.; Oike, H.; Ito, Y. *J. Am. Chem. Soc.* **1995**, *117*, 1665−1666.

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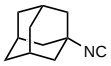
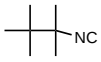
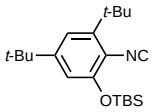
Table 1. Oligomerization of 1a in the Presence of $(RNC)_2Pd^0$ (2) in Benzene-d_6

entry no.	catalyst **2**	isocyanide	time (days), temp (°C)	ratio of oligomers $\mathbf{3a}_n$, %							total % yield
				$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	$n=8$	
1	**2a**	*t*-BuNC	6, 50	9	44	30	12	5	0		66
2[a]	**2a**	*t*-BuNC	6, 80	26	41	22	7	4	0		53
3[b]	**2a**	*t*-BuNC	6, 80	32	44	18	6	0			41
4	**2b**		6, 80	10	24	26	15	10	8	6	62
5	**2c**		4, 80	81	19	0					27
6	**2d**	*i*-PrNC	6, 50	50	40	10	0				50
7	**2e**	2,6-XyNC	6, 50	91	9	0					46
8	**2f**		6, 50	100	0						46

[a] Addition of *t*-BuNC (1 equiv based on **2a**). [b] Addition of *t*-BuNC (2 equiv based on **2a**).

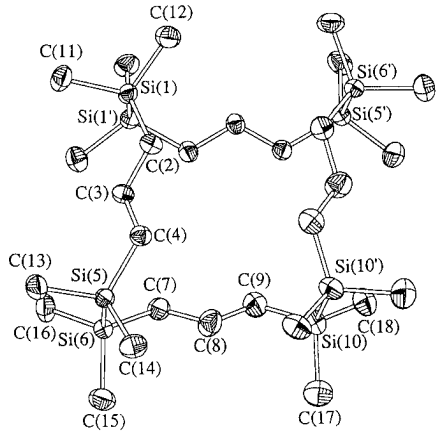
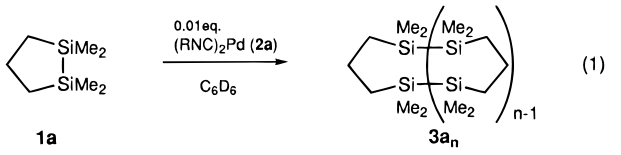


Figure 1. ORTEP drawing of the tetramer $\mathbf{3a_4}$ (30% probability). Hydrogen atoms are omitted for clarity.

Results and Discussion

Ring-Enlargement Oligomerization of Cyclic Disilanes. 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (**1a**) was reacted in the presence of 1 mol % of $(t\text{-BuNC})_2Pd^0$ (**2a**) in C_6D_6 under argon in an NMR sample tube fitted with a rubber septum (eq 1; Table 1, entry 1). Though no reaction took place at room temperature,



(1)

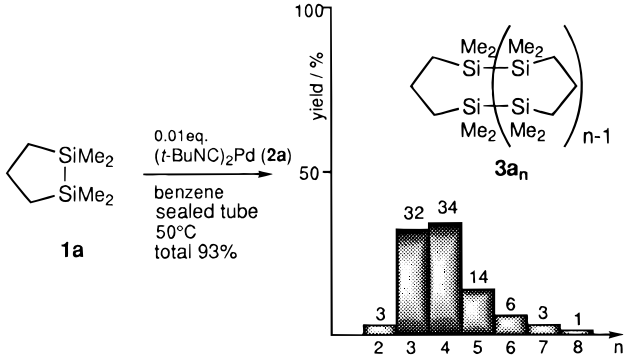
heating the mixture at 50 °C resulted in slow conversion of **1a** into a mixture of oligomeric products, which included the literature-known cyclic dimer $\mathbf{3a_2}$. After 6 days at this temperature, the oligomeric products were subjected to gel permeation chromatography to separate and isolate the cyclic oligomers $\mathbf{3a}_n$ up to a 30-membered hexamer. The cyclic structure of the tetramer $\mathbf{3a_4}$ was established by single-crystal X-ray diffraction, which showed that the four Si−Si bonds in the ring were in a nearly parallel arrangement (Figure 1 and Table 2). The oligomerization was significantly retarded by addition of a small amount (1 or 2 equiv based on palladium) of *tert*-butyl isocyanide, although the reaction at 80 °C gave the cyclic oligomers in nearly the same distribution (entries 2 and 3). Among the various isocyanides examined, *tert*-alkyl isocyanides except for 1,1,2,2-tetramethylpropyl isocyanide (in catalyst **2c**), which might be too bulky for the reaction to proceed, were the ligands of choice, giving higher oligomers (entries 4 and 5). Use of *sec*-alkyl isocyanide as well as aryl isocyanides resulted in formation of the oligomers only up to the tetramer $\mathbf{3a_4}$ (entries 6−8).

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for $\mathbf{3a_4}$

Bond Distances			
Si(1)−Si(1′)	2.352(2)	Si(1)−C(2)	1.882(4)
C(2)−C(3)	1.531(5)	C(3)−C(4)	1.530(4)
C(4)−Si(5)	1.886(4)	Si(5)−Si(6)	2.356(1)
Si(6)−C(7)	1.869(4)	C(7)−C(8)	1.589(6)
C(8)−C(9)	1.500(6)	C(9)−Si(10)	1.858(5)
Si(10)−Si(10′)	2.366(2)		

Bond Angles			
Si(1′)−Si(1)−C(2)	110.7(1)	Si(1)−C(2)−C(3	115.6(2)
C(2)−C(3)−C(4)	115.0(3)	C(3)−C(4)−Si(5)	115.8(3)
C(4)−Si(5)−Si(6)	113.0(1)	Si(5)−Si(6)−C(7)	112.6(1)
Si(6)−C(7)−C(8)	112.7(2)	C(7)−C(8)−C(9)	115.2(3)
C(8)−C(9)−Si(10)	114.1(3)	C(9)−Si(10)−Si(10′)	115.3(2)

Scheme 1



The yields of the oligomers were largely improved by carrying out the reaction in a sealed tube under higher concentration (see Experimental Section). Thus, in the presence of **2a**, the mixture of oligomers $\mathbf{3a}_n$ was obtained in 93% total yield, consisting of the dimer $\mathbf{3a_2}$ (3%), trimer $\mathbf{3a_3}$ (32%), tetramer $\mathbf{3a_4}$ (34%), pentamer $\mathbf{3a_5}$ (14%), hexamer $\mathbf{3a_6}$ (6%), heptamer $\mathbf{3a_7}$ (3%), and octamer $\mathbf{3a_8}$ (1%) (Scheme 1).

Unlike the reaction of **1a**, the cyclic disilanes **1b**−**g** showed much lower reactivities. 1,2-Disilacyclopentane **1b** gave dimer $\mathbf{3b_2}$ (50% yield, 3:3:2:2 mixture of four

Scheme 2

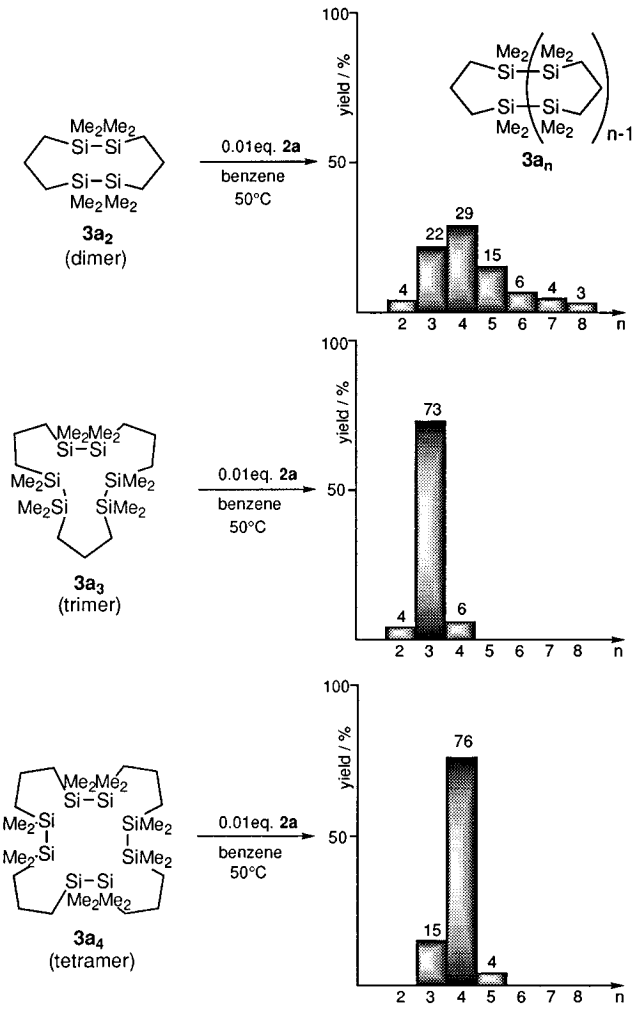
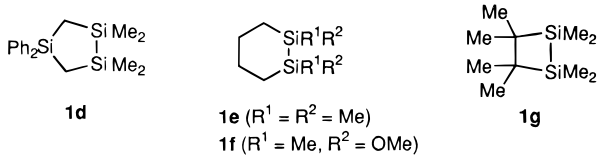
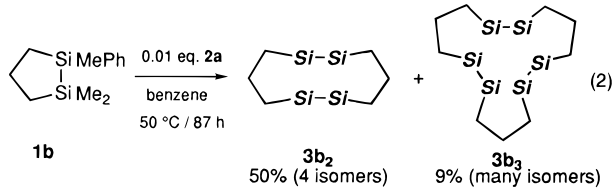
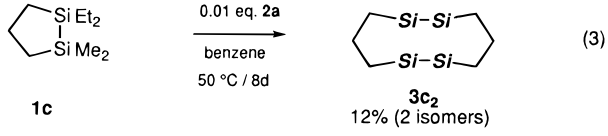


Chart 1



regio- and stereoisomers) and trimer $\mathbf{3b_3}$ (9% yield, many isomers), while **1c** gave only dimer $\mathbf{3c_2}$ under conditions identical with those employed for **1a** (eqs 2 and 3). Other cyclic disilanes **1d**−**g** listed in Chart 1 failed to give oligomers.





Mechanistic Interpretation. Treatment of the isolated oligomer $\mathbf{3a_2}$, $\mathbf{3a_3}$, or $\mathbf{3a_4}$ under the reaction conditions employed for the oligomerization of **1a** revealed that the present ring-enlargement oligomerization was reversible (Scheme 2). Thus, the reaction starting with the dimer $\mathbf{3a_2}$ afforded a mixture of oligomers in a distribution almost identical with that of the reaction with **1a**. Deoligomerization of the dimer followed by oligomerization of the resultant **1a** may be presumed. The cyclic trimer $\mathbf{3a_3}$ and tetramer $\mathbf{3a_4}$ underwent the deoligomerization and oligomerization only to the $(n - 1)$-mer and $(n + 1)$-mer, respectively, to a lesser extent. These findings imply that the cyclooligomerization did not proceed by σ-bond metathesis between the two oligomers produced but between the five-membered cyclic disilane **1a** and the oligomers.

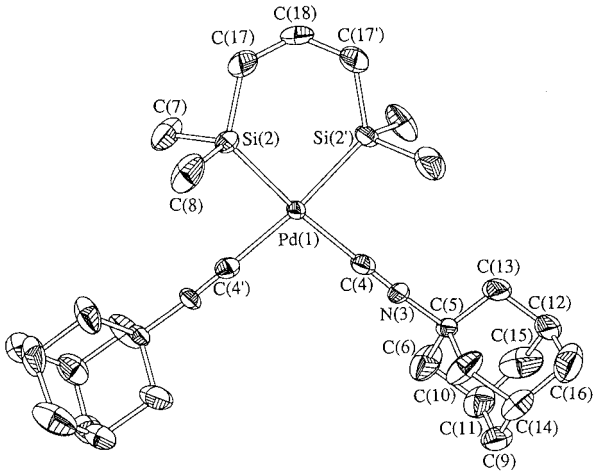


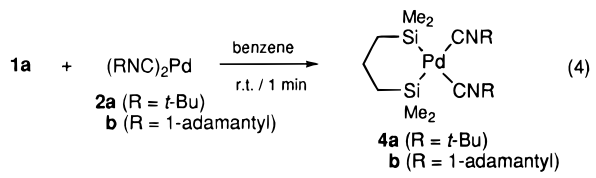
Figure 2. ORTEP drawing of **4b** (30% probability). One of the two orientations of the disordered C(18) atom is shown. Hydrogen atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for 4b

Bond Distances			
Pd(1)−Si(2)	2.358(5)	Pd(1)−C(4)	2.059(16)
Si(2)−C(7)	1.88(3)	Si(2)−C(8)	1.90(3)
Si(2)−C(17)	1.89(3)	N(3)−C(4)	1.14(2)
N(3)−C(5)	1.466(19)		

Bond Angles			
Si(2)−Pd(1)−Si(2′)	85.8(2)	Si(2)−Pd(1)−C(4′)	88.3(5)
Si(2)−Pd(1)−C(4)	173.7(5)	C(4)−Pd(1)−C(4′)	97.6(6)
Pd(1)−Si(2)−C(7)	109.1(9)	Pd(1)−Si(2)−C(8)	107.6(10)
Pd(1)−Si(2)−C(17)	126.3(9)	C(4)−N(3)−C(5)	176.7(15)
Pd(1)−C(4)−N(3)	179.9	N(3)−C(5)−C(6)	108.1(15)
N(3)−C(5)−C(10)	107.1(14)	N(3)−C(5)−C(13)	108.7(14)

Concerning the intermediary palladium species, we found that **2a** reacted with **1a** at room temperature to give the six-membered cyclic bis(organosilyl)bis(*tert*-butyl isocyanide)palladium(II) complex **4a** (eq 4). This



very rapid, quantitative formation of **4a** may also be involved in the catalytic cycle of the oligomerization. The structure of the corresponding adamantyl isocyanide complex **4b** was determined by a single-crystal X-ray diffraction study (Figure 2 and Table 3). In the square-planar complex, the angle Pd(1)−Si(2)−C(17) (>125°) was relatively large for sp_3 hybridization on the Si atoms.

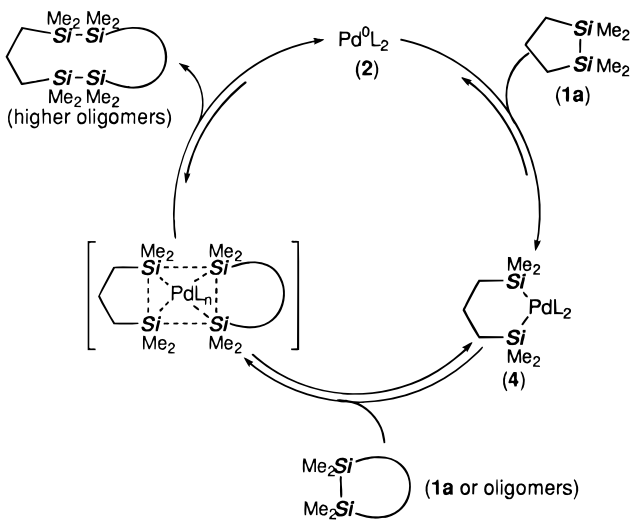
The reaction of the dimer $\mathbf{3a_2}$ with 2 equiv of **2a** at room temperature was also noteworthy; it slowly gave

Table 4

entry no.	5	time (days)	% yield[a] of linear oligomers $\mathbf{6}_n$ $n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6$	$n=7$	total % yield[a]	selectivity[b] $\mathbf{6}_n$:$\mathbf{3a}_n$
1[c]	**b**	2	30	20	9	4	1.4	0.5	0.2	65	67:33
2[c]	**c**	6	33	13	5	0.9	0.3			52	46:54
3[d]	**d**	3	22	20	12	6	3	1.4		64	66:34

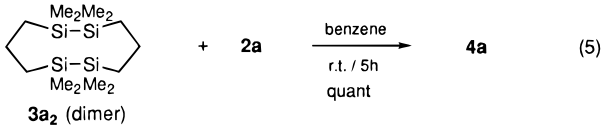
[a] Isolated yields based on the linear disilanes **5**. [b] Ratios of the yields based on **1a**. [c] 2.0 equiv of **1a** was used. [d] 2.5 equiv of **1a** was used.

Scheme 3[a]



[a] L = *t*-RNC.

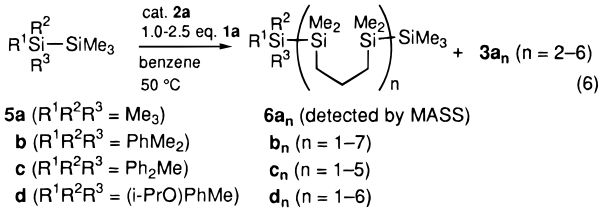
the complex **4a** in quantitative yield (eq 5), while the tetramer $\mathbf{3a}_4$ failed to give **4a**. Presumably, the ar-



rangement of the Si−Si bonds of the dimer was more appropriate than that of the tetramer for intramolecular metathesis of the Si−Si bonds in the ring,[6] which resulted in deoligomerization giving the respective (n − 1)-mer and **4a**.

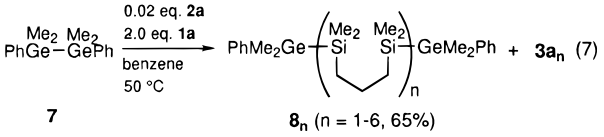
A schematic illustration is presented for the ring-enlargement oligomerization of **1a** (Scheme 3). Oxidative addition of **1a** onto **2a** affords the six-membered bis(silyl)palladium complex **4**, which may react with the Si−Si bond of **1a** or the oligomers via five-centered activation, to give higher cyclic oligomers. Though the cycle is reversible, the monomer **1a** is completely consumed to produce higher oligomers, since the oligomers higher than the cyclic trimer hardly undergo deoligomerization by intramolecular metathesis.

Oligomerization of 1a with Linear Disilanes. Cross-oligomerization of **1a** with any linear disilanes according to the mechanism shown in Scheme 3 may expand synthetic utilities of the present metathesis. We found that linear disilanes **5** underwent insertion of **1a** to give acyclic cross-oligomerization products **6** along with the cyclic oligomers $\mathbf{3a}_n$ derived from the ring-enlargement oligomerization of **1a** (eq 6). In the reaction of hexamethyldisilane (**5a**) with 1 equiv of **1a**, tris(disilane) $\mathbf{6a_2}$ ($n=2$) was detected by mass spectroscopy, though it could not be separated from the cyclic oligomers $\mathbf{3a}_n$ because of their low polarity. Use of the disilanes **5b**−**d**, bearing a phenyl or isopropoxy group, made isolation of the oligomeric, linear products $\mathbf{6}_n$

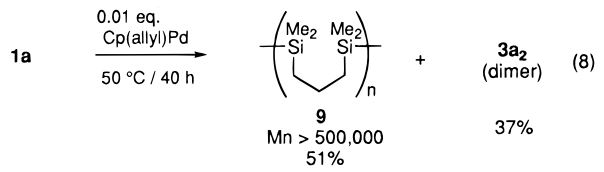


possible (Table 4). In the cases with **5b** and **5d**, insertion of **1a** into the Si−Si bonds of the linear disilanes occurred preferentially over the ring-enlargement oligomerization of **1a** (entries 1 and 3).

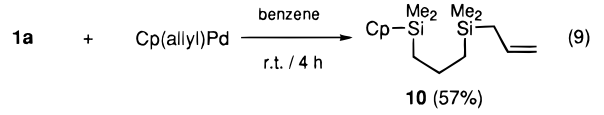
Noteworthy was that insertion of **1a** into 1,1,2,2-tetramethyl-1,2-diphenyldigermane (**7**) also took place to give a mixture of oligomers $\mathbf{8}_n$ ($n = 1-6$) bearing the dimethylphenylgermyl groups at both ends (eq 7).



Polymerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (1a). Of particular interest is that, unlike **2a**, the (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) (Cp(allyl)Pd) catalyst induced polymerization of **1a** to give polymers **9** with very high molecular weights (51%, $M_n > 500\,000$), which were accompanied only by the cyclic dimer $\mathbf{3a_2}$ (37%) without formation of any other oligomers (eq 8). A separate experiment indicated that



$\mathbf{3a_2}$, once isolated, remained intact under the polymerization conditions employing the Cp(allyl)Pd catalyst. A similar polymerization has also been reported by Suzuki's[9] and Tanaka's[10] group, who carried out the reaction of **1a** in the presence of palladium−phosphine complexes. The mechanistic discrepancy between the polymerization and the ring-enlargement oligomerization cannot be reasonably explained at this moment. It may be relevant to the mechanism that a stoichiometric reaction of Cp(allyl)Pd with **1a** gave the ring-opening product **10** (eq 9).



(9) Suzuki, M.; Obayashi, T.; Amii, H.; Saegusa, T. *Polym. Prep. Jpn.* **1991**, *40*, 355.
(10) Uchimaru, Y.; Tanaka, Y.; Tanaka, M. *Chem. Lett.* **1995**, 164.

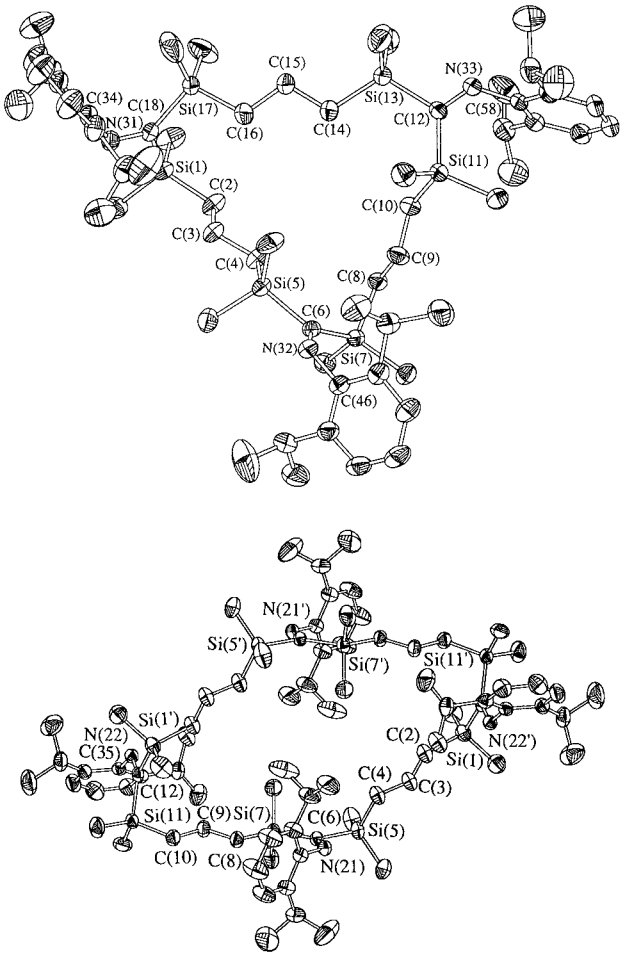


Figure 3. ORTEP drawings of **11a** (top) and **11b** (bottom) (30% probability). Hydrogen atoms are omitted for clarity.

Synthesis of Cyclic Organosilicon Compounds via Insertion Reactions with Si−Si Linkages of the Cyclic Oligomers. The cyclic oligomers thus far prepared, which contain Si−Si linkages in the ring, were further elaborated by virtue of the high but controllable reactivities of Si−Si toward transition-metal complex catalysts, as demonstrated by insertion reactions of unsaturated molecules into the Si−Si bonds. Thus, in the presence of $Pd(OAc)_2$ catalyst, 2,6-diisopropylphenyl isocyanide inserted into all the Si−Si bonds of the trimer and tetramer to give the 18-membered triimine **11a** and 24-membered tetraimine **11b**, respectively (eqs 10 and 11).[11] Single-crystal X-ray diffraction studies of **11a** and **11b** showed planar triangle and lozenge shapes, respectively, with each side occupied by the $-Me_2Si(CH_2)_3SiMe_2-$ unit (Figure 3, Tables 5 and 6).

Unexpectedly, reaction of the trimer with phenylacetylene in the presence of a palladium catalyst prepared from $Pd(OAc)_2$ and 1,1,2,2-tetramethylbutyl isocyanide did not give the corresponding cyclic trienes but resulted in formation of the the cyclic monoene **12a** and dienes **12b**, in which the one or two Si−Si linkages remained unchanged (eq 12).[12] The isolated cyclic **12b** failed to undergo further insertion of phenylacetylene.

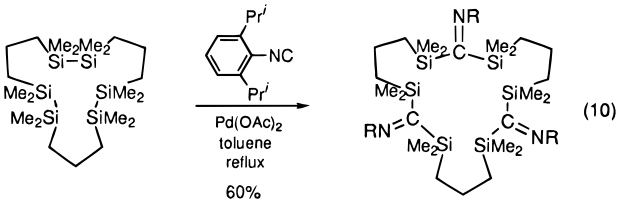
The cyclic oligomers also underwent insertion of oxygen atoms by oxidation of the Si−Si linkages with trimethylamine oxide in refluxing benzene.[13] The reactions of the trimer and tetramer cleanly proceeded without ring opening, affording tris(disiloxane) **13a** and

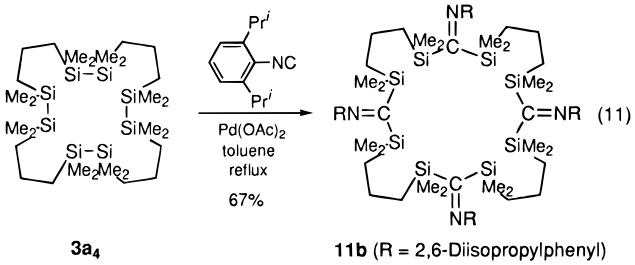
Table 5. Selected Bond Distances (Å) and Bond Angles (deg) for 11a

Bond Distances			
Si(1)−C(18)	1.919(3)	Si(1)−C(2)	1.870(4)
C(2)−C(3)	1.534(6)	C(3)−C(4)	1.533(6)
C(4)−Si(5)	1.870(4)	Si(5)−C(6)	1.927(3)
C(6)−Si(7)	1.923(3)	C(6)−N(32)	1.283(4)
Si(7)−C(8)	1.878(4)	C(8)−C(9)	1.520(6)
C(9)−C(10)	1.521(6)	C(10)−Si(11)	1.883(4)
Si(11)−C(12)	1.917(4)	C(12)−Si(13)	1.919(4)
C(12)−N(33)	1.282(4)	Si(13)−C(14)	1.868(6)
C(14)−C(15)	1.530(7)	C(15)−C(16)	1.532(8)
C(16)−Si(17)	1.859(6)	Si(17)−C(18)	1.936(3)
C(18)−N(31)	1.283(4)	N(31)−C(34)	1.430(5)
N(32)−C(46)	1.428(4)	N(33)−C(58)	1.428(4)
Bond Angles			
C(2)−Si(1)−C(18)	111.5(2)	Si(1)−C(2)−C(3)	115.1(3)
C(2)−C(3)−C(4)	113.5(3)	C(3)−C(4)−Si(5)	114.3(3)
C(4)−Si(5)−C(6)	114.8(2)	Si(5)−C(6)−Si(7)	124.7(2)
Si(7)−C(6)−N(32)	128.5(2)	Si(5)−C(6)−N(32)	106.8(2)
C(6)−Si(7)−C(8)	105.9(2)	Si(7)−C(8)−C(9)	113.7(3)
C(8)−C(9)−C(10)	114.8(3)	C(9)−C(10)−Si(11)	114.8(3)
C(10)−Si(11)−C(12)	105.6(2)	Si(11)−C(12)−Si(13)	122.6(2)
Si(11)−C(12)−N(33)	128.0(3)	Si(13)−C(12)−N(33)	109.3(2)
C(12)−Si(13)−C(14)	113.8(2)	Si(13)−C(14)−C(15)	114.6(3)
C(14)−C(15)−C(16)	112.7(4)	C(15)−C(16)−Si(17)	116.5(4)
C(16)−Si(17)−C(18)	106.0(2)	Si(1)−C(18)−Si(17)	123.4(2)
Si(1)−C(18)−N(31)	109.6(2)	Si(17)−C(18)−N(31)	127.0(2)
C(18)−N(31)−C(34)	123.7(3)	C(6)−N(32)−C(46)	122.7(3)
C(12)−N(33)−C(58)	123.4(3)		

Table 6. Selected Bond Distances (Å) and Bond Angles (deg) for 11b

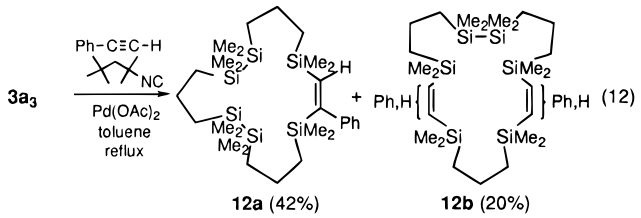
Bond Distances			
Si(1)−C(2)	1.870(3)	Si(1)−C(12′)	1.918(2)
C(2)−C(3)	1.527(4)	C(3)−C(4)	1.530(4)
C(4)−Si(5)	1.867(3)	Si(5)−C(6)	1.915(2)
C(6)−Si(7)	1.914(2)	C(6)−N(21)	1.286(3)
Si(7)−C(8)	1.875(3)	C(8)−C(9)	1.535(4)
C(9)−C(10)	1.535(4)	C(10)−Si(11)	1.872(3)
Si(11)−C(12)	1.917(2)	C(12)−N(22)	1.289(3)
N(21)−C(23)	1.422(3)	N(22)−C(35)	1.424(3)
Bond Angles			
C(2)−Si(1)−C(12′)	106.8 (1)	Si(1)−C(2)−C(3)	116.3(2)
C(2)−C(3)−C(4)	112.8(2)	C(3)−C(4)−Si(5)	117.4(2)
C(4)−Si(5)−C(6)	104.4(1)	Si(5)−C(6)−Si(7)	124.0(1)
Si(5)−C(6)−N(21)	106.8(2)	Si(7)−C(6)−N(21)	129.2(2)
C(6)−Si(7)−C(8)	116.0(1)	Si(7)−C(8)−C(9)	113.6(2)
C(8)−C(9)−C(10)	112.9(2)	C(9)−C(10)−Si(11)	114.3(2)
C(10)−Si(11)−C(12)	106.5(1)	Si(1′)−C(12)−Si(11)	124.0(1)
Si(11)−C(12)−N(22)	128.6(2)	Si(1′)−C(12)−N(22)	107.3 (2)
C(6)−N(21)−C(23)	124.0(2)	C(12)−N(22)−C(35)	122.3(2)





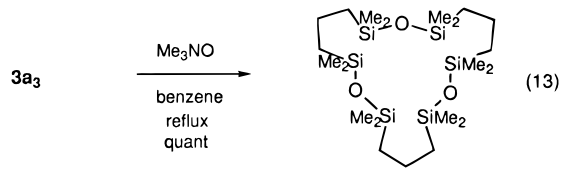
(11) Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899−8908.

(12) The expression "Ph,H" in eq 12 means that there are two positional isomers.

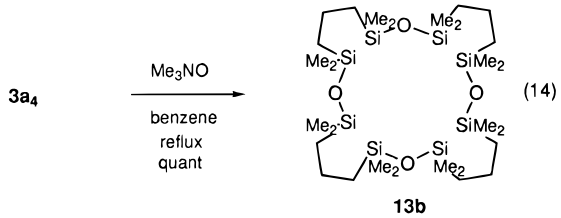


(12)

tetrakis(disiloxane) **13b**, respectively, in quantitative yield (eqs 13 and 14).



(13)



(14)

Conclusion

Oligomeric as well as polymeric organosilicon compounds with regularly arranged Si−Si linkages were synthesized from 1,1,2,2-tetramethyl-1,2-disilacyclopentane in the presence of palladium catalyst. Especially, ring-enlargement oligomerization of the cyclic disilane gave cyclic oligomers up to the 40-membered octamer. Bis(*tert*-alkyl isocyanide)palladium(0) complexes, which give cyclic bis(organosilyl)palladium intermediates on reaction with 1,2-disilacyclopentanes, were essential for the ring-enlargement oligomerization and the cross-oligomerization with linear disilanes.

Experimental Section

General Considerations. All reactions were carried out under a dry nitrogen or an argon atmosphere. Solvents were purified by distillation from appropriate drying agents under argon. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Varian VXR-200. Proton chemical shifts (ppm) are referenced to internal residual solvent protons: $CDCl_3$, 7.25; C_6D_6, 7.20. Carbon chemical shifts (ppm) are referenced to the carbon signal of the deuterated solvents: $CDCl_3$, 77.0; C_6D_6, 128.0. Silicon chemical shifts are referenced to the signals of tetramethylsilane. Preparative gel permeation chromatography was performed on a JAI LC-908 (Japan Analytical Industry Co., Ltd.) equipped with JAIGEL-1H and -2H columns.

Preparation of Bis(isonitrile)palladium(0) (2). The procedure reported by Otsuka et al.[14] was followed with slight modification. To a pentane solution of (η^5-cyclopentadienyl)-(η^3-allyl)palladium(II) (117 mg, 0.55 mmol) was added the corresponding isocyanide (2.2 mmol) at −10 °C under argon. After 10 min, removal of supernatant liquid gave **2** as an orange solid, which was washed twice with pentane, dried in vacuo, and used for further reaction. Complex **2** was obtained nearly quantitatively, though the yield was not determined for each reaction.

Oligomerization of 1,1,2,2-Tetramethyl-1,2-disilacyclopentane (1a) in the Presence of 2. (a) General Procedure for the Reactions in an NMR Sample Tube. A mixture of **2** (5 μmol) and **1a** (79 mg, 0.5 mmol) in benzene-d_6 (0.6 mL) was heated at 50−80 °C under argon for the period described in Table 1. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers **3a**$_n$, which was subjected to preparative gel permeation chromatography to separate each oligomer.

(**b) Procedure for the Reaction in a Sealed Tube.** A mixture of **1a** (158 mg, 1.0 mmol) and **2** (freshly prepared 0.5 M solution in benzene, 20 μL, 10 μmol) was heated at 50 °C under argon in a sealed tube for 90 h. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers **3a**$_n$, which was subjected to preparative gel permeation chromatography to separate dimer **3a$_2$** (4 mg, 3%), trimer **3a$_3$** (51 mg, 32%), tetramer **3a$_4$** (53 mg, 34%), pentamer **3a$_5$** (22 mg, 14%), hexamer **3a$_6$** (10 mg, 6%), heptamer **3a$_7$** (4 mg, 3%), and octamer **3a$_8$** (2 mg, 1%).

1,1,2,2,6,6,7,7-Octamethyl-1,2,6,7-tetrasilacyclodecane (3a$_2$): mp 71.0−72.0 °C; ^{1}H NMR (C_6D_6) δ 0.14 (s, 24 H, CH_3), 0.80−0.88 (m, 8 H, SiCH_2), 1.52−1.70 (m, 4 H, SiCH$_2$CH_2); ^{13}C NMR (C_6D_6) δ −2.7, 20.3, 21.5; IR (KBr) 2916, 1248, 796 cm^{-1}; MS (20 eV) *m*/*z* 316 (M^+). Anal. Calcd for $C_{14}H_{36}Si_4$: C, 53.08; H, 11.45. Found: C, 52.80; H, 11.51.

1,1,2,2,6,6,7,7,11,11,12,12-Dodecamethyl-1,2,6,7,11,12-hexasilacyclopentadecane (3a$_3$): mp 34.5−35.0 °C; ^{1}H NMR (C_6D_6) δ 0.17 (s, 36 H), 0.81−0.91 (m, 12 H), 1.50−1.66 (m, 6 H); ^{13}C NMR (C_6D_6) δ −3.2, 21.1, 21.6; IR (neat) 2956, 1246, 800 cm^{-1}; MS (20 eV) *m*/*z* 474 (M^+). Anal. Calcd for $C_{21}H_{54}Si_6$: C, 53.08; H, 11.45. Found: C, 52.81; H, 11.62.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17-Hexadecamethyl-1,2,6,7,11,12,16,17-octasilacycloeicosane (3a$_4$): mp 94.5−95.5 °C; ^{1}H NMR (C_6D_6) δ 0.19 (s, 48 H), 0.81−0.91 (m, 16 H), 1.51−1.67 (m, 8 H); ^{13}C NMR (C_6D_6) δ −3.6, 20.6, 20.9; IR (KBr) 2912, 1246, 828 cm^{-1}; MS (20 eV) *m*/*z* 632 (M^+). Anal. Calcd for $C_{28}H_{72}Si_8$: C, 53.08; H, 11.45. Found: C, 53.03; H, 11.53. Recrystallization from $CHCl_3$ gave crystals suitable for the X-ray diffraction study.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22-Eicosamethyl-1,2,6,7,11,12,16,17,21,22-decasilacyclopentacosane (3a$_5$): ^{1}H NMR (C_6D_6) δ 0.21 (s, 60 H), 0.83−0.92 (m, 20 H), 1.53−1.69 (m, 10 H); ^{13}C NMR (C_6D_6) δ −3.5, 20.5, 20.7; IR (neat) 2956, 1246, 792 cm^{-1}; MS (20 eV) *m*/*z* 790 (M^+). Anal. Calcd for $C_{35}H_{90}Si_{10}$: C, 53.08; H, 11.45. Found: C, 52.80; H, 11.60.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22,26,26,27,27-Tetracosamethyl-1,2,6,7,11,12,16,17,21,22,26,27-dodecasilacyclotriacontane (3a$_6$): mp 46.0−47.0 °C; ^{1}H NMR (C_6D_6) δ 0.22 (s, 72 H), 0.84−0.94 (m, 24 H), 1.54−1.71 (m, 12 H); ^{13}C NMR (C_6D_6) δ −3.5, 20.5, 20.7; IR (neat) 2956, 1246, 790 cm^{-1}; FABMS *m*/*z* 948 (M^+). Anal. Calcd for $C_{42}H_{108}Si_{12}$: C, 53.08; H, 11.45. Found: C, 53.09; H, 11.58.

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22,26,26,27,27,31,31,32,32-Octacosamethyl-1,2,6,7,11,12,16,17,21,22,26,27,31,32-tetradecasilacyclopentatriacontane (3a$_7$): ^{1}H NMR (C_6D_6) δ 0.22 (s, 84 H), 0.84−0.93 (m, 28 H), 1.53−1.72 (m, 14 H); ^{13}C NMR (C_6D_6) δ −3.5, 20.5, 20.7; IR (neat) 2956, 1246, 792 cm^{-1}; FABMS *m*/*z* 1107 (M^+).

1,1,2,2,6,6,7,7,11,11,12,12,16,16,17,17,21,21,22,22,26,26,27,27,31,31,32,32,36,36,37,37-Dotriacontamethyl-1,2,6,7,11,12,16,17,21,22,26,27,31,32,36,37-hexadecasilacyclotetracontane (3a$_8$): ^{1}H NMR (C_6D_6) δ 0.23 (s, 96 H), 0.85−0.93 (m, 32 H), 1.54−1.72 (m, 16 H); ^{13}C NMR (C_6D_6) δ −3.4, 20.5, 20.7; IR (neat) 2956, 1245, 792 cm^{-1}; FABMS *m*/*z* 1266 [$(M + 1)^+$].

Oligomerization of 1,2,2-Trimethyl-1-phenyl-1,2-disilacyclopentane (1b) in the Presence of 2a. A mixture of **1b** (220 mg, 1.0 mmol) and **2a** (freshly prepared 0.25 M solution in benzene, 40 μL, 10 μmol) was stirred at 50 °C under argon

(13) Ishikawa, M.; Hatano, T.; Hasegawa, Y.; Horio, T.; Kunai, A.; Miyai, A.; Ishida, T.; Tsukihara, T.; Yamanaka, T.; Koike, T.; Shioya, J. *Organometallics* **1992**, *11*, 1604−1618.

(14) Otsuka, S.; Nakamura, A.; Tatsuno, Y. *J. Am. Chem. Soc.* **1969**, *91*, 6994−6999.

in a sealed tube for 87 h. The cooled mixture was passed through a short column of silica gel (hexane/ether, 10/1) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers **3b$_n$**, which was subjected to preparative gel permeation chromatography to separate dimers **3b$_2$** (a mixture of four isomers, 110 mg, 50%), trimers **3b$_3$** (a mixture of many isomers, 19 mg, 9%), and **1b** (78 mg, 35% recovered). Recrystallization of the dimers from ethanol gave one of the four isomers, which was determined to be (*1R*,6S**)-1,2,2,6,7,7-hexamethyl-1,6-diphenyl-1,2,6,7-tetrasilacyclodecane by the single-crystal X-ray method (see Supporting Information).

3b$_2$: ^{1}H NMR for the (*1R*,6S**) isomer ($CDCl_3$) δ −0.02 (s, 6 H, $SiCH_3CH_3$), 0.10 (s, 6 H, $SiCH_3CH_3$), 0.35 (s, 6 H, $PhSiCH_3$), 0.74−1.26 (m, 8 H, $SiCH_2$), 1.64−1.80 (m, 4 H, $SiCH_2CH_2$), 7.30−7.36 (m, 6 H, Ar *H*), 7.40−7.48 (m, 4 H, Ar *H*); MS (23 eV) *m*/*z* 440 (M^+). Elemental analysis was carried out for the mixture of isomers. Anal. Calcd for $C_{24}H_{40}Si_4$: C, 65.38; H, 9.14. Found: C, 65.44; H, 9.37.

3b$_3$: MS (23 eV) *m*/*z* 660 (M^+). Anal. Calcd for $C_{36}H_{60}Si_6$: C, 65.38; H, 9.14. Found: C, 65.44; H, 9.32.

Oligomerization of 1,1-Diethyl-2,2-dimethyl-1,2-disilacyclopentane (1c) in the Presence of 2a. A mixture of **1c** (186 mg, 1.0 mmol) and **2a** (freshly prepared 0.25 M solution in benzene, 40 μL, 10 μmol) was stirred at 50 °C under argon in a sealed tube for 8 days. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. After evaporation of the resulting colorless solution, the residue was subjected to preparative gel permeation chromatography to furnish dimer **3c$_2$** (a mixture of two isomers, 23 mg, 12%). **3c$_2$**: ^{1}H NMR (C_6D_6) δ 0.15 (s, 12 H for the minor isomer), 0.20 (s, 12 H for the major isomer), 0.60-0.78 (m, 8 H for both isomers), 0.82−0.94 (m, 8 H for both isomers), 1.05 (t, J = 7.4 Hz, 12 H for the major isomer), 1.06 (t, J = 7.7 Hz, 12 H for the minor isomer), 1.56−1.74 (m, 4 H for both isomers); MS (23 eV) *m*/*z* 372 (M^+). Anal. Calcd for $C_{18}H_{44}Si_4$: C, 57.98; H, 11.89. Found: C, 57.80; H, 12.10.

General Procedure for the Reactions of Isolated Oligomers 3a$_2$, 3a$_3$, and 3a$_4$. The oligomer **3a$_n$** (79 mg, 0.50 mmol of the $-Me_2Si(CH_2)_3SiMe_2-$ unit), **2a** (freshly prepared 0.1 M solution in benzene, 50 μL, 5 μmol), and benzene (0.2 mL) was stirred at 50 °C under argon for 40 h. The cooled mixture was passed through a short column of silica gel (hexane) to remove the palladium catalyst. Evaporation of the resulting colorless solution gave a mixture of oligomers, which was subjected to preparative gel permeation chromatography to separate into each oligomer.

Preparation of Bis(organosilyl)palladium−Isocyanide Complex 4b. To a benzene (1 mL) solution of **2b** (0.2 mmol) was added **1a** (32 mg, 0.2 mmol) at room temperature under an argon atmosphere. After 30 min, evaporation of the solvent followed by recrystallization from benzene/pentane (1/4) afforded **4b** (114 mg, 97%) as a crystalline solid. Recrystallization from benzene/pentane (4/1) gave crystals suitable for the X-ray diffraction study. **4b**: ^{1}H NMR (C_6D_6) δ 0.79 (s, 12 H), 1.16−1.25 (m, 4 H), 1.26 (br, 12 H), 1.66 (br, 6 H), 1.80 (br, 12 H), 2.28−2.42 (m, 2 H); ^{13}C NMR (C_6D_6) δ 7.1, 22.3, 22.8, 28.8, 35.3, 43.0, 56.1, 146.7; ^{29}Si NMR (C_6D_6) δ −0.3; IR (benzene) 2146 cm^{-1}. Anal. Calcd for $C_{29}H_{48}N_2PdSi_2$: C, 59.31; H, 8.24; N, 4.77. Found: C, 59.15; H, 8.37; N, 4.74.

Stoichiometric Reaction of Cyclic Dimer 3a$_2$ with 2a. To a benzene-d_6 (0.3 mL) solution of **2a** (0.05 mmol) in an NMR sample tube was added a benzene-d_6 (0.3 mL) solution of **3a$_2$** (7.9 mg, 0.025 mmol) at room temperature under an argon atmosphere. After 5 h at room temperature, ^{1}H NMR showed quantitative formation of **4a**.

Reaction of Hexamethyldisilane (5a) with 1a in the Presence of 2a. A mixture of **5a** (37 mg, 0.25 mmol), **1a** (40 mg, 0.25 mmol), and **2a** (freshly prepared 0.1 M solution in benzene, 50 μL, 5 μmol) in benzene (0.4 mL) was heated at 50 °C for 20 h. The cooled mixture was passed through a short column of silica gel (hexane). After evaporation of the solvent, the residue was subjected to preparative GPC to give five fractions. The third fraction was analyzed by mass spectroscopy, which revealed the existence of **6a$_2$** (*m*/*z* 462) along with cyclic tetramer **3a$_4$** (*m*/*z* 632).

Reaction of Pentamethylphenyldisilane (5b) with 1a in the Presence of 2a. A mixture of **5b** (83 mg, 0.4 mmol), **1a** (158 mg, 1.0 mmol), and **2a** (freshly prepared 0.1 M solution in benzene, 100 μL, 10 μmol) in benzene (0.4 mL) was heated in a sealed tube at 50 °C for 90 h. Preparative TLC (hexane) afforded mixtures of **6b$_n$** and cyclic oligomers **3a$_n$** (n = 2−6, 29 mg, 0.18 mmol of the $-Me_2Si(CH_2)_3SiMe_2-$ unit). The mixture of **6b$_n$** was subjected to preparative gel permeation chromatography to give **6b$_1$** (30 mg, 20%), **6b$_2$** (28 mg, 13%), **6b$_3$** (22 mg, 8%), **6b$_4$** (16 mg, 5%), **6b$_5$** (8 mg, 2%), **6b$_6$** (4 mg, 1%), and **6b$_7$** (3 mg, 0.6%). Elemental analyses were carried out for **6b$_1$**, **6b$_2$**, and **6b$_3$**.

6b$_1$: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 6 H), 0.03 (s, 15 H), 0.34 (s, 6 H), 0.56−0.70 (m, 4 H), 1.24−1.40 (m, 2 H), 7.30−7.36 (m, 3 H), 7.42−7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.3, −4.0, −3.6, −2.0, 19.8, 127.7, 128.2, 133.7, 139.8; MS (23 eV) *m*/*z* 366 (M^+). Anal. Calcd for $C_{18}H_{38}Si_4$: C, 58.94; H, 10.44. Found: C, 59.00; H, 10.35.

6b$_2$: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 6 H), 0.01 (s, 6 H), 0.02 (s, 6 H), 0.04 (s, 6 H), 0.05 (s, 9 H), 0.34 (s, 6 H), 0.56−0.70 (m, 8 H), 1.22−1.44 (m, 4 H), 7.30−7.36 (m, 3 H), 7.42−7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −4.0, −3.8, −3.6, −2.0, 19.78, 19.81, 19.9, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8; MS (23 eV) *m*/*z* 524 (M^+). Anal. Calcd for $C_{25}H_{56}Si_6$: C, 57.17; H, 10.75. Found: C, 57.35; H, 10.97.

6b$_3$: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 6 H), 0.00 (s, 6 H), 0.017 (s, 6 H), 0.022 (s, 12 H), 0.03 (s, 6 H), 0.05 (s, 9 H), 0.34 (s, 6 H), 0.56−0.70 (m, 12 H), 1.24−1.46 (m, 6 H), 7.30−7.36 (m, 3 H), 7.42−7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −4.0, −3.8, −3.6, −2.0, 19.79, 19.85, 19.91, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8; MS (23 eV) *m*/*z* 682 (M^+). Anal. Calcd for $C_{32}H_{74}Si_8$: C, 56.22; H, 10.91. Found: C, 56.12; H, 11.11.

6b$_4$: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 6 H), 0.01 (s, 6 H), 0.02 (s, 30 H), 0.03 (s, 6 H), 0.05 (s, 9 H), 0.34 (s, 6 H), 0.56−0.70 (m, 16 H), 1.22−1.48 (m, 8 H), 7.30−7.36 (m, 3 H), 7.42−7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −4.0, −3.8, −3.6, −2.0, 19.76, 19.85, 19.90, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8.

6b$_5$: ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 6 H), 0.00 (s, 6 H), 0.02 (s, 42 H), 0.03 (s, 6 H), 0.05 (s, 9 H), 0.33 (s, 6 H), 0.56−0.70 (m, 20 H), 1.22−1.46 (m, 10 H), 7.30−7.36 (m, 3 H), 7.42-7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −4.0, −3.8, −3.6, −2.0, 19.75, 19.85, 19.89, 20.1, 20.2, 127.7, 128.2, 133.7, 139.8.

6b$_6$: ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 6 H), 0.00 (s, 6 H), 0.02 (s, 60 H), 0.04 (s, 9 H), 0.33 (s, 6 H), 0.56−0.70 (m, 24 H), 1.24−1.46 (m, 12 H), 7.30−7.36 (m, 3 H), 7.42−7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −4.0, −3.8, −3.6, −2.0, 19.8, 19.9, 20.2, 127.7, 128.2, 133.7, 139.8.

6b$_7$: ^{1}H NMR ($CDCl_3$) δ −0.02 (s, 6 H), 0.00 (s, 6 H), 0.02 (s, 72 H), 0.04 (s, 9 H), 0.33 (s, 6 H), 0.56−0.70 (m, 28 H), 1.24−1.48 (m, 14 H), 7.30−7.36 (m, 3 H), 7.42−7.48 (m, 2 H).

Reaction of 1,2,2,2-Tetramethyl-1,1-diphenyldisilane (5c) with 1a in the Presence of 2a. By a procedure similar to that used for the synthesis of **6b**, reaction of **5c** (135 mg, 0.50 mmol) with **1a** (158 mg, 1.0 mmol) in the presence of **2a** (10 μmol) was carried out to give **6c$_1$** (71 mg, 33%), **6c$_2$** (39 mg, 13%), **6c$_3$** (18 mg, 5.0%), **6c$_4$** (4.2 mg, 0.9%), and **6c$_5$** (1.4 mg, 0.3%).

6c$_1$: ^{1}H NMR (C_6D_6) δ 0.05 (s, 6 H), 0.11 (s, 9 H), 0.22 (s, 6 H), 0.65 (s, 3 H), 0.58−0.71 (m, 2 H), 0.78−0.94 (m, 2 H), 1.36−1.52 (m, 2 H), 7.15−7.30 (m, 6 H), 7.55−7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −4.5, −4.3, −3.5, −2.0, 19.7, 19.8, 20.1, 127.8, 128.6, 134.8, 137.6; MS (23 eV) *m*/*z* 428 (M^+). Anal. Calcd for $C_{23}H_{40}Si_4$: C, 64.41; H, 9.40. Found: C, 64.04; H, 9.39.

6c$_2$: ^{1}H NMR (C_6D_6) δ 0.12 (s, 6 H), 0.14 (s, 6 H), 0.15 (s, 6 H), 0.16 (s, 9 H), 0.24 (s, 6 H), 0.66 (s, 3 H), 0.68−0.92 (m, 8 H), 1.42−1.64 (m, 4 H), 7.15−7.32 (m, 6 H), 7.55−7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −4.5, −4.2, −3.91, −3.86, −3.5, −2.0, 19.7, 19.9, 20.1, 127.8, 128.7, 134.8, 137.6. Anal. Calcd for $C_{30}H_{58}Si_6$: C, 61.35; H, 9.95. Found: C, 61.31; H, 10.11.

6c$_3$: ^{1}H NMR (C_6D_6) δ 0.12 (s, 6 H), 0.15 (s, 6 H), 0.16 (s, 15 H), 0.20 (s, 12 H), 0.24 (s, 6 H), 0.66 (s, 3 H), 0.76−0.92 (m, 12 H), 1.46−1.68 (m, 6 H), 7.15−7.30 (m, 6 H), 7.55−7.65 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −4.5, −4.2, −3.9, −3.8, −3.5, −2.0, 19.7, 19.8, 19.9, 20.1, 20.2, 127.8, 128.6, 134.8, 137.6. Anal. Calcd for $C_{37}H_{76}Si_8$: C, 59.60; H, 10.27. Found: C, 59.72; H, 10.49.

6c$_4$: ^{1}H NMR (C_6D_6) δ 0.13 (s, 6 H), 0.15 (s, 6 H), 0.17 (s, 15 H), 0.210 (s, 6 H), 0.213 (s, 18 H), 0.25 (s, 6 H), 0.67 (s, 3 H), 0.78−0.94 (m, 16 H), 1.48−1.71 (m, 8 H), 7.15−7.30 (m, 6 H), 7.55−7.65 (m, 4 H).

6c$_5$: ^{1}H NMR (C_6D_6) δ 0.13 (s, 6 H), 0.15 (s, 6 H), 0.17 (s, 12 H), 0.21 (s, 9 H), 0.22 (br s, 30 H), 0.25 (s, 6 H), 0.67 (s, 3 H), 0.79−0.93 (m, 20 H), 1.47−1.68 (m, 10 H), 7.15−7.31 (m, 6 H), 7.53−7.65 (m, 4 H).

Reaction of 1-Isopropoxy-1,2,2,2-tetramethyl-1-phenyldisilane (5d) with 1a in the Presence of 2a. By a procedure similar to that used for the synthesis of **6b**, reaction of **5d** (126 mg, 0.50 mmol) with **1a** (228 mg, 1.3 mmol) in the presence of **2a** (13 μmol) was carried out to give **6d$_1$** (18 mg, 22%), **6d$_2$** (33 mg, 20%), **6d$_3$** (30 mg, 12%), **6d$_4$** (20 mg, 6%), **6d$_5$** (11 mg, 3%), and **6d$_6$** (6.6 mg, 1.4%).

6d$_1$: ^{1}H NMR (C_6D_6) δ 0.11 (s, 6 H), 0.14 (s, 9 H), 0.21 (s, 6 H), 0.57 (s, 3 H), 0.67−0.88 (m, 4 H), 1.15 (d, J = 6.1 Hz, 6 H), 1.42−1.62 (m, 2 H), 3.96 (septet, J = 6.1 Hz, 1 H), 7.18−7.33 (m, 3 H), 7.65−7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.3, −3.8, −2.0, −1.2, 19.7, 19.8, 19.9, 25.9, 26.0, 66.2, 127.7, 128.9, 133.6, 139.5. Anal. Calcd for $C_{20}H_{42}OSi_4$: C, 58.46; H, 10.30. Found: C, 58.59; H, 10.57.

6d$_2$: ^{1}H NMR (C_6D_6) δ 0.14 (s, 6 H), 0.16 (s, 9 H), 0.17 (s, 6 H), 0.18 (s, 6 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.72−0.92 (m, 8 H), 1.15 (d, J = 6.1 Hz, 6 H), 1.46−1.66 (m, 4 H), 3.98 (septet, J = 6.1 Hz, 1 H), 7.20−7.35 (m, 3 H), 7.66−7.73 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −3.9, −3.84, −3.75, −2.0, −1.2, 19.7, 19.9, 20.1, 20.2, 25.9, 66.2, 127.7, 128.9, 133.6, 139.5. Anal. Calcd for $C_{27}H_{60}OSi_6$: C, 56.92; H, 10.62. Found: C, 56.66; H, 10.43.

6d$_3$: ^{1}H NMR (C_6D_6) δ 0.15 (s, 6 H), 0.16 (s, 9 H), 0.17 (s, 6 H), 0.19 (s, 6 H), 0.198 (s, 6 H), 0.200 (s, 6 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.73−0.92 (m, 12 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.46−1.69 (m, 6 H), 3.94 (septet, J = 6.1 Hz, 1 H), 7.15−7.35 (m, 3 H), 7.65−7.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −3.82, −3.75, −2.0, −1.2, 19.6, 19.8, 19.9, 20.1, 20.2, 25.90, 25.94, 66.2, 127.7, 128.9, 133.6, 139.5. Anal. Calcd for $C_{34}H_{78}OSi_8$: C, 56.12; H, 10.80. Found: C, 56.25; H, 10.93.

6d$_4$: ^{1}H NMR (C_6D_6) δ 0.15 (s, 6 H), 0.17 (s, 6 H), 0.18 (s, 6 H), 0.19 (s, 6 H), 0.20 (s, 6 H), 0.21 (br s, 21 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.76−0.92 (m, 16 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.46−1.70 (m, 8 H), 3.90 (septet, J = 6.1 Hz, 1 H), 7.15−7.34 (m, 3 H), 7.65−7.72 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −3.9, −3.8, −2.0, −1.3, 19.6, 19.8, 19.9, 20.1, 20.2, 25.89, 25.94, 66.2, 127.7, 128.9, 133.6, 139.5. Anal. Calcd for $C_{41}H_{96}OSi_{10}$: C, 55.58; H, 10.92. Found: C, 55.61; H, 11.19.

6d$_5$: ^{1}H NMR (C_6D_6) δ 0.15 (s, 6 H), 0.17 (s, 6 H), 0.18 (s, 6 H), 0.20 (s, 6 H), 0.21 (s, 6 H), 0.22 (s, 33 H), 0.58 (s, 3 H), 0.72−0.93 (m, 20 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.45-1.71 (m, 10 H), 3.97 (septet, J = 6.1 Hz, 1 H), 7.15−7.36 (m, 3 H), 7.65−7.74 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ −4.2, −3.8, −2.0, −1.2, 19.6, 19.8, 20.2, 25.9, 66.2, 127.7, 128.9, 133.6, 139.5.

6d$_6$: ^{1}H NMR (C_6D_6) δ 0.16 (s, 6 H), 0.17 (s, 6 H), 0.18 (s, 6 H), 0.19 (s, 6 H), 0.20 (s, 6 H), 0.21 (br s, 45 H), 0.23 (s, 6 H), 0.58 (s, 3 H), 0.74−0.94 (m, 24 H), 1.16 (d, J = 6.1 Hz, 6 H), 1.47−1.72 (m, 12 H), 3.96 (septet, J = 6.1 Hz, 1 H), 7.15−7.32 (m, 3 H), 7.66−7.73 (m, 2 H).

Reaction of 1,1,2,2-Tetramethyl-1,2-diphenyldigermane (7) with 1a in the Presence of 2a. By a procedure similar to that used for the synthesis of **6b**, reaction of **7** (180 mg, 0.50 mmol) with **1a** (158 mg, 1.0 mmol) in the presence of **2a** (10 μmol) was carried out to give **8$_1$** (67 mg, 26%), **8$_2$** (63 mg, 19%), **8$_3$** (50 mg, 11%), **8$_4$** (35 mg, 7.2%), **8$_5$** (10 mg, 1.7%), and **8$_6$** (5.1 mg, 0.8%).

8$_1$: ^{1}H NMR (C_6D_6) δ 0.12 (s, 12 H, SiCH_3), 0.48 (s, 12 H, GeCH_3), 0.64−0.75 (m, 4 H, SiCH_2), 1.27−1.46 (m, 2 H, SiCH$_2$CH_2), 7.18−7.35 (m, 6 H, Ar H), 7.43−7.59 (m, 4 H, Ar H); ^{13}C NMR ($CDCl_3$) δ −4.1, −3.4, 19.6, 20.2, 127.6, 127.9, 133.5, 142.5; MS (23 eV) m/z 518 (M^+). Anal. Calcd for $C_{23}H_{40}Ge_2Si_2$: C, 53.34; H, 7.78. Found: C, 53.22; H, 7.93.

8$_2$: ^{1}H NMR (C_6D_6) δ 0.13 (s, 12 H), 0.18 (s, 12 H), 0.51 (s, 12 H), 0.66−0.81 (m, 8 H), 1.35−1.59 (m, 4 H), 7.19−7.36 (m, 6 H), 7.47−7.58 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −4.1, −3.9, −3.3, 19.7, 20.0, 20.4, 127.6, 127.9, 133.5, 142.5; MS (23 eV) m/z 676 (M^+). Anal. Calcd for $C_{30}H_{58}Ge_2Si_4$: C, 53.28; H, 8.64. Found: C, 53.00; H, 8.91.

8$_3$: ^{1}H NMR (C_6D_6) δ 0.16 (s, 12 H), 0.18 (s, 24 H), 0.52 (s, 12 H), 0.70−0.88 (m, 12 H), 1.41−1.67 (m, 6 H), 7.21−7.34 (m, 6 H), 7.50−7.59 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ −4.1, −3.9, −3.3, 19.7, 19.8, 20.0, 20.1, 20.4, 127.6, 127.9, 133.5, 142.6; MS (23 eV) m/z 834 (M^+). Anal. Calcd for $C_{37}H_{76}Ge_2Si_6$: C, 53.24; H, 9.18. Found: C, 53.11; H, 9.43.

8$_4$: ^{1}H NMR (C_6D_6) δ 0.16 (s, 12 H), 0.18 (s, 24 H), 0.21 (s, 12 H), 0.52 (s, 12 H), 0.70−0.91 (m, 16 H), 1.41−1.69 (m, 8 H), 7.15−7.32 (m, 6 H), 7.46−7.54 (m, 4 H).

8$_5$: ^{1}H NMR (C_6D_6) δ 0.17 (s, 12 H), 0.19 (s, 24 H), 0.22 (s, 24 H), 0.52 (s, 12 H), 0.72−0.93 (m, 20 H), 1.44−1.75 (m, 10 H), 7.19−7.35 (m, 6 H), 7.48−7.56 (m, 4 H).

8$_6$: ^{1}H NMR (C_6D_6) δ 0.17 (s, 12 H), 0.19 (s, 24 H), 0.22 (br s, 36 H), 0.53 (s, 12 H), 0.78−0.93 (m, 24 H), 1.46−1.72 (m, 12 H), 7.16−7.33 (m, 6 H), 7.47−7.58 (m, 4 H).

Polymerization of 1a in the Presence of Cp(π-allyl)Pd. A mixture of **1a** (158 mg, 1.0 mmol) and (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) (2 mg, 10 μmol) was stirred at 50 °C under argon for 40 h. The cooled gummy mixture was dissolved into $CHCl_3$ and passed through a filter to remove the palladium catalyst. Evaporation of the resulting colorless solution and separation by preparative gel permeation chromatography gave the cyclic dimer **3** (n = 2, 51 mg, 37%) and polymers **9** (80 mg, 51%). GPC analysis of the polymer showed molecular weights >500 000 (polystyrene standard). Spectral data for the polymers: ^{1}H NMR (C_6D_6) δ 0.25 (s, 12n H), 0.85−0.96 (m, 4n H), 1.56−1.74 (m, 2n H); ^{13}C NMR (C_6D_6) δ −3.6, 20.5, 20.7; IR (neat) 2960, 1246, 788 cm^{-1}.

Stoichiometric Reaction of 1a with Cp(π-allyl)Pd. A mixture of **1a** (32 mg, 0.2 mmol) and (η^5-cyclopentadienyl)(η^3-allyl)palladium(II) (42 mg, 0.2 mmol) was stirred at room temperature under argon for 4 h. The mixture was passed through a short column of silica gel (hexane). Evaporation of the resulting colorless solution gave crude material, which was further purified by preparative HPLC to give pure **10** (30 mg, 57%). **10**: ^{1}H NMR (C_6D_6) for major positional isomer, i.e., 1-(*2,4*-cyclopentadienyl)-1,1,2,2-tetramethyl-2-(2-propenyl)-disilane; δ −0.09 (s, 6 H), 0.01 (s, 6 H), 0.50−0.64 (m, 4 H), 1.28−1.45 (m, 2 H), 1.50 (dt, J = 8.2, 1.2 Hz, 2 H), 3.34 (br, 1 H), 4.89−5.02 (m, 2 H), 5.70−5.94 (m, 1 H), 6.46−6.74 (br, 4 H); ^{13}C NMR (C_6D_6) for the major positional isomer δ −3.9, −3.6, 18.9, 19.6, 20.2, 23.5, 51.4, 113.1, 130.6, 133.3, 135.3; HRMS calcd for $C_{15}H_{28}Si_2$ 264.1729, found 264.1744.

Synthesis of Cyclic Triimine 11a. A mixture of the trimer **3a$_3$** (79 mg, 0.17 mmol), 2,6-diisopropylphenyl isocyanide (140 mg, 0.75 mmol), and $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) in toluene (0.5 mL) was heated under reflux for 26 h. The cooled mixture was passed through a short column of Et_3N-pretreated Florisil (hexane) to remove the palladium catalyst. Crystallization from dry EtOH afforded triimine **11a** (103 mg, 60%) as yellow crystals. Recrystallization from benzene/EtOH (1/5) gave crystals suitable for the X-ray diffraction study. **11a**: mp 156.0−157.0 °C (sealed tube); ^{1}H NMR (toluene-d_8, 100 °C) δ 0.44 (s, 36 H, SiCH_3), 1.28−1.56 (m, 12H, SiCH_2), 1.50 (d, J = 6.6 Hz, 36 H, CHCH_3), 1.74−2.00 (m, 6 H, SiCH$_2$CH_2), 3.08−3.30 (m, 6 H, CHCH$_3$), 7.24−7.46 (m, 9 H, Ar H); IR (KBr) 3068, 2968, 1544, 1252, 830 cm^{-1}; FABMS m/z 1036 (M^+). Anal. Calcd for $C_{60}H_{105}N_3Si_6$: C, 69.49; H, 10.21; N, 4.05. Found: C, 69.39; H, 10.48; N, 3.86.

Synthesis of Cyclic Tetraimine 11b. A mixture of the tetramer **3a$_4$** (63 mg, 0.1 mmol), 2,6-diisopropylphenyl isocyanide (112 mg, 0.6 mmol), and $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) in toluene (0.5 mL) was heated under reflux for 36 h. The

Table 7. Summary of Crystallographic Data

	$3a_4$	4b	11a	11b
formula	$C_{28}H_{72}Si_8$	$C_{29}H_{48}N_2PdSi_2$	$C_{60}H_{105}N_3Si_6$	$C_{80}H_{140}N_4Si_8$
fw	633.6	587.3	1037.0	1380.0
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No. 15)	*Pna*21 (No. 33)	*P*21/*a* (No. 14)
a, Å	21.700(8)	22.761(7)	18.862(4)	18.603(4)
b, Å	13.598(6)	11.268(3)	26.369(4)	13.669(3)
c, Å	15.336(9)	14.379(6)	13.889(3)	18.345(3)
β, deg	107.88(4)	121.26(2)		94.28(2)
cell vol, Å^3	4307(3)	3152(2)	6908(2)	4652(2)
Z	4	4	4	2
ρ(calcd), g cm^{-3}	0.98	1.24	1.00	0.99
F(000)	1408	1240	2280	1520
cryst size, mm	0.50 × 0.50 × 0.30	0.60 × 0.30 × 0.35	0.50 × 0.45 × 0.40	0.25 × 0.35 × 0.40
μ, cm^{-1}	2.27	57.239	12.94	12.81
radiation	Mo Kα	Cu Kα	Cu Kα	Cu Kα
$2\theta_{max}$, deg	50	130	130	130
no. of rflns measd	5432	2999	6477	8584
no. of indep rflns	4953	2641	5902	7768
no. of rflns used	3417	2380	5730	7046
no. of variables	277	182	940	629
R, R_w	0.065, 0.071	0.081, 0.108	0.040, 0.039	0.068, 0.047

cooled mixture was passed through a short column of Et_3N-pretreated Florisil (hexane) to remove the palladium catalyst. Crystallization from dry EtOH afforded tetraimine **11b** (92 mg, 67%) as yellow crystals. Recrystallization from benzene/EtOH (1/5) gave crystals suitable for the X-ray diffraction study. **11b**: mp 150.0−151.0 °C (sealed tube); ^{1}H NMR (toluene-d_8, 90 °C) δ 0.49 (s, 48 H), 1.20−1.45 (m, 16H), 1.51 (br s, 48 H), 1.76−1.98 (m, 8 H), 3.10-3.30 (m, 8 H), 7.25−7.46 (m, 12 H); IR (KBr) 3072, 2972, 1540, 1258, 1250, 1138, 928 cm^{-1}; FABMS *m*/*z* 1381 (M$^+$). Anal. Calcd for $C_{80}H_{140}N_4Si_8$: C, 69.49; H, 10.21; N, 4.05. Found: C, 69.48; H, 10.44; N, 3.91.

Palladium-Catalyzed Reaction of the Cyclic Trimer with Phenylacetylene. To a mixture of $Pd(OAc)_2$ (2.2 mg, 0.01 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (21 mg, 0.15 mmol) was added trimer **3a$_3$** (79 mg, 0.17 mmol) and phenylacetylene (77 mg, 0.75 mmol) under a nitrogen atmosphere. The mixture was stirred under reflux for 26 h, cooled to room temperature, and then subjected to preparative TLC (hexane) to furnish **12b** (23 mg, 20%) and another fraction containing **12a**. The crude fraction was further purified by preparative GPC to give pure **12a** (40 mg, 42%). **12a**: ^{1}H NMR ($CDCl_3$) δ 0.01 (s, 12 H), 0.04 (s, 6 H), 0.05 (s, 6 H), 0.10 (s, 6 H), 0.18 (s, 6 H), 0.60−0.86 (m, 12 H), 1.24−1.52 (m, 6 H), 6.42 (s, 1 H), 6.98−7.04 (m, 2 H), 7.14−7.30 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ −3.9, −3.8, −3.7, −0.5, 19.2, 19.3, 20.5, 20.6, 20.7, 21.1, 21.2, 22.1, 125.5, 126.3, 127.7, 148.7, 151.1, 164.1; IR (neat) 3064, 2960, 1490, 1248, 832 cm^{-1}. Anal. Calcd for $C_{29}H_{60}Si_6$: C, 60.34; H, 10.48. Found: C, 60.10; H, 10.55. **12b** (mixture of three isomers): ^{1}H NMR ($CDCl_3$) δ 0.01−0.21 (many singlets, 36 H), 0.64−0.90 (m, 12 H), 1.26−1.56 (m, 6 H), 6.41-6.44 (three singlets, 2H), 6.96−7.04 (m, 4 H), 7.14−7.30 (m, 6 H); IR (neat) 3080, 2960, 1490, 1250, 832 cm^{-1}. Anal. Calcd for $C_{37}H_{66}Si_6$: C, 65.41; H, 9.79. Found: C, 65.21; H, 10.06.

Synthesis of Compound 13a. A mixture of the trimer **3a$_3$** (79 mg, 0.17 mmol) and trimethylamine oxide (38 mg, 0.5 mmol) in benzene (3 mL) was heated under reflux for 46 h. The reaction mixture was cooled to room temperature and then subjected to column chromatography on silica gel (hexane) to furnish tris(disiloxane) **13a** (87 mg, quantitative). **13a**: ^{1}H NMR (C_6D_6) δ 0.20 (s, 36 H), 0.82−0.92 (m, 12 H), 1.58−1.78 (m, 6 H); ^{13}C NMR (C_6D_6) δ 0.76, 17.7, 23.2; IR (KBr) 2964, 1412, 1254, 1070 cm^{-1}; MS *m*/*z* 522 (M$^+$). Anal. Calcd for $C_{21}H_{54}O_3Si_6$: C, 48.21; H, 10.40. Found: C, 48.14; H, 10.60.

Synthesis of Compound 13b. By a procedure similar to that used for the synthesis of **13a**, reaction of the tetramer **3a$_4$** (79 mg, 0.125 mmol) with trimethylamine oxide (45 mg, 0.60 mmol) was carried out to give tetrakis(disiloxane) **13b** (87 mg, quantitative). **13b**: ^{1}H NMR (C_6D_6) δ 0.21 (s, 48 H), 0.85−0.95 (m, 16 H), 1.56−1.75 (m, 8 H); ^{13}C NMR (C_6D_6) δ 0.77, 17.8, 23.3; IR (KBr) 2968, 1414, 1256, 1064 cm^{-1}; MS *m*/*z* 696 (M$^+$). Anal. Calcd for $C_{28}H_{72}O_4Si_8$: C, 48.21; H, 10.40. Found: C, 48.50; H, 10.66.

X-ray Diffraction Studies. Single crystals of the compounds were mounted on glass fibers (for **3a$_4$**, **11a**, and **11b**) or sealed in a glass capillary (for **4b**). Intensity data collections were carried out with a Mac Science MXC3 diffractometer using graphite-monochromated Cu Kα (λ = 1.541 78 Å) or Mo Kα (λ = 0.710 69 Å) radiation at 293 K. Intensity data were collected using $\omega/2\theta$ scans and corrected for Lorentz−polarization and for absorption by an analytical function. Details of crystal and data collection parameters are shown in Table 7. Structure solutions and refinements were carried out with the program package CrystanG (Mac Science). All non-hydrogen atoms were refined anisotropically by full-matrix least squares. For compound **4b**, C(18) was split into two sites, i.e., both sides of the square plane around the Pd atom, and was refined with an occupation factor of 0.5. For compounds **3a$_4$**, **11a**, and **11b**, all hydrogen atoms except for those on C(21) and C(53) of **11a** and C(30) and C(31) of **11b** were located on a difference electron density map and refined with isotropic thermal parameters calculated from those of the bonded atoms. For compound **4b**, all hydrogen atoms except for those on C(18) were included in the refinement at the calculated positions (0.96 Å) with isotropic thermal parameters.

Supporting Information Available: Tables of final atomic coordinates, thermal parameters, bond distances, and bond angles for compounds **3a$_4$**, **4b**, **11a**, and **11b**, and a figure giving the crystal structure of (*1R**,*6S**)-**3b$_2$** (17 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Intermet access instructions.

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