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Preface

The study presented in this thesis has been carried out under the direction of Professor Yoshihiko Ito at Kyoto University during 1988-1993. The study is concerned with the reactions of organosilicon compounds having silicon-silicon linkages with various unsaturated compounds promoted by a palladium–isocyanide catalyst.

Finally, the author expresses his appreciation to his family, especially his parents, Dr. Hiroshi Suginome and Mrs. Yasuko Suginome, and his wife, Mrs. Yoko Suginome for their constant assistance and encouragement.

<div align="right">Michinori Suginome</div>

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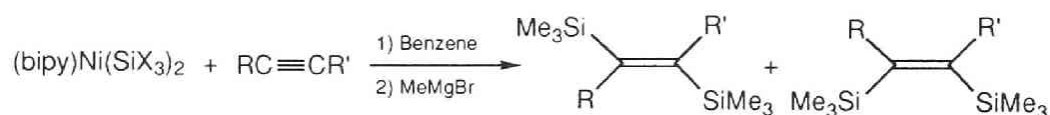Kyoto University
January, 1993.

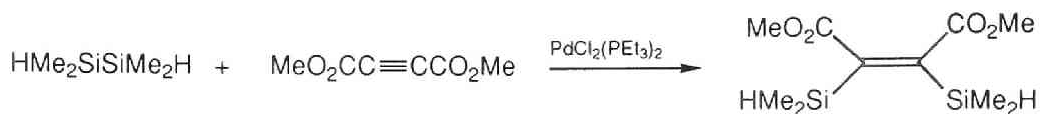# Contents

General Introduction

Organosilicon chemistry has rapidly developed in the last half a century and organosilicon compounds are now widely used as synthetic tools and as functional materials.[1] Therefore, development of new method for synthesis of organosilicon compounds is desired earnestly.

Silicon-carbon bond formation, which is one of the most important step in synthesis of organosilicon compounds, has been achieved by various methods. They can be divided into three categories: 1) The reaction of carbanion with silyl halides. 2) The reaction of silyl anion with carbon electrophiles. 3) Transition metal catalyzed reaction of silicon compounds with unsaturated organic compounds. Much attention is now paid to the third, because this type of reaction generally proceeds with high selectivities under mild conditions by appropriate choice of a catalyst. Hydrosilation is a good example of such reactions, and has been frequently used for formation of silicon-carbon bond.

Transition metal-catalyzed bis-silylation, on the other hand, has gained little attention for the last decade, in spite of one-step formation of two silicon-carbon bonds. A prototype of catalytic bis-silylation was found by Kumada *et al.* in 1974.[2] They reported that the reaction of bis(trichlorosilyl)-bipyridylnickel(II) with alkynes followed by methylation with methylmagnesium bromide afforded bis(trimethylsilyl)alkenes. This was regarded as a consequence of the insertion of a carbon-carbon triple bond into an intermediary nickel-silicon bond followed by reductive elimination. Next year they

$$(bipy)Ni(SiX_3)_2 \ + \ RC{\equiv}CR' \ \xrightarrow[\text{2) MeMgBr}]{\text{1) Benzene}} \ \substack{Me_3Si \\ R} {>}{=}{<} \substack{R' \\ SiMe_3} \ + \ \substack{R \\ Me_3Si} {>}{=}{<} \substack{R' \\ SiMe_3}$$

showed the first example of transition metal-catalyzed bis-silylation with disilanes, in which catalytic amount of dichlorobis(triethylphosphine)-

$$\text{HMe}_2\text{SiSiMe}_2\text{H} \quad + \quad \text{MeO}_2\text{CC}{\equiv}\text{CCO}_2\text{Me} \quad \xrightarrow{\text{PdCl}_2(\text{PEt}_3)_2} \quad \begin{array}{c} \text{MeO}_2\text{C} \diagdown \quad \diagup \text{CO}_2\text{Me} \\ \diagup\diagdown \\ \text{HMe}_2\text{Si} \quad \quad \text{SiMe}_2\text{H} \end{array}$$

palladium(II) promoted the reaction of 1,2-dihydrotetramethyldisilane with dimethyl acetylenedicarboxylate giving cis-disilylmaleate in moderate yield.[3] In 1975, Sakurai and co-workers also reported bis-silylation of dimethyl acetylenedicarboxylate by using strained disilacyclopentanes.[4] The reaction

$$\begin{array}{c} \diagup\text{SiMe}_2 \\ \Big\langle \quad \Big| \\ \diagdown\text{SiMe}_2 \end{array} \quad + \quad \text{RC}{\equiv}\text{CR'} \quad \xrightarrow{\text{PdCl}_2(\text{PPh}_3)_2} \quad \begin{array}{c} \text{Me}_2 \\ \text{Si} \diagdown \text{R} \\ \Big| \qquad \Big\| \\ \text{Si} \diagdown \text{R'} \\ \text{Me}_2 \end{array}$$
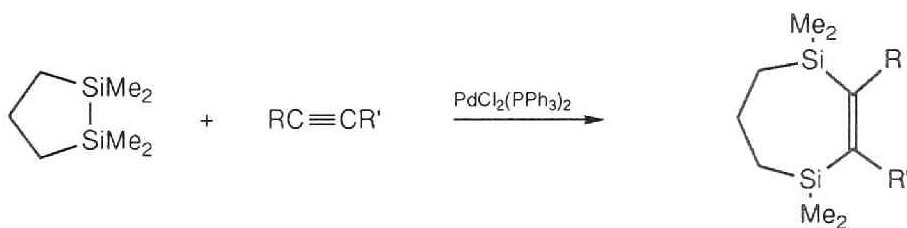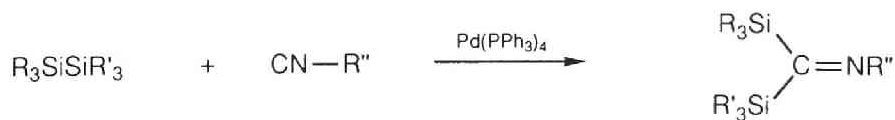
mechanism was considered to involve an oxidative addition of a disilane to palladium(0) generated in situ[5], followed by insertion of carbon-carbon triple bond and reductive elimination affording a 1,2-bis(silyl)alkene.[6] Since then, bis-silylations of carbon-carbon triple bonds with fluorodisilanes,[7] chlorodisilanes[8] and alkoxydisilanes[9] have been reported. However, a palladium-phosphine catalyst, which was used in these early works, was not effective for the bis-silylation with unreactive disilanes having no electron-withdrawing substituents on silicon atoms.[10] Moreover, the palladium-phosphine complex showed no catalytic activity for bis-silylation of alkenes at all.[11]

A direct lead of this thesis appeared in 1987. Ito and co-workers reported that palladium-catalyzed 1,1-bis-silylation of isocyanides afforded bis-(silyl)imines in moderate to good yield.[12] Then, they extended it to higher

$$\text{R}_3\text{SiSiR'}_3 \quad + \quad \text{CN}{-}\text{R''} \quad \xrightarrow{\text{Pd}(\text{PPh}_3)_4} \quad \begin{array}{c} \text{R}_3\text{Si} \diagdown \\ \quad \quad \text{C}{=}\text{NR''} \\ \text{R'}_3\text{Si} \diagup \end{array}$$

oligosilanes, e.g., octamethyltrisilane and decamethyltetrasilane.[13]

Chapter 1 describes regular insertion of aryl isocyanides into silicon-silicon linkages of oligosilanes in the presence of palladium(II) acetate in detail. It has been demonstrated that the mode of insertion can be controlled by change of the amount of isocyanides, and the sterically crowded substituents on isocyanides as well as oligosilanes. This is a rare example of transition metal-catalyzed reaction of oligosilanes, because oligosilanes generally undergo extrusion of silylene and cleavage of silicon-silicon linkages in the presence of transition metal complexes to give a complex mixture.
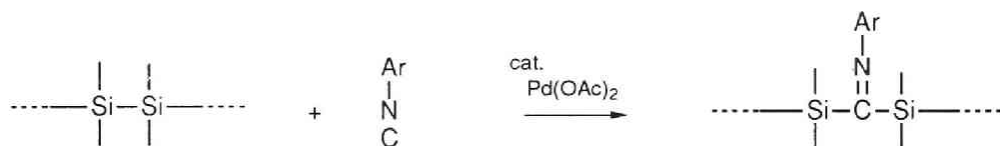
Chapter 2 deals with novel skeletal rearrangement reaction of tetrasilanes and hexasilanes with aryl isocyanides in the presence of palladium(II) acetate. Although it is known that oligosilanes themselves undergo skeletal rearrangement catalyzed by Lewis acid as well as transition metals,[14] the reaction mentioned in this chapter is unique in that the product is properly reconstituted from four fragments of oligosilanes and two fragments of aryl isocyanides. Furthermore, it is remarked that this rearrangement is promoted by an addition of *tert*-alkyl isocyanides, which is never taken in the products.
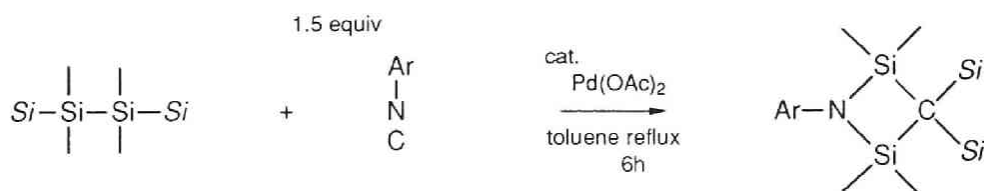
Chapter 3 describes bis-silylation of cabon-carbon triple bonds which is accomplished by using palladium–*tert*-alkyl isocyanide catalyst. Noteworthy is that tert-alkyl isocyanides do not insert into silicon-silicon linkages unlike

aryl isocyanides as well as primary and secondary alkyl isocyanides. The employment of *tert*-alkyl isocyanides for a *ligand* of palladium catalyst permits bis-silylation of alkynes with unreactive disilanes, such as hexamethyldisilane. Octamethyltrisilane and decamethyltetrasilane give double and triple bis-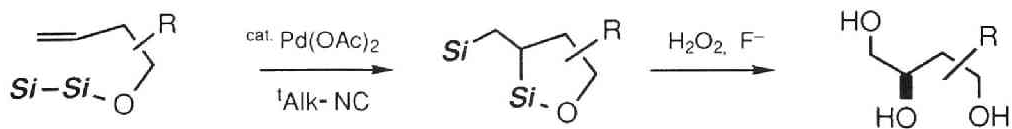silylated products respectively. In addition, the intramolecular bis-silylation of carbon-carbon triple bonds was first achieved by means of this catalyst system. Even internal alkynes, which is unreactive under the ordinary conditions, afford bis-silylated products in good yield.
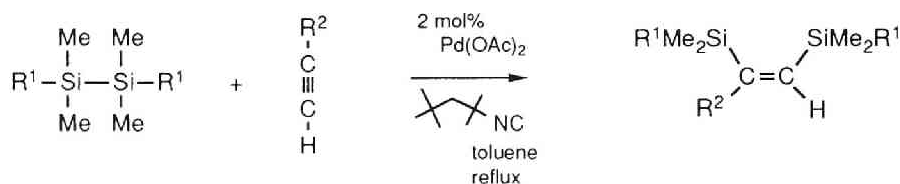
Chapter 4 is concerned with the stereoselective intramolecular bis-silylation of alkenes leading to synthesis of polyols. Alkenes tethered to disilanyl groups through chain of 2 or 3 atoms undergo intramolecular bis-silylation in the presence of palladium–*tert*-alkyl isocyanide complex. Especially in the case of alkenes connected with disilanyl groups by chain of 3 atoms, the reaction proceeds in highly stereoselective manner; alkenes having an allylic substituent afford five-membered ring products with 1,2-trans stereoselection whereas alkenes having a homoallylic substituent afford ring products with 1,3-cis stereoselection. Since silicon-carbon bonds are oxidatively transformed into oxygen-carbon bonds by hydrogenperoxide in the presence of fluoride anion,[15] intramolecular bis-silylation can be regarded as a synthetic equivalent to stereoselective dihydroxylation of alkenes. Stereoselective syn-

theses of polyhydroxylated compounds have been demonstrated by the oxidation of the intramolecular bis-silylation products.

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Chapter 1

Palladium-Catalyzed Insertion of Isocyanides into Silicon-Silicon Linkage of Oligosilanes

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.

Introduction

The application of organosilicon compounds to organic synthesis has exploded in the last two decades.[1] The unique chemical reactivities of organo-silicons, 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., photoresists and photoconducting films, due to their chemical and physical properties.[2]

From the view-points 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, Ito and co-workers preliminarily documented a palladium catalyzed insertion of isocyanides into Si–Si linkage of oligosilanes giving bis(organosilyl) imine derivatives.[3] The synthesis of bis(organosilyl) imines, which are nitrogen analogs of bis(organosilyl) ketones and otherwise difficult to synthesize, provided an entry to a new field of organosilicon chemistry. Herein, the author presents full details of the study on the insertion reactions of isocyanides into oligosilanes promoted by palladium catalyst.

Complete Insertion of Isocyanides into Oligosilanes

The insertion of isocyanide intothe Si-Si linkage of disilanes was originally discovered by use of tetrakis(triphenylphosphine)palladium catalyst. Later it was 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 **3b** obtained from hexamethyldisilane (**1a**) were thermally so stable as to be isolated by distillation, although exposure to the air caused gradual decomposition.(Scheme I).

Scheme I

2a Ar = 2,6-xylyl	(Xy-)
2b Ar = 2,6-di(isopropyl)phenyl	(Dip-)
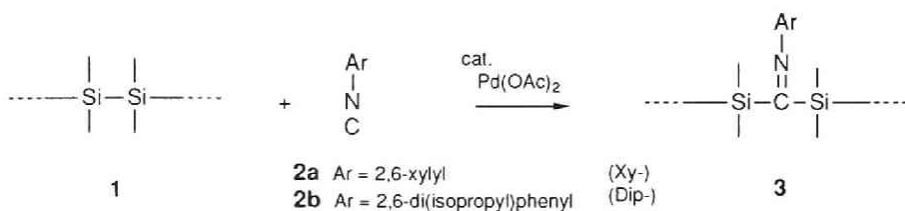
An isocyanide molecule was regularly inserted into all Si–Si linkages of the trisilanes (Table I, entries 3–6). Products **3c–f** were yellow solids, which were isolated by filtration of the reaction mixture through a short column under nitrogen atmosphere to remove the palladium catalyst, followed by re-crystallization 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).

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 at 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, 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 I, together

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Table I. The Regular Insertion of Aryl Isocyanides into Oligosilanes
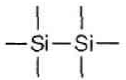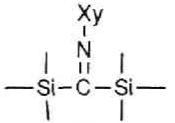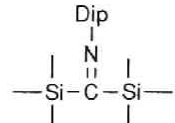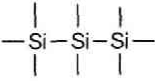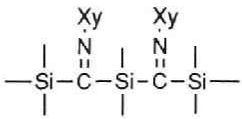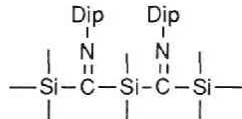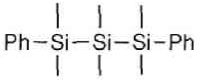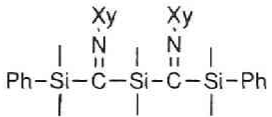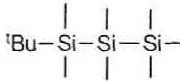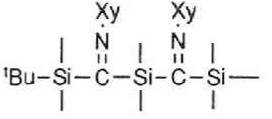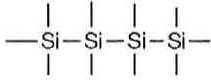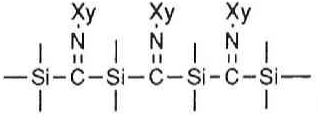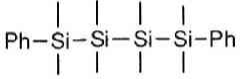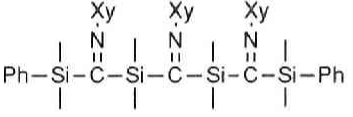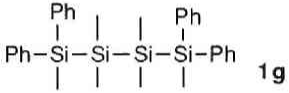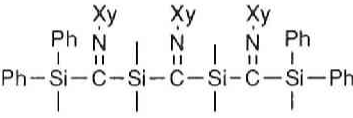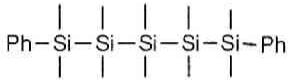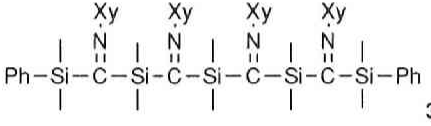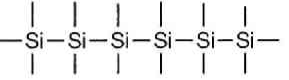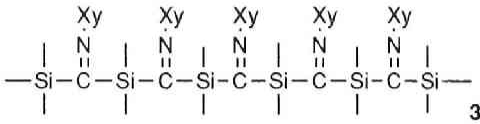
entry	1	2 (equiv)	conditions	3	yield, %
1	—Si—Si— **1a**	2a (1.0)	toluene reflux, 1 h	(Xy)N=C inserted: —Si—C—Si— **3a**	66
2	**1a**	2b (1.0)	toluene reflux, 1 h	(Dip)N=C inserted: —Si—C—Si— **3b**	81
3	—Si—Si—Si— **1b**	2a (2.5)	toluene reflux, 4 h	(Xy)(Xy) —Si—C—Si—C—Si— **3c**	57
4	**1b**	2b (7.1)	toluene reflux, 40 h	(Dip)(Dip) —Si—C—Si—C—Si— **3d**	64
5	Ph—Si—Si—Si—Ph **1c**	2a (3.0)	DMF, 70 °C, 5 h	(Xy)(Xy) Ph—Si—C—Si—C—Si—Ph **3e**	62
6	ᵗBu—Si—Si—Si— **1d**	2a (3.1)	toluene, 150 °C, 6 h	(Xy)(Xy) ᵗBu—Si—C—Si—C—Si— **3f**	82

Table I. (continued)

entry	1 (equiv)	2 (equiv)	conditions	3	yield, %
7	—Si—Si—Si—Si— **1e**	**2a** (3.5)	toluene, 70 °C, 22.5 h	Xy–N=C bridged: —Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si— **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	Ph—Si—Si—Si—Si—Ph **1f**	**2a** (4.5)	DMF, 70 °C, 9 h	Ph—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—Ph **3h**	43
14	Ph(Ph)Si—Si—Si—Si(Ph)—Ph **1g**	**2a** (3.9)	DMF, 70 °C, 15 h	Ph—Si(Ph)—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si(Ph)—Ph **3i**	28
15	Ph—Si—Si—Si—Si—Si—Ph **1h**	**2a** (6.5)	DMF, 70 °C, 30 h	Ph—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—Ph **3j**	40
16	—Si—Si—Si—Si—Si—Si— **1i**	**2a** (10.1)	DMF, 70 °C, 46 h	—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si—C(=N–Xy)—Si— **3k**	28
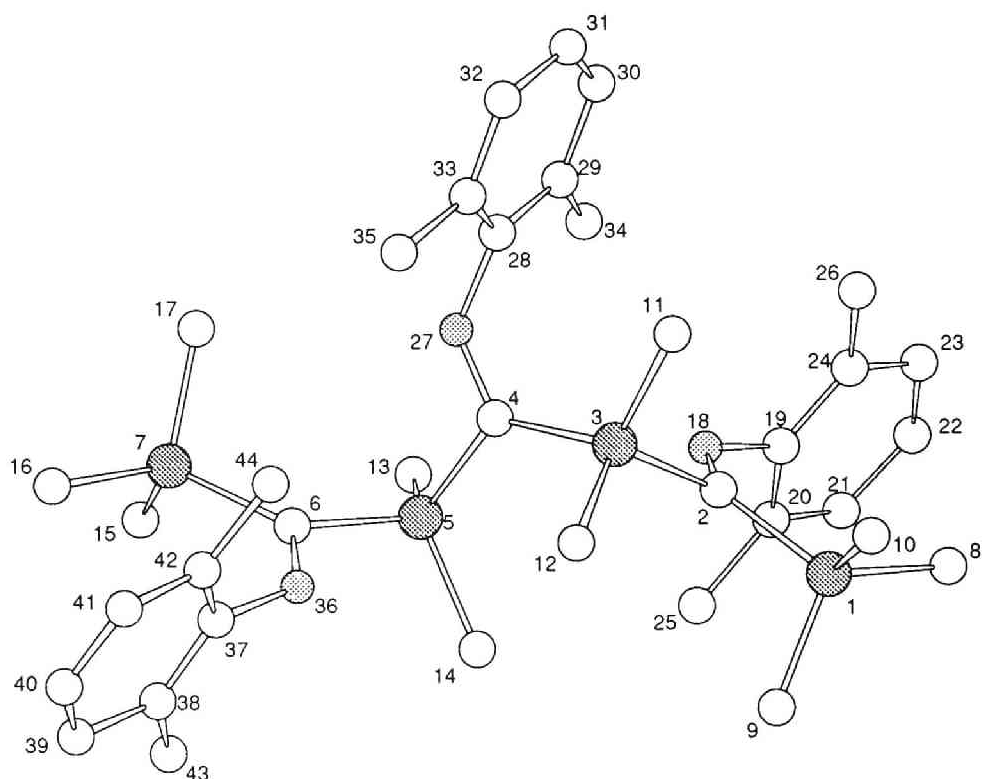
Figure I. Crystal structure of **3g**. Hydrogen atoms have been omitted for clarity. Some bond distances (Å) and angles (deg) are as follows. Si(1)–C(2) = 1.90(1), C(2)–Si(3) = 1.94(1), Si(3)–C(4) = 1.92(1), C(4)–Si(5) = 1.88(1), Si(5)–C(6) = 1.87(1), C(6)–Si(7) = 1.91(1), C(2)–N(18) = 1.27(1), C(4)–N(27) = 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).

Table II. Atomic coordinates (x10⁴) and isotropic temperature factors ($Å^2$x10) with e.s.d. values in parentheses for **3g**.

	x	y	z	B
Si (1)	-1287 (3)	2951 (2)	4968 (3)	44.3 (9)
C (2)	-305 (8)	2273 (6)	3729 (8)	24 (2)
Si (3)	1219 (3)	2229 (2)	3951 (3)	33.9 (8)
C (4)	1720 (8)	2003 (7)	2349 (9)	30 (2)
Si (5)	1239 (3)	2857 (2)	1307 (3)	34.0 (8)
C (6)	2413 (8)	3263 (7)	1094 (9)	30 (2)
Si (7)	3318 (3)	2814 (2)	-256 (3)	40.7 (8)
C (8)	-2510 (13)	2529 (11)	4916 (15)	78 (4)
C (9)	-1721 (13)	4204 (11)	4784 (15)	92 (5)
C (10)	-565 (13)	2836 (10)	6526 (14)	82 (4)
C (11)	1883 (10)	1310 (8)	4880 (11)	45 (3)
C (12)	1475 (10)	3379 (8)	4807 (11)	44 (3)
C (13)	715 (10)	2184 (8)	-200 (11)	49 (3)
C (14)	133 (9)	3967 (7)	1929 (10)	45 (3)
C (15)	2401 (12)	3053 (10)	-1716 (14)	72 (4)
C (16)	3898 (11)	1535 (9)	-321 (12)	52 (3)
C (17)	4429 (10)	3341 (8)	-219 (12)	51 (3)
N (18)	-478 (7)	1729 (5)	2720 (7)	38 (2)
C (19)	-1459 (8)	1426 (7)	2383 (9)	33 (2)
C (20)	-2276 (9)	1934 (7)	1647 (10)	38 (3)
C (21)	-3179 (9)	1571 (8)	1257 (11)	51 (3)
C (22)	-3244 (10)	779 (8)	1555 (11)	54 (3)
C (23)	-2405 (10)	298 (8)	2296 (11)	53 (3)
C (24)	-1492 (9)	622 (7)	2679 (10)	41 (3)

Table II. (Continued)

	x	y	z	B
C (25)	-2265 (11)	2816 (9)	1304 (12)	63 (3)
C (26)	-597 (10)	108 (8)	3469 (12)	63 (3)
N (27)	2385 (7)	1231 (6)	1794 (8)	46 (2)
C (28)	2854 (9)	372 (8)	2238 (10)	49 (3)
C (29)	2320 (10)	-348 (8)	1863 (11)	54(3)
C (30)	2824 (12)	-1186 (9)	2301 (13)	77 (4)
C (31)	3780 (11)	-1268 (9)	3002 (12)	71 (4)
C (32)	4302 (11)	-560 (9)	3310 (12)	64(3)
C (33)	3831 (10)	297 (8)	2957 (11)	52 (3)
C (34)	1313 (11)	-229 (9)	1054 (12)	70 (4)
C (35)	4394 (11)	1061 (8)	3314 (12)	63 (3)
N (36)	2500 (7)	3971 (6)	2016 (8)	41 (2)
C (37)	3238 (8)	4530 (7)	2182 (9)	35 (3)
C (38)	2985 (9)	5280 (8)	1618 (10)	50 (3)
C (39)	3739 (11)	5867 (9)	1831 (12)	64 (3)
C (40)	4643 (10)	5644 (8)	2611 (11)	59 (3)
C (41)	4875 (10)	4924 (8)	3203 (11)	53 (3)
C (42)	4186 (9)	4318 (7)	2998 (10)	44 (3)
C (43)	2017 (10)	5512 (8)	750 (11)	57 (3)
C (44)	4391 (11)	3502 (9)	3602 (12)	68 (3)

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 hexacosanemethyl-dodecasilane, 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 in chapter 2.

Partial Insertion of Isocyanides into Oligosilanes

Next, the author attempted the partial insertion of isocyanides into oligosilanes by control of the stepwise multiple insertion. Some examples of partial insertion are summarized in Table III. Insertion reactions were carried out with varying molar ratios of oligosilane to isocyanide (**1** / **2**). Use of 1.2 equiv of isocyanide to trisilanes resulted in the selective formation of mono-insertion products (Table III, entries 1-4). Similarly, a reaction of 2.0 equiv of isocyanide **2a** with tetrasilane **1e** in DMF afforded a bis-insertion product **8**, wherein 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 **4**, **5**, and **8** with isocyanide led to the formation of the complete insertion products **3c**, **3d**, and **3g**, respectively (Scheme II). These results may suggest that the multiple insertion proceeds stepwise to accomplish the complete insertion and that isocyanide **2a** is inserted preferentially into terminal Si–Si linkages of tetrasilane **1e**, which are sterically less crowded than the internal one. Isocyanide **2a** inserted into a Si–Si linkage

15

Table III. The Partial Insertion of Aryl Isocyanide into Oligosilanes
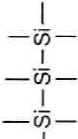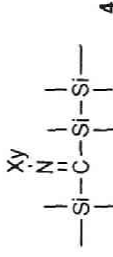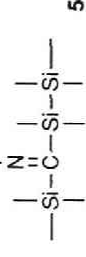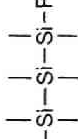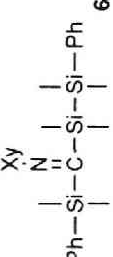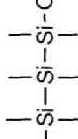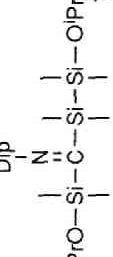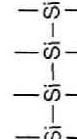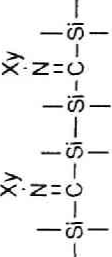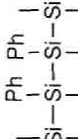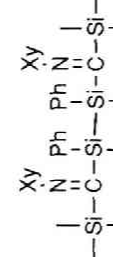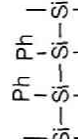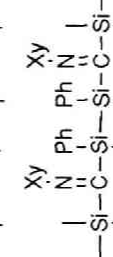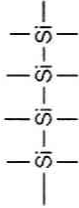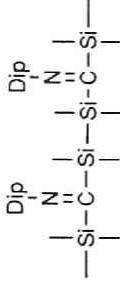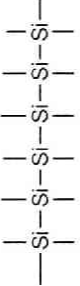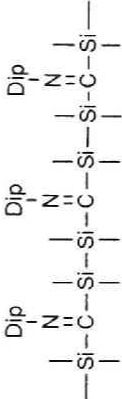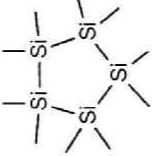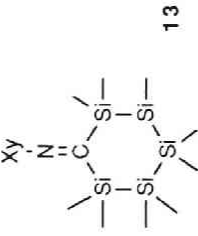
entry	oligosilane	aryl isocyanide (equiv)	conditions	product	yield, %
1	—Si–Si–Si— (1b)	2a (1.2)	toluene reflux, 4 h	**4**	64
2	1b	2b (1.2)	toluene reflux, 4 h	**5**	64
3	Ph—Si–Si–Ph (1c)	2a (1.2)	DMF, 70 °C, 5 h	**6**	61
4	iPrO—Si–Si–OiPr (1j)	2b (1.2)	toluene, 80 °C, 14 h	**7**	51
5	—Si–Si–Si— (1e)	2a (2.0)	DMF, 70 °C, 9 h	**8**	50
6	Ph Ph −Si–Si–Si— (1k)	2a (3.5)	toluene, 70 °C, 22.5 h	**9**	48
7	Ph Ph —Si–Si–Si— Ph Ph (1l)	2a (4.5)	toluene reflux, 3 h	**10**	55

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Table III. (continued)

entry	oligosilane	aryl isocyanide (equiv)	conditions	product	yield, %
8	1e	2b (3.5)	DMF, 70 °C, 26 h	11	60
9	1i	2b (4.0)	DMF, 70 °C, 1 d	12	16
10	1m	2a (3.1)	toluene reflux, 6.5 h	13	29

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.

Scheme II
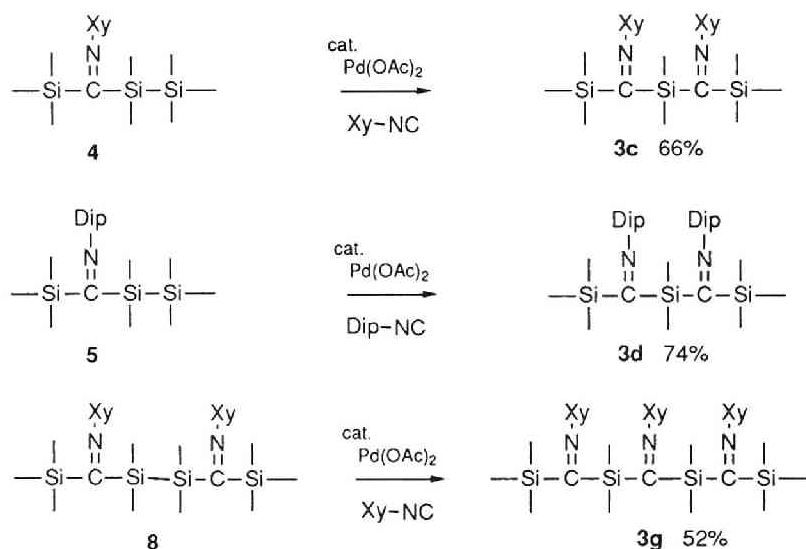
As supposed, the insertion process was much influenced by the steric bulkiness of substituents on both reactants. Tetrasilanes **1k** and **1l** having phenyl groups on internal silicon atoms gave partial insertion products **9** and **10**, respectively, even with the use of excess isocyanide **2a**. In addition, a branched oligosilane such as 2,3-bis(trimethylsilyl)-1,1,1,2,3,4,4,4-octa-methyltetrasilane 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 iso-cyanide 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 **11**. In contrast, 2,6-xylyl isocyanide (**2a**) gave a complete

insertion product **3g** under the same reaction conditions as stated above (entry 11 in Table I). Noteworthy was that 2,6-di(isopropyl)phenyl isocyanide (**2b**) was selectively inserted into every other Si–Si linkage of tetradecamethyl-hexasilane (**1i**) to afford a tris-insertion product **12**. It might be that 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 **9**, **10**, and **11** 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 a 6-membered **13** as an isolable product, wherein only one Si–Si linkage of **1m** participated in the insertion reaction. However, an analogous 6-membered cyclic oligosilane, dodecamethyl-cyclohexasilane, as well as the isolated **13** failed to react with isocyanide at all. Formation of 7-membered bis(organosilyl)palladium complex, which is proposed in a possible mechanism mentioned later, might be disfavored.

Mechanistic Interpretations

Tetrakis(triphenylphosphine)palladium(0)[3] as well as palladium(II) acetate showed a comparable catalyst activity in the insertion reaction of iso-cyanides with oligosilanes, suggesting that an actual effective catalyst might be a palladium(0) species. A mechanism involving the catalytic cycle as depicted in Scheme III 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 iso-cyanide,[5] to give bis(organosilyl)palladium complex **14**,[6] (ii) insertion of iso-cyanide into the Pd-Si linkage of **14** to afford **15**, and (iii) reductive elimination resulting in the formation of an insertion product along with regeneration of the Pd(0) catalyst . Reversibility of the insertion of isocyanide into Si-Si linkages of oligosilanes was suggested by a palladium-catalyzed reaction of 5 with 2,6-xylyl isocyanide, which gave **3c** along with **3l** (Scheme IV).

Scheme III.

Pd(OAc)$_2$

Ar—NC

"(Ar-NC)$_n$Pd(0)"

Ar
|
N
||
·····—Si—C—Si—····
| |

·····—Si—Si—····   **1**

\Si/
·····—C
    \\N—Ar
·····—Si/   **15**
Pd(CN-Ar)$_n$

·····—Si\
        Pd(CN-Ar)$_n$
·····—Si/   **14**

Ar—NC   **2**

Scheme IV.

Dip
|
N
||
—Si—C—Si—Si—
| | | |
5

2equiv.
Xy—NC
cat.
Pd(OAc)$_2$
toluene
reflux
20h

Xy   Xy
| |
N   N
|| ||
—Si—C—Si—C—Si—
| | | | |
3c 26%

+

Dip   Xy
| |
N   N
|| ||
—Si—C—Si—C—Si—
| | | | |
3l 43%
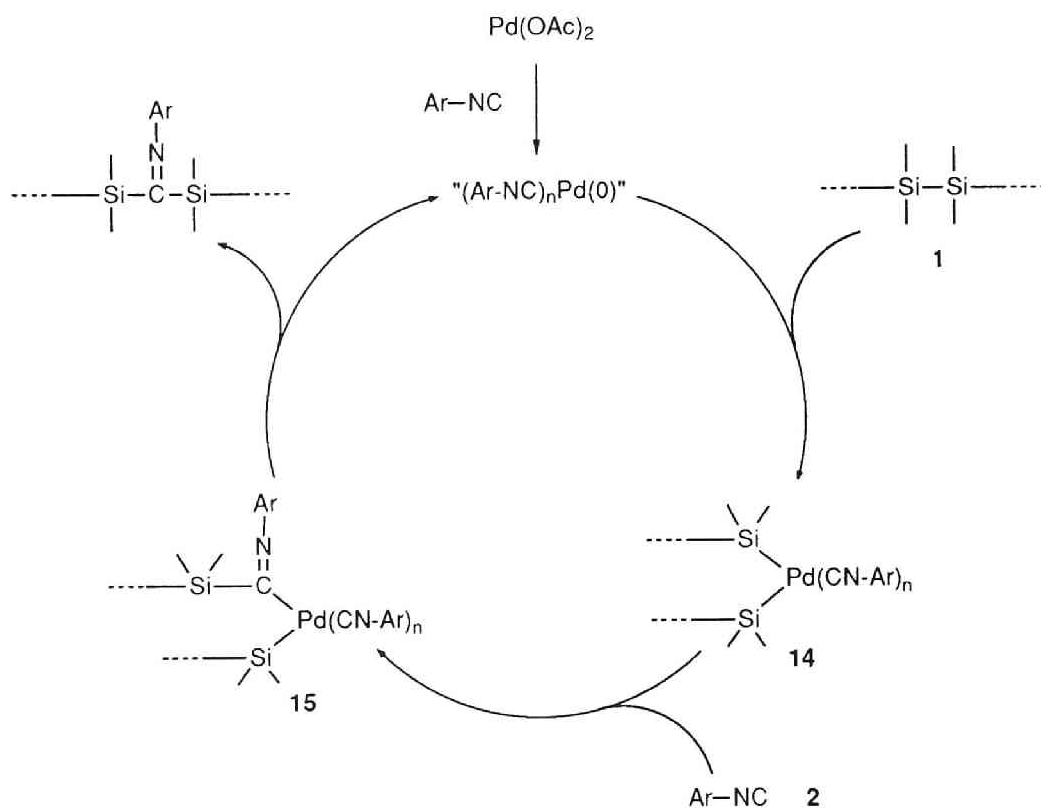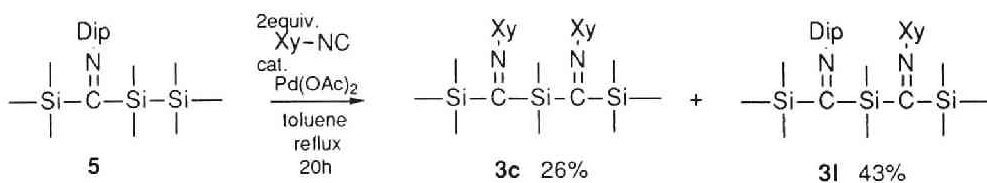
Spectral Properties of Oligo(silylimine) Derivatives

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 of 1610–1680 cm^{-1}.[7a] Oligo(silylimine) derivatives absorbed at remarkably long wavelengths near the visible range of 400–410 nm. These absorptions which are attributable to n–π* transition are remarkably different from those of ordinary imines with absorptions at around 240 nm.[7b] On the analogy of electronic spectra of acylsilanes,[8] the major origin of this bathochromic shift may be mixing of the sigma orbitals of the silicon-carbon bond with the n-orbital on nitrogen which gives rise to considerable σ–π* character for the excitation.[9]

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 (**16**) in 85% yield with disappearance of yellow color (Scheme V), whose UV spectra of **16** exhibited no absorption in the range 400–410 nm.
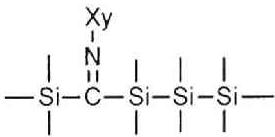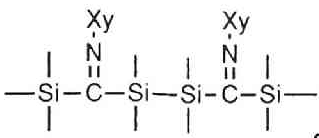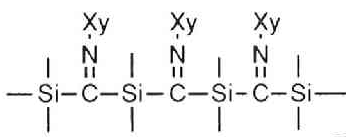
Scheme V
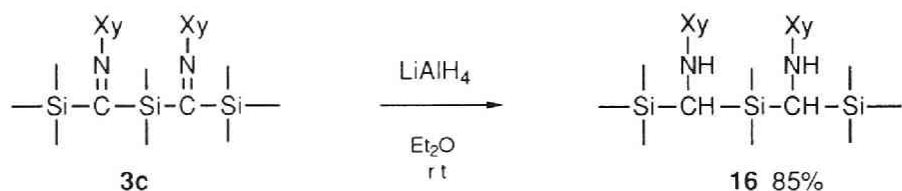
The vibrational frequencies and UV absorption maxima of the imino groups in mono-, bis-, and tris-insertion products **17**, **8**, and **3g** are summarized in Table III. The mono-insertion product **17** was prepared by trans-metalation of [(trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**18**) followed by coupling with chloroheptamethyltrisilane(Scheme VI).[10] 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 ^{1}H NMR spectrum of **3k** is notable; the

Table IV. Spectral Data of **17**, **8**, and **3g**

compound	UV λ$_{max}$, nm (ε)	IR ν, cm^{-1}
`` Xy	N			‖			—Si—C—Si—Si—Si—				17```	400 (226)	1542
`` Xy Xy		N N ‖		‖	—Si—C—Si—Si—C—Si—				8```	405 (420)	1546
`` Xy Xy Xy			N N N ‖ ‖ ‖	—Si—C—Si—C—Si—C—Si—			3g```	407 (540)	1544

Scheme VI

```
   Xy                    Xy
   |                     |
   N                     N                  | | |              Xy
   ‖         nBuLi        ‖                 Cl—Si—Si—Si—        |
—Si—C—SnMe3   ——→    [ —Si—C—Li ]          | | |          N  | | |
   |                     |              ——————————→        ‖  | | |
   18                                                   —Si—C—Si—Si—Si—
                                                           |  | | |
                                                           17
```
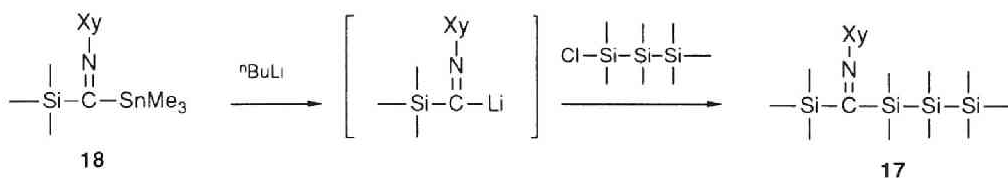
very broad signal, assigned to the Me$_3$Si and Me$_2$Si groups, appeared between δ -0.40 and 1.20 at room temperature, which split into three slightly broad singlet signals at δ -0.18, 0.24 and 0.50 with a relative intensity of 3:2:2 at 80 °C(Figure II). This observation showed that the *syn-anti* interconversion of 2,6-xylyl group on the imino nitrogen became rapid enough to sharpen the Me$_3$Si and Me$_2$Si signals at 80 °C. Similar temperature dependence of ^{1}H NMR spectra was observed for **12**.
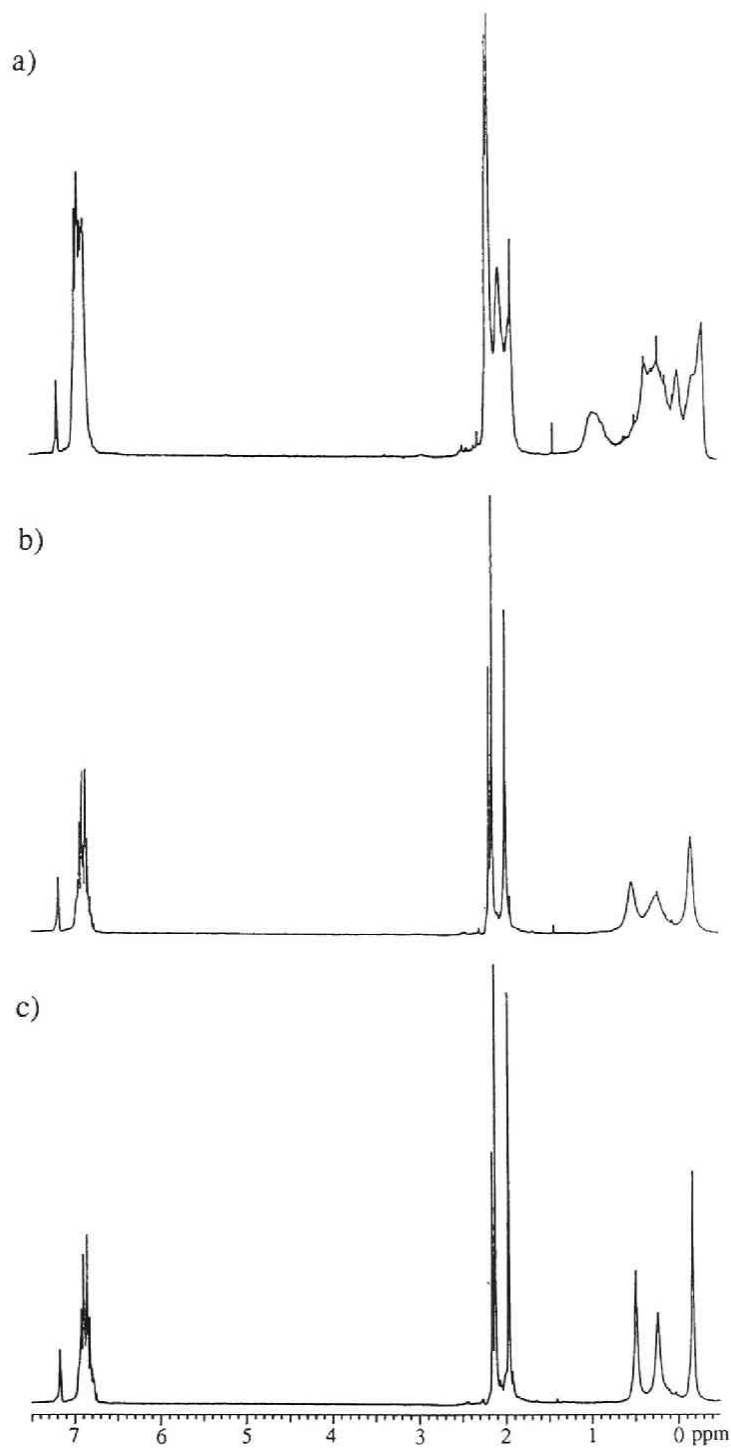
Figure II. The temperature dependent ^{1}H NMR spectrum of **3k**.

a) 20 °C b) 65 °C c) 80 °C.

Conclusion

Complete insertion of isocyanide into all silicon–silicon linkage of oligo-silanes was promoted by palladium catalyst giving oligo(silylimine) derivatives. Partial insertion of isocyanide into oligosilane was also achieved by virtue of steric hindrance.The reactions disclosed in the present study are not only interesting from synthetic viewpoint but also provide a simple and convenient entry into a novel class of organosilicon compounds which 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-perform-ance liquid chromatography (HPLC) was done using a 10 mm × 25 cm Merck LiChrosorb NH$_2$ column. The analytical and preparative recycling gel per-meation chromatography was performed with JAI LC-908 equipped with JAIGEL-1H and -2H columns. ^{1}H and ^{13}C NMR spectra were acquired with a Varian VXR-200 spectrometer in chloroform-*d* unless otherwise noted. Carbon chemical shift were recorded relative to chloroform-*d* (δ 77.0). Infra-red spectra were recorded with a Hitachi 270-30 spectrometer. UV spectra were obtained with 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 with a Yamato-MP apparatus and are uncorrected. MgSO$_4$ was used to dry organic layers after extraction.

All reactions were performed under dry nitrogen atmosphere.
Material Tetrahydrofuran (THF), diethyl ether, toluene and benzene were distilled from LiAlH$_4$, and CH$_2$Cl$_2$, dimethylformamide, ethanol, and aceto-

nitrile from CaH_2. 2,6-Xylyl isocyanide (**2a**) and 2-methylphenyl isocyanide were prepared according to the literature procedure.[11] 2,6-Di(isopropyl)phenyl isocyanide (**2b**) and 1-adamantyl isocyanide were prepared by the similar procedure from 1-formamido-2,6-di(isopropyl)benzene and 1-(formamido)adamantane, respectively. 1,1,3,3-Tetramethylbutyl isocyanide and hexamethyldisilane (**1a**) were purchased from commercial source. Octamethyltrisilane (**1b**),[12] decamethyltetrasilane (**1e**),[13] 1,4-diphenyloctamethyltetrasilane (**1f**),[14] and decamethylcyclopentasilane (**1m**)[15] were prepared as reported in the literature. 1,3-Diphenylhexamethyltrisilane (**1c**) was prepared by coupling of 1-chloro-2-phenyl-1,1,2,2,-tetramethyldisilane with dimethylphenylsilyl lithium. 1,1,4,4,-Tetraphenylhexamethyltetrasilane (**1g**) was synthesized by coupling of 1,2-dichlorotetramethyldisilane with dimethylphenylsilyl lithium. 1,5-Diphenyldecameethylpentasilane (**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-Di(isopropoxy)hexamethyltrisilane (**1j**) was prepared by reaction of 1,3-dichlorohexamethyltrisilane with 2-propanol. [(Trimethylsilyl)(2,6-xylylimino)methyl]trimethylstannane (**18**) was prepared by the reported procedure.[10] 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 crystal: 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}; ^{1}H 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-Di(isopropyl)phenylimino]-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 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}; ^{1}H 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), palladium(II) acetate (165 mg, 0.73 mmol) 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 column of Florisil pretreated with Et$_3$N 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}; ^{1}H NMR δ -0.25–0.70 (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-di(isopropyl)phenylimino]-2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane (3d). A mixture of 2,6-di(isopropyl)phenyl isocyanide (**2b**,

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913 mg, 6.98 mmol), octamethyltrisilane (**1b**, 200 mg, 0.98 mmol), palladium(II) acetate (22 mg, 0.98 μmol) in toluene (2 mL) was heated at reflux for 40 h. The cooled mixture was passed through column of Florisil pretreated with Et$_3$N (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}; ^{1}H 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$_2$Si$_3$: 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-trisila-heptane (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 column of Florisil pretreated with Et$_3$N 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}; ^{1}H NMR δ -0.3–0.7 (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$_2$Si$_3$: 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$_3$N under nitrogen

(elution with *n*-hexane), and the filtrate was condensed. Kugelrohr distillation of the residue gave **3f** as 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}; ^{1}H 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 the similar procedure (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 acetate (8.6 mg, 38 µmol) as a yellow crystal (55%): mp 110–112 °C (sealed tube). IR (KBr) 3068, 3020, 2960, 1592, 1544, 1250, 1176 cm^{-1}; ^{1}H NMR δ -0.41–0.82 (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 acetate (11.6 mg, 52 µmol) in DMF (1 mL) was heated at 70 °C for 9 h. The cooled mixture was passed through column of Florisil pretreated with Et$_3$N under nitrogen (elution with dry *n*-hexane). The filtrate was condensed and the residue was purified by HPLC to give **3h** as yellow viscous oil (43%): IR (neat) 3072, 3024, 2964, 2932, 2864, 1592, 1540, 1254, 1176 cm^{-1}; ^{1}H NMR δ -0.4–0.7 (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 the similar procedure (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 acetate (8.8 mg, 39 μmol) as yellow viscous oil (28%): IR (neat) 3072, 3052, 3020, 2964, 2908, 1592, 1540, 1254, 1176 cm^{-1}; ^{1}H NMR δ -0.5–0.7 (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 the similar procedure (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 acetate (10.1 mg, 45 μmol) as yellow viscous oil (40%). Yellow crystallines 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 the similar procedure (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 acetate (14.6 mg, 65 μmol) as 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.

2,2,4,4,5,5-Hexamethyl-3-(2,6-xylylimino)-2,4,5-trisilahexane (4). A mixture of octamethyltrisilane (**1b**, 300 mg, 1.47 mmol), 2,6-xylyl isocyanide (**2b**, 231 mg, 1.76 mmol), and palladium(II) acetate (14 mg, 0.15 mmol) in toluene (5 mL) was heated at reflux for 4 h. The cooled reaction mixture was filtered through Florisil column pretreated with Et$_3$N (elution with n-hexane) and the filtrate was condensed. Kugelrohr distillation of the residue afforded **5** as yellow viscous oil (64%): 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.

3-[2,6-Di(isopropyl)phenylimino]-2,2,4,4,5,5-hexamethyl-2,4,5-trisila-hexane (5). A mixture of octamethyltrisilane (**1b**, 200 mg, 0.98 mmol), 2,6-di(isopropyl)phenyl 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 Florisil column pretreated with Et$_3$N (elution with n-hexane) and the filtrate was condensed. Kugelrohr distillation of the residue gave **5** 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 (9). 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 Florisil column pretreated with Et$_3$N (elution with n-hexane) and the filtrate was condensed. Kugelrohr distillation of the residue gave **5** 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-di(isopropyl)phenylimino]-2,4,4,5-tetramethyl-2,4,5-trisilahexane (7). A mixture of 1,3-di(isopropoxy)hexamethyltrisilane (**1j**, 200 mg, 0.68 mmol), 2,6-di(isopropyl)phenyl 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 **7** as a yellow viscous oil: 51% yield after Kugelrohr 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$_2$Si$_3$: 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 (8). By the similar procedure (70 °C, 2 h) to that used to prepare **3e**, the title compound (**8**) was obtained from decamethyltetrasilane

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(**1e**, 219 mg, 0.83 mmol), **2a** (219 mg, 1.67 mmol), and palladium acetate (17 mg, 76 μmol) as 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$_2$Si$_4$: 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 (9). 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 Florisil column pretreated with Et$_3$N (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$_2$Si$_4$: C, 70.31, ; H, 8.07; N, 4.32. Found: C, 70.03; H, 8.37; N, 4.06. One diastereomer (**9a**) was preferentially recrystallized from n-hexane–ethanol and the other diastereomer (**9b**) was obtained from the mother liquor. **9a**: mp 238.5–240.0 °C (sealed tube). IR (KBr) 3076, 3028, 2960, 2928, 2904, 1592, 1538, 1246, 1176 cm^{-1}; ^{1}H 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$^+$). **9b**: mp. 158–163 °C (sealed tube). IR (KBr) 3072, 2964, 2908, 1592, 1538, 1248, 1176 cm^{-1}; ^{1}H 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 (10). A mixture of 2,2,3,3-tetraphenylhexamethyl-tetrasilane (**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 precipitate, which was washed with cold dichloromethane to give **14** as yellow solids (55%): mp 286–287 °C (sealed tube). IR (KBr) 3060, 3020, 2980, 2960, 2900, 1590, 1538, 1248, 1174 cm^{-1}; ^{1}H 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-di(isopropyl)phenylimino]-2,2,4,4,5,5,7,7-octamethyl-2,4,5,7-tetrasilaoctane (11). A mixture of decamethyltetrasilane (**1e**, 200 mg, 0.76 mmol), 2,6-di(isopropyl)phenyl 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 precipitate, which was successively washed with DMF and ethanol to give **11** as yellow solids (60%): mp 194–195 °C (sealed tube). IR (neat) 3064, 2968, 2908, 2876, 1546, 1252, 1242, 1168 cm^{-1}; ^{1}H 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-di(isopropyl)phenylimino]-2,2,4,4,5,5,7,7,8,8,10,10-do-decamethyl-2,4,5,7,8,10-hexasilaundecane (12). A mixture of tetradeca-methylhexasilane (**1i**, 100 mg, 0.26 mmol), 2,6-di(isopropyl)phenyl 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 Florisil column pretreated with Et$_3$N (elution with *n*-hexane) under

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nitrogen. The filtrate was condensed and the residue was purified by preparative GPC to give **12** as a yellow viscous oil (16%): IR (neat) 3068, 2968, 2936, 2876, 1536, 1252, 1168 cm^{-1}; ^{1}H 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$_3$Si$_6$ 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-pentasila-cyclohexane (13). By the similar procedure (reflux, 6.5 h) to that used to prepare **9**, the title compound (**13**) was obtained from decamethylcyclopenta-silane (**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}; ^{1}H NMR (benzene-d_6) δ -0.2–0.6 (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$_4$Si 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.

X-ray Crystal Structure Analysis of 3g. Crystal data: C$_{37}$H$_{57}$N$_3$Si$_4$, M = 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 K_α radiation (λ = 1.54178 Å), μ = 14.9 cm^{-1}. Intensity data were measured on a Rigaku AFC-5R diffractometer using 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 3 standard reflections monitored every 50 reflections. Structure was solved by the direct method (MULTAN 87)[16]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 ($\sigma = 0.01–0.02$ Å) and angles ($0.5–1.4°$) with less accuracy were observed, but not significantly deviated from their normal values.

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Chapter 2

Novel Skeletal Rearrangement Reaction of Oligosilanes with Aryl Isocyanide

Abstract

A novel skeletal rearrangement of oligosilanes in the palladium catalyzed reaction with aryl isocyanides gives 3,3-disilyl-2,4-disila-1-azacyclobutane derivatives, whose structure has been determined by X-ray crystallography. The rearrangement, which is unique and intriguing in that the product is properly reconstituted from four fragments of the oligosilane and two fragments of the isocyanide, was promoted in the presence of a *tert*-alkyl isocyanide.

Introduction

Organopolysilanes have been known to undergo skeletal rearrangements catalyzed by Lewis acid as well as transition metal complexes.[1] During the course of the study on the partial insertion of isocyanide into tetrasilane catalyzed by palladium(II) acetate, novel skeletal rearrangement of oligosilanes was found.

Results and Discussion

As described in chapter 1, the reaction of decamethyltetrasilane (**1a**) with 3.5 equiv of 2,6-di(isopropyl)phenyl isocyanide (**2a**) in DMF afforded the

Scheme I

3.5 equiv

Dip
|
N
|||
C

1a   **2a**

cat.
Pd(OAc)$_2$
DMF 80°C

3

Scheme II

1.5 equiv

Ar
|
N
|||
C

1   **2a**; Ar=2,6-diisopropyl phenyl
2b; Ar=2,6-xylyl

cat.
Pd(OAc)$_2$
toluene reflux
6h

4
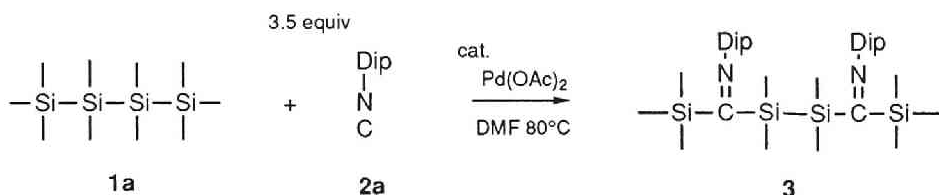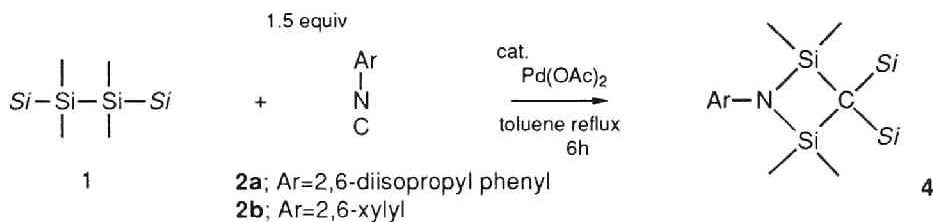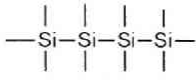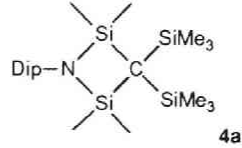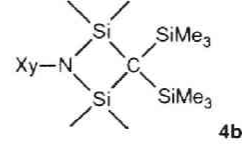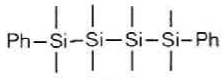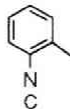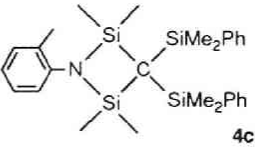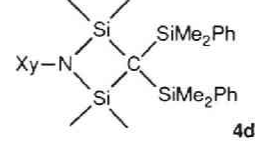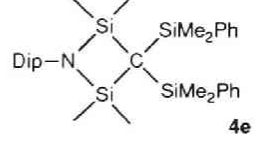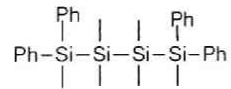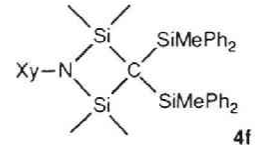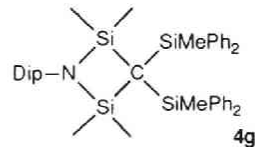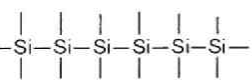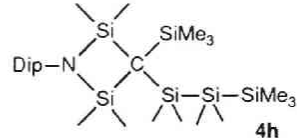
bis-insertion product **3** (Scheme I). However, attempts to synthesize a mono-insertion product from tetrasilane by use of 1.5 equiv of **2a** in DMF did not give mono-insertion product but bis-insertion product **3** in 22% yield along with 6% of an unexpected skeletal rearranged product **4a**. The yield of the rearranged product **4a** significantly increased up to 40% when the reaction was carried out in toluene (Scheme II). Representative results of the skeletal rearrangement reaction are summarized in Table I. The rearrangement took place with 2,6-disubstituted aryl isocyanide, but not with *o*-tolyl isocyanide under the same reaction conditions. *Prim*- 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 one equiv of *tert*-alkyl isocyanide and 1.5 equiv of 2,6-disubstituted aryl isocyanide improved the yields of the rearranged products **4** in some cases (entries 2, 3, 5, and 6). Especially, it is remarked that *o*-tolyl isocyanide reacted with tetrasilane **1a** in the presence of palladium(II) acetate–1,1,3,3-tetramethylbutyl isocyanide to afford the rear-

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Table I. The Sckeletal Rearrangement of Oligosilanes

entry	1	2	product (18)	yield, %[a]
1	—Si—Si—Si—Si— **1a**	2a	Dip—N〈Si/Si〉C〈SiMe₃/SiMe₃〉 **4a**	40, 45
2	**1a**	2b	Xy—N〈Si/Si〉C〈SiMe₃/SiMe₃〉 **4b**	9, 40
3	Ph—Si—Si—Si—Si—Ph **1b**	(o-tolyl isocyanide)	(o-tolyl)N〈Si/Si〉C〈SiMe₂Ph/SiMe₂Ph〉 **4c**	0, 24
4	**1b**	2b	Xy—N〈Si/Si〉C〈SiMe₂Ph/SiMe₂Ph〉 **4d**	37, 31
5	**1b**	2a	Dip—N〈Si/Si〉C〈SiMe₂Ph/SiMe₂Ph〉 **4e**	50, 62
6	Ph—Si(Ph)—Si—Si—Si(Ph)—Ph **1c**	2b	Xy—N〈Si/Si〉C〈SiMePh₂/SiMePh₂〉 **4f**	10, 28
7	**1c**	2a	Dip—N〈Si/Si〉C〈SiMePh₂/SiMePh₂〉 **4g**	54, 48
8	—Si—Si—Si—Si—Si—Si— **1d**	2a	Dip—N〈Si/Si〉C〈SiMe₃/Si—Si—SiMe₃〉 **4h**	-, 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.

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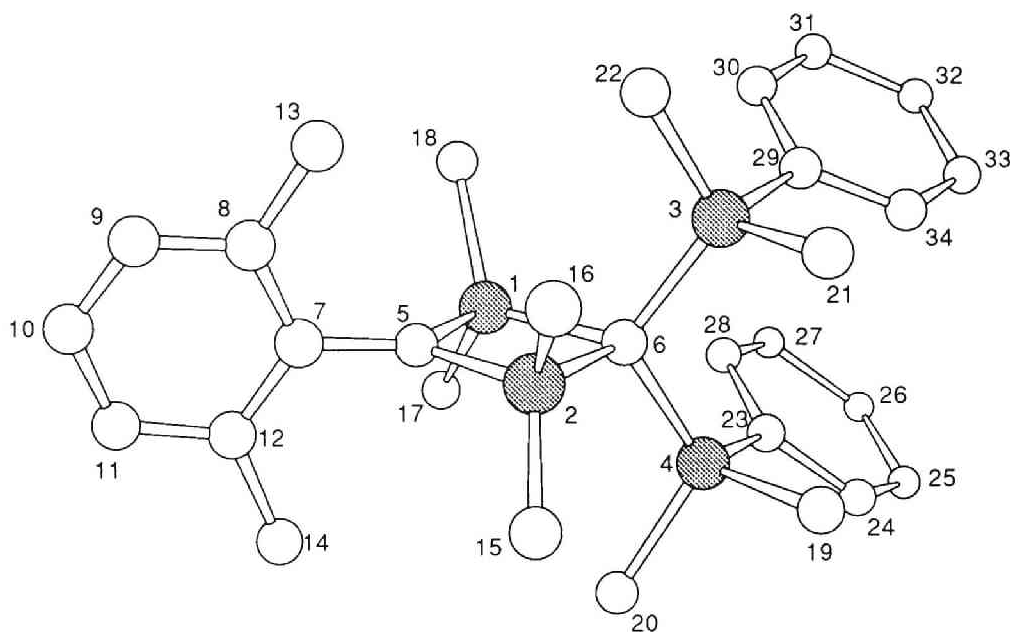
Figure I. Crystal structure of **4d**. Hydrogen atoms have been omitted for clarity. Some bond distances (Å) and angles (deg) are as follows. Si(1)–N(5) = 1.733(3), Si(1)–C(6) = 1.925(3), Si(2)–N(5) = 1.746(3), Si(2)–C(6) = 1.913(3), N(5)–C(7) = 1.436(4), Si(1)–C(6)–Si(2) = 84.9(1), Si(1)–N(5)–Si(2) = 96.2(1), N(5)–Si(1)–C(6) = 89.4(1), N(5)–Si(2)–C(6) = 89.5(1).
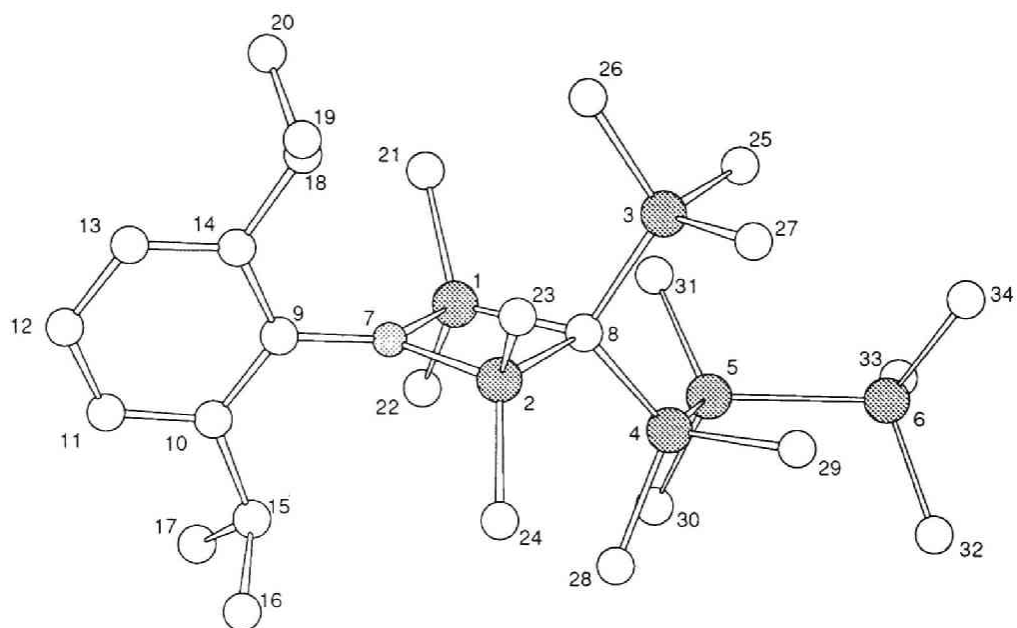
Figure II. Crystal structure of **4h**. Hydrogen atoms have been omitted for clarity. Some bond distances (Å) and angles (deg) are as follows. Si(1)–N(7) = 1.738(3), Si(1)–C(8) = 1.907(4), Si(2)–N(7) = 1.734(3), Si(2)–C(8) = 1.909(4), N(7)–C(9) = 1.446(5), Si(1)–C(8)–Si(2) = 84.9(2), Si(1)–N(7)–Si(2) = 95.8(2), N(7)–Si(1)–C(8) = 89.4(2), N(7)–Si(2)–C(8) = 89.4(2).

Table II. Atomic coordinates (x10⁴) and isotropic temperature factors (Å²x10) with e.s.d. values in parentheses for **4d**.

	x	y	z	B
Si (1)	2561.4 (5)	-778.5 (4)	1608.7 (2)	366 (2)
Si (2)	1817.1 (5)	417.4 (4)	835.9 (2)	281 (1)
Si (3)	4518.8 (5)	1337.6 (5)	1463.9 (2)	348 (2)
Si (4)	1447.9 (5)	1571.4 (5)	1943.6 (2)	353 (2)
N (5)	1780 (2)	-958 (1)	1013 (1)	360 (5)
C (6)	2636 (2)	772 (1)	1486 (1)	317 (5)
C (7)	1269 (2)	-1875 (2)	722 (1)	444 (7)
C (8)	-179 (3)	-2191 (2)	760 (1)	520 (8)
C (9)	-690 (4)	-3030 (2)	444 (1)	730 (11)
C (10)	177 (4)	-3548 (2)	110 (1)	831 (13)
C (11)	1605 (4)	-3265 (2)	81 (1)	805 (13)
C (12)	2184 (3)	-2429 (2)	387 (1)	576 (8)
C (13)	-1195 (3)	-1651 (2)	1119 (1)	620 (10)
C (14)	3732 (4)	-2168 (3)	349 (1)	774 (12)
C (15)	4282 (3)	-1542 (2)	1708 (1)	637 (10)
C (16)	1470 (3)	-1307 (2)	2152 (1)	588 (9)
C (17)	2882 (2)	685 (2)	248 (1)	432 (7)
C (18)	33 (2)	981 (2)	656 (1)	426 (7)
C (19)	5347 (2)	1357 (3)	2118 (1)	651 (10)
C (20)	5804 (2)	541 (2)	1058 (1)	548 (8)
C (21)	2062 (3)	1448 (2)	2624 (1)	563 (9)
C (22)	-470 (2)	1101 (2)	1948 (1)	525 (8)
C (23)	4653 (2)	2767 (2)	1202 (1)	462 (7)
C (24)	3691 (2)	3227 (2)	851 (1)	500 (8)

Table II. (Continued)

	x	y	z	B
C (25)	3908 (3)	4253 (2)	643 (1)	712 (11)
C (26)	5085 (4)	4856 (2)	784 (2)	929 (16)
C (27)	6028 (3)	4450 (3)	1129 (2)	954 (16)
C (28)	5835 (3)	3398 (2)	1338 (1)	743 (12)
C (29)	1379 (2)	3078 (2)	1788 (1)	409 (6)
C (30)	348 (2)	3506 (2)	1453 (1)	481 (7)
C (31)	324 (3)	4599 (2)	1324 (1)	597 (9)
C (32)	1298 (3)	5312 (2)	1525 (1)	618 (10)
C (33)	2303 (3)	4932 (2)	1862 (1)	598 (9)
C (34)	2333 (2)	3829 (2)	1996 (1)	497 (8)

Table III. Atomic coordinates ($\times 10^4$) and isotropic temperature factors ($Å^2 \times 10$) with e.s.d. values in parentheses for **4h**.

	x	y	z	B
Si (1)	1208.9 (4)	1735 (1)	5994 (1)	406 (4)
Si (2)	1600.9 (4)	3245 (1)	4603 (1)	430 (4)
Si (3)	680.3(4)	2558 (1)	3378 (1)	539 (4)
Si (4)	1446.9 (4)	851 (1)	3081 (1)	476 (4)
Si (5)	1119.8 (4)	-944(1)	3342 (1)	496 (4)
Si (6)	888.5 (5)	-1750(1)	1342(2)	666 (5)
N (7)	1520 (1)	2934 (3)	6272 (3)	375 (9)
C (8)	1219 (1)	2039 (3)	4129 (4)	380 (1)
C (9)	1661 (1)	3454 (3)	7502 (4)	390 (1)

Table III. (Continued)

	x	y	z	B
C (10)	2051 (1)	3114 (4)	8139 (4)	450 (1)
C (11)	2171 (2)	3617 (5)	9342 (5)	560 (2)
C (12)	1921 (2)	4434 (5)	9899 (5)	610 (2)
C (13)	1540 (2)	4789 (5)	9263 (5)	580 (2)
C (14)	1404 (1)	4304 (4)	8072 (4)	440 (1)
C (15)	2359 (2)	2232 (4)	7583 (5)	500 (1)
C (16)	2798 (2)	2742 (6)	7177 (7)	670 (2)
C (17)	2440 (2)	1251 (6)	8532 (7)	690 (2)
C (18)	981 (2)	4727 (4)	7435 (5)	500 (1)
C (19)	584 (2)	4544 (6)	8332 (7)	700 (2)
C (20)	1019 (3)	5979 (5)	7057 (8)	800 (2)
C (21)	678 (2)	1691 (6)	6892 (6)	680 (2)
C (22)	1491 (2)	431(5)	6554 (6)	670 (2)
C (23)	1432 (3)	4682 (5)	4104 (6)	710 (2)
C (24)	2190 (2)	3208 (5)	4073 (6)	620 (2)
C (25)	304 (2)	1371 (6)	3007 (8)	760 (2)
C (26)	350 (2)	3522 (6)	4447 (8)	800 (2)
C (27)	769 (3)	3392 (8)	1831 (8)	940 (3)
C (28)	2050 (2)	580 (6)	3350 (1)	910 (3)
C (29)	1422 (3)	1180 (7)	1261 (8)	900 (3)
C (30)	1560 (2)	-1934 (6)	3970 (1)	960 (3)
C (31)	654 (2)	-1107 (7)	4562 (6)	800 (2)
C (32)	1388 (5)	-1990 (1)	310 (1)	1570 (6)
C (33)	670 (4)	-3168 (7)	1780 (1)	1080 (4)
C (34)	446 (5)	-980 (1)	450 (1)	1520 (5)

ranged product **4c** in 24% (entry 3). *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 **4** was favored by bulkiness of the aromatic group of the isocyanide (entries 3-5). Hexasilane **1d** also underwent a similar rearrangement giving 3-silyl-3-trisilyl-1-aza-2,4-disilacyclobutane **4h** in 15% as an isolable product (entry 8).

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

It may be relevant to the reaction mechanism that mono-insertion product **5** underwent the skeletal rearrangement in the presence of palladium(II) acetate to give **4**. A toluene solution of **5**, which was prepared from 1-chloro-

Scheme III

5a Ar = Dip
5b Ar = Xy

cat.
Pd(OAc)$_2$
^{t}Alk-NC

toluene
reflux
5h

4a Ar = Dip 47%
(^{t}Alk = 1,1,3,3-tetramethylbutyl)
4b Ar = Xy 37%
(^{t}Alk = adamantyl)
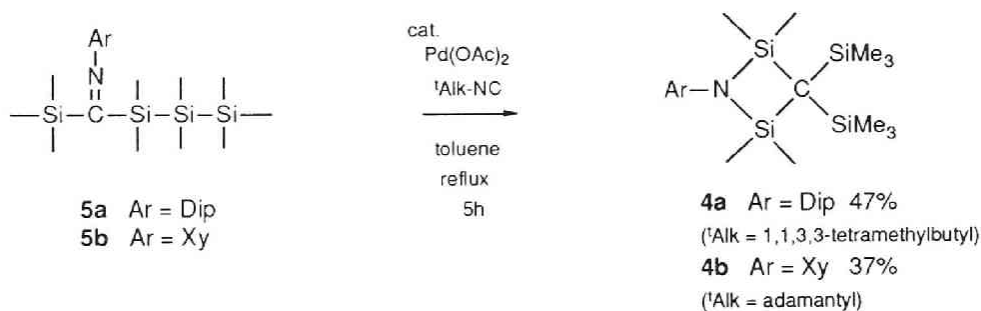
heptamethyltrisilane and [(arylimino)(trimethylsilyl)methyl]lithium,[2] was heated with palladium(II) acetate in the presence of *tert*-alkyl isocyanide to afford the rearranged product **4** in moderate yield (Scheme III). This suggested the mono-insertion product **5** is a possible intermediate of the rearrangement, although the subsequent pathway leading to **4** remains to be clarified. Intermediacy of silylene-palladium complex[3] might be presumed for the rearrangement step. By use of $Pd(PPh_3)_4$ in stead of $Pd(OAc)_2$–tert-alkyl isocyanide, the mono-insertion product **5** 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 palladium species, serving favorably for formation and stabilization of bis(organosilyl)palladium without being incorporated in 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.

Conclusion

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 achievement of the complete insertion of isocyanide into higher polysilanes.

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). ^{1}H and ^{13}C NMR spectra were acquired with a Varian VXR-200 spectrometer in chloroform-*d* unless otherwise noted. Carbon chemical shift were recorded relative to chloroform-*d* (δ 77.0). Infrared spectra were recorded with a

Hitachi 270-30 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 with a Yamato-MP apparatus and are uncorrected. $MgSO_4$ was used to dry organic layers after extraction.

All reactions were performed under dry nitrogen atmosphere.

Material   Toluene was distilled from $LiAlH_4$, and dimethylformamide, from CaH_2. 2,6-Di(isopropyl)phenyl isocyanide (**2a**) and 1-adamantyl isocyanide were prepared by the similar procedure from 1-formamido-2,6-di-(isopropyl)benzene and 1-(formamido)adamantane, respectively. 2,6-Xylyl isocyanide (**2b**) and 2-methylphenyl isocyanide were prepared according to the literature procedure.[4] 1,1,3,3-Tetramethylbutyl isocyanide was purchased from commercial source. Decamethyltetrasilane (**1a**)[5] and 1,4-diphenyloctamethyltetrasilane (**1b**)[6] were prepared as reported in the literature. 1,1,4,4,-Tetraphenylhexamethyltetrasilane (**1c**) was synthesized by coupling of 1,2-dichlorotetramethyldisilane with dimethylphenylsilyl lithium. Tetradecamethylhexasilane (**1d**) was synthesized by treatment of 1-chloroheptamethyltrisilane with an alloy of sodium and potassium. Palladium(II) acetate was purchased from a commercial source and used without further purification.

1-[2,6-Di(isopropyl)phenyl]-2,2,4,4-tetramethyl-3,3-bis(trimethylsilyl)-1-aza-2,4-disilacyclobutane (4a).   A mixture of decamethyltetrasilane (**1e**, 100 mg, 0.38 mmol), 2,6-di(isopropyl)phenyl 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, 0.38 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 **4a** as a colorless solid (45%): mp 194–195 °C. IR (KBr) 2980, 2956, 2908, 2876, 1466, 1442, 1320, 1254, 1208, 870 cm^{-1}; ^{1}H 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-tis(trimethylsilyl)-1-(2,6-xylyl)-1-aza-2,4-disilacyclobutane (4b). By the similar procedure to that used to prepare **4a**, the title compound (**4b**) 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, 0.38 μmol) as a colorless solid (40%): mp 192.5–193.0 °C. IR (KBr) 2950, 1600, 1450, 1272, 1256, 1234, 878 cm^{-1}; ^{1}H 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 (4c). By the similar procedure to that used to prepare **4a**, the title compound (**4c**) 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, 0.26 μmol) as a colorless solid (24%): mp 124–125 °C. IR (KBr) 3076, 2964, 2908, 1488, 1430, 1290, 1260, 1106 cm^{-1}; ^{1}H 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 (4d). 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, 0.38 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 **4d** 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}; ^{1}H 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-[Di(isopropyl)phenyl]-3,3-bis(dimethylphenylsilyl)-2,2,4,4-tetramethyl-1-aza-2,4-disilacyclobutane (4e). By the similar procedure to that used to prepare **4a**, the title compound (**4e**) was obtained from 1,4-diphenyloctamethyltetrasilane (**1f**, 100 mg, 0.26 mmol), 2,6-di(isopropyl)phenyl isocyanide (**2b**, 73 mg, 0.39 mmol), 1,1,3,3-tetramethyl-butyl isocyanide (36 mg, 0.26 mmol), and palladium(II) acetate (5.8 mg, 0.26 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}; ^{1}H 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 (4f). By the similar procedure to that used to prepare **4a**, the title compound (**4f**) 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, 0.20 μmol) as a colorless solid (28%): mp 264.5–265.0 °C. IR (KBr) 3076, 3048, 3016, 1430, 1260, 1230, 1100, 966 cm^{-1}; ^{1}H 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-[Di(isopropyl)phenyl]-2,2,4,4-tetramethyl-3,3-bis(methyldiphenyl-silyl)-1-aza-2,4-disilacyclobutane (4g). By the similar procedure to that used to prepare **4d**, the title compound (**4g**) was obtained from 1,1,4,4-tetraphenyl-1,2,2,3,3,4-hexamethyltetrasilane (**1g**, 100 mg, 0.20 mmol), 2,6-di(isopropyl)phenyl isocyanide (**2b**, 55 mg, 0.29 mmol), and palladium(II) acetate (4.4 mg, 0.20 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}; ^{1}H 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-Di(isopropyl)phenyl]-3-heptamethyltrisilyl-2,2,4,4-tetramethyl-3-trimethylsilyl-1-aza-2,4-disilacyclobutane (4h). By the similar procedure to that used to prepare **4a**, the title compound (**4h**) was obtained from tetra-decamethylhexasilane (**1i**, 100 mg, 0.26 mmol), 2,6-di(isopropyl)phenyl iso-cyanide (**2b**, 49 mg, 0.26 mmol), 1,1,3,3-tetramethylbutyl isocyanide (55 mg, 0.40 mmol), and palladium(II) acetate (6 mg, 0.26 μmol) as 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

(5b). To a solution of [(trimethylsilyl)(2,6-xylylimino)methyl]trimethyl-stannane (447 mg, 1.21 mmol) in THF (6 mL) was added a *n*-hexane solution of *n*-butyllithium (1.33 mmol) at -78 °C under nitrogen. After stirring for 50 min, 1-chloroheptamethyltrisilane (377 mg, 1.68 mmol) was added 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 **5b** as yellow viscous oil (73%): bp 150–160 °C (0.5 mmHg). IR (neat) 2956, 1594, 1542, 1250 cm^{-1}; ^{1}H NMR δ -0.25–0.55 (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-Di(isopropyl)phenylimino]-2,2,4,4,5,5,6,6-octamethyl-2,4,5,6-tetra-silaheptane (5a).** 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 4h. Crystal data: C$_{27}$H$_{59}$NSi$_6$, $M =$ 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 K_α radiation (λ = 0.71069 Å), μ = 2.07 cm^{-1}. Intensity data were measured on a Mac Science MXC3 diffractometer using ω–2θ scan technique. 8419 unique reflections within 3≤2θ≤55° were collected. Structure was solved by the Monte Carlo direct method based on MULTAN 78[7] and refined anisotropically by the full-matrix least-squares to $R = 0.066$, $R_w =$ 0.078, and $S = 1.45$ for 4256 reflections with $F_o > 4σ(F_o)$. 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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Chapter 3

Palladium(II) Acetate - *tert*-Alkyl Isocyanide as a Highly Efficient Catalyst for the Inter- and Intramolecular Bis-silylation of Carbon-Carbon Triple Bonds

Abstract

A new catalyst, palladium(II) acetate - *tert*-alkyl isocyanide, permitted *intermolecular* bis-silylation of alkynes by otherwise unreactive disilanes, such as hexamethyldisilane and 1,2-diphenyl-1,1,2,2-tetramethyldisilane, to give bis-silylated alkenes in yields up to 98%. The bis-silylation of alkynes by octamethyltrisilane and decamethyltetrasilane was also achieved. Furthermore, the catalyst was successfully applied to *intra*molecular bis-silylation, and thus permitted bis-silylation of disubstituted alkynes for the first time.

Introduction

Much interest has been focused on the development of methodology for the introduction of silicon into organic molecules because such new methodology would be valuable for both the synthetic elaboration of organic molecules via organosilicon compounds and the synthesis of new silicon containing materials.[1] Recently, new bis-silylation reactions of isocyanides[2] and alkenes[3] have been discovered. The bis-silylation of alkynes by disilanes has also been reported.[4] However, satisfactory bis-silylations of alkynes were achieved only by disilanes with electron-withdrawing substituents (such as alkoxy and halogen) on silicon, and a few cyclic disilanes. Hexaalkyldisilanes, such as hexa-

methyldisilane, have afforded bis-silylation products in low yield (26% at most).[3c] The low reactivity of hexaalkyldisilanes discouraged attempts to employ other peralkylpolysilanes. Also, the *intra*molecular version of the reaction was unknown. The author presents here that a new catalyst, palladium(II) acetate *tert*-alkyl isocyanide, permitted the *inter*molecular bis-silylation of alkynes by otherwise unreactive disilanes, such as hexamethyldisilane and 1,2-diphenyl-1,1,2,2-tetramethyldisilane, to give bis-silylated alkenes products in yields up to 98%. Extension of the reaction to the *intra*molecular bis-silylation of carbon-carbon triple bonds led to the regioselective formation of cyclic organosilicon compounds in good yield.

Results and Discussion

Heating a toluene solution of hexamethyldisilane and phenylethyne (1.5 equiv) in the presence of palladium(II) acetate (0.02 equiv)[5] and 1,1,3,3-tetramethylbutyl isocyanide (*tert*-octyl isocyanide) (0.30 equiv) at reflux for 6 h, followed by preparative TLC of the cooled reaction mixture on silica gel, furnished 1,2-bis(trimethylsilyl)-1-phenylethene (**2a**) ($Z : E$ = 96 : 4) in 82% yield. The results of similar bis-silylations of selected alkynes are summarized in Table I. Z-isomers, which arose from *cis*-addition of the Si-Si linkage to the carbon-carbon triple bond, were predominantly produced. Not only phenylethyne, but also other alkyl-substituted terminal alkynes, and acetylene itself, afforded Z-1,2-bis(organosilyl)alkenes in good yield. However, disubstituted alkynes were unreactive.(Scheme I)

Scheme I
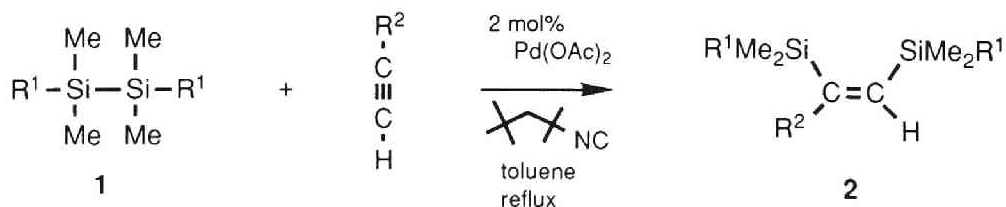
Table I. Bis-silylation of Alkynes with Disilanes

entry	R¹	R²	product	% yield	Z : E
1	Me	Ph	**2a**	82	96 : 4
2	Me	*n*-Hex	**2b**	81	95 : 5
3	Ph	*n*-Hex	**2c**	96	100 : 0
4	Ph	H	**2d**	98	97 : 3

A significant feature of the palladium catalyst is the use of excess *tert*-alkyl isocyanide as a ligand. However, the role of the isocyanide in the remarkable promotion of bis-silylation is yet to be clarified. 1-Adamantyl and *tert*-butyl isocyanides also efficiently promoted the catalytic activity of palladium(II) acetate. In the absence of *tert*-alkyl isocyanide, reaction failed to occur.

The reaction was extended to include bis-silylation by octamethyltrisilane (**3**) and decamethyltetrasilane (**5**). The reaction of **3** with phenylethyne (3

Scheme II

95%   **4a** : **4b** : **4c** = 4 : 2 : 3

Me Me Me Me   Ph
 | | | | |
Me—Si—Si—Si—Si—Me   +   C   3 mol% Pd(OAc)$_2$
 | | | | ||| ───────────────────►
Me Me Me Me   C   ⤢⤢ NC
                          | toluene
         5   H   80°C

Me₃Si Me   Me Me   Me
     \ \Si/   \Si/   \SiMe₃
      C=C   C=C   C=C   +   **4a**   +   **4b**
     Ph, H   Ph, H   Ph, H

                                          10%   31%
         6 47%
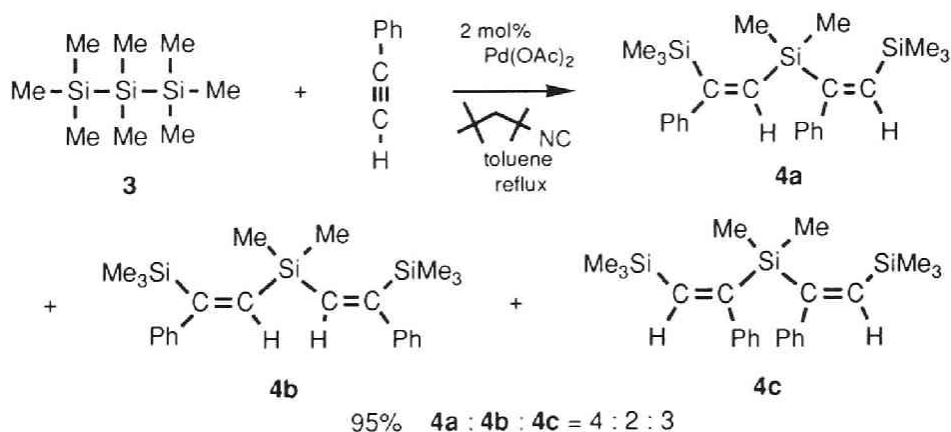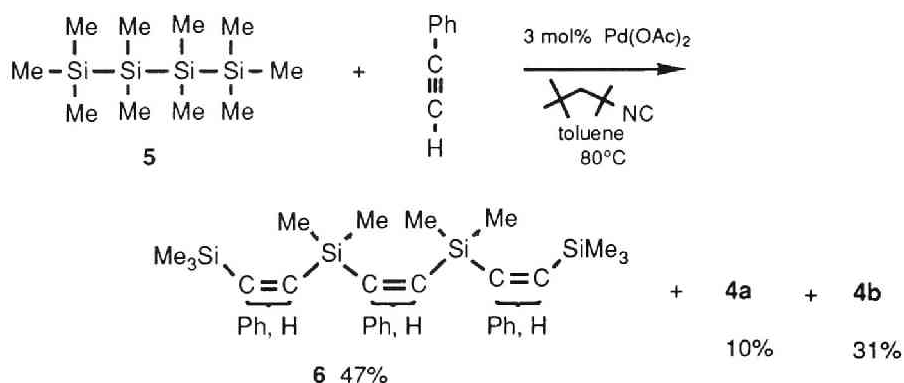
equiv) gave a mixture of regioisomeric double bis-silylation products **4** in high
total yield. Bis-silylation with **5** gave the desired triple bis-silylation product
6[6] in 47% yield, together with the double bis-silylation products **4a** and **4b**
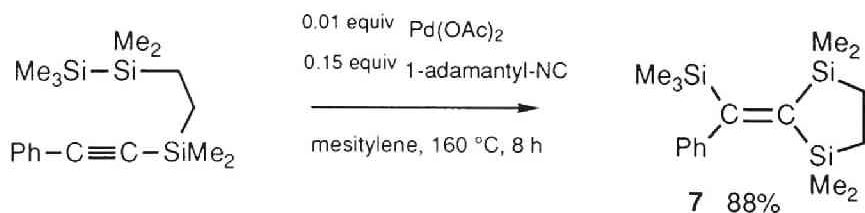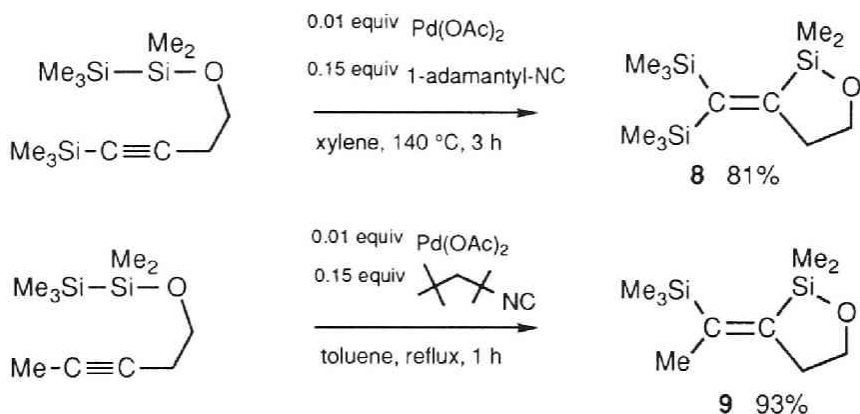(41%). The latter may possibly have been formed by fragmentation of **5** to **3**,
and subsequent bis-silylation by **3**.(Scheme II)

Furthermore, palladium(II) acetate - *tert*-alkyl isocyanide catalyzed the first
known *intra*molecular bis-silylations, that is, cyclizations of pentaalkyldisilyl-
substituted alkynes, which permitted bis-silylation of disubstituted alkynes for
the first time. Thus, intramolecular regioselective *cis*-addition of the Si-Si
linkage to the carbon-carbon triple bond furnished the exocyclic olefins **7-9** in
good yield. Of particular note was that olefins **7** and **8**, which are sterically
very congested, were easily formed.(Scheme III)

Scheme III

                Me₂
Me₃Si—Si─┐   0.01 equiv Pd(OAc)$_2$ Me₃Si   Me₂
          >   \   Si
Ph—C≡C—SiMe₂   0.15 equiv 1-adamantyl-NC   C=C /   \
                    ─────────────────────►   Ph/   \Si──┘
                    mesitylene, 160 °C, 8 h   Me₂

                                                         7 88%

The synthetic transformations possible for the bis-silylation products are exemplified by the ring-opening of **8** to yield silyl-substituted homoallylic alcohol **10** and by the oxidation of **9** to afford epoxide **11**.(Scheme IV)

Scheme IV
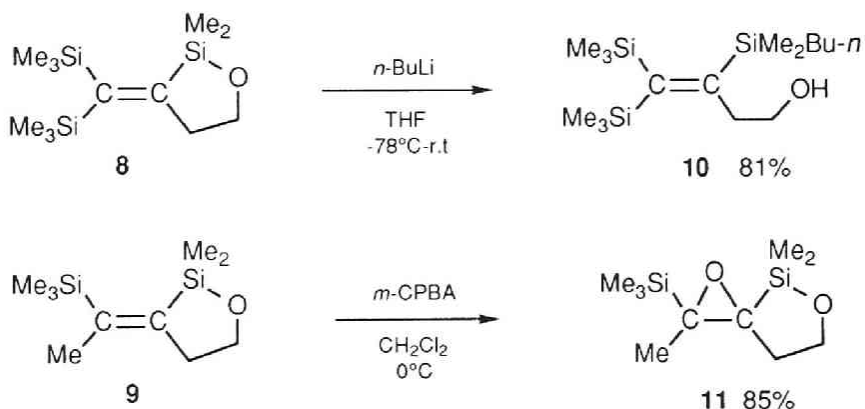
A new catalyst, palladium(II) acetate *tert*-alkyl isocyanide, thus has made the bis-silylation of alkynes a synthetically useful reaction. Studies of a variety of synthetically useful transformations of the bis-silylation products are now in progress.

Experimental Section

Electron impact mass spectra (EIMS) were recorded with a JEOL JMS-D300 spectrometer and a JMA-2000 data system. Fast atom bombardment mass spectra (FABMS) were recorded with a JEOL JMS-SX102 spectrometer and a JMA-DA6000 data system. A Xe beam source (10 kV acceleration potential) was used. The spectra of 2-hydroxyethyl disulfide solutions. Melting points are uncorrected.

1,1,3,3,-Tetramethylbutyl isocyanide was purchased from Aldrich. 1-Adamantyl isocyanide was prepared by dehydration of N-formyl-1-adamantan-amine with thionyl chloride-triethylamine. Toluene, xylene, and mesitylene were freshly distilled under nitrogen from lithium aluminium hydride before use.

1,2-Bis(trimethylsilyl)-1-phenylethene (2a). A toluene solution (1 mL) of hexamethyldisilane (100 mg, 0.68 mmol), phenylethyne (105 mg, 1.03 mmol), palladium(II) acetate (3.1 mg, 0.014 mmol), and 1,1,3,3-tetramethyl-butyl isocyanide (29 mg, 0.21 mmol) was heated at reflux for 6 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (n-hexane) afforded 1,2-bis(trimethylsilyl)-1-phenylethene (2a, 140 mg, 82%, Z : E = 96 : 4).

1,2-Bis(trimethylsilyl)-1-octene (2b). Bis-silylation product (2b) was obtained from 1-octyne and hexamethyldisilane, by the procedure described for 2a, in 81% yield (Z : E = 95 : 5): IR (neat) 2932, 1466, 1250, 844 cm^{-1}; ^{1}H NMR of the Z-isomer (200 MHz, CDCl$_3$) δ 0.12 (s, 9 H), 0.15 (s, 9 H), 0.88 (t, J = 6.2 Hz, 3 H), 1.23-1.42 (m, 8 H), 2.12-2.22 (m, 2 H), 6.26 (s, 1 H); ^{13}C NMR of the Z-isomer (CDCl$_3$) δ 0.81, 1.08, 14.10, 22.67, 29.15, 30.26, 31.77, 44.30, 143.33, 162.72; MS (EI, 20 eV) m/z 256 (M$^+$). Anal. Calcd for C$_{14}$H$_{32}$Si$_2$: C, 65.54; H, 12.37. Found: C, 65.80; H, 12.54.

1,2-Bis(dimethylphenylsilyl)-1-octene (2c). Bis-silylation product (2c)

was obtained from 1-octyne and 1,1,2,2-tetramethyl-1,2-diphenyldisilane, by the procedure described for **2a**, in 96% yield ($Z : E = 100 : 0$): IR (neat) 2932, 1430, 1252, 1112, 844 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 6 H), 0.27 (s, 6 H), 0.87 (t, $J = 6.2$ Hz, 3 H), 1.19-1.47 (m, 8 H), 2.21-2.31 (m, 2 H), 6.60 (s, 1 H), 7.25-7.36 (m, 3 H), 7.41-7.50 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -0.35, 0.22, 14.09, 22.66, 29.12, 30.30, 31.70, 44.13, 127.60, 128.64, 128.79, 133.88, 134.18, 139.55, 140.41, 143.20, 162.05; EIMS (20 eV) m/z 380 (M^+). Anal. Calcd for $C_{24}H_{36}Si_2$: C, 75.72; H, 9.53. Found: C, 75.85; H, 9.64.

1,2-Bis(dimethylphenylsilyl)ethene (2d). To a toluene solution (5 mL) of 1,1,2,2-tetramethyl-1,2-diphenyldisilane (100 mg, 0.37 mmol), palladium(II) acetate (1.7 mg, 0.0076 mmol), and 1,1,3,3-tetramethylbutyl iso-cyanide (15 mg, 0.11 mmol) in an autoclave cooled in a liquid N_2 bath was introduced gaseous ethyne to a pressure of 10 kg/cm^2. The autoclave was heated at 120 °C for 60 h. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded 1,2-bis(dimethylphenylsilyl)ethene (**2d**, 108 mg, 98%, $Z : E = 97 : 3$).: IR (neat) 2964, 1430, 1252, 1114 cm^{-1}; ^1H NMR of the Z-isomer (200 MHz, $CDCl_3$) δ 0.35 (s, 12 H), 7,16 (s, 2 H), 7.39-7.46 (m, 3 H), 7.54-7.60 (m, 2 H); ^{13}C NMR of the Z-isomer ($CDCl_3$) δ -0.93, 127.71, 128.89, 133.96, 139.22, 151.41; EIMS (20 eV) m/z 296 (M^+). Anal. Calcd for $C_{18}H_{24}Si_2$: C, 72.90; H, 8.16. Found: C, 72.64; H, 8.22.

Reaction of Phenylethyne with Octamethyltrisilane. A toluene solu-tion (1 mL) of octamethyltrisilane (100 mg, 0.49 mmol), phenylethyne (150 mg, 1.47 mmol), palladium(II) acetate (2.2 mg, 0.0098 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (21 mg, 0.15 mmol) was heated at reflux for 6 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded a mixture of regioisomeric double bis-silylation products (**4a+4b+4c**, 190 mg, 95%). Anal. Calcd for $C_{24}H_{36}Si_3$: C, 70.51; H, 8.88. Found: C, 70.72; H, 9.12. The regiochemistry of each isomer was determined from the ^1H NMR spectra of authentic samples.[7] **4a**: ^1H NMR (200 MHz,

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CDCl$_3$) δ 0.08 (s, 9 H), 0.18 (s, 9 H), 0.34 (s, 6 H), 6.47 (s, 1 H), 6.56 (s, 1 H), 6.9-7.3 (m, 10 H). **4b**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.14 (s, 18 H), 0.37 (s, 6 H), 6.56 (s, 2 H), 7.0-7.3 (m, 10 H). **4c**: ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.13 (s, 18 H), 0.41 (s, 6 H), 6.38 (s, 2 H), 6.8-7.3 (m, 10 H).

Reaction of Phenylethyne with Decamethyltetrasilane. A toluene solution (0.7 mL) of decamethyltetrasilane (67 mg, 0.25 mmol), phenylethyne (116 mg, 1.14 mmol), palladium(II) acetate (1.7 mg, 0.0076 mmol), and 1,1,3,3-tetramethylbutyl isocyanide (15 mg, 0.11 mmol) was heated at 80 °C for 4 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded **6** (68 mg, 47%) and **4a+4b** (42 mg, 41%). **6**: IR (neat) 2968, 1596, 1490, 1250 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.08 (s, 9 H), 0.12 (s, 9 H), 0.388 (s, 6 H), 0.394 (s, 6 H), 6.53 (s, 1 H), 6.57 (s, 1 H), 6.64 (s, 1 H), 6.87-7.32 (m, 15 H); ^{13}C NMR (CDCl$_3$) δ 0.96, 1.07, 1.78, 2.21, 125.59, 125.83, 126.10, 126.15, 126.64, 127.75, 127.80, 147.93, 148.36, 149.25, 150.49, 150.57, 150.73, 163.54, 164.69, 164.75. HRFABMS. Calcd for C$_{34}$H$_{48}$Si$_4$ + Li: 575.2993. Found: 575.2997.

Synthesis of 7 by Intramolecular Bis-silylation. A mesitylene solution (0.5 mL) of 3,3,6,6,7,7-hexamethyl-1-phenyl-3,6,7-trisila-1-octyne (103 mg, 0.32 mmol), palladium(II) acetate (1.4 mg, 0.0062 mmol), and 1-adamantyl isocyanide (15 mg, 0.093 mmol) was heated at 160 °C for 8 h under nitrogen. Preparative TLC of the cooled reaction mixture on silica gel (*n*-hexane) afforded **7** (91 mg, 88%): mp 53.4-54.4 °C. IR (KBr) 2960, 1248, 840 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ -0.37 (s, 6 H), 0.04 (s, 9 H), 0.28 (s, 6 H), 0.55-0.80 (m, 4 H), 6.81-6.87 (m, 2 H), 7.10-7.25 (m, 3 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ -0.13, 0.27, 0.90, 9.84, 11.35, 125.28, 127.06, 127.33, 149.44, 161.92, 177.58. HREIMS (20 eV). Calcd for C$_{17}$H$_{30}$Si$_3$: 318.1655. Found: 318.1627.

Synthesis of 8 by Intramolecular Bis-silylation. A xylene solution

(0.5 mL) of 4-(pentamethyldisilyloxy)-1-trimethylsilyl-1-butyne (138 mg, 0.51 mmol), palladium(II) acetate (1.2 mg, 0.0053 mmol), and 1-adamantyl iso-cyanide (13 mg, 0.081 mmol) was heated at 140 °C for 3 h under nitrogen. Kugelrohr distillation [120-125 °C (1 mmHg)] of the reaction mixture afforded **8** (112 mg, 81%): IR (neat) 2964, 1252, 1084 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.16 (s, 9 H), 0.21 (s, 9 H), 0.35 (s, 6 H), 2.75 (t, J = 6.3 Hz, 2 H), 3.91 (t, J = 6.3 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 1.37, 2.46, 2.90, 42.49, 63.97, 157.26, 172.62; EIMS (20 eV) m/z 272 (M$^+$). Anal. Calcd for C$_{12}$H$_{28}$OSi$_3$: C, 52.87; H, 10.35. Found: C, 52.60; H, 10.56.

Synthesis of 9 by Intramolecular Bis-silylation. A toluene solution (1.2 mL) of 5-(pentamethyldisilyloxy)-2-pentyne (137 mg, 0.64 mmol), palladium(II) acetate (1.4 mg, 0.0062 mmol), and 1,1,3,3-tetramethylbutyl iso-cyanide (13 mg, 0.093 mmol) was heated at reflux for 1 h under nitrogen. Kugelrohr distillation [140-150 °C (10 mmHg)] of the reaction mixture afforded **9** (128 mg, 93%): IR (neat) 2968, 1252, 1066 cm^{-1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.11 (s, 9 H), 0.30 (s, 6 H), 1.81 (t, J = 1.3 Hz, 3 H), 2.55 (t q, J = 6.6 and 1.3 Hz, 2 H), 3.96 (t, J = 6.6 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ -0.21, 0.86, 20.71, 35.77, 64.28, 148.45, 150.67; MS (EI, 20 eV) m/z 214 (M$^+$). Anal. Calcd for C$_{10}$H$_{22}$OSi$_2$: C, 56.01; H, 10.34. Found: C, 56.21; H, 10.57.

Synthesis of Homoallylic Alcohol 10. To a THF solution (1 mL) of **8** (67 mg, 0.25 mmol) was added a hexane solution of n-butyllithium (0.49 mmol) at -78 °C under nitrogen. The temperature of the mixture was allowed to rise to room temperature over 12 h, and then 1 N aqueous HCl (1 mL) was added. Extraction with ether and preparative TLC of the extract (n-hexane : ether = 9 : 1) afforded **10** (66 mg, 81%): IR (neat) 3324, 2964, 1252, 1040 cm^{-} ^{1}; ^{1}H NMR (200 MHz, CDCl$_3$) δ 0.20 (s, 6 H), 0.21 (s, 9 H), 0.24 (s, 9 H), 0.65-0.74 (m, 2 H), 0.89 (t, J = 6.6 Hz, 3 H), 1.26-1.43 (m, 4 H), 2.87 (t, J = 6.8 Hz, 2 H), 3.62 (t, J = 6.8 Hz, 2 H); ^{13}C NMR (50 MHz, CDCl$_3$) δ 0.33, 3.50, 3.72, 13.64, 17.67, 26.21, 26.48, 46.78, 62.24, 167.99, 174.64. HREIMS

(20 eV). Calcd for $C_{16}H_{38}OSi_3$: 330.2231. Found: 330.2221.

Epoxidation of 9. To a dichloromethane solution (1 mL) of *m*-chloroperbenzoic acid (45 mg, 0.26 mmol) was added **9** (47 mg, 0.22 mmol) at 0 °C. The mixture was stirred for 45 min,. and was then extracted with ether. Evaporation of solvent from the extract afforded **11** (43 mg, 85%): IR (neat) 2968, 1254, 1064 cm^{-1}; ^{1}H NMR (200 MHz, C_6D_6) δ 0.05 (s, 9 H), 0.31 (s, 3 H), 0.42 (s, 3 H), 1.25 (s, 3 H), 1.57 (d d d, J = 14.1, 4.5, and 2.1 Hz, 1 H), 1.86-2.03 (m, 1 H), 3.88-4.05 (m, 2 H); ^{13}C NMR (50 MHz, C_6D_6) δ -2.02, 1.61, 0.36, 18.55, 36.83, 56.94, 63.42; EIMS (20 eV) *m/z* 230 (M$^+$). Anal. Calcd for $C_{10}H_{22}O_2Si_2$: C, 52.12; H, 9.62. Found: C, 51.84; H, 9.60.

References and Notes

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(5) The use of tetrakis(triphenylphosphine)palladium(0) and *tert*-octyl isocyanide gave unsatisfactory results. The catalytic species in the bis-silylation reaction thus may be a palladium(0) isocyanide complex, to which otherwise unreactive hexaalkyldisilanes can undergo oxidative addition. In the case of tetrakis(triphenylphosphine)palladium(0),

triphenylphosphine may possibly coordinate to palladium(0) species so strongly as to seriously retard the exchange of ligands.

(6) ^{1}H and ^{13}C NMR indicate that the product (**6**) is a single isomer of unknown regiochemistry.

(7) Bis-silylation of phenylethyne (1 equiv) by **3** afforded Z-2-pentamethyl-disilyl-1-phenyl-1-(trimethylsilyl)ethene (34%) and Z-1-pentamethyl-disilyl-1-phenyl-2-(trimethylsilyl)ethene (29%). The two were separated by HPLC and were identified by a ^{1}H NMR NOE experiment. The regioisomers were transformed to **4a+4c** and **4a+4b** by further reaction with phenylethyne.

Chapter 4

Stereoselective Intramolecular Bis-Silylation of Alkenes Promoted by Palladium–Isocyanide Catalyst Leading to Polyol Synthesis

Abstract

Details of a study on the intramolecular bis-silylation of terminal alkenes promoted by a palladium–*tert*-alkyl isocyanide catalyst are described. With a disilanyl ether derived from a homoallylic alcohol, intramolecular regioselective addition of the Si–Si linkage to the C=C bond took place to furnish an *exo*-ring closure product, *i.e.*, 1,2-oxasilolane. The bis-silylation of alkenes having substituents α to the C=C bond gave *trans*-3,4-disubstituted oxasilolanes, while substituents β to the C=C bond favored *cis*-3,5-disubstituted oxasilolanes. The stereoselectivity trends are formulated as arising through a preference for a chair-like transition state over boat-like one. A substituent, either α or β to the C=C bond, prefers the equatorial position in a chair-like transition state. The 1,2-oxasilolanes thus produced stereoselectively were oxidatively converted to the corresponding 1,2,4-triols. The present methodology for the synthesis of 1,2,4-triols was successfully extended to the stereoselective synthesis of 1,2,4,5,7- and 1,2,4,6,7-pentaols through a sequence of the intramolecular bis-silylation. The bis-silylation was also performed with alkenes linked to disilanyl groups through a 3-carbon chain and through an amide linkage. Both 1,2- and 1,3-stereoselections analogous to the ether substrates were observed. Alkenes tethered to disilanyl groups through chains of 2 atoms underwent similar intramolecular bis-silylation. In conclusion, the intramolecular bis-silylation of C=C bonds followed by oxidation constitutes a new synthetic transformation equivalent to the stereoselective dihydroxylation of olefins.

Introduction

The addition of organosilicon compounds to unsaturated organic substrates is a fundamental process in organosilicon chemistry. The utility of the hydrosilation as s synthetic tool has been demonstrated to the extent of a enantioselective reaction.[1] The addition of Si–Si bond across C–C multiple bonds giving 1,2-bis(organosilyl)alkane (or -alkene), that is, the *bis-silylation* is a particularly attractive transformation in that two Si–C bonds are created at once, although less attention has been paid to the bis-silylation than to the hydrosilation. The bis-silylation of C–C triple bonds with disilanes has been achieved by palladium catalyst.[2] In contrast, more difficulties were encountered with C–C double bonds. While the catalytic bis-silylation of ethene using platinum complex was recently reported,[3] the synthetic utilities have been limited.

In chapter 3, the author disclosed results concerning the bis-silylation of carbon–carbon triple bonds catalyzed by palladium(II) acetate–*tert*-alkyl isocyanide.[4] This new catalyst was so highly efficient that less reactive disilanes such as hexamethyldisilane readily underwent the bis-silylation of alkynes. A further investigation of this catalyst system was directed toward the bis-silylation of C–C double bonds. Although the catalyst failed to promote the intermolecular bis-silylation of alkenes, the possibility to carry out *intra*-molecular variant was next examined. Herein the author describes the detail of the study on the stereoselective intramolecular bis-silylation of C–C double bonds which provides new methodology for polyol synthesis.[5]

Results and Discussion

Intramolecular bis-silylation was examined with alkenes tethered to disilanyl groups through chains of 2 and 3 atoms. With alkenes tethered to disilanyl groups by chains of more than 4 atoms, bis-silylation did not occur at
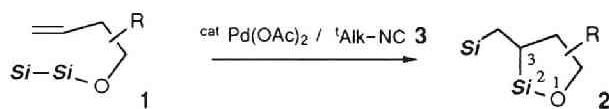
all. Since the intermolecular bis-silylation of alkenes by the present catalyst system was intrinsically unsuccessful, a C=C bond appropriately juxtaposed with a disilanyl group is endowed with an enhanced reactivity toward bis-silylation.(Scheme I)

Scheme I

Intermolecular

$$
\begin{array}{ccc}
Si & & C \\
| & + & || \\
Si & & C
\end{array}
\quad ----//---\!\!\!\rightarrow \quad
\begin{array}{c}
Si-C \\
| \\
Si-C
\end{array}
$$

Intramolecular

n = 2 or 3

$$
\begin{array}{cc}
Si & C \\
| & || \\
Si & C \\
\multicolumn{2}{c}{\underset{n}{(X)}}
\end{array}
\quad \Longrightarrow \quad
\begin{array}{c}
Si-C \\
| \\
Si-C \\
\underset{n}{(X)}
\end{array}
$$

Intramolecular Bis-silylation of Alkenes Tethered to a Disilanyl Group by a Chain of 3 Atoms Through Ether Linkage 1. Disilanyl alkenes **1** were prepared in good yield by the reaction of homoallylic alcohols with chlorodisilanes in the presence of an amine. The bis-silylation reaction of **1** was carried out in the presence of a catalytic amount of palladium(II) acetate (0.01–0.05 equiv) and *tert*-alkyl isocyanide **3** (0.15–0.75 equiv) in toluene under the conditions specified in Table I. Intramolecular regioselective addition of the Si–Si linkage to the C=C bond took place to furnish *exo*-ring closure product, *i.e.*, 1,2-oxasilolane **2** in good yield. Tertiary alkyl carbon–silicon bonds were readily formed by the bis-silylation of geminally disubstituted olefins, although heating at 80 °C was required (entries 26, 27). In contrast, vicinally disubstituted olefins were found not to undergo the bis-silylation. Ester and allylic benzyloxy groups did not encumber the desired bis-silylation reaction (entries 10, 11).

Table I. Intramolecular Bis-silylation of C=C Bonds

entry	1	tAlk-NC 3	conditions	product 2	yield, %	cis : trans
1	1a	3b	r.t., 10 h	2a	94	—
2	1b	3a	r.t., 6h	2b	90	7 : 93
3	1c	3a	r.t., 1h	2c	95	7 : 93
4	1c	3a	111°C, 0.5 h	2c	88	10 : 90
5	1c	3b	r.t., 3 h	2c	97	11 : 89
6	1c	3c	r.t., 9 h	2c	77	8 : 92
7	1d	3a	r.t., 2 h	2d	84	3 : 97
8	1d	3b	r.t., 2 h	2d	95	4 : 96
9	1e	3a	35°C, 4 h	2e	90	5 : 95
10	1f	3a	r.t., 12 h	2f	92	3 : 97
11	1g	3a	r.t., 8h	2g	85	1 : >99

Table I. (Continued)
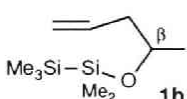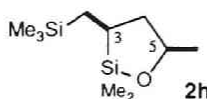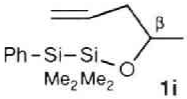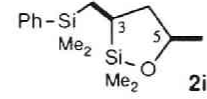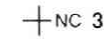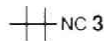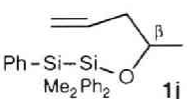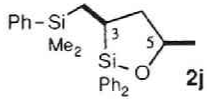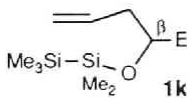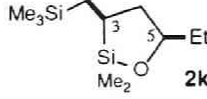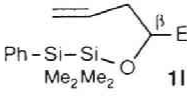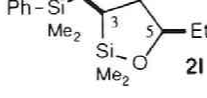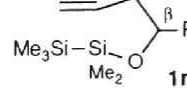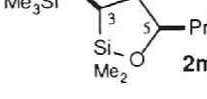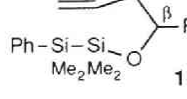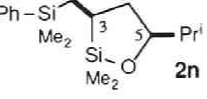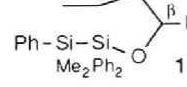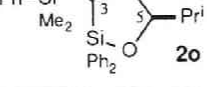
entry	1	¹Alk-NC **3**	conditions	product **2**	yield, %	cis : trans
12	Me₃Si–Si–O / Me₂ / β **1h**	$\times\times$ NC **3a**	35°C, 10 h	Me₃Si ... Si–O / Me₂ **2h**	91	92 : 8
13	Ph–Si–Si–O / Me₂Me₂ / β **1i**	**3a**	r.t., 2 h	Ph–Si / Me₂ / Si–O / Me₂ **2i**	90	93 : 7
14	**1i**	**3a**	111°C, 0.5 h	**2i**	91	90 : 10
15	**1i**	NC **3b**	r.t., 2 h	**2i**	90	90 : 10
16	**1i**	NC **3c**	r.t., 6 h	**2i**	86	92 : 8
17	Ph–Si–Si–O / Me₂Ph₂ / β **1j**	**3b**	r.t., 6 h	Ph–Si / Me₂ / Si–O / Ph₂ **2j**	90	96 : 4
18	Me₃Si–Si–O / Me₂ / β Et **1k**	**3a**	r.t., 8 h	Me₃Si ... Si–O / Me₂ Et **2k**	88	92 : 8
19	Ph–Si–Si–O / Me₂Me₂ / β Et **1l**	**3a**	r.t., 2 h	Ph–Si / Me₂ / Si–O / Me₂ Et **2l**	93	91 : 9
20	Me₃Si–Si–O / Me₂ / β Pr^i **1m**	**3a**	35°C, 10 h	Me₃Si ... Si–O / Me₂ Pr^i **2m**	97	93 : 7
21	Ph–Si–Si–O / Me₂Me₂ / β Pr^i **1n**	**3a**	r.t., 2 h	Ph–Si / Me₂ / Si–O / Me₂ Pr^i **2n**	98	93 : 7
22	Ph–Si–Si–O / Me₂Ph₂ / β Pr^i **1o**	**3a**	r.t., 1 h	Ph–Si / Me₂ / Si–O / Ph₂ Pr^i **2o**	92	96 : 4

Table I. (Continued)

| entry	1	^{t}Alk-NC 3	conditions	product 2	yield, %	cis : trans
23	Me$_3$Si–Si(Me$_2$)–O–...–Bu^t (β) **1p**	**3a**	r.t., 10 h	Me$_3$Si...Si(Me$_2$)O ring, 3,5 positions, –Bu^t **2p**	92	93 : 7
24	Me$_3$Si–Si(Me$_2$)–O–...–Ph (β) **1q**	**3a**	75°C, 6 h	Me$_3$Si...Si(Me$_2$)O ring, 3,5, –Ph **2q**	95	97 : 3
25	Ph–Si–Si(Me$_2$Me$_2$)–O–...(β)–O–Si–Bu^t(Me$_2$) **1r**	**3a**	r.t., 6 h	Ph–Si(Me$_2$)...Si(Me$_2$)O ring, O–Si–Bu^t(Me$_2$) **2r**	96	93 : 7
26	Ph–Si–Si(Me$_2$Me$_2$)–O–... (β) **1s**	**3a**	80°C, 2 h	Ph–Si(Me$_2$)...Si(Me$_2$)O ring **2s**	97	96 : 4
27	Ph–Si–Si(Me$_2$Me$_2$)–O–...(β)–Ph **1t**	**3a**	80°C, 2 h	Ph–Si(Me$_2$)...Si(Me$_2$)O ring, –Ph **2t**	99	96 : 4

It is noteworthy that the bis-silylation of an alkene having an asymmetric center in the tether proceeds with high diastereoselection. Alkenes having substituents in allylic positions, *i.e.*, α to the C=C bond, gave *trans*-3,4-disubstituted **2** (entries 2–11). On the other hand, substituents β to the C=C bond favored *cis*-3,5-disubstituted **2** (entries 12–27). Very similar selectivities in a range of 92 : 8 – 93 : 7 were observed with β-substituents of a variety of bulkiness from methyl to *tert*-butyl groups (entries 12, 18, 20, 23). Geminal disubstitution of the C=C bond improved the selectivity slightly (entries 13, 26). The reaction at refluxing temperature of toluene resulted in only a little decrease in the selectivity (entries 3, 4, 13, 14). Use of THF as solvent gave similar chemical yield and stereoselectivity. Among *tert*-alkyl isocyanides examined, 1,1,3,3-tetramethylbutyl isocyanide (**3a**) was the isocyanide of choice

in terms of the reaction rate and the stereoselectivity (entries 3, 5, 6, 13, 15, 16).

The influence of the silicon substituents on the stereoselectivity was examined; significant difference in the selectivity was not observed among pentamethyldisilanyl, 2-phenyl-1,1,2,2-tetramethyldisilanyl, and 2-(isopropoxy)-1,1,2,2-tetramethyldisilanyl groups, indicating that the stereochemical outcome was not affected by the substituents on the silicon atom distal to the ether oxygen (entries 2, 3, 9). In contrast, the two phenyl groups on the silicon atom proximal to the ether oxygen increased the selectivity slightly (entries 7, 17, 22).[6]

The stereoselectivity trends observed are formulated as arising through a preference for a chair-like transition state **Tc** over boat-like one **Tb**. In a chair-like transition state **Tc**, a substituent, either α or β to the C=C bond, prefers the equatorial position. In consequence, the α-substituent of the C=C bond leads to *trans*-3,4-disubstituted oxasilolane and β-substituent to *cis*-3,5-disubstituted oxasilolane (Scheme II).
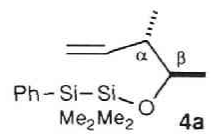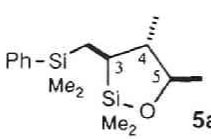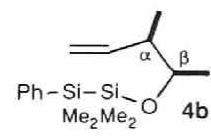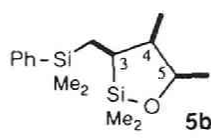
Scheme II

Tc favored   Tb

3,4-*trans*

3,5-*cis*
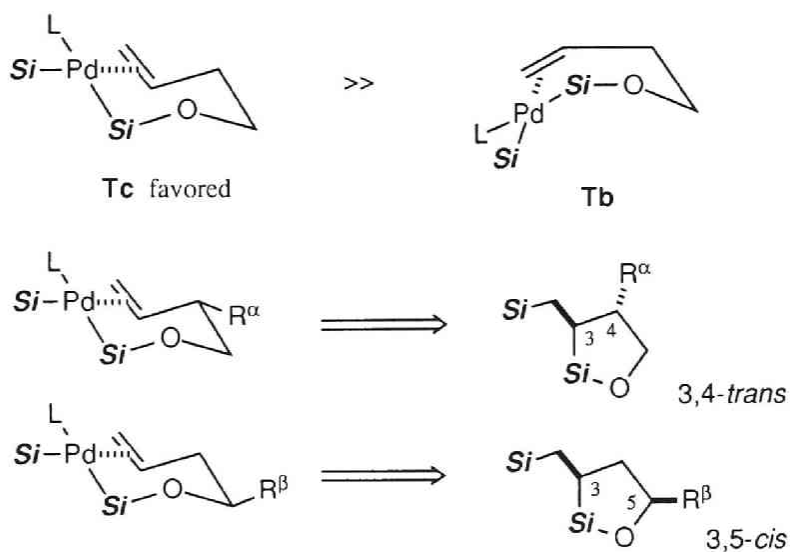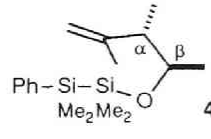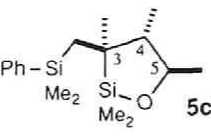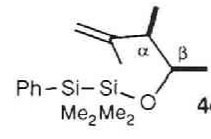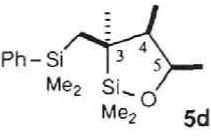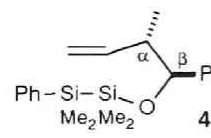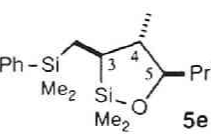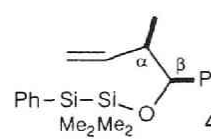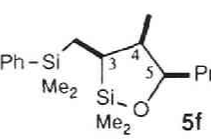
The bis-silylation reaction with a pair of diastereomers **4**, in which two substituents are introduced in the tether, is interesting in terms of stereodifferenciation: In case of one diastereomer (**4a,c,e,g**), both substituents in the tether can occupy equatorial positions in the proposed chair-like transition state, reinforcing the inherent stereochemical preferences. In case of the other diastereomer (**4b,d,f,h**), it is impossible for the two substituents to be equatorial concurrently and, in consequence, the stereochemical preferences of the two substituents are opposing. A series of those substrates were prepared and subjected to the protocol for the bis-silylation mentioned above (Table II). In the reactions of **4a,c,e,g**, the two substituents in the tether both favored (3R^*,4R^*,5R^*)-configuration improving the selectivity. In particular case of **4g**, the C=C bond and the disilanyl group were fixed on a cyclohexane ring by *trans*-1,2-substitution, which would result in a stable conformation of the tether. The fact that complete diastereoselection was attained with **4g** may support the strong preference of chair-like transition state **Tc** over boat-like one **Tb** (entry 7). In the reaction of **4b,d,f,h**, the substituent β to the C=C bond predominantly governed the stereochemistry at the new stereocenter (5-position) favoring (3R^*,4S^*,5R^*)-configuration, although the other substituent α to the C=C bond worked in a cross direction decreasing the selectivity.
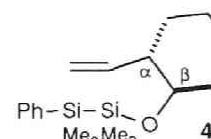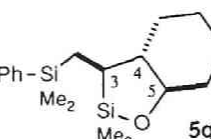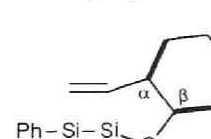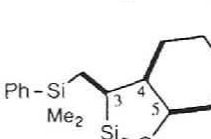
The Palladium Catalyst. Stirring a mixture of palladium(II) acetate and *tert*-alkyl isocyanide resulted in a dramatic change in the color from orange to dark red in a minute probably due to the formation of palladium(0) isocyanide complex. An excess of the isocyanide (*tert*-alkyl isocyanide / Pd(OAc)$_2$ = 6 – 15) was required. Use of less than 6 equiv of isocyanide to Pd(OAc)$_2$ did not bring the reaction to completion. A catalyst prepared from Pd(acac)$_2$ and *tert*-alkyl isocyanide exhibited similar catalytic activity. In the absence of *tert*-alkyl isocyanide, all palladium compounds examined [Pd(OAc)$_2$, Pd(PPh$_3$)$_4$, PdCl$_2$(PPh$_3$)$_2$, Pd(OAc)$_2$ / PPh$_3$ (1 : 2), Pd$_2$(dba)$_3$·CHCl$_3$ / PPh$_3$ (1 : 4), and Pd$_2$(dba)$_3$·CHCl$_3$ / P(OEt)$_3$ (1 : 4)] did not promote the intramolecular bis-silylation at all. Palladium species prepared by mixing Pd(OAc)$_2$ with other

Table II. Intramolecular Bis-silylation of Disubstituted Disilanyl Alkenes **4**

entry	**4**	conditions	product **5**	yield, %	cis : trans[a]
1	**4a**	r t 70 min	**5a**	94	96 : 4
2	**4b**	r t 70 min	**5b**	96	82 : 18
3	**4c**	80 °C 2 h	**5c**	90	99 : 1
4	**4d**	80 °C 2 h	**5d**	90	92 : 8
5	**4e**	r t 2 h	**5e**	93	97 : 3
6	**4f**	r t 3.5 h	**5f**	91	91 : 9
7	**4g**	r t 2 h	**5g**	99	100 : 0
8	**4h**	r t 12 h	**5h**	99	82 : 18

[a] Referring to the stereochemistry of 3,5-substituents of the 1,2-oxasilolane.

isocyanides shown below exhibited no catalytic activity.

$$Ph\underset{H}{\overset{}{-\!\!\!\!|\!\!\!\!-}}NC \qquad Ph\underset{SiMe_3}{\overset{}{-\!\!\!\!|\!\!\!\!-}}NC \qquad \underset{CO_2Me}{\overset{}{-\!\!\!\!|\!\!\!\!-}}NC \qquad R\text{-}\!\!\!\bigcirc\!\!\!\text{-}NC$$

Although the precise mechanism is not clear, we assume that the oxidative insertion of palladium(0) species, initially formed by reduction of palladium(II) acetate with isocyanide,[7] into Si–Si linkage takes place first to give bis(organosilyl)palladium(II) complex.[8] Insertion of the C=C bond into the Pd–Si bond followed by reductive elimination of palladium(0) species would complete the catalytic cycle.

Oxidative Transformations of the 1,2-Oxasilolanes into 1,2,4-Triols.
It has been reported that the oxidative cleavage of a Si–C bond furnishing a hydroxyl group proceeds with retention of configuration at the cleaved carbon atom and that at least one functional group bound to the silicon such as an alkoxy group or a halogen is required for the oxidation.[9] The silicon having phenyl substituents also undergoes the oxidation via prior cleavage of the Ph–Si bond.

The 1,2-oxasilolanes **2** and **5** comprise two Si–C bonds and, in particular, those derived from 2-phenyldisilanyl ethers are possible precursors of 1,2,4-triols because both Si–C bonds fulfill the requirement for the oxidation mentioned above. The Si–Ph bonds were cleaved in the following ways prior to the oxidation by hydrogen peroxide (Table III). For **2c,d,i,j,n,s**, **5a,c,e,g**, and **11**, the cleavage was carried out by treatment with an acid as reported previously.[10] Subsequent treatment with hydrogen peroxide accomplished the oxidative transformation to the corresponding 1,2,4-triols, which were isolated as di- or triacetates **6** in moderate to good yield. When **2t** was reacted with trifluoroacetic acid, intramolecular migration of the phenyl group from the silicon to the benzylic carbon occurred to give 2-methyl-4,4-diphenylbutan-
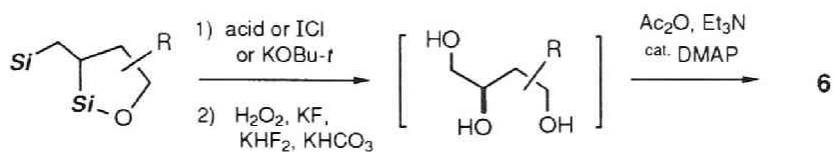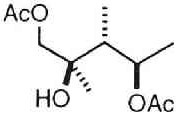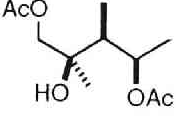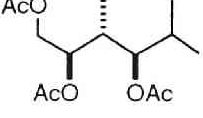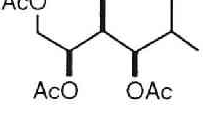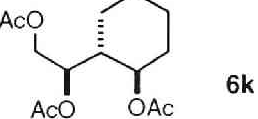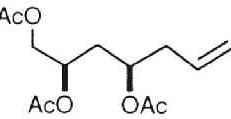
Table III. Oxidation of 1,2-Oxasilolanes into 1,2,4-Triols

entry	oxasilolane	reagent [a]	6	yield, %
1	**2c**	CF_3CO_2H	**6a**	77
2	**2d**	CF_3CO_2H	**6a**	76
3	**2i**	CF_3CO_2H	**6b**	74
4	**2j**	CF_3CO_2H	**6b**	64
5	**2n**	HBF_4	**6c**	81
6	**2s**	CF_3CO_2H	**6d**	82
7	**2t**	ICl	**6e**	67
8	**2t**	$KOBu^t$	**6e**	78
9	**5a**	CF_3CO_2H	**6f**	91

[a] Reagent used for cleavage of Si–Ph bond.

75

Table III. (Continued)

entry	oxasilolane	reagent [a]	6	yield, %
10	**5c**	CF$_3$CO$_2$H	**6g**	90
11	**5d**	KOBu^t	**6h**	78
12	**5e**	CF$_3$CO$_2$H	**6i**	91
13	**5f**	KOBu^t	**6j**	90
14	**5g**	CF$_3$CO$_2$H	**6k**	83
15	**11**	CF$_3$CO$_2$H	**6l**	80

[a] Reagent used for cleavage of Si–Ph bond.

1,2-diol after oxidation.[11] In order to prevent this Friedel-Crafts type reaction, an electrophilic ICl was used instead of an acid for cleavage of the Si–Ph bond (entry 7).[12] The alternative method for cleavage of the Si–Ph bond of the 1,2-oxasilolane has been also devised. Treatment of the 1,2-oxasilolane with potassium *tert*-butoxide in dimethyl sulfoxide (DMSO) successfully cleaved the Si–Ph bond presumably via ring opening reaction (entries 8, 11, 13).[13] For **5d** and **5f**, cleavage with potassium *tert*-butoxide gave much better yield of

1,2,4-triols than with trifluoroacetic acid. Thus, the stereoselective bis-silyla-
tion of C=C bonds followed by oxidation constitutes a new synthetic transfor-
mation equivalent to the stereoselective dihydroxylation of olefins.

Synthesis of Pentaols. The new method for the synthesis of 1,2,4-triols
was extended to the stereoselective synthesis of 1,2,4,6,7-pentaol through a
sequence of the intramolecular bis-silylation procedure (Scheme III). On treat-
ment with palladium(II) acetate–*tert*-alkyl isocyanide, a disilanyl ether **7** de-
rived from 1,6-heptadien-4-ol produced 3,5-*cis*-disubstituted oxasilolane **8** se-
lectively (cis : trans = 93 : 7). The ring opening of **8** with phenyllithium in
ether gave a homoallylic alcohol **9**, which was separated from the minor iso-
mer by HPLC. Introduction of a disilanyl group followed by the second bis-
silylation reaction afforded 3,5-*cis*-disubstituted oxasilolane **11** selectively (cis
: trans = 92 : 8). Finally, oxidative transformation of all C–Si bonds into
C–OH bonds gave rise to 1,2,4,6,7-pentaol, which was isolated as a
pentaacetate **12**.

Scheme III
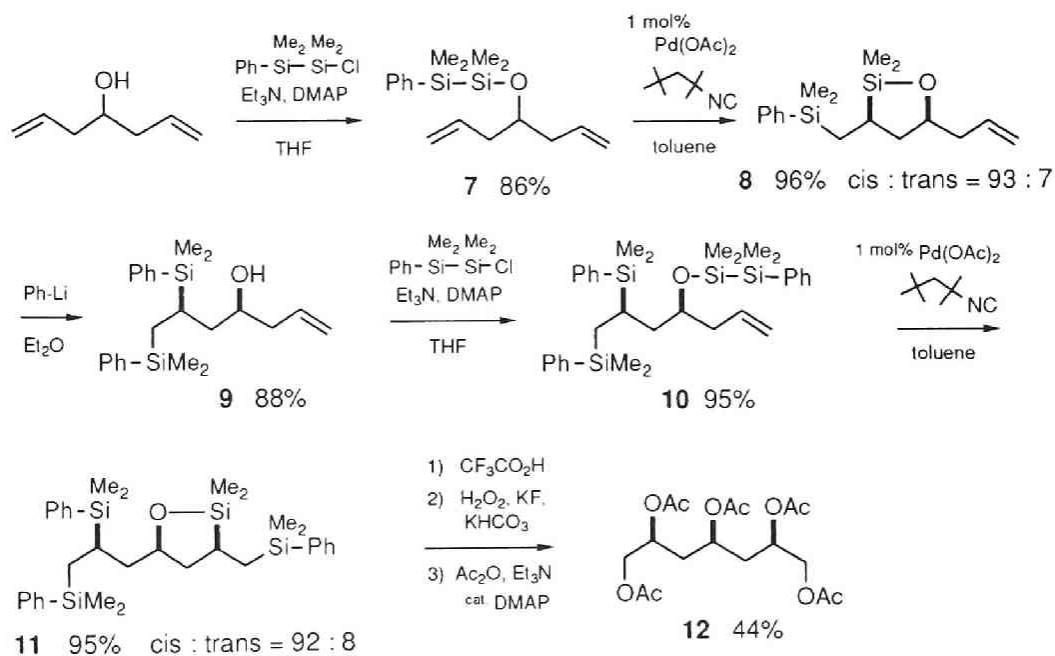
Another example was presented by the synthesis of 1,2,4,5,7-pentaol, which involved elongation of the carbon chain (Scheme IV). A triacetate **6d**, obtained from a homoallylic alcohol via 3,5-*cis*-disubstituted oxasilolane **2o** as mentioned above, was hydrolyzed to the corresponding 1,2,4-triol. After selective protection of the primary hydroxyl group with *tert*-butyldiphenylsilyl chloride, the two secondary hydroxyl groups of **13** were benzylated. The Si–O bond was cleaved by TBAF giving the primary alcohol **14**, which was separated from the minor isomer by HPLC. Swern oxidation of **14** produced α-benzyloxy aldehyde **15**. Notably, allylation of **15** with an allyltin reagent

Scheme IV
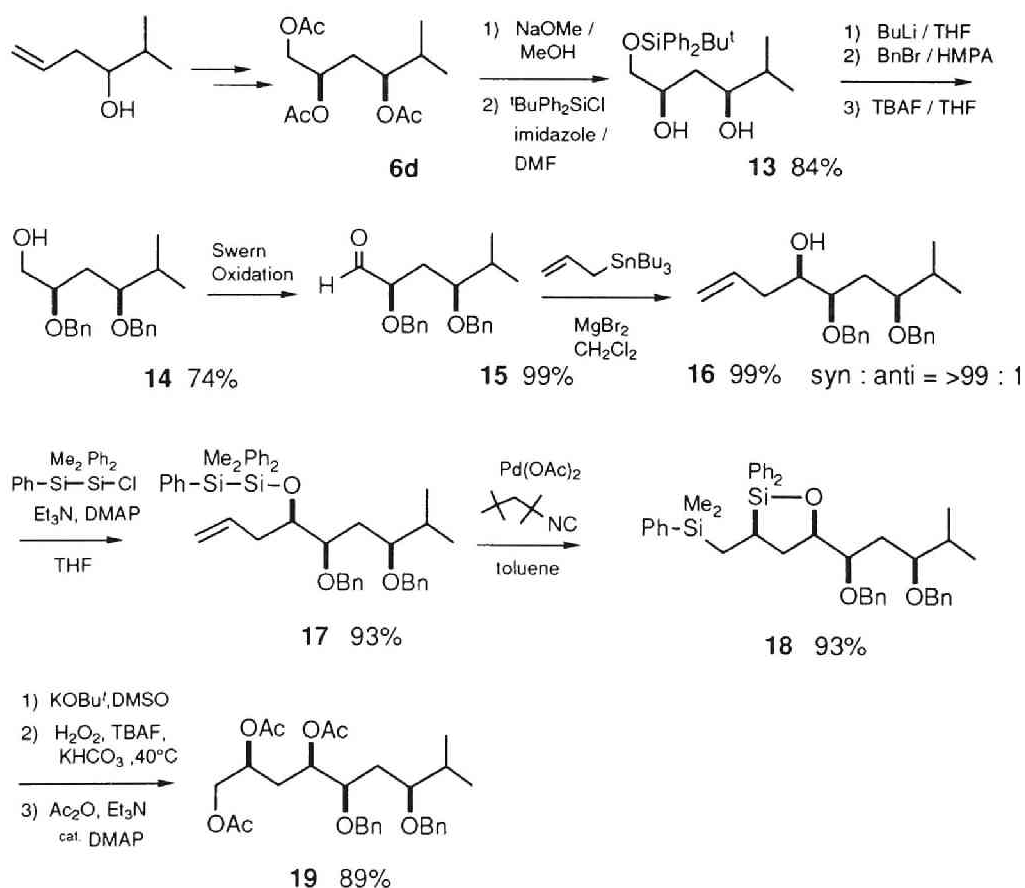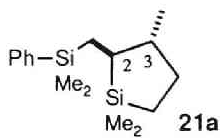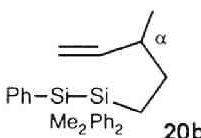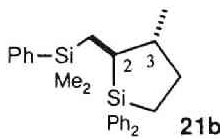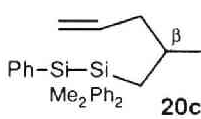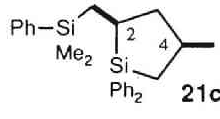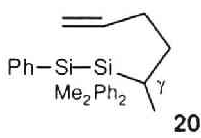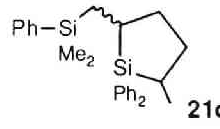
afforded a homoallylic alcohol **16** as a single stereoisomer in 91% yield. This selectivity was accounted for by the chelation model.[14] Introduction of a disilanyl group and the subsequent intramolecular bis-silylation gave 3,5-*cis*-disubstituted oxasilolane **18** selectively. The following oxidative transformation of C–Si bonds into C–OH bonds furnished 1,2,4,5,7-pentaol derivative **19**. In the course of the transformation from **6d** to **19**, an elongation of the skeleton by 3 carbon chain as well as a stereoselective intro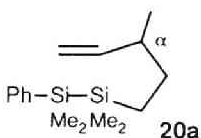duction of two hydroxyl groups has been achieved. The repetition of this sequence would provide an access to stereoselective construction of highly polyoxygenated skeleton.

Intramolecular Bis-silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Three Carbon Atoms 20. In the bis-silylation of C–C multiple bonds reported so far,[2,3] disilanes bearing electron withdrawing substituents such as fluoro and alkoxy groups gave much better yield of bis-silylated products than ordinary hexaalkyldisilane. In contrast, the present intramolecular bis-silylation promoted by a palladium–*tert*-alkyl isocyanide catalyst requires no electron withdrawing group on the silicon atom and, hence, the bis-silylation was successfully performed with an alkene linked to a disilanyl group through a 3 carbon chain. Such a disilanyl alkene **20** was prepared by the reaction of an olefinic Grignard reagent with a chlorodisilane in THF. The intramolecular bis-silylation of **20** led to the formation of silolane **21** (Table IV). Both 1,2- and 1,3-stereoselections analogous to the ether substrates **1** were observed; alkenes having substituents α to the C=C bond gave *trans*-2,3-disubstituted silolane (entries 1, 2), while a substituent β to the C=C bond led to *cis*-2,4-disubstituted silolane **21c** (entry 3). However, poor selectivity was obtained with a disilanyl alkene **20d** possessing a substituent γ to the C=C bond, the reason being unclear so far (entry 4). The two phenyl groups on the silicon atom proximal to the C=C bond improved the selectivity analogously to the ether substrates **1** (entries 1, 2).

Oxidative elaboration of the silolanes **21b** and **21c** furnished the corresponding 1,2,5-triols **22** (Scheme V).

Table IV. Intramolecular Bis-silylation of Alkenes Tethered to Disilanyl Group through Chains of 3 Carbon Atoms **20**

entry	**20**	conditions	product **21**	yield, %	cis : trans
1	**20a**	50 °C 2 h	**21a**	87	14 : 86
2	**20b**	30 °C 4 h	**21b**	99	1 : >99
3	**20c**	r t 1 h	**21c**	92	96 : 4
4	**20d**	40 °C 2 h	**21d**	89	40 : 60 [a]

[a] The assignment of the stereochemistry is tentative.

Scheme V
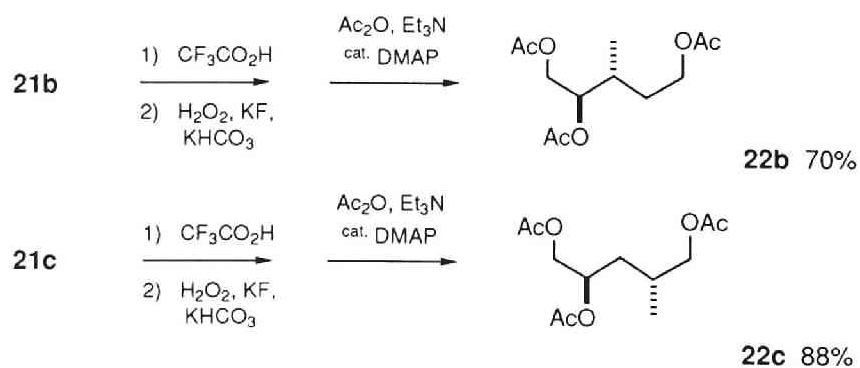
Intramolecular Bis-silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Three Atoms Through Amide Linkage 23. The present method for the polyol synthesis was next applied to the synthesis of amino diols. Disilanyl amides **23** were readily prepared by the reaction of primary homoallylic amines with 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane in the presence of triethylamine, and Kugelrohr distillation allowed their isolation.[15] The intramolecular bis-silylation of the disilanyl amide **23** also took place on treatment with a palladium–*tert*-alkyl isocyanide catalyst. After removal of the catalyst by filtration, the crude cyclic silyl amide **24** was subjected to the oxidation procedure without purification since the silyl amide linkage is generally unstable. 4-Amino-1,2-diol triacetates **25** were produced and their stereoselectivity trends were analogous to that observed with disilanyl alkenes **1** and **20**. Protection of the remaining amide hydrogen of **23** with a trimethylsilyl group resulted in a loss of stereoselectivity in the bis-silylation reaction,

Scheme VI

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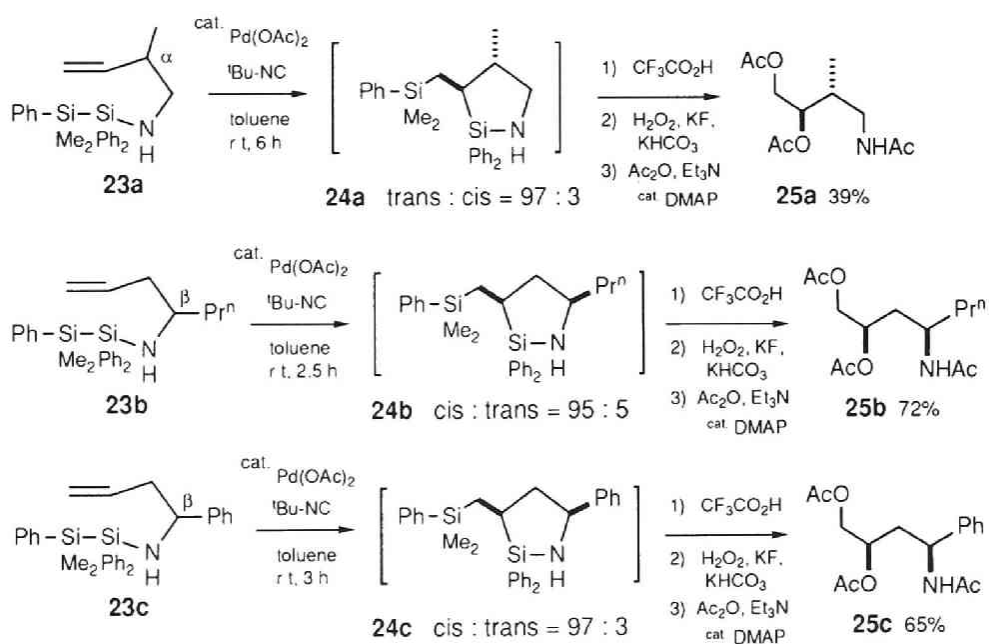
which might be in line with the poor selectivity observed with the disilanyl alkene **20d** bearing a γ-substituent (Scheme VI).

Intramolecular Bis-silylation of Alkenes Tethered to a Disilanyl Group by a Chain of Two Atoms 26. Next, the bis-silylation of alkenes tethered to disilanyl groups through chains of 2 atoms **26** was examined. A disilanyl alkene **26a** underwent the intramolecular bis-silylation analogously to alkenes tethered to disilanyl groups through chains of 3 atoms, affording a 4-membered *exo*-ring closure product **27a**. An alkene **26b** having a substituent α to the C=C bond gave *trans*-3,4-disubstituted siletane **27b** predominantly. A substituent β to the C=C bond favored *cis*-2,4-disubstituted siletane **27c**. Although the bis-silylation took place also with the disilanyl ethers **26d–f**, the products were difficult to isolate. Therefore, the reaction mixture was directly oxidized after removal of the catalyst by filtration, giving the corresponding triol triacetates **28d–f** with moderate stereoselection. On the basis of the formation of the 4-membered siletanes **27a–c** from **26a–c** and the stereochemistry of the oxidized products **28d–f**, it is likely that 4-membered and *trans*-

Scheme VII
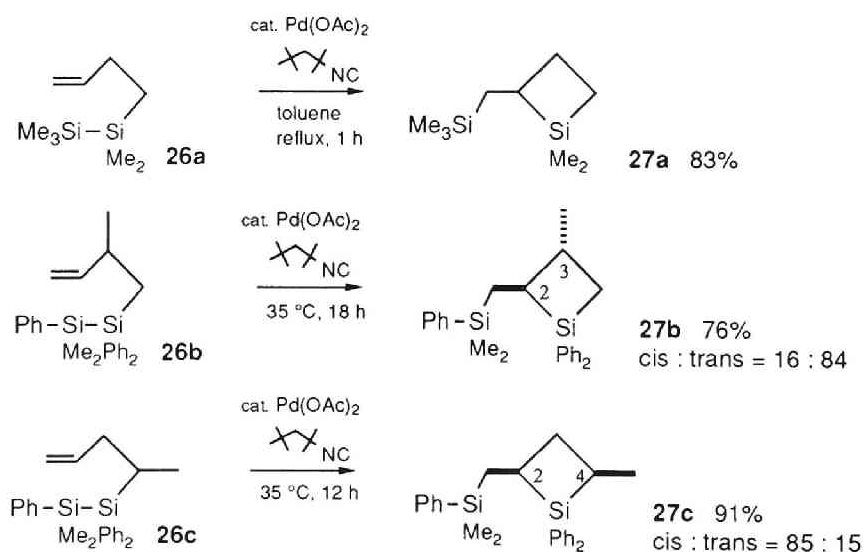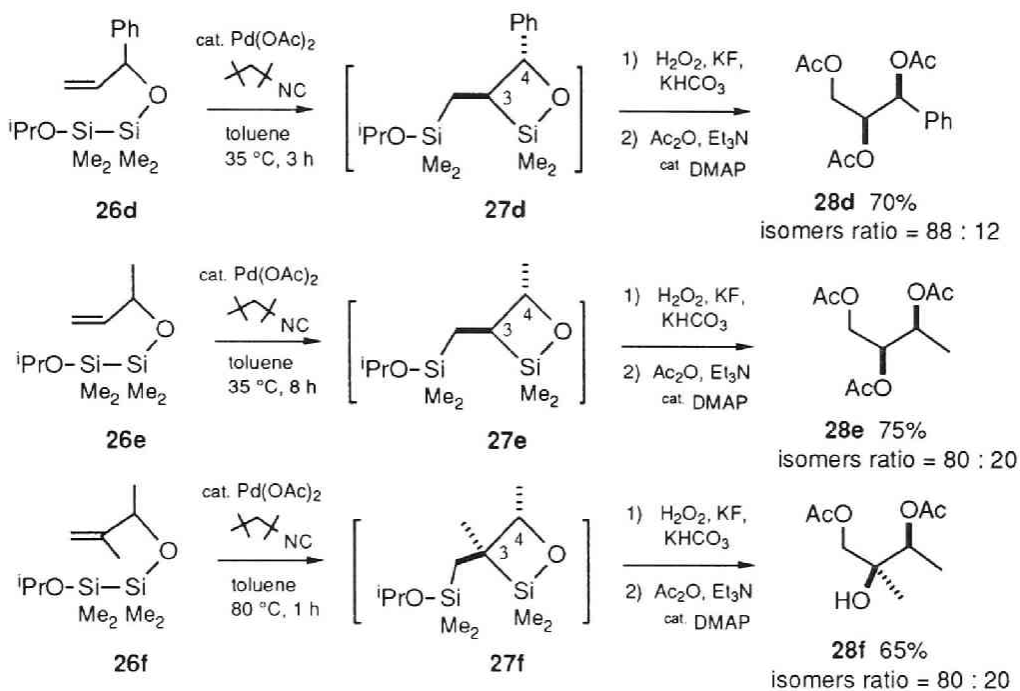
3,4-disubstituted 1,2-oxasiletanes **27d–f** are the primary products (Scheme VII).

Stereochemical Assignments. The stereochemistry of the 1,2-oxasilolanes **2b,f,g,s,t**, **5c**, and **5d** was deduced by NOE experiments, the
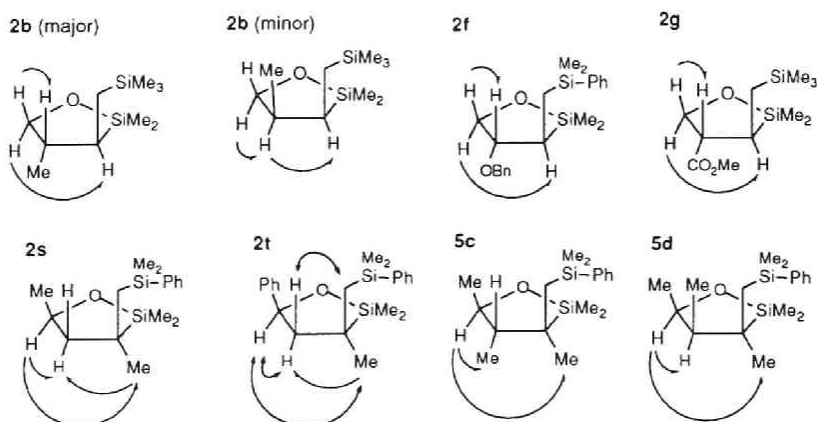
results shown in the chart. For **2b**, NOE experiment was also carried out on the minor isomer to ascertain the assignment.

The 1,2-oxasilolanes **2c–e** were converted to the 1,3-dioxolane **29** through a triol and comparison with the literature data[16] established the stereochemistry of **2c–e** (Scheme VIII).

Scheme VIII
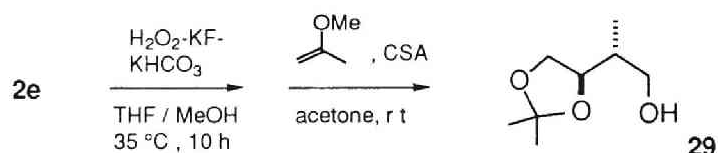
The 1,2-oxasilolanes **2h,m,q**, **5e–h**, **8**, and **11** were converted to 1,3-dioxanes **30** via 1,3-diols formed by partial oxidation of the Si–C bonds of the oxasilolane rings with the Me$_3$Si–C and PhMe$_2$Si–C bonds on the side chains retained. For **30a** obtained from **2q**, NOE experiment together with the coupling constants ($^3J_{H1,H3}$ and $^3J_{H3,H4}$) in ^{1}H NMR clearly showed *cis*-relationship between 4- and 6-substituents (Scheme IX).

Scheme IX
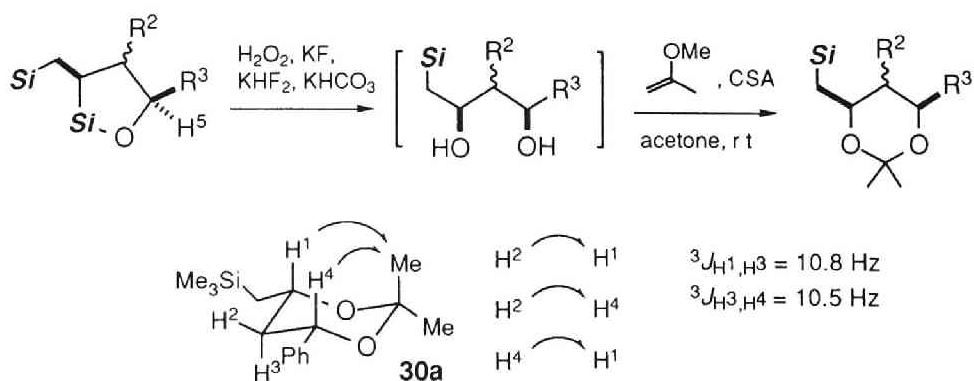
For 4,6-disubstituted 1,3-dioxanes **30b–e**, *cis*-relationships between 4-

and 6-substituents were elucidated according to the ^{13}C NMR chemical shift correlation method reported recently.[17a] The ^{13}C NMR chemical shifts of the three acetonide carbons fall adequately within the distinguished ranges of 4,6-*cis*-disubstitution [δ (ppm): axial acetonide Me = 19.5±0.2; equatorial acetonide Me = 30.1±0.2; ketal carbon = 98.3±0.7]. The stereochemistry of 4,5,6-trisubstituted 1,3-dioxanes **30f–i** was determined in a similar manner[17b] (Table V).

Table V. ^{13}C NMR Chemical Shifts of the Three Acetonide Carbons of **30**

30	1,2-oxa silolane	^{13}C NMR chemical shifts acetonide Me carbons		ketal carbon
30b	**2h**	19.7	30.3	98.2
30c	**2m**	19.7	30.3	98.1
30d	**8**	19.6	30.2	98.4
30e	**11**	19.7	30.1	98.1
30f	**5e**	19.2	30.0	97.6
30g	**5f**	19.5	30.0	98.6
30h	**5g**	19.2	30.0	97.6
30i	**5h**	19.5	30.0	98.9

[a] The parent 1,2-oxasilolane from which **30** was prepared.

Thus, *cis*-relationships between 3- and 5-substituents have been established for 3,5-disubstituted and 3,4,5-trisubstituted 1,2-oxasilolanes (**2h,m,q,**

5e–h, **8**, and **11**). Listed in Table VI are ^{1}H NMR chemical shifts of the proton at 5-position (H^{5}) of those 3,5-*cis*-disubstituted 1,2-oxasilolanes and of the corresponding 3,5-*trans*-disubstituted 1,2-oxasilolanes obtained as minor isomers. Inspection of the chemical shifts in Table VI demonstrates a stereoregular pattern that a 3,5-*cis*-disubstituted 1,2-oxasilolane resonates at higher field than its *trans*-isomer. Application of this correlation to 1,2-oxasilolanes **2i–l,n–p,r**, **5a**, and **5b** revealed that all the major isomers have *cis*-relationships between 3- and 5-substituents without an exception.

Table VI. ^{1}H NMR Chemical Shifts of H^{5} of 1,2-Oxasilolanes

1,2-oxa-silolane	^{1}H NMR chemical shifts(δ)	
	cis-isomer	*trans*-isomer
2h	3.81-4.00	4.10-4.27
2m	3.48-3.60	3.64-3.80
2q	4.83	5.10
8	3.72-3.88	3.97-4.12
11	3.34-3.56	3.61-3.86
5e	3.24	3.35
5f	3.14	3.42
5g	3.16	–
5h	3.84-3.93	3.95-4.04

Reduction of a γ-lactone **31**[18] afforded the (2R*,3S*)-isomer of **22b**. Similarly, an authentic sample of **22c** was prepared from γ-lactone **32**. Comparison of **22b** and **22c** with those samples established the stereochemistry of the parent silolanes **21b** and **21c** (Scheme X).

Scheme X
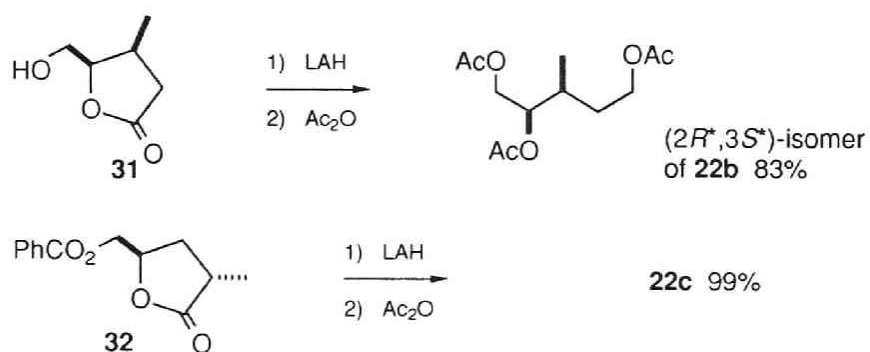
The 4-amino-1,2-diol triacetate **25a** was found to be identical with an authentic sample synthesized from 1,2-oxasilolane **2d** via a route shown in Scheme XI. The stereochemistry of the 4-amino-1,2-diol triacetate **25c** was elucidated by coupling constants in ¹H NMR of a cyclic carbamate **33** derived from the cyclic amide **24c**.

Scheme XI

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33 26% from **24c**

$$^3J_{H1,H2} = 2.0 \text{ Hz}, \quad ^3J_{H1,H3} = 11.0 \text{ Hz}$$
$$^3J_{H2,H4} = 4.6 \text{ Hz}, \quad ^3J_{H3,H4} = 11.0 \text{ Hz}$$
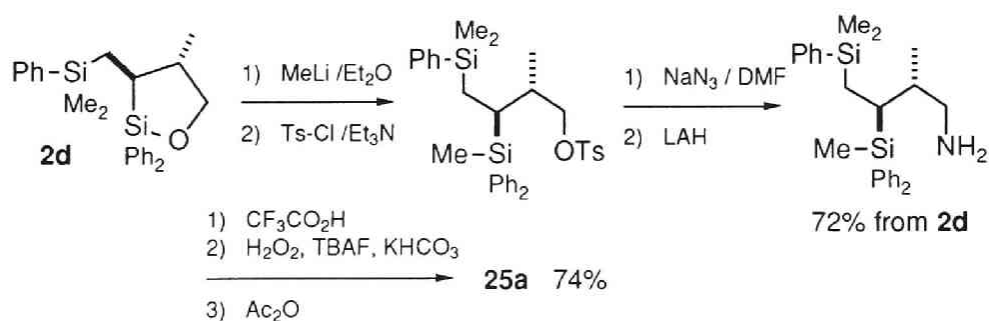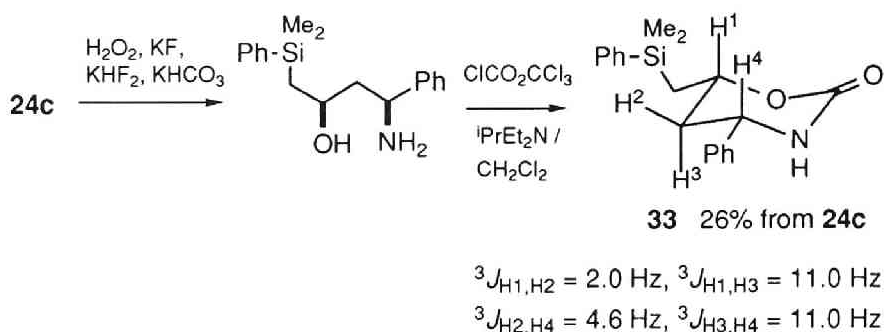
Oxidation of the siletanes **27b** and **27c** with alkaline hydrogen peroxide led to a facile cleavage of strained 4-membered rings to afford diols **34b** and **34c**, which have the same configuration with those obtained by partial oxidation of **2d** and **2j**, respectively (Scheme XII). The stereochemistry of 1,2,3-triol triacetates **28d–f** was determined by comparison with samples prepared by OsO_4-catalyzed *cis*-dihydroxylation of allylic alcohol derivatives.

Scheme XII
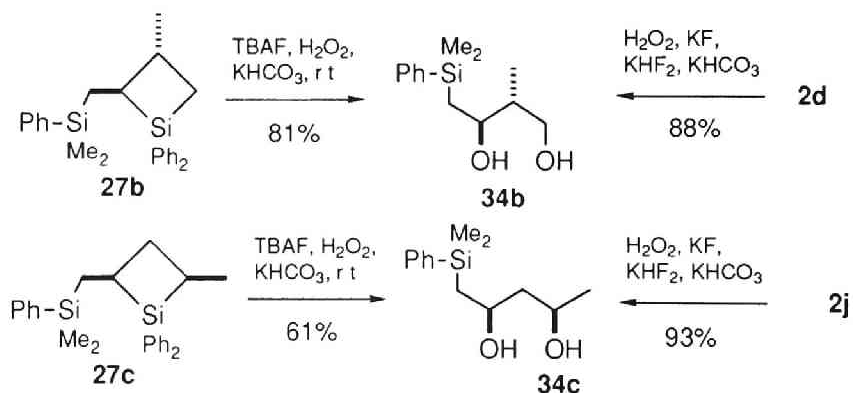
Conclusion

The diastereoselective introduction of silicons into a carbon framework was accomplished in predictable manner by the intramolecular bis-silylation of C=C bonds. The subsequent oxidation of C–Si bonds constitutes a new synthetic transformation equivalent to the stereoselective dihydroxylation of olefins. The present method would provide a new access to the stereoselective construction of a highly polyoxygenated skeleton.

Experimental Section

General. Column chromatography was performed with silica gel 60 (E. Merck, Darmstadt), 230–400 mesh. Preparative thin-layer chromatography (TLC) was performed with silica gel 60 PF_{254} (E. Merck, Darmstadt). ^{1}H and ^{13}C NMR spectra were acquired in chloroform-d. Carbon chemical shifts were recorded relative to chloroform-d (δ 77.0). Where appropriate, NMR data only for the major stereoisomer were described. K_2CO_3 was used to dry organic layers after extraction. All reactions were performed under dry nitrogen atmosphere.

Unless otherwise noted, materials were obtained from commercial sources. THF was distilled from $LiAlH_4$, and HMPA from CaH_2. 1,1,2,2-Tetramethylpropyl isocyanide (**3c**) was prepared according to the procedure in literature.[19]

Preparation of Disilanyl Ethers 1 and 7. The following describes the general procedure for the synthesis of disilanyl ethers **1** and **7** except **1d,e,j,o**. To a mixture of a homoallylic alcohol (4.3 mmol), Et_3N (6.4 mmol), and a catalytic amount of 4-(dimethylamino)pyridine in THF (10 mL) was added chlorodisilane (4.3 mmol) at rt. The reaction was monitored by GC and/or TLC and, after completion, hexane (10 mL) was added to the mixture, which

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was filtered to remove salts. Kugelrohr distillation or column chromatography (silica gel) of the filtrate afforded a disilanyl ether.

Disilanyl alkenes **1d,j,o** were prepared according to the following procedure. To a mixture of a homoallylic alcohol (5.7 mmol) and 1-chloro-2,2-dimethyl-1,1,2-triphenyldisilane (5.7 mmol) in DMF (3.5 mL) was added imidazole (11.4 mmol), which was stirred at rt. After completion, the mixture was purified by column chromatography to afford **1**.

Disilanyl alkene **1e** was prepared according to the following procedure. To a mixture of 1,2-dichlorotetramethyldisilane (2.0 g, 10.7 mmol), Et$_3$N (2.2 g, 22 mmol) and THF (15 ml) at -10°C was slowly added isopropyl alcohol (0.64 g, 10.7 mmol) in THF (5 ml). The mixture was stirred at -10°C for 4.5 h, then 2-methyl-3-butene-1-ol (0.92 g, 10.7 mmol) was added. The mixture was stirred for 1.5 h, and insoluble salt was filtered off. Evapolation and distillation afforded crude product (2.6 g, 80 % pure by GC). Pure **1e** was obtained by purification with preparative GC.

3-[(Dimethylphenylsilyl)methyl]-2,2-dimethyl-1,2-oxasilolane (2a). To a mixture of palladium(II) acetate (25 mg, 0.11 mmol) and *tert*-butyl isocyanide (142 mg, 1.71 mmol) in toluene (3.8 mL) was added **1a** (1.50 g, 5.70 mmol). The mixture was stirred at rt for 10 h. Kugelrohr distillation afforded **2a** (1.41 g, 94%) as a colorless liquid: ^{1}H NMR δ 0.06 (s, 3 H), 0.09 (s, 3 H), 0.30 (s, 6 H), 0.76–0.97 (m, 2 H), 1.00–1.15 (m, 1 H), 1.44–1.65 (m, 1 H), 1.93–2.10 (m, 1 H), 3.65 (dt, J = 4.8, 9.5 Hz, 1 H), 3.92 (ddd, J =3.3, 6.3, 9.5 Hz, 1 H), 7.31–7.40 (m, 3 H), 7.48–7.55 (m, 2 H); ^{13}C NMR δ -3.0, -2.6, -2.4, -1.0, 15.6, 19.4, 36.8, 65.9, 127.8, 129.0, 133.6, 139.4; IR (neat) 2968, 1430, 1252, 1114, 1042, 834 cm^{-1}. Anal. Calcd for C$_{14}$H$_{24}$OSi$_2$: C, 63.57; H, 9.14. Found: C, 63.48; H, 9.16.

The following intramolecular bis-silylation reactions producing **2** and **5** were carried out according to the preceding procedure for **2a**. 1,2-Oxasilolanes **2d,j,o** were isolated by column chromatography.

(3R*,4R*)-2,2,4-Trimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane

(2b). ^{1}H NMR δ 0.00 (s, 9 H), 0.12 (s, 3 H), 0.12 (s, 3 H), 0.49–0.60 (m, 2 H), 0.67–0.85 (m, 1 H), 0.94 (d, J = 6.4 Hz, 3 H), 1.61–1.84 (m, 1 H), 3.26 (dd, J = 9.4, 10.4 Hz, 1 H), 3.98 (dd, J = 6.3, 9.4 Hz, 1 H); ^{13}C NMR δ -2.4, -1.2, 0.2, 14.6, 15.5, 28.3, 43.2, 72.7; IR (neat) 2968, 2876, 1252, 1038, 856, 820 cm^{-1}. Anal. Calcd for $C_{10}H_{24}OSi_2$: C, 55.49; H, 11.18. Found: C, 55.61; H, 11.40.

(3R*,4R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,4-trimethyl-1,2-oxasilolane (2c). ^{1}H NMR δ 0.028 (s, 3 H), 0.035 (s, 3 H), 0.30 (s, 3 H), 0.32 (s, 3 H), 0.50 (dt, J = 2.8, 11.3 Hz, 1 H), 0.81 (dd, J = 11.3, 14.7 Hz, 1 H), 0.93 (d, J = 6.5 Hz, 3 H), 1.04 (dd, J = 2,8, 14.7 Hz, 1 H), 1.60–1.88 (m, 1 H), 3.24 (dd, J = 9.4, 10.5 Hz, 1 H), 3.97 (dd, J = 6.2, 9.4 Hz, 1 H), 7.32–7.60 (m, 5 H); ^{13}C NMR δ -2.8, -2.6, -0.5, 13.9, 15.5, 28.1, 43.2, 72.6, 127.8, 129.0, 133.7, 139.0; IR (neat) 2968, 2876, 1430, 1252, 1114, 1036, 838 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.42; H, 9.67.

(3R*,4R*)-3-[(Dimethylphenylsilyl)methyl]-4-methyl-2,2-diphenyl-1,2-oxasilolane (2d). ^{1}H NMR δ 0.16 (s, 3 H), 0.19 (s, 3 H), 0.78–1.08 (m, 2 H), 1.02 (d, J = 6.5 Hz, 3 H), 1.18 (dt, J = 3.5, 10.0 Hz, 1 H), 1.90–2.14 (m, 1 H), 3.53 (dd, J = 9.4, 10.3 Hz, 1 H), 4.28 (dd, J = 6.3, 9.4 Hz, 1 H), 7.26–7.70 (m, 15 H); ^{13}C NMR δ -2.7, -2.2, 13.8, 15.8, 26.6, 43.4, 73.3, 127.7, 127.8, 128.9, 130.0, 130.2, 132.7, 133.6, 134.2, 135.0, 135.5, 139.0; IR (neat) 3076, 2964, 2876, 1592, 1432, 1252, 1118, 1026, 836, 796, 734, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}OSi_2$: C, 74.57; H, 7.51. Found: C, 74.50; H, 7.56.

(3R*,4R*)-3-[(Isopropoxydimethylsilyl)methyl]-2,2,4-trimethyl-1,2-oxasilolane (2e). Pd(OAc)$_2$ (12.9 mg, 0.058 mmol), **3a** (120 mg, 0.86 mmol), toluene (2.3 mL), **1e** (460 mg, 1.8 mmol): ^{1}H NMR δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.14 (s, 3 H), 0.24 (s, 3 H), 0.48–0.56 (m, 2 H), 0.75–0.83 (m, 1 H), 0.93 (d, J = 6.5 Hz, 3 H), 1.13 (d, J = 6.1 Hz, 6 H), 1.58–1.82 (m, 1 H), 3.24 (dd, J = 9.5, 10.5 Hz, 1 H), 3.84–4.04 (m, 2 H); ^{13}C NMR δ -2.4, -1.2, -1.1, -0.2, 15.2, 15.4, 25.8, 27.6, 43.0, 64.9, 72.7; IR (neat) 2974, 2880, 1252, 1126,

1038, 838, 782 cm^{-1}. Anal. Calcd for C$_{12}$H$_{28}$O$_2$Si$_2$: C, 55.32; H, 10.83. Found: C, 55.33; H, 11.06.

(3R*,4R*)-4-(Benzyloxy)-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2f). ^{1}H NMR δ 0.05 (s, 3 H), 0.12 (s, 3 H), 0.297 (s, 3 H), 0.300 (s, 3 H), 0.83 (dd, J = 9.8, 14.8 Hz, 1 H), 0.97 (dd, J = 4.9, 14.8 Hz, 1 H), 1.26 (ddd, J = 4.9, 6.5, 9.8 Hz, 1 H), 3.60 (ddd, J = 4.4, 5.6, 6.5 Hz, 1 H), 3.69 (dd, J = 5.6, 9.9 Hz, 1 H), 3.98 (dd, J = 4.4, 9.9 Hz, 1 H), 4.46 (s, 2 H), 7.27–7.40 (m, 8 H), 7.48–7.53 (m, 2 H); ^{13}C NMR δ -2.8, -2.7, -2.4, 0.0, 13.3, 25.8, 68.4, 71.3, 86.0, 127.4, 127.8, 128.17, 128.24, 129.0, 133.6, 138.6, 138.9; IR (neat) 2964, 2872, 1252, 1114, 1046, 836, 732, 700 cm^{-1}. Anal. Calcd for C$_{21}$H$_{30}$O$_2$Si$_2$: C, 68.05; H, 8.16. Found: C, 67.78; H, 8.39.

(3R*,4R*)-4-(Methoxycarbonyl)-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2g). ^{1}H NMR δ -0.01 (s, 9 H), 0.15 (s, 3 H), 0.29, (s, 3 H), 0.65 (dd, J = 11.6, 14.7 Hz, 1 H), 0.78 (dd, J = 3.3, 14.7 Hz, 1 H), 1.41 (ddd, J = 3.3, 11.1, 11.6 Hz, 1 H), 2.69 (ddd, J = 6.9, 10.5, 11.1 Hz, 1 H), 3.69 (s, 3 H), 3.74 (dd, J = 9.4, 10.5 Hz, 1 H), 4.12 (dd, J = 6.9, 9.4 Hz, 1 H); ^{13}C NMR δ -2.4, -1.3, -0.5, 15.6, 24.8, 51.7, 54.1, 67.4, 174.2; IR (neat) 2964, 2900, 1740, 1254, 1198, 1040, 858 cm^{-1}. Anal. Calcd for C$_{11}$H$_{24}$O$_3$Si$_2$: C, 50.72; H, 9.29. Found: C, 50.55; H, 9.51.

(3R*,5R*)-2,2,5-Trimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2h). ^{1}H NMR δ 0.01 (s, 9 H), 0.10 (s, 3 H), 0.20 (s, 3 H), 0.51–0.76 (m, 2 H), 1.07–1.20 (m, 2 H), 1.23 (d, J = 6.0 Hz, 3 H), 1.99–2.23 (m, 1 H), 3.81–4.00 (m, 1 H); ^{13}C NMR δ -2.7, -1.3, -1.0, 16.5, 21.3, 23.3, 45.2, 73.2; IR (neat) 2968, 2864, 1252, 1100, 1048, 940 cm^{-1}; MS m/z 216 (M$^+$). Anal. Calcd for C$_{10}$H$_{24}$OSi$_2$: C, 55.49; H, 11.18. Found: C, 55.46; H, 11.03.

(3R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,5-trimethyl-1,2-oxasilolane (2i). ^{1}H NMR δ 0.06 (s, 3 H), 0.10 (s, 3 H), 0.30 (s, 3 H), 0.31 (s, 3 H), 0.80–1.28 (m, 4 H), 1.23 (d, J = 6.0 Hz, 3 H), 2.00–2.21 (m, 1 H), 3.75–4.00 (m, 1 H), 7.32–7.60 (m, 5 H); ^{13}C NMR δ -2.7, -2.5, -2.2, -0.9, 16.0,

21.3, 23.4, 45.4, 73.1, 127.8, 129.0, 133.6, 139.3; IR (neat) 2968, 2860, 1252, 1116, 940, 824 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.42; H, 9.53.

(3R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-5-methyl-2,2-diphenyl-1,2-oxasilolane (2j). ^{1}H NMR δ 0.31 (s, 3 H). 0.32 (s, 3 H), 0.75 (dd, J = 9.5, 15.2 Hz, 1 H), 1.13 (dd, J = 4.8, 15.2 Hz, 1 H), 1.22–1.42 (m, 1 H), 1.47 (d, J = 6.0 Hz, 3 H), 1.74–1.94 (m, 1 H), 2.31 (ddd, J = 3.7, 7.3, 12.4 Hz, 1 H), 4.06–4.30 (m, 1 H), 7.30–7.80 (m, 15 H); ^{13}C NMR δ -2.5, –2.2, 15.7, 20.2, 23.3, 44.4, 74.2, 127.67, 127.72, 127.9, 128.9, 130.0, 130.2, 133.1, 133.6, 134.4, 134.7, 135.3, 139.3; IR (neat) 3076, 2972, 2864, 1592, 1432, 1250, 1120, 938, 832, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}OSi_2$: C, 74.57; H, 7.51. Found: C, 74.45; H, 7.61.

(3R*,5R*)-5-Ethyl-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2k). ^{1}H NMR δ 0.01 (s, 9 H), 0.10 (s, 3 H), 0.22 (s, 3 H), 0.54–0.77 (m, 2 H), 0.91 (t, J = 7.4 Hz, 3 H), 1.00–1.26 (m, 2 H), 1.37–1.70 (m, 2 H), 2.07–2.20 (m, 1 H), 3.63–3.79 (m, 1H); ^{13}C NMR δ -2.6, -1.0, -0.8, 9.9, 16.8, 20.9, 30.6, 42.5, 78.4; IR (neat) 2968, 1252, 876, 864, 840 cm^{-1}. Anal. Calcd for $C_{11}H_{26}OSi_2$: C, 57.32; H, 11.37. Found: C, 57.05; H, 11.52.

(3R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-5-ethyl-2,2-dimethyl-1,2-oxasilolane (2l). ^{1}H NMR δ 0.04 (s, 3 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.31 (s, 3 H), 0.78–0.97 (m, 5 H), 1.07–1.23 (m, 2 H), 1.31–1.70 (m, 2 H), 2.04–2.17 (m, 1 H), 3.60–3.76 (m, 1 H), 7.30–7.41 (m, 3 H), 7.45–7.56 (m, 2 H); ^{13}C NMR δ -2.7, -2.6, -2.3, -0.9, 9.8, 16.0, 20.8, 30.6, 42.6, 78.3, 127.8, 128.9, 133.6, 139.4; IR (neat) 2968, 1430, 1252, 1116, 878, 832, 780 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.56; H, 9.77.

(3R*,5S*)-5-Isopropyl-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2m). ^{1}H NMR δ 0.00 (s, 9 H), 0.08 (s, 3 H), 0.22 (s, 3 H), 0.52–0.76 (m, 2 H), 0.86 (d, J = 6.7 Hz, 3 H), 0.92 (d, J = 6.7 Hz, 3 H), 1.06–1.30 (m, 2 H), 1.54–1.76 (m, 1 H), 1.98–2.10 (m, 1 H), 3.48–3.60 (m, 1

H); ^{13}C NMR δ -2.7, -1.1, -0.8, 16.7, 17.8, 18.7, 20.9, 34.2, 39.5, 82.1; IR (neat) 2968, 2856, 1252, 1038, 864, 840 cm^{-1}; MS *m/z* 230 (M$^+$). Anal. Calcd for C$_{12}$H$_{28}$Si$_2$O: C, 58.94; H, 11.54. Found: C, 58.75; H, 11.47.

(3*R****,5***S****)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2-dimethyl-1,2-oxasilolane (2n).** ^{1}H NMR δ 0.03 (s, 3 H), 0.09 (s, 3 H), 0.30 (s, 3 H), 0.31 (s, 3 H), 0.84 (d, *J* = 6.7 Hz, 3 H), 0.90 (d, *J* = 6.8 Hz, 3 H), 0.70–1.38 (m, 4 H), 1.50–1.80 (m, 1 H), 1.95–2.09 (m, 1 H), 3.46–3.58 (m, 1 H), 7.32–7.64 (m, 5 H); ^{13}C NMR δ -2.7, -2.3, -0.9, 16.0, 17.8, 18.7, 20.7, 34.1, 39.5, 81.9, 127.8, 128.9, 133.6, 139.4; IR (neat) 2968, 1472, 1430, 1252, 1114, 1038, 834 cm^{-1}. Anal. Calcd for C$_{17}$H$_{30}$OSi$_2$: C, 66.60; H, 9.86. Found: C, 66.50; H, 9.92.

(3*R****,5***S****)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2-diphenyl-1,2-oxasilolane (2o).** ^{1}H NMR δ 0.24 (s, 6 H), 0.71 (dd, *J* = 9.4, 15.1 Hz, 1 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 1.04 (d, *J* = 6.8 Hz, 3 H), 0.90–1.14 (m, 1 H), 1.30 (dt, *J* = 11.1, 12.5 Hz, 1 H), 1.62–1.90 (m, 2 H), 2.19 (ddd, *J* = 3.9, 7.4, 12.5 Hz, 1 H), 3.65 (ddd, *J* = 3.9, 6.9, 11.1 Hz, 1 H), 7.30–7.60 (m, 15 H); ^{13}C NMR δ -2.4, -2.2, 15.9, 18.3, 19.4, 20.1, 34.9, 39.8, 83.3, 127.7, 127.8, 127.9, 128.9, 129.9, 130.1, 133.4, 133.6, 133.9, 134.8, 135.4, 139.5; IR (neat) 3144, 2964, 1592, 1432, 1250, 1120, 1032, 1000, 836, 700 cm^{-1}. Anal. Calcd for C$_{27}$H$_{34}$OSi$_2$: C, 75.29; H, 7.96. Found: C, 75.06; H, 8.05.

(3*R****,5***S****)-5-*tert*-Butyl-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2p).** ^{1}H NMR δ 0.00 (s, 9 H), 0.06 (s, 3 H), 0.23 (s, 3 H), 0.59 (dd, *J* = 7.0, 14.7 Hz, 1 H), 0.70 (dd, *J* = 7.7, 14.7 Hz, 1 H), 0.88 (s, 9 H), 0.97–1.16 (m, 1 H), 1.25 (dt, *J* = 10.9, 12.2 Hz, 1 H), 1.97 (ddd, *J* = 4.2, 7.0, 12.2 Hz, 1 H), 3.48 (dd, *J* = 4.2, 10.9 Hz, 1 H); ^{13}C NMR δ –2.8, -1.0, -0.7, 16.7, 21.1, 25.7, 34.3, 37.5, 84.8; IR (neat) 2964, 1252, 1028, 886, 862, 834 cm^{-1}. Anal. Calcd for C$_{13}$H$_{30}$OSi$_2$: C, 60.39; H, 11.69. Found: C, 60.38; H, 11.75.

(3R*,5S*)-2,2-Dimethyl-5-phenyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2q). ^{1}H NMR δ 0.02 (s, 9 H), 0.24 (s, 3 H), 0.32 (s, 3 H), 0.56–0.81 (m, 2 H), 1.20–1.58 (m, 2 H), 2.33–2.47 (m, 1 H), 4.83 (dd, J = 4.1, 10.6 Hz, 1 H), 7.18–7.37 (m, 5 H); ^{13}C NMR δ -2.7, –1.0, -0.8, 16.4, 21.9, 46.5, 78.7, 125.2, 127.0, 128.2, 144.6; IR (neat) 3040, 2964, 2908, 2860, 1252, 1078, 1040, 864, 840 cm^{-1}. Anal. Calcd for $C_{15}H_{26}OSi_2$: C, 64.68; H, 9.41. Found: C, 64.65; H, 9.59.

(3R*,5S*)-5-[(tert-Butyldimethylsiloxy)methyl]-2,2-dimethyl-3-[(trimethylsilyl)methyl]-1,2-oxasilolane (2r). ^{1}H NMR δ 0.03 (s, 3 H), 0.04 (s, 6 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.84–0.99 (m, 2 H), 0.89 (s, 9 H), 1.01–1.41 (m, 2 H), 2.08 (ddd, J = 4.5, 6.8, 12.2 Hz, 1 H), 3.52 (d, J = 5.4, 10.3 Hz, 1 H), 3.64 (d, J = 4.4, 10.3 Hz, 1 H), 3.71–3.87 (m, 1 H), 7.31–7.40 (m, 3 H), 7.47–7.56 (m, 2 H); ^{13}C NMR δ -5.3, –2.7, -2.3, -1.0, 16.0, 18.4, 20.4, 26.0, 39.4, 67.5, 77.2, 127.8, 129.0, 133.6, 139.3; IR (neat) 2964, 1254, 1114, 1092, 836 cm^{-1}. Anal. Calcd for $C_{21}H_{40}O_2Si_2$: C, 61.70; H, 9.86. Found: C, 61.70; H, 10.04.

(3R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,3,5-tetramethyl-1,2-oxasilolane (2s). ^{1}H NMR δ 0.02 (s, 3 H), 0.09 (s, 3 H), 0.34 (s, 3 H), 0.35 (s, 3 H), 1.00 (d, J = 15.1 Hz, 1 H), 1.05 (s, 3 H), 1.07 (d, J = 15.1 Hz, 1 H), 1.19 (d, J = 6.0 Hz, 3 H), 1.42 (dd, J = 10.9, 12.9 Hz, 1 H), 1.63 (dd, J = 2.2, 10.9 Hz, 1 H), 3.93–4.10 (m, 1 H), 7.32–7.39 (m, 3 H), 7.48–7.58 (m, 2 H); ^{13}C NMR δ -3.6, -1.1, -0.6, 23.2, 23.6, 25.8, 26.2, 53.3, 71.0, 127.8, 128.8, 133.6, 140.2; IR (neat) 2968, 2912, 1252, 1114, 824 cm^{-1}. Anal. Calcd for $C_{16}H_{28}OSi_2$: C, 65.69; H, 9.65. Found: C, 65.49; H, 9.79.

(3R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,3-trimethyl-5-phenyl-1,2-oxasilolane (2t). ^{1}H NMR δ 0.12 (s, 3 H), 0.25 (s, 3 H), 0.37 (s, 3 H), 0.39 (s, 3 H), 0.99–1.44 (m, 2 H), 1.17 (s, 3 H), 1.74 (dd, J = 11.1, 13.2 Hz, 1 H), 1.92 (dd, J = 4.7, 13.2 Hz, 1 H), 4.95 (dd, J = 4.7, 11.1 Hz, 1 H), 7.20–7.65 (m, 10 H); ^{13}C NMR δ -3.7, -1.3, -0.7, -0.6, 23.0, 26.0, 26.2, 54.4, 76.7, 125.2, 126.9, 127.8, 128.2, 128.9, 133.6, 140.0, 144.8; IR (neat) 3076, 2964, 1256,

1114, 1044, 860, 832, 788 cm^{-1}. Anal. Calcd for C$_{21}$H$_{30}$OSi$_2$: C, 71.12; H, 8.53. Found: C, 70.98; H, 8.66.

(3R*,4R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,4,5-tetramethyl-1,2-oxasilolane (5a). ^{1}H NMR δ -0.01 (s, 3 H), 0.01 (s, 3 H), 0.28 (s, 3 H), 0.29 (s, 3 H), 0.55 (dt, J = 2.2, 11.7 Hz, 1 H), 0.79 (dd, J = 11.7, 14.6 Hz, 1 H), 0.94 (d, J = 6.3 Hz, 3 H), 0.99 (dd, J = 2.2, 14.6 Hz, 1 H), 1.22 (d, J = 6.0 Hz, 3 H), 1.11–1.32 (m, 1 H), 3.42 (dq, J = 9.5, 6.0 Hz, 1 H), 7.31–7.40 (m, 3 H), 7.46–7.55 (m, 2 H); ^{13}C NMR δ -2.8, -2.6, -2.3, -0.6, 14.3, 15.7, 21.7, 29.0, 50.4, 78.9, 127.8, 129.0, 133.7, 139.1; IR (neat) 2968, 2872, 1430, 1378, 1252, 1114, 1042, 938, 834 cm^{-1}. Anal. Calcd for C$_{16}$H$_{28}$OSi$_2$: C, 65.69; H, 9.65. Found: C, 65.57; H, 9.84.

(3R*,4S*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,4,5-tetramethyl-1,2-oxasilolane (5b). ^{1}H NMR δ 0.03 (s, 3 H), 0.08 (s, 3 H), 0.29 (s, 3 H), 0.31 (s, 3 H), 0.80 (d, J = 7.1 Hz, 3 H), 0.85–1.02 (m, 2 H), 1.18 (d, J = 6.4 Hz, 3 H), 1.20–1.33 (m, 1 H), 1.93 (d-quintet, J = 3.6, 7.1 Hz, 1 H), 3.93 (dq, J = 3.6, 6.4 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.46–7.56 (m, 2 H); ^{13}C NMR δ 2.8, -2.4, -1.1, -0.1, 9.1, 12.5, 19.8, 27.2, 43.3, 75.9, 127.8, 129.0, 133.6, 139.2; IR (neat) 2976, 2896, 1430, 1380, 1252, 1114, 1010, 930, 830 cm^{-1}. Anal. Calcd for C$_{16}$H$_{28}$OSi$_2$: C, 65.69; H, 9.65. Found: C, 65.58; H, 9.93.

(3R*,4R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,3,4,5-pentamethyl-1,2-oxasilolane (5c). ^{1}H NMR δ -0.05 (s, 3 H), 0.07 (s, 3 H), 0.329 (s, 3 H), 0.335 (s, 3 H), 0.78 (d, J = 6.8 Hz, 3 H), 0.82 (d, J = 15.0 Hz, 1 H), 0.82 (s, 3 H), 1.08 (d, J = 15.0 Hz, 1 H), 1.20 (d, J = 6.0 Hz, 3 H), 1.26–1.42 (m, 1 H), 3.57 (dq, J = 9.9, 6.0 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.47–7.57 (m, 2 H); ^{13}C NMR δ -3.1, -1.1, -0.8, 8.2, 16.9, 22.1, 24.2, 27.3, 53.1, 76.5, 127.8, 128.9, 133.8, 139.9; IR (neat) 2972, 1456, 1430, 1380, 1252, 1116, 1076, 936, 824 cm^{-1}. Anal. Calcd for C$_{17}$H$_{30}$OSi$_2$: C, 66.60; H, 9.86. Found: C, 66.64; H, 9.88.

(3R*,4S*,5R*)-3-[(Dimethylphenylsilyl)methyl]-2,2,3,4,5-pentam-ethyl-1,2-oxasilolane (5d). ^{1}H NMR δ -0.01 (s, 3 H), 0.16 (s, 3 H), 0.357 (s, 3 H), 0.363 (s, 3 H), 0.88 (d, J = 7.3 Hz, 3 H), 1.00–1.12 (m, 2 H), 1.13 (s, 3 H), 1.17 (d, J = 6.4 Hz, 3 H), 1.43 (dq, J = 3.9, 7.3 Hz, 1 H), 4.33 (dq, J = 3.9, 6.4 Hz, 1 H), 7.30–7.40 (m, 3 H), 7.49–7.60 (m, 2 H); ^{13}C NMR δ -2.7, -0.43, 0.38, 0.0, 10.6, 19.6, 22.5, 25.1, 29.5, 50.8, 73.1, 127.8, 128.8, 133.6, 140.4; IR (neat) 2976, 1456, 1430, 1380, 1254, 1114, 1072, 932, 832 cm^{-1}. Anal. Calcd for $C_{17}H_{30}OSi_2$: C, 66.60; H, 9.86. Found: C, 66.43; H, 9.96.

(3R*,4R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2,4-tri-methyl-1,2-oxasilolane (5e). ^{1}H NMR δ -0.02 (s, 3 H), 0.00 (s, 3 H), 0.28 (s, 3 H), 0.29 (s, 3 H), 0.54 (dt, J = 2.2, 11.4 Hz, 1 H), 0.79 (d, J = 6.8 Hz, 3 H), 0.86 (d, J = 6.4 Hz, 3 H), 0.99 (d, J = 7.0 Hz, 3 H), 0.71–1.09 (m, 2 H), 1.32–1.56 (m, 1 H), 1.64–1.82 (m, 1 H), 3.24 (dd, J = 2.0, 9.6 Hz, 1 H), 7.32–7.40 (m, 3 H), 7.42–7.58 (m, 2 H); ^{13}C NMR δ -2.8, -2.5, -0.5, 14.2, 14.7, 16.3, 21.0, 28.9, 30.1, 44.5, 87.3, 127.8, 129.0, 133.7, 139.2; IR (neat) 2968, 2892, 1472, 1430, 1386, 1252, 1114, 1006, 834 cm^{-1}. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.13; H, 10.09.

(3R*,4S*,5R*)-3-[(Dimethylphenylsilyl)methyl]-5-isopropyl-2,2,4-tri-methyl-1,2-oxasilolane (5f). ^{1}H NMR δ 0.03 (s, 3 H), 0.08 (s, 3 H), 0.29 (s, 3 H), 0.31 (s, 3 H), 0.71–1.04 (m, 2 H), 0.77 (d, J = 7.1 Hz, 3 H), 0.79 (d, J = 6.7 Hz, 3 H), 0.99 (d, J = 6.5 Hz, 3 H), 1.21 (dt, J = 8.8, 6.6 Hz, 1 H), 1.52–1.79 (m, 1 H), 2.04 (ddq, J = 2.9, 6.6, 6.7 Hz, 1 H), 3.14 (dd, J = 2.9, 9.6 Hz, 1 H), 7.28–7.42 (m, 3 H), 7.43–7.60 (m, 2 H); ^{13}C NMR δ -2.8, -2.3, -1.0, 0.1, 8.7, 12.7, 18.5, 21.9, 27.5, 30.8, 40.7, 86.4, 127.8, 129.0, 133.7, 139.4; IR (neat) 2968, 2900, 1472, 1430, 1382, 1252, 1116, 988, 832 cm^{-1}. Anal. Calcd for $C_{18}H_{32}OSi_2$: C, 67.43; H, 10.06. Found: C, 67.20; H, 10.27.

(1R*,6R*,9R*)-9-[(Dimethylphenylsilyl)methyl]-8,8-dimethyl-7-oxa-8-silabicyclo[4.3.0]nonane (5g). ^{1}H NMR δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.28 (s, 3 H), 0.29 (s, 3 H), 0.54–0.91 (m, 3 H), 0.96–1.38 (m, 5 H), 1.65–1.85 (m,

2 H), 1.97–2.12 (m, 2 H), 3.16 (dt, J = 4.0, 10.2 Hz, 1 H), 7.31–7.41 (m, 3 H), 7.45–7.55 (m, 2 H); ^{13}C NMR δ -2.8, -2.7, -2.6, -0.6, 13.2, 24.8, 26.1, 26.7, 29.4, 34.4, 54.0, 80.7, 127.8, 129.0, 133.7, 139.1; IR (neat) 2940, 2864, 1450, 1430, 1252, 1114, 1016, 836 cm^{-1}. Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.63; H, 9.74.

(1S*,6R*,9R*)-9-[(Dimethylphenylsilyl)methyl]-8,8-dimethyl-7-oxa-8-silabicyclo[4.3.0]nonane (5h).

^{1}H NMR δ 0.05 (s, 3 H), 0.12 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.82–2.10 (m, 12 H), 3.84–3.93 (m, 1 H), 7.31–7.45 (m, 3 H), 7.45–7.60 (m, 2 H); ^{13}C NMR δ -2.8, -2.4, -1.2, 0.1, 11.4, 20.0, 24.3, 25.5, 27.6, 31.3, 44.8, 75.5, 127.8, 129.0, 133.6, 139.3; IR (neat) 2940, 2864, 1450, 1430, 1252, 1114, 974, 834 cm^{-1}. Anal. Calcd for $C_{18}H_{30}OSi_2$: C, 67.86; H, 9.49. Found: C, 67.75; H, 9.76.

(2R*,3R*)-3-Methylbutan-1,2,4-triol Triacetate (6a).

A mixture of **2c** (112 mg, 0.40 mmol) and trifluoroacetic acid (917 mg, 8.0 mmol) was stirred at 50 °C for 2.5 h. After removal of trifluoroacetic acid under reduced pressure, KHF$_2$ (125 mg, 1.6 mmol), MeOH (0.7 mL), KF (47 mg, 0.80 mmol), THF (0.7 mL), H$_2$O$_2$ (30% in water, 0.48 mL), and KHCO$_3$ (322 mg, 3.2 mmol) were added, and the mixture was stirred at 40 °C for 4 h. Excess Na$_2$S$_2$O$_3$ was added and abolition of H$_2$O$_2$ was ascertained by test paper. After evaporation of volatiles, THF (2 mL), Et$_3$N (609 mg, 6.0 mmol), acetic anhydride (410 mg, 4.0 mmol), and a catalytic amount of 4-(dimethylamino)pyridine were added and the mixture was stirred for 10 h. Column chromatography (hexane : ether = 2 : 1 – 1 : 1) afforded **6a** (76 mg, 77%).

The following oxidative transformations producing **6b,d,f,g,i,k,** and **l** were carried out according to the preceding procedure for **6a**.

(2R*,4R*)-Pentan-1,2,4-triol Triacetate (6b).

^{1}H NMR δ 1.25 (d, J = 6.3 Hz, 3 H), 1.77 (dt, J = 5.8, 14.4 Hz, 1 H), 1.88–2.04 (m, 1 H), 2.03 (s, 3 H), 2.06 (s, 6 H), 4.02 (dd, J = 6.1, 12.0 Hz, 1 H), 4.27 (dd, J = 3.5, 12.0 Hz, 1

H), 4.88–5.04 (m, 1 H), 5.08–5.20 (m, 1 H); ^{13}C NMR δ 19.9, 20.7, 21.0, 21.3, 36.6, 64.8, 67.5, 68.6, 170.3, 170.4, 170.7; IR (neat) 2988, 1738, 1442, 1376, 1240, 1086, 1050 cm^{-1}. Anal. Calcd for $C_{11}H_{18}O_6$: C, 53.65; H, 7.37. Found: C, 53.56; H, 7.48.

(2R*,4R*)-1,4-Diacetoxy-2-methylpentan-2-ol (6d). ^{1}H NMR δ 1.23 (s, 3 H), 1.28 (d, J = 6.2 Hz, 3 H), 1.66 (dd, J = 3.3, 15.1 Hz, 1 H), 1.94 (dd, J = 8.7, 15.1 Hz, 1 H), 2.04 (s, 3 H), 2.11 (s, 3 H), 2.12–2.60 (br, 1 H), 3.95 (s, 2 H), 5.08–5.27 (m, 1 H); ^{13}C NMR δ 20.8, 21.5, 21.6, 24.5, 44.5, 67.8, 70.8, 70.9, 170.7, 171.0; IR (neat) 3504, 2988, 1740, 1378, 1256, 1048 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_5$: C, 55.03; H, 8.31. Found: C, 54.97; H, 8.48.

(2R*,3R*,4R*)-3-Methyl-1,2,4-triol Triacetate (6f). ^{1}H NMR δ 0.96 (d, J = 7.1 Hz, 3 H), 1.17 (d, J = 6.5 Hz, 3 H), 2.04 (s, 3 H), 2.05 (s, 3 H), 2.08 (s, 3 H), 2.00–2.22 (m, 1 H), 4.03 (dd, J = 7.0, 12.2 Hz, 1 H), 4.35 (dd, J = 2.9, 12.2 Hz, 1 H), 4.94 (m, 1 H), 5.07 (dt, J = 2.9, 7.0 Hz, 1 H); ^{13}C NMR δ 19.7, 24.1, 28.2, 28.4, 28.6, 43.5, 65.2, 71.4, 72.7, 157.9, 158.0, 158.2; IR (neat) 2992, 1740, 1444, 1378, 1252, 1050, 1028 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.49; H, 8.02.

(2R*,3R*,4R*)-1,4-Diacetoxy-2,3-dimethylpentan-2-ol (6g). ^{1}H NMR δ 0.92 (d, J = 7.1 Hz, 3 H), 1.12 (s, 3 H), 1.25 (d, J = 6.4 Hz, 3 H), 1.95–2.12 (m, 1 H), 2.04 (s, 3 H), 2.11 (s, 3 H), 2.15–2.55 (br, 1 H), 3.96 (d, J = 11.4 Hz, 1 H), 4.04 (d, J = 11.4 Hz, 1 H), 5.15 (quintet, J = 6.4 Hz, 1 H); ^{13}C NMR δ 10.6, 17.5, 20.8, 21.5, 43.2, 70.2, 71.6, 73.4, 170.3, 171.0; IR (neat) 3508, 2992, 1740, 1380, 1250, 1046 cm^{-1} Anal. Calcd for $C_{11}H_{20}O_5$: C, 56.88; H, 8.68. Found: C, 56.73; H, 8.89.

(2R*,3R*,4R*)-3,5-Dimethylhexan-1,2,4-triol Triacetate (6i). ^{1}H NMR δ 0.83 (d, J = 6.7 Hz, 3 H), 0.91 (d, J = 6.7 Hz, 3 H), 0.92 (d, J = 7.3 Hz, 3 H), 1.82–2.28 (m, 2 H), 2.01 (s, 3 H), 2.04 (s, 3 H), 2.08 (s, 3 H), 4.05 (dd, J = 8.6, 12.0 Hz, 1 H), 4.33 (dd, J = 2.7, 12.0 Hz, 1 H), 4.71 (t, J = 6.5 Hz, 1 H), 5.16 (ddd, J = 2.7, 4.3, 8.6 Hz, 1 H); ^{13}C NMR δ 12.1, 17.0, 19.4, 20.7, 20.8,

21.0, 29.5, 36.5, 63.2, 71.5, 78.8, 170.2, 170.68, 170.71; IR (neat) 2980, 1754, 1468, 1442, 1376, 1240, 1088, 1048 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O_6$: C, 58.32; H, 8.39. Found: C, 58.04; H, 8.62.

(1R*,2R*,1'R*)-2-(1',2'-Diacetoxyethyl)cyclohexanol Acetate (6k).
^{1}H NMR δ 1.03–1.40 (m, 4 H), 1.55–1.75 (m, 2 H), 1.75–1.91 (m, 2 H), 1.91–2.12 (m, 1 H), 1.98 (s, 3 H), 2.03 (s, 3 H), 2.04 (s, 3 H), 4.02 (dd, J = 8.3, 11.9 Hz, 1 H), 4.21 (dd, J = 3.5, 11.9 Hz, 1 H), 4.65 (dt, J = 4.5, 10.1 Hz, 1 H), 5.17 (dt, J = 8.3, 3.5 Hz, 1 H); ^{13}C NMR δ 20.7, 20.9, 21.3, 23.9, 24.7, 26.6, 31.7, 43.5, 63.8, 71.7, 72.7, 170.3, 170.7; IR (neat) 2948, 2872, 1740, 1454, 1372, 1236, 1040 cm^{-1}. Anal. Calcd for $C_{14}H_{22}O_6$: C, 58.73; H, 7.74. Found: C, 58.57; H, 7.96.

(4R*,6R*)-Hept-6-en-1,2,4-triol Triacetate (6l). ^{1}H NMR δ 1.80–1.91 (m, 2 H), 2.01 (s, 3 H), 2.026 (s, 3 H), 2.031 (s, 3 H), 2.18–2.44 (m, 2 H), 4.00 (dd, J = 6.0, 12.1 Hz, 1 H), 4.23 (dd, J = 3.4, 12.1 Hz, 1 H), 4.86–5.18 (m, 4 H), 5.58–5.81 (m, 1 H); ^{13}C NMR δ 20.6, 21.0, 21.1, 34.3, 38.4, 64.6, 68.6, 69.7, 118.4, 132.8, 170.2, 170.3, 170.5; IR (neat) 2984, 1740, 1442, 1376, 1240, 1048, 1026 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_6$: C, 57.34; H, 7.40. Found: C, 57.36; H, 7.49.

(2R*,4S*)-5-Methylhexan-1,2,4-triol Triacetate (6c). To a solution of **2n** (717 mg, 2.34 mmol) in CH_2Cl_2 (10 mL) at 0 °C was added HBF$_4$•OEt$_2$ (85%, 1.1 g, 5.7 mmol), and the mixture was stirred for 1 h. After evaporation of volatiles, THF (10 mL), MeOH (10 mL), KF (273 mg, 4.7 mmol), KHCO$_3$ (1.17 g, 11.7 mmol), H_2O_2 (30% in water, 2.34 mL) were added, and the mixture was stirred at 40 °C for 4 h. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a similar procedure to that used for **6a** to give **6c** (519 mg, 81%): ^{1}H NMR δ 0.87 (d, J = 6.8 Hz, 3 H), 0.88 (d, J = 6.9 Hz, 3 H), 1.70–1.95 (m, 3 H), 2.037 (s, 3 H), 2.043 (s, 3 H), 2.05 (s, 3 H), 4.05 (dd, J = 5.9, 12.1 Hz, 1 H), 4.27 (dd, J = 3.2, 12.1 Hz, 1 H), 4.78 (q, J = 5.9 Hz, 1

H), 5.00–5.13 (m, 1 H); ^{13}C NMR δ 17.4, 18.1, 20.7, 21.0, 31.4, 32.0, 64.5, 69.1, 74.6, 170.3, 170.6, 170.7; IR (neat) 2980, 1740, 1376, 1240 cm^{-1}. Anal. Calcd for $C_{13}H_{22}O_6$: C, 56.92; H, 8.08. Found: C, 56.70; H, 8.31.

(1R*,4S*)-1,4-Diacetoxy-4-phenylbutan-2-ol (6e). (method A) To a solution of **2t** (100 mg, 0.282 mmol) in CH_2Cl_2 (0.5 mL) at 0 °C was added ICl (1 M in CH_2Cl_2, 0.3 mmol), and the mixture was stirred for 3 h. After evaporation of volatiles, THF (1 mL), ^{i}PrOH (51 mg, 0.85 mmol), and Et_3N (86 mg, 0.85 mmol) were added. The mixture was stirred at rt for 10 h and then passed through a short column of silica gel. After evaporation, TBAF (1 M in THF, 1.1 mmol), MeOH (1 mL), H_2O_2 (30% in water, 0.34 mL), and $KHCO_3$ (56 mg, 0.56 mmol) were added to the residue, which was stirred at 40 °C for 4 h. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a similar procedure to that used for **6a** to give **6e** (53 mg, 67%).

(Method B) To a solution of **2t** (100 mg, 0.282 mmol) in DMSO (0.5 mL) at rt was added KOBu^t (35 mg, 0.31 mmol). The mixture was stirred for 4 h, then diluted with ether (10 mL) and phosphate buffer solution (pH 7), and extracted with ether. After evaporation, oxidation and acetylation of the residue were carried out by a similar procedure to the method A to give **6e** (62 mg, 78%): ^{1}H NMR (C_6D_6) δ 1.09 (s, 3 H), 1.68 (s, 3 H), 1.69 (s, 3 H), 1.79 (dd, J = 3.5, 14.9 Hz, 1 H), 2.20 (dd, J = 9.2, 14.9 Hz, 1 H), 2.30–2.70 (br, 1 H), 3.94–4.06 (m, 2 H), 6.29 (dd, J = 3.5, 9.2 Hz, 1 H), 7.02–7.40 (m, 5 H); ^{13}C NMR (C_6D_6) δ 19.3, 19.9, 24.1, 44.6, 69.7, 70.0, 71.7, 125.9, 126.8, 127.3, 141.2, 168.7, 169.4; IR (neat) 3492, 2984, 1740, 1378, 1248, 1046 cm^{-1}. Anal. Calcd for $C_{15}H_{20}O_5$: C, 64.27; H, 7.19. Found: C, 64.26; H, 7.15.

(2R*,3S*,4R*)-1,4-Diacetoxy-2,3-dimethylpentan-2-ol (6h). ^{1}H NMR δ 1.04 (d, J = 7.2 Hz, 3 H), 1.18 (s, 3 H), 1.22 (d, J = 6.5 Hz, 3 H), 1.70 (dq, J = 1.6, 7.2 Hz, 1 H), 2.01 (s, 3 H), 2.07 (s, 3 H), 3.95 (d, J = 11.4 Hz, 1 H), 4.05 (d, J = 11.4 Hz, 1 H), 5.29 (dq, J = 1.6, 6.5 Hz, 1 H); ^{13}C NMR δ 7.8, 19.3, 20.8, 21.4, 23.0, 44.9, 69.2, 69.3, 73.3, 170.6, 171.1; IR (neat) 3504,

2988, 1740, 1378, 1248 cm^{-1}. Anal. Calcd for C$_{11}$H$_{20}$O$_5$: C, 56.88; H, 8.68. Found: C, 56.70; H, 8.82.

(2R*,3S*,4R*)-3,5-Dimethylhexan-1,2,4-triol Triacetate (6j). ^{1}H NMR δ 0.87 (d, J = 6.6 Hz, 3 H), 0.89 (d, J = 6.8 Hz, 3 H), 0.95 (d, J = 7.0 Hz, 3 H), 1.85–2.20 (m, 2 H), 2.05 (s, 3 H), 2.07 (s, 3 H), 2.09 (s, 3 H), 4.11 (dd, J = 6.5, 12.1 Hz, 1 H), 4.34 (dd, J = 3.3, 12.1 Hz, 1 H), 4.75 (dd, J = 4.4, 7.4 Hz, 1 H), 4.99 (dt, J = 3.3, 6.5 Hz, 1 H); ^{13}C NMR δ 9.6, 17.8, 19.1, 20.6, 20.8, 29.7, 35.2, 63.4, 72.5, 77.4, 170.3, 170.5, 170.7; IR (neat) 2988, 1746, 1374, 1240, 1048, 1022 cm^{-1}. Anal. Calcd for C$_{14}$H$_{24}$O$_6$: C, 58.32; H, 8.39. Found: C, 58.25; H, 8.54.

(3S*,5S*)-5-Allyl-3-[(dimethylphenylsilyl)methyl]-2,2-dimethyl-1,2-oxasilolane (8). By a procedure similar to that used to prepare **2a**, the intramolecular bis-silylation of **7** was carried out using 1,1,3,3-tetramethylbutyl isocyanide (**3a**) to give **8** (96%): ^{1}H NMR δ 0.05 (s, 3 H), 0.09 (s, 3 H), 0.29 (s, 3 H), 0.30 (s, 3 H), 0.76–1.30 (m, 4 H), 2.02–2.12 (m, 1 H), 2.12–2.40 (m, 2 H), 3.72–3.88 (m, 1 H), 4.99–5.11 (m, 2 H), 5.69–5.91 (m, 1 H), 7.32–7.40 (m, 3 H), 7.46–7.60 (m, 2 H); ^{13}C NMR δ -2.8, -2.7, -2.3, -0.9, 16.0, 20.7, 42.1, 42.7, 76.2, 116.7, 127.8, 129.0, 133.6, 135.0, 139.2; IR (neat) 3076, 2964, 2856, 1646, 1430, 1252, 1116, 828 cm^{-1}. Anal. Calcd for C$_{17}$H$_{28}$OSi$_2$: C, 67.04; H, 9.27. Found: C, 66.85; H, 9.51.

(4S*,6S*)-6,7-Bis(dimethylphenylsilyl)hept-1-en-4-ol (9). To a solution of **8** (263 mg, 0.863 mmol) in ether (3 mL) at rt was added PhLi (0.56 M, 1.9 mL, 1.0 mmol). The mixture was stirred for 2 h and then diluted with water. Extraction with ether followed by column chromatography on silica gel (ether : hexane = 1 : 9) afforded **9** (290 mg, 88%) as a mixture of diastereomers. The major isomer was isolated by HPLC: ^{1}H NMR δ 0.23 (s, 3 H), 0.26 (s, 6 H), 0.30 (s, 3 H), 0.60 (dd, J = 7.4, 15.4 Hz, 1 H), 0.90–1.38 (m, 4 H), 1.47–1.61 (m, 1 H), 1.78–2.10 (m, 2 H), 3.22–3.38 (m, 1 H), 4.95–5.09 (m, 2 H), 5.44–5.66 (m, 1 H), 7.34–7.60 (m, 10 H); ^{13}C NMR δ -4.8, -4.3, -3.0, -2.2,

15.2, 16.0, 40.7, 42.2, 68.8, 117.6, 127.2, 127.8, 128.9, 129.0, 133.7, 134.1, 135.1, 138.7, 139.7; IR (neat) 3592, 3484, 3076, 2964, 2908, 1644, 1430, 1250, 1114, 818, 700 cm^{-1}. Anal. Calcd for C$_{23}$H$_{34}$OSi$_2$: C, 72.19; H, 8.95. Found: C, 72.25; H, 9.03.

(4S*,6S*)-6,7-Bis(dimethylphenylsilyl)-4-[(1',1',2',2'-tetramethyl-2'-phenyldisilan-1'-yl)oxy]hept-1-ene (10). According to the general procedure for the synthesis of disilanyl ethers **1**, the title compound **10** was obtained in 89% yield from **9**: ^{1}H NMR δ 0.10 (s, 3 H), 0.13 (s, 3 H), 0.22 (s, 3 H), 0.26 (s, 6 H), 0.29 (s, 3 H), 0.34 (s, 6 H), 0.59 (dd, J = 10.0, 15.1 Hz, 1 H), 0.85–1.11 (m, 2 H), 1.30–1.60 (m, 2 H), 1.72–1.90 (m, 1 H), 1.93–2.10 (m, 1 H), 3.38–3.53 (m, 1 H), 4.79–5.00 (m, 2 H), 5.38–5.59 (m, 1 H), 7.32–7.60 (m, 15 H); ^{13}C NMR δ -4.3, -3.8, -3.7, -2.3, −1.9, 0.3, 0.6, 16.2, 17.0, 41.0, 42.0, 72.0, 116.4, 127.7, 128.4, 128.8, 133.6, 133.9, 134.0, 135.4, 139.3, 139.8; IR (neat) 2964, 1430, 1250, 1112, 1062, 830, 814, 790, 700 cm^{-1}. Anal. Calcd for C$_{33}$H$_{50}$OSi$_4$: C, 68.92; H, 8.76. Found: C, 68.86; H, 8.85.

(3R*,5R*,2'S*)-5-[2',3'-Bis(dimethylphenylsilyl)propyl]-3-[(dimethylphenylsilyl)methyl]-2,2-dimethyl-1,2-oxasilolane (11). By a procedure similar to that used to prepare **2a**, the intramolecular bis-silylation of **10** was carried out using 1,1,3,3-tetramethylbutyl isocyanide **3a** to give **11** (95%): ^{1}H NMR δ -0.05 (s, 3 H), 0.02 (s, 3 H), 0.18 (s, 3 H), 0.20 (s, 3 H), 0.23 (s, 3 H), 0.25 (s, 3 H), 0.27 (s, 6 H), 0.54 (dd, J = 8.9, 15.3, 1 H), 0.65–0.99 (m, 5 H), 1.00–1.16 (m, 1 H), 1.17–1.83 (m, 1 H), 1.55–1.82 (m, 2 H), 3.38–3.53 (m, 1 H), 7.28–7.55 (m, 15 H); ^{13}C NMR δ -4.6, -4.3, -2.7, -2.6, -2.3, -1.0, 15.75, 15.84, 16.2, 20.7, 42.3, 43.3, 75.4, 127.6, 127.7, 127.8, 128.8, 128.9, 133.6, 134.0, 139.2, 139.5, 139.9; IR (neat) 2964, 1430, 1250, 1114, 832 cm^{-1}. Anal. Calcd for C$_{33}$H$_{50}$OSi$_4$: C, 68.92; H, 8.76. Found: C, 69.02; H, 8.96.

(2S*,4R*,6R*)-Heptan-1,2,4,6,7-pentaol Pentaacetate (12). By a procedure similar to that used to prepare **6a**, the title compound **12** was obtained

in 44% yield from **11**: ^{1}H NMR δ 1.81–1.99 (m, 4 H), 2.05 (s, 9 H), 2.06 (s, 6 H), 4.01 (dd, J = 5.9, 12.0 Hz, 2 H), 4.24 (dd, J = 3.5, 12.0 Hz, 2 H), (quintet, J = 6.2 Hz, 1 H), 5.03–5.16 (m, 2 H); ^{13}C NMR δ 20.7, 21.0, 21.1, 34.8, 64.5, 67.5, 68.3, 170.3, 170.6; IR (neat) 2964, 1740, 1444, 1376, 1240, 1048 cm^{-1} .Anal. Calcd for $C_{17}H_{26}O_{10}$: C, 52.30; H, 6.71. Found: C, 52.01; H, 6.70.

(2R*,4S*)-1-(*tert*-Butyldimethylsiloxy)-5-methylhexan-2,4-diol (13). To **6d** (443 mg, 1.61 mmol) in MeOH (10 mL) was added NaOMe (2.6 M in MeOH, 31 μL, 0.081 mmol), and the mixture was stirred for 5 h at rt. After the volatiles were evaporated, ClSiMe$_2$Bu^t (531 mg, 1.93 mmol), DMF (3 mL), and imidazole (274 mg, 4.03 mmol) were added and the mixture was stirred at rt for 1 h. Column chromatography on silica gel (ether : hexane = 1 : 1) afforded **13** (524 mg, 84%): ^{1}H NMR δ 0.89 (d, J = 6.8 Hz, 3 H), 0.90 (d, J = 6.8 Hz, 3 H), 1.07 (s, 9 H), 1.30–1.78 (m, 3 H), 2.6–3.0 (br, 2 H), 3.49–3.68 (m, 3 H), 3.90–4.05 (m, 1 H), 7.35–7.50 (m, 6 H), 7.62–7.71 (m, 4 H); ^{13}C NMR δ 17.5, 18.2, 19.2, 26.8, 33.9, 35.4, 68.0, 73.3, 76.9, 127.8, 129.9, 133.0, 135.5; IR (neat) 3416, 2968, 2868, 1474, 1430, 1114, 1070, 702 cm^{-1}.

(2R*,4S*)-2,4-Bis(benzyloxy)-5-methylhexan-1-ol (14). To **13** (325 mg, 0.84 mmol) in THF (1.5 mL) at -78 °C was added butyllithium (1.62 M in hexane, 1.09 mL, 1.77 mmol). After the mixture stirred for 1 h at -78 °C, benzyl bromide (431 mg, 2.52 mmol) in HMPA (1.5 mL) was added. The mixture was stirred for 30 min at 0 °C and for 2 d at rt, extracted with ether, dried over K$_2$CO$_3$, and evaporated. To the residue dissolved in THF (3 mL) was added TBAF (1.0 M in THF, 1.26 mL, 1.26 mmol), and the mixture was stirred at rt for 1 d. Column chromatography on silica gel (ether : hexane = 1 : 1) afforded **14** (204 mg, 74%): ^{1}H NMR δ 0.95 (d, J = 7.0 Hz, 6 H), 1.69–1.95 (m, 2 H), 1.98–2.18 (m, 1 H), 2.1–2.5 (br, 1 H), 3.31–3.43 (m, 1 H), 3.48–3.63 (m, 1 H), 3.64–3.76 (m, 2 H), 4.44 (d, J = 11.4 Hz, 1 H), 4.52 (d, J = 11.7 Hz, 1 H), 4.59 (d, J = 11.4 Hz, 1 H), 4.63 (d, J = 11.7 Hz, 1 H), 7.25–7.47 (m, 10 H); ^{13}C NMR δ 16.8, 18.5, 29.8, 30.6, 63.8, 71.0, 71.2, 77.0, 80.3, 127.6, 127.7, 127.8, 128.3, 128.4, 138.4, 138.5; IR (neat) 3448, 2968, 2880, 1458,

1070, 736, 698 cm^{-1}. Anal. Calcd for C$_{21}$H$_{28}$O$_3$: C, 76.79; H, 8.59. Found: C, 76.97; H, 8.66.

(2R*,4S*)-2,4-Bis(benzyloxy)-5-methylhexanal (15). To oxalyl chloride (121 mg, 0.95 mmol) in CH$_2$Cl$_2$ (2 mL) at -78 °C was slowly added DMSO (107 mg, 1.37 mmol) in CH$_2$Cl$_2$ (0.5 mL), and the mixture was stirred for 10 min. Then, **14** (195 mg, 0.59 mmol) in CH$_2$Cl$_2$ (1.5 mL) was added and stirring was continued for 10 min at -78 °C and for 50 min at -50 °C. Et$_3$N (481 mg, 4.8 mmol) was added, and the mixture was stirred at 0 °C for 20 min and then diluted with sat. *aq*. NH$_4$Cl. Extraction with ether followed by column chromatography on silica gel (ether : hexane = 1 : 2) afforded **15** (192 mg, 99%): ^{1}H NMR δ 0.93 (d, J = 6.8 Hz, 3 H), 0.94 (d, J = 7.0 Hz, 3 H), 1.89–2.11 (m, 3 H), 3.52 (dt, J = 8.3, 4.6 Hz, 1 H), 3.94 (dt, J = 1.1, 5.2 Hz, 1 H), 4.45 (d, J = 11.2 Hz, 1 H), 4.52 (d, J = 11.2 Hz, 1 H), 4.58 (d, J = 11.9 Hz, 1 H), 4.73 (d, J = 11.9 Hz, 1 H), 7.20–7.45 (m, 10 H), 9.61 (d, J = 1.1 Hz, 1 H); ^{13}C NMR δ 16.9, 18.4, 30.0, 31.8, 71.3, 72.1, 79.0, 80.7, 127.4, 127.7, 127.8, 128.1, 128.2, 128.5, 137.5, 138.5, 202.5; IR (neat) 2968, 1736, 1092, 1072, 734 cm^{-1}. Anal. Calcd for C$_{21}$H$_{26}$O$_3$: C, 77.27; H, 8.03. Found: C, 76.99; H, 8.13.

(4R*,5R*,7S*)-5,7-Bis(benzyloxy)-8-methylnon-1-en-4-ol (16). To a mixture of MgBr$_2$, prepared by the reaction of Mg (6.0 mg, 0.25 mmol) with excess 1,2-dibromoethane in ether, and **15** (54 mg, 0.17 mmol) in CH$_2$Cl$_2$ (0.7 mL) at -25 °C was added allyltributyltin (60 mg, 0.18 mmol). The mixture was allowed to warm up gradually to rt and stirred for 10 h at rt. Extraction with ether followed by column chromatography on silica gel (ether : hexane = 1 : 2) afforded **16** (60 mg, 99%): ^{1}H NMR δ 0.96 (d, J = 6.8 Hz, 6 H), 1.70–1.99 (m, 2 H), 2.00–2.20 (m, 1 H), 2.23–2.42 (m, 3 H), 3.36 (dt, J = 8.8, 4.0 Hz, 1 H), 3.50 (dt, J = 7.5, 4.1 Hz, 1 H), 3.51–3.70 (m, 1 H), 4.41 (d, J = 11.5 Hz, 1 H), 4.46 (d, J = 11.5 Hz, 1 H), 4.60 (d, J = 11.5 Hz, 1 H), 4.67 (d, J = 11.5 Hz, 1 H), 4.97–5.18 (m, 2 H), 5.66–5.88 (m, 1 H), 7.24–7.43 (m, 10 H); ^{13}C NMR δ 16.9, 18.4, 30.0, 30.1, 38.3, 71.2, 71.5, 71.8, 78.0, 80.2, 117.2,

127.5, 127.7, 127.8, 128.0, 128.29, 128.34, 135.1, 138.3, 138.7; IR (neat) 3464, 2968, 1644, 1068, 736, 698 cm^{-1}. Anal. Calcd for $C_{24}H_{32}O_3$: C, 78.22; H, 8.75. Found: C, 78.02; H, 8.71.

(4R*,5R*,7S*)-5,7-Bis(benzyloxy)-4-(2,2-dimethyl-1,1,2-triphenyl-disilanyl)oxy-8-methylnon-1-ene (17). To a mixture of **16** (94 mg, 0.26 mmol) and $Me_2PhSi–SiPh_2Cl$ (108 mg, 0.31 mmol) in DMF (1 mL) at rt was added imidazole (35 mg, 0.51 mmol), and the mixture was stirred for 6 h. Column chromatography on silica gel (ether : hexane = 1 : 4) afforded **17** (164 mg, 93%): ^1H NMR δ 0.46 (s, 3 H), 0.47 (s, 3 H), 0.80 (d, J = 6.7 Hz, 6 H), 1.49–1.67 (m, 1 H), 1.72 (ddd J = 6.8, 8.3, 14.6 Hz, 1 H), 1.90 (ddd, J = 4.0, 6.8, 14.6 Hz, 1 H), 2.13–2.31 (m, 1 H), 2.36–2.53 (m, 1 H), 3.13 (dt, J = 3.8, 6.8 Hz, 1 H), 3.31 (dt, J = 8.3, 4.0 Hz, 1 H), 4.01 (dt, J = 4.0, 5.6 Hz, 1 H), 4.16 (d, J = 11.9 Hz, 1 H), 4.29 (d, J = 11.9 Hz, 1 H), 4.33 (d, J = 11.8 Hz, 1 H), 4.38 (d, J = 11.8 Hz, 1 H), 4.86–5.00 (m, 2 H), 5.55–5.78 (m, 1 H), 7.08–7.62 (m, 25 H); ^{13}C NMR δ -2.72, -2.67, 16.9, 18.9, 30.2, 30.4, 36.9, 71.1, 71.4, 73.7, 78.7, 81.0, 116.7, 127.1, 127.3, 127.5, 127.6, 127.7, 128.08, 128.13, 128.7, 129.5, 129.7, 134.4, 135.1, 135.4, 135.6, 136.3, 136.4, 138.2, 138.9, 139.3; IR (neat) 2968, 1430, 1108, 1070, 734, 700 cm^{-1}.

(3R*,5R*)-3-[(Dimethylphenylsilyl)methyl]-5-[(1'R*,3'S*)-1',3'-bis-(benzyloxy)-4-methylpentyl]-2,2-diphenyl-1,2-oxasilolane (18). By a procedure similar to that used to prepare **2a**, the intramolecular bis-silylation of **17** was carried out using 1,1,3,3-tetramethylbutyl isocyanide (**3a**) to give **18** (93%): ^1H NMR δ 0.22 (s, 6 H), 0.66 (dd, J = 9.3, 15.1 Hz, 1 H), 0.90 (d, J = 6.8 Hz, 3 H), 0.92 (d, J = 6.8 Hz, 3 H), 1.03 (dd, J = 4.3, 15.1 Hz, 1 H), 1.43–2.07 (m, 6 H), 3.27–3.40 (m, 1 H), 3.41–3.52 (m, 1 H), 3.88–4.01 (m, 1 H), 4.43 (d, J = 11.7 Hz, 1 H), 4.52 (d, J = 11.7 Hz, 1 H), 4.65 (d, J = 11.7 Hz, 1 H), 4.72 (d, J = 11.7 Hz, 1 H), 7.20–7.62 (m, 25 H); ^{13}C NMR δ -2.4, -2.3, 15.8, 17.8, 17.9, 19.7, 30.3, 31.1, 38.0, 71.0, 72.3, 79.0, 79.3, 80.2, 127.3, 127.6, 127.7, 127.9, 128.0, 128.2, 128.9, 129.9, 130.1, 133.2, 133.6, 134.7, 135.5, 139.1, 139.4; IR (neat) 2968, 1458, 1120, 1068, 832, 724, 698 cm^{-1}.

Anal. Calcd for $C_{44}H_{52}O_3Si_2$: C, 77.14; H, 7.65. Found: C, 77.11; H, 7.69.

(2S*,4R*,5R*,6S*)-5,6-Bis(benzyloxy)-8-methylnonan-1,2,4-triol Triacetate (19). By a procedure similar to that used to prepare **6f** by use of KOBu^t in DMSO, the title compound **19** was obtained in 89% yield from **18**: ^{1}H NMR δ 0.86 (d, J = 6.7 Hz, 3 H), 0.88 (d, J = 6.6 Hz, 3 H), 1.56–2.00 (m, 5 H), 2.00 (s, 3 H), 2.02 (s, 3 H), 2.06 (s, 3 H), 3.21 (dt, J = 7.4, 4.4 Hz, 1 H), 3.59 (dt, J = 3.4, 6.1 Hz, 1 H), 3.92 (dd, J = 5.8, 12.0 Hz, 1 H), 4.12 (dd, J = 3.3, 12.0 Hz, 1 H), 4.43 (d, J = 11.4 Hz, 1 H), 4.49 (d, J = 11.4 Hz, 1 H), 4.53 (d, J = 11.4 Hz, 1 H), 4.61 (d, J = 11.4 Hz, 1 H), 4.85–5.00 (m, 1 H), 5.04–5.16 (m, 1 H), 7.20–7.43 (m, 10 H); ^{13}C NMR δ 17.3, 17.9, 20.7, 21.0, 29.8, 30.1, 31.0, 64.5, 69.0, 70.0, 71.2, 71.4, 75.3, 80.1, 127.4, 127.7, 127.8, 128.3, 137.9, 138.9, 170.2, 170.4, 170.6; IR (neat) 2968, 1740, 1374, 1238, 1068, 736, 700 cm^{-1}. Anal. Calcd for $C_{30}H_{40}Si_8$: C, 68.16; H, 7.63. Found: C, 68.28; H, 7.69.

Preparation of Disilanyl Alkenes 20. The following describes the general procedure for the synthesis of disilanyl alkenes **20a–c**. To a solution of Grignard reagent (6 mmol) in THF (3 mL) at rt was added chlorodisilane (3.4 mmol). The mixture was stirred for 10 h, diluted with hexane, and filtered to remove insoluble materials. Column chromatography on silica gel (hexane) afforded the corresponding disilanyl alkene.

Disilanyl alkene **20d** was prepared from secondary Grignard reagent as follows. To a solution of Grignard reagent, prepared from 5-bromo-1-hexene (1.60 g, 10 mmol) and Mg (0.27 g, 11.0 mmol) in THF (5 mL) at 0 °C were successively added CuCN (70 mg, 1.0 mmol) and 1-chloro-2,2-dimethyl-1,2,2-triphenyldisilane (2.8 g, 8.0 mmol).[20] The mixture was stirred at 0 °C for 3h and at rt for 10 h, diluted with hexane, and filtered to remove insoluble materials. Column chromatography on silica gel (hexane) afforded **20d** (2.3g, 70%).

(2R*,3R*)-2-[(Dimethylphenylsilyl)methyl]-1,1,3-trimethylsilolane (21a). To a mixture of palladium(II) acetate (2.2 mg, 10 μmol) and 1,1,3,3-

tetramethylbutyl isocyanide (21 mg, 0.15 mmol) in toluene (0.5 mL) was added **20a** (100 mg, 0.36 mmol). The mixture was stirred at 50 °C for 2 h. Preparative TLC of silica gel (hexane) afforded **21a** (87 g, 87%) as a colorless liquid: ^{1}H NMR δ -0.04 (s, 3 H), -0.01 (s, 3 H), 0.21 (dt, J = 2.9, 10.5 Hz, 1 H), 0.30 (s, 6 H), 0.42 (ddd, J = 8.2, 12.4, 14.4 Hz,1 H), 0.67 (ddd, J = 2.0, 6.8, 14.4 Hz, 1 H), 0.73-1.10 (m, 3 H), 0.95 (d, J = 6.3 Hz, 3 H), 1.15-1.38 (m, 1 H), 1.80-1.95 (m, 1H), 7.30-7.40 (m, 3 H), 7.49-7.60 (m, 2 H) ; ^{13}C NMR δ 3.4, -2.6, -2.5, -1.3, 12.4, 14.7, 19.9, 29.0. 34.1, 45.2, 127.6, 128.7, 133.6, 139.9. IR(neat) 2960, 1250, 1114, 836; Anal. Calcd for $C_{16}H_{28}Si_2$: C, 69.49; H, 10.20. Found: C, 69.32; H, 10.46.

The following intramolecular bis-silylation reactions of **20b–d** producing **21b–d** were carried out according to the preceding procedure for **21a**.

(2R*,3R*)-2-[(Dimethylphenylsilyl)methyl]-3-methyl-1,1-diphenylsilolane (21b). ^{1}H NMR δ 0.09 (s, 3 H), 0.14 (s, 3 H), 0.80-1.33 (m, 6 H), 1.01 (d, J = 6.6 Hz, 3 H), 1.51-1.70 (m, 1 H), 2.02-2.18 (m, 1 H), 7.20–7.60 (m, 15 H); ^{13}C NMR δ -2.6, -2.1, 12.0, 15.3, 20.3, 27.4, 33.9, 46.1, 127.6, 127.7, 128.7, 129.1, 133.7, 134.9, 135.2, 135.9, 136.3, 139.7; IR(neat) 3076, 2960, 1440, 1258, 1110, 840, 738, 700; Anal. Calcd for $C_{26}H_{32}OSi_2$: C, 77.93; H, 8.05. Found: C, 78.01; H, 7.96.

(2R*,4R*)-2-[(Dimethylphenylsilyl)methyl]-4-methyl-1,1-diphenylsilolane (21c). ^{1}H NMR δ 0.23 (s, 3 H), 0.25 (s, 3 H), 0.66 (dd, J = 10.3, 14.8 Hz, 1 H), 0.79 (dd, J = 12.0, 14.8 Hz, 1 H), 0.96–1.10 (m, 1 H), 0.99 (dd, J = 4.2, 8.3 Hz, 1 H), 1.12 (d, J = 6.4 Hz, 3 H), 1.35 (ddd, J = 2.2, 6.1, 15.1 Hz, 1 H), 1.45–1.65 (m, 1 H), 1.65–1.88 (m, 1 H), 2.05–2.20 (m, 1 H), 7.25–7.60 (m, 15 H); ^{13}C NMR δ -2.4, -1.9, 17.1, 21.7, 22.0, 23.7, 34.3, 47.1, 127.7, 127.8, 128.7, 129.2, 133.6, 134.9, 135.2, 135.6, 136.5, 139.9; IR (neat) 3050, 2940, 1450, 1260, 1135, 850, 750, 720 cm^{-1}. Anal. Calcd for $C_{26}H_{32}Si_2$: C, 77.93; H, 8.05. Found: C, 77.92; H, 8.03.

2-[(Dimethylphenylsilyl)methyl]-5-methyl-1,1-diphenylsilolane (21d).

^{13}C NMR (a mixture of isomers) δ -2.5, -2.3, -2.2, -2.1, 16.2, 16.8, 17.1, 17.4, 19.7, 20.4, 21.0, 35.1, 35.5, 35.9, 36.4, 127.5, 127.7, 127.8, 128.7, 129.1, 129.2, 133.6, 133.8, 134.76, 134.83, 135.7, 135.8, 139.9, 140.0. Anal. Calcd for $C_{26}H_{32}Si_2$: C, 77.93; H, 8.05. Found: C, 77.83; H, 8.17.

(2R*,3R*)-3-Methylpentan-1,2,5-triol Triacetate (22b). By a procedure similar to that used to prepare **6a**, the oxidation of **21b** was carried out to give **22b** (70%): ^{1}H NMR δ 0.97 (d, J = 6.9 Hz, 3 H), 1.34–1.58 (m, 1 H), 1.69–2.10 (m, 2 H), 2.04 (s, 6 H), 2.08 (s, 3 H), 3.98–4.19 (m, 3 H), 4.30 (dd, J = 3.1, 10.8 Hz, 1 H), 4.96 (dt, J = 3.1, 6.9 Hz, 1 H); ^{13}C NMR δ 15.2, 20.7, 20.9, 30.8, 31.2, 62.2, 63.3, 74.7, 170.5, 170.8, 171.0; IR (neat) 2976, 1740, 1374, 1248, 1052 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.16; H, 7.51.

(2R*,4R*)-4-Methylpentan-1,2,5-triol Triacetate (22c). By a procedure similar to that used to prepare **6a**, the oxidation of **21c** was carried out to give **22c** (88%): ^{1}H NMR δ 0.96 (d, J = 6.8 Hz, 3 H), 1.22–1.43 (m, 1 H), 1.68–1.97 (m, 2 H), 2.06 (s, 9 H), 3.94 (d, J = 5.9 Hz, 2 H), 4.01 (dd, J = 6.8, 11.8 Hz, 1 H), 4.24 (dd, J = 3.6, 11.8 Hz, 1 H), 5.22 (m, 1 H); ^{13}C NMR δ 16.3, 20.7, 20.8, 20.9, 29.0, 34.4, 65.5, 69.1, 170.5, 170.7, 171.0; IR (neat) 2972, 1738, 1376, 1240, 1040 cm^{-1}. Anal. Calcd for $C_{12}H_{20}O_6$: C, 55.37; H, 7.74. Found: C, 55.24; H, 7.83.

Preparation of Disilanyl Amides 23. The following describes the general procedure for the preparation of disilanyl amides **23a–c**. To a mixture of chlorodisilane (3.0 mmol) and Et_3N (4.5 mmol) in MeCN (5 mL) at rt was added a homoallylic amine (3.0 mmol). The mixture was stirred for 3 h, diluted with ether, and filtered to remove insoluble materials. Kugelrohr distillation afforded the corresponding disilanyl amide **23**.

(2R*,3R*)-4-Acetamido-3-methylbutan-1,2-diol Diacetate (25a). To a mixture of palladium(II) acetate (4.5 mg, 20 μmol) and *tert*-butyl isocyanide

(25 mg, 0.30 mmol) in toluene (0.7 mL) was added **23a** (400 mg, 1.00 mmol). The mixture was stirred at rt for 4 h, and then evaporated. The residue dissolved in hexane was treated with activated carbon, filtered through a pad of Celite®, and evaporated. A mixture of the residue and trifluoroacetic acid (2.27 g, 20 mmol) was stirred at 45 °C for 10 h. After removal of trifluoroacetic acid under reduced pressure, KHF_2 (622 mg, 8.0 mmol), MeOH (1.5 mL), KF (116 mg, 2.0 mmol), H_2O_2 (30% in water, 1.0 mL), and $KHCO_3$ (800 mg, 8.0 mmol) were added, and the mixture was stirred at rt for 1 d. Excess $Na_2S_2O_3$ was added and abolition of H_2O_2 was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a similar procedure to that used for **6a**, and the title compound **25a** was isolated by column chromatography on silica gel ($CHCl_3$: MeOH : *aq* NH_3 = 250 : 15 : 1, 94 mg, 39%): ^1H NMR δ 0.96 (d, J = 7.1 Hz, 3 H), 1.95–2.10 (m, 1 H), 1.97 (s, 3 H), 2.05 (s, 3 H), 2.09 (s, 3 H), 3.08 (dt, J = 14.0, 5.5 Hz, 1 H), 3.43 (ddd, J = 5.3, 6.9, 14.0 Hz, 1 H), 4.05 (dd, J = 6.7, 12.1 Hz, 1 H), 4.33 (dd, J = 2.8, 12.1 Hz, 1 H), 4.95 (ddd, J = 2.8, 6.7, 7.8 Hz, 1 H), 5.75–6.00 (br, 1 H); ^{13}C NMR δ 13.8, 20.7, 21.0, 23.3, 34.5, 41.0, 63.5, 73.2, 170.3, 170.8, 171.0; IR (neat) 3304, 2980, 1740, 1660, 1558, 1442, 1376, 1230, 1050 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO_5$: C, 53.87; H, 7.81; N, 5.71. Found: C, 53.68; H, 7.54; N, 5.75.

The following syntheses of **25b** and **25c** were carried out according to the preceding procedure for **25a**.

(2R*,4R*)-4-Acetamidoheptan-1,2-diol Diacetate (25b). ^1H NMR δ 0.80–0.93 (m, 3 H), 1.18–1.50 (m, 4 H), 1.57–1.82 (m, 2 H), 1.95 (s, 3 H), 2.02 (s, 6 H), 3.84–4.60 (m, 1 H), 4.08 (dd, J = 6.2, 12.2 Hz, 1 H), 4.24 (dd, J = 3.2, 12.2 Hz, 1 H), 4.93–5.07 (m, 1 H), 5.50–5.85 (br, 1 H); ^{13}C NMR δ 13.8, 18.9, 20.7, 21.1, 23.3, 35.8, 37.3, 45.9, 64.6, 69.5, 169.8, 170.7; IR (neat) 3288, 2968, 1740, 1658, 1548, 1446, 1376, 1244, 1048 cm^{-1}. Anal. Calcd for $C_{13}H_{23}NO_5$: C, 57.01; H, 8.35; N, 4.91. Found: C, 57.13; H, 8.48; N, 5.12.

(2R*,4S*)-4-Acetamido-4-phenylbutan-1,2-diol Diacetate (25c). ^{1}H NMR δ 1.92–2.23 (m, 2 H), 1.96 (s, 3 H), 1.97 (s, 3 H), 2.03 (s, 3 H), 4.09 (dd, J = 5.7, 12.1 Hz, 1 H), 4.24 (dd, J = 3.4, 12.1 Hz, 1 H), 4.84–4.98 (m, 1 H), 5.05 (q, J = 8.0 Hz, 1 H), 6.41 (d, J = 8.0 Hz, 1 H), 7.18–7.40 (m, 5 H); ^{13}C NMR δ 20.6, 20.9, 23.2, 36.9, 50.2, 64.5, 69.3, 126.3, 127.6, 128.7, 141.0, 169.4, 170.5, 170.6; IR (neat) 3304, 3024, 1740, 1660, 1546, 1374, 1220, 1050, 768 cm^{-1}. Anal. Calcd for $C_{11}H_{19}NO_5$: C, 62.53; H, 6.89; N, 4.56. Found: C, 62.25; H, 6.69; N, 5.75.

Preparation of Disilanyl Alkenes 26. Disilanyl alkenes **26a** and **26b** were prepared from the corresponding Grignard reagents by a procedure similar to that used to prepare **20a–c**. Disilanyl alkenes **26c** was prepared from (1-penten-4-yl)magnesium bromide by a procedure similar to that used to prepare **20d**. Disilanyl alkene **26d–f** were prepared by a procedure similar to that used to prepare **1e**.

1,1-Dimethyl-2-(trimethylsilylmethyl)siletane (27a). By a procedure similar to that used to prepare **21a**, the intramolecular bis-silylation of **26a** was carried out to give **27a** (83%): ^{1}H NMR δ -0.06 (s, 9 H), 0.20 (s, 3 H), 0.25 (s, 3 H), 0.61–0.70 (m, 2 H), 0.75–0.86 (m, 2 H), 1.25–1.65 (m, 2 H), 2.34–2.52 (m, 1 H); ^{13}C NMR δ -5.1, -1.5, 1.0, 11.0, 18.8, 24.8, 29.5; IR (neat) 2964, 1250, 840 cm^{-1}; MS m/z: 186 (M$^+$). Anal. Calcd for $C_9H_{22}Si_2$: C, 57.98; H, 11.89. Found: C, 58.26; H, 12.05.

(2R*,3R*)-2-[(Dimethylphenylsilyl)methyl]-3-methyl-1,1-diphenylsiletane (27b). By a procedure similar to that used to prepare **21a**, the intramolecular bis-silylation of **26b** was carried out to give **27b** (76%): ^{1}H NMR δ 0.14 (s, 3 H), 0.18 (s, 3 H), 0.80–1.08 (m, 3 H), 1.20 (d, J = 6.3 Hz, 3 H), 1.39 (dt, J = 10.7, 3.3 Hz, 1 H), 1.69 (dd, J = 7.9, 14.1 Hz, 1 H), 1.94–2.20 (m, 1 H), 7.20–7.60 (m, 15 H); ^{13}C NMR δ -2.7, -2.5, 16.4, 20.1, 24.2, 33.0, 38.4, 127.6, 127.8, 128.7, 129.5, 133.7, 134.8, 135.5, 135.7, 136.4, 139.4; IR (neat) 3076, 2960, 1430, 1250, 1114, 838, 734, 700 cm^{-1}. Anal. Calcd for

$C_{25}H_{30}Si_2$: C, 77.65; H, 7.82. Found: C, 77.78; H, 7.78.

(2R*,4R*)-2-[(Dimethylphenylsilyl)methyl]-4-methyl-1,1-diphenylsiletane (27c). By a procedure similar to that used to prepare **21a**, the intramolecular bis-silylation of **26c** was carried out to give **27c** (91%): ^{1}H NMR δ 0.02 (s, 6 H), 1.11 (dd, J = 7.8, 14.8 Hz, 1 H), 1.18 (d, J = 7.2 Hz, 3 H), 1.27 (dd, J = 7.8, 14.8 Hz, 1 H), 1.45–1.70 (m, 1 H), 1.72–1.95 (m, 2 H), 2.82 (dt, J = 10.6, 9.2 Hz, 1 H), 7.27–7.69 (m, 15 H); ^{13}C NMR δ -2.6, -2.4, 15.7, 17.8, 20.9, 22.2, 40.0, 127.7, 127.9, 128.7, 129.5, 133.6, 134.6, 135.7, 136.1, 137.1, 139.7. IR (neat) 3076, 2960, 1430, 1250, 1114, 834, 700 cm^{-1}. Anal. Calcd for $C_{25}H_{30}Si_2$: C, 77.65; H, 7.82. Found: C, 77.47; H, 7.61.

Synthesis of (1R*,2S*)-1-Phenyl-1,2,3-propantriol (28d). To a mixture of palladium(II) acetate (3.3 mg, 0.015 mmol) and 1,1,3,3-tetramethylbutyl isocyanide (31 mg, 0.22 mmol) in toluene (0.6 mL) was added **26d** (140 mg, 0.46 mmol). The mixture was stirred at 35 °C for 3 h, and then passed through Florisil®. After evaporation of volatiles, THF (1 mL), MeOH (1 mL), KF (110 mg, 1.9 mmol), KHCO$_3$ (93 mg, 0.93 mmol) and H$_2$O$_2$ (30% in water, 0.47 mL) were added, and the mixture was stirred at 35 °C for 10 h. Excess Na$_2$S$_2$O$_3$ was added and abolition of H$_2$O$_2$ was ascertained by test paper. After evaporation of volatiles, the residue was acetylated by a similar procedure to that used for **6a** to give **28d** (95 mg, 70%).

The syntheses of **28e** and **28f** were carried out according to the preceding procedure for **28d**.

References and Notes

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Price, C. C.; Sowa, J. R. *J. Org. Chem.* **1967**, *32*, 4126. However, cleavage of the Ph–Si bond of PhSiMe$_2$Bu^n with ^{t}BuOK in DMSO was found to be much slower than that of a 1,2-oxasilolane. It has been also reported that an alkoxide anion assists intramolecularly to cleave an unactivated C–Si bond: Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1982**, *104*, 6808; Hudrlik, P. F.; Abdallah, Y. M.; Hudrlik, A. M. *Tetrahedron Lett.* **1992**, *33*, 6743, 6747. In the present case, ^{t}BuOK might cause ring opening reaction of the 1,2-oxasilolane to produce an alkoxide anion, which assists cleavage of the Ph–Si bond intramolecularly. The failure of the cleavage in aprotic ether solvents may suggest that DMSO acts as an effective scavenger of the resulting phenyl anion to shift the reaction forward.
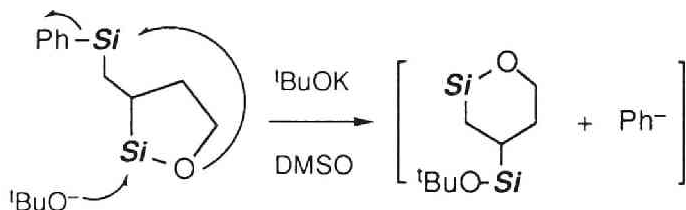
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List of Publications

Chapter 1
Palladium–Catalyzed Insertion of Isocyanides into Silicon-Silicon Linkage of Oligosilanes
Ito, Y.; Suginome, M.; Matsuura, T.; Murakami, M. *J. Am. Chem. Soc.* **1991**, *113*, 8899-8908.

Chapter 2
Novel Skeletal Rearrangement Reaction of Oligosilanes with Aryl Isocyanides
Ito, Y.; Suginome, M.; Murakami, M.; Shiro, M. *J. Chem. Soc., Chem. Commun.* **1989,** 1494-1495.

Chapter 3
Palladium(II) Acetate–*tert*-Alkyl Isocyanide as a Highly Efficient Catalyst for the Inter- and Intramolecular Bis-silylation of Carbon-Carbon Triple Bonds
Ito, Y.; Suginome, M.; Murakami, M. *J. Org. Chem.* **1991**, *56*, 1948-1951.

Chapter 4
Intramolecular Bis-silylation of Carbon-Carbon Double Bonds Leading to Stereoselective Synthesis of 1,2,4-Triols
Murakami, M.; Andersson, P. G.; Suginome, M.; Ito, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3987-3988.

Stereoselective Intramolecular Bis-silylation of Alkenes Promoted by Palladium-Isocyanide Catalyst Leading to Polyol Synthesis.
Murakami, M.; Suginome, M.; Andersson, P. G.; Nakamura, H.; Fujimoto, K.; Ito, Y., to be submitted

Other Publications

(1)   Convenient Preparative Method and Crystal Structures of (Triphenyl-
       phosphine)Gold(I) Enolate and Homoenolate Complexes
       Ito, Y.; Inouye, M.; Suginome, M.; Murakami, M. *J. Organomet. Chem.*
       1988, *342*, C41-C44.

(2)   Reaction of (Triphenylphosphine)Gold(I) Enolate and Homoenolates
       Murakami, M.; Inouye, M.; Suginome, M.; Ito, Y. *Bull. Chem. Soc. Jpn.*
       1988, *61*, 3649-3652.

(3)   Stereoselective Synthesis of 1,2,4-Triols via Intramolecular Bis-silylation
       of Carbon-Carbon Triple Bonds Followed by Hydrogenation
       Murakami, M.; Oike, H.; Sugawara, M.; Suginome, M.; Ito, Y.
       Tetrahedron, in press.