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Mixed reagent (aminosilyl)lithium/*i*-PrMgBr for the synthesis of functionalized oligosilanes

Atsushi Kawachi, Kohei Tamao *

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

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Abstract

Mixed reagents prepared in situ from the (aminosilyl)lithiums with *i*-PrMgBr undergo coupling reactions with chloro-oligosilanes without Si–Si bond cleavage, which is a serious side reaction with the (aminosilyl)lithiums themselves. Based on the coupling reaction and the amino-to-chloro transformation, functionalized tetrasilanes and hexasilanes are synthesized. The analysis of the ^{1}H- and ^{29}Si-NMR spectra indicates that these oligosilanes include three configurational isomers, *ll*, *ul*, and *uu*. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Oligosilanes; Magnesium; Stereoisomers

1. Introduction

Polysilanes have received much attention due to their interesting chemical and physical properties [1]. To investigate these properties, synthetic methodologies for structurally well-defined oligo- and polysilanes have been developed. The standard method for the Si–Si chain elongation is based on a combination of two steps: (1) coupling of (organosilyl)lithiums [2] with silanes bearing good leaving groups such as halogens and the trifluoromethane sulfonate group, and (2) conversion of the organic groups such as the phenyl and methyl groups on the silicon atom(s) into good leaving groups. Based on this methodology, Lambert et al. [3a], Suzuki et al. [3b], and Sekiguchi et al. [3c] independently had a remarkable success in the syntheses of dendric polysilanes with regular three-dimensional structures.

We previously reported that the (aminosilyl)lithiums **1**–**3** readily react with chlorosilanes to yield a variety of amino-disilanes and trisilanes [4]. By treatment with an acyl chloride [4] or hydrogen chloride [5], these amino-oligosilanes can be converted into the chloro-oligosilanes, which work as precursors for further Si–Si chain elongation reaction. This facile functional group transformation is one of the most remarkable features in the aminosilyl anion chemistry. In the reaction of the (aminosilyl)lithiums with chloro-oligosilanes, however, cleavage of the Si–Si bond often occurs to lower the yields of the desired coupling products. To overcome this problem, we have tried to control the reactivity of the aminosilyl anions by changing the counter cation Li^{+} to other metal cations. Considering the electronegativity [6], Mg (1.23), Zn (1.66), and Cu (1.75) were expected to form more covalent bonding to Si (1.74) than Li (0.97), so that the reactivity of silyl–magnesium [7], silyl–zinc [8], and silyl–copper [9] species could be different from that of the silyllithiums. Among the metals examined so far, we found that magnesium is the most suitable for our purpose. We report here the preparation of the mixed reagents of the (aminosilyl)lithium and *i*-PrMgBr and their application to the synthesis of functionalized oligosilanes based on the facile amino-to-chloro transformation.

* Corresponding author. Tel.: +81-774-383180; fax: +81-774-383186.

E-mail address: tamao@sc1.kyoto-u.ac.jp (K. Tamao)

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2. Results and discussion

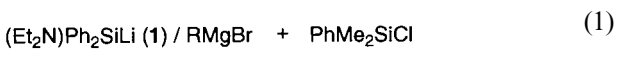
2.1. Preparation and reaction of mixed (aminosilyl)lithium/i-PrMgBr reagents

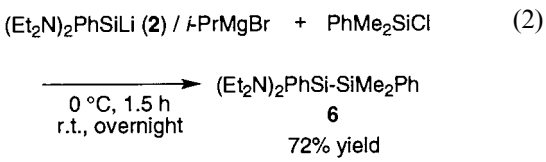
The mixed reagents were prepared in situ by mixing the (aminosilyl)lithiums **1**–**3** [4] with alkyl Grignard reagents, RMgBr, at 0°C based on the method reported by Oshima and co-workers [7d]. The reagents might involve the (aminosilyl)(alkyl)magnesium moieties as previously proposed [7b], and thus potentially may offer two reaction modes, that is, silylation and alkylation, which depend on the transfer ability of the silyl group and the alkyl group. The reactions of a series of reagents **1**/RMgBr (R = Me, Et, *i*-Pr) with $PhMe_2SiCl$ in THF–Et_2O were examined (Eq. (1)). In all cases, the silylation product, $(Et_2N)Ph_2Si$–$SiMe_2Ph$ (**4**), was more preferred than the alkylation product, R–$SiMe_2Ph$ (**5**), as shown in Table 1. Selectivity of the silylation increased as the alkyl group became bulkier. The alkylation was completely suppressed in the case of the isopropyl group. It is noted that the silylation should regenerate *i*-PrMgX (X = Cl, Br), but no alkylation of the chlorosilane was observed under the reaction condition. Two other mixed reagents, **2**/*i*-PrMgBr and **3**/*i*-PrMgBr, also exhibited sufficient reactivity toward $PhMe_2SiCl$ under mild conditions (0°C, 0.5–1.5 h) to afford **6** and **7** in 72 and 57% yields, respectively, without formation of the alkylation product **5**, as shown in Eqs. (2) and (3).

Other examined species are mentioned for comparison. While a silyl–magnesium species prepared from **1** with $MgBr_2$ (**1**–$MgBr_2$ = 1:1 and 2:1 mol ratio) afforded **4** in much lower yields, other mixed-metal reagents prepared from **1** with CuCN, $ZnCl_2$, $ZnCl_2$·tmeda, or *n*-Bu_2Zn afforded only a complex mixture during the reaction with chlorosilanes.

$(Et_2N)Ph_2SiLi$ **1** $(Et_2N)_2PhSiLi$ **2** $(Et_2N)PhMeSiLi$ **3**

Chart 1





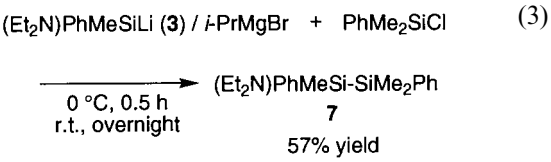
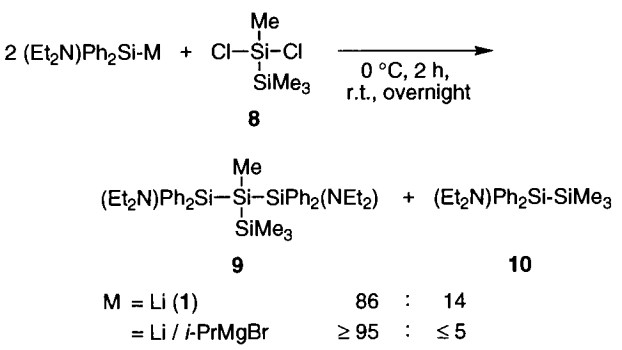


Table 1
Products from reactions of the mixed reagent **1**/RMgBr with $PhMe_2SiCl$ according to Eq. (1)

	Product(s)	
RMgBr	Total yield (%) [a]	Silylation (**4**):Alkylation (**5**) [b]
MeMgBr	80	87:13
EtMgBr	88	88:12
i-PrMgBr	80	100:0

[a] Isolated yields by bulb-to-bulb distillation.
[b] The ratio was determined by ^{1}H-NMR analysis of the reaction mixture.

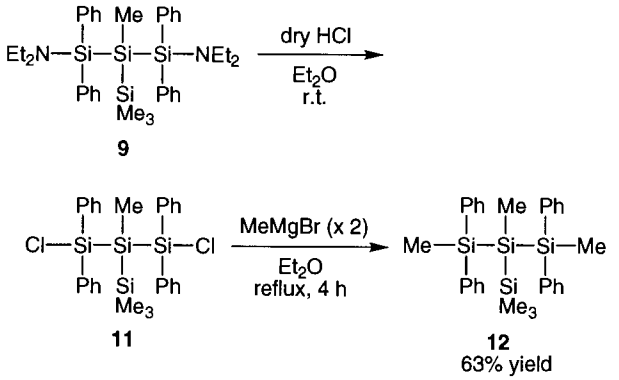


Scheme 1.

2.2. Synthesis of oligosilanes

Using the (aminosilyl)lithium/*i*-PrMgBr mixed reagents, the undesired Si–Si bond cleavage was almost completely suppressed, as shown in Scheme 1. Thus, the mixed reagent **1**/*i*-PrMgBr (2 mol) reacted with the 1,1-dichlorodisilane **8** [10] to afford the desired coupling product **9** in higher than 95% chemoselectivity, whereas the lithium reagent **1** itself significantly caused the Si–Si bond cleavage, yielding **10** in addition to **9** (**9**:**10** = 86:14). We found that the hydrolysis of the reaction mixture of **9** under alkaline conditions using a 1 M NaOH aq. solution at 0°C was successful to decompose the regenerated Grignard reagent by keeping the silicon–nitrogen bond intact.

For the amino-to-chloro transformation, **9** was treated with an excess of dry hydrogen chloride in Et_2O at room temperature to yield the corresponding dichlorotetrasilane **11**, as shown in Scheme 2. For isolation, **11** was methylated with MeMgBr in Et_2O to afford **12** in 63% overall yield based on **8**. The ^{29}Si-NMR spectrum of **12** showed signals at δ −11.5 (−*Si*Me_3), −16.1 (−*Si*Ph_2Me), and −85.3 (+*Si*Me), which are consistent with the reported chemical shift ranges for the polydimethylsilanes, e.g. −9 to



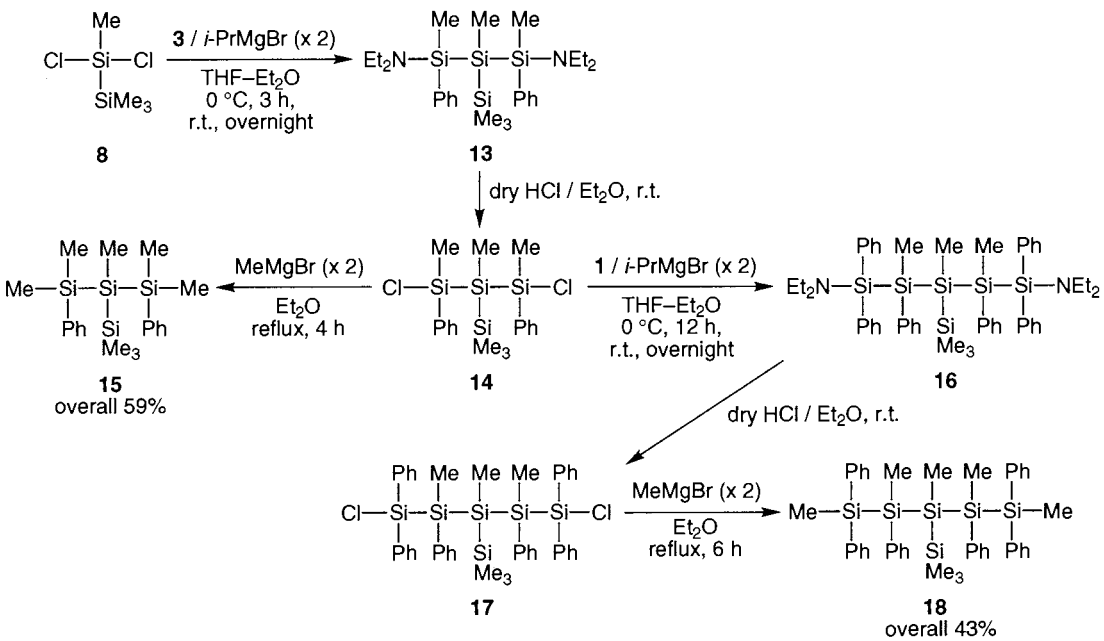
Scheme 2.

−20 ppm for $-SiMe_3$ and −79 to −81 ppm for +SiMe [11].

An example of the synthesis of functionalized hexasilanes by reiteration of this methodology is shown in Scheme 3. The reaction of the mixed reagent, **3**/*i*-PrMgBr (2 mol amt.), with **8** in THF–Et_2O at 0°C afforded the desired branched tetrasilane **13**. After decomposition of the regenerated Grignard reagent using a 1 M NaOH aq. solution followed by the usual work-up, the reaction mixture of **13** was treated with an excess of dry hydrogen chloride in Et_2O at room temperature, yielding the dichlorotetrasilane **14**. For isolation, **14** was methylated with MeMgBr in Et_2O to afford **15** in 59% overall yield based on **8**. The ^{29}Si-NMR spectrum of **15** showed signals at δ −11.9 ($-SiMe_3$), −15.5 ($-SiPhMe_2$), and −86.4 (+*Si*Me). The second silylation was performed on **14** using the reagent **1**/*i*-PrMgBr (2 mol amt.) in THF–Et_2O at 0°C, which afforded the branched hexasilane **16**. The amino-to-chloro transformation of **16** and subsequent methylation of the resulting dichlorohexasilane **17** afforded the corresponding hexasilane **18** in 43% overall yield based on **8** as a mixture of the configurational isomers (see below).

2.3. Identification of the stereoisomers of *14* and *18*

The stereoisomers of **14** and **18** were identified as follows. Due to the two chiral silicon centers, there are



Scheme 3.

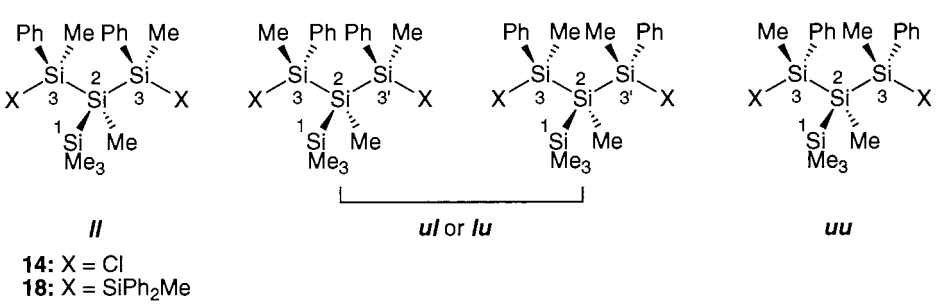


Fig. 1. Configurational isomers of **14** and **18**.

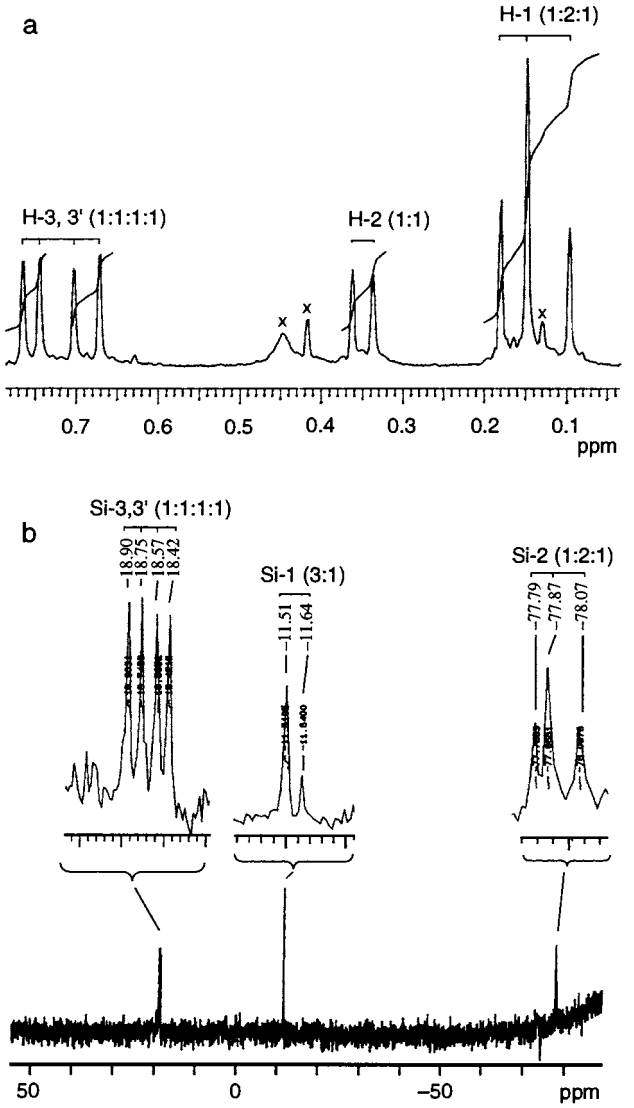


Fig. 2. ^{1}H- and ^{29}Si-NMR spectra of a mixture of **14*ll***, **14*ul***, and **14*uu***: (a) ^{1}H-NMR, and (b) ^{29}Si-NMR. The marked (×) peaks in the ^{1}H-NMR spectrum are due to impurities.

three possible configurational isomers, *ll*, *ul* and its enantiomer *lu*, and *uu*, in **14** and **18**, as shown in Fig. 1, where *l* and *u* denote 'like' and 'unlike', respectively [12,13].

According to the ^{1}H- and ^{29}Si-NMR spectra of the crude product **14** (Fig. 2), all of the three isomers are present in the ratio of 1:2:1. The ^{1}H-NMR spectrum (Fig. 2(a)) displays three signals of the methyl protons on the Me_3Si group (H-1) at δ 0.096, 0.15, and 0.18 in the ratio of 1:2:1, which is consistent with the statistical distribution of the three isomers. The methyl protons appear on the branched silicon atoms (H-2) at δ 0.34 and 0.36 in the ratio of 1:1, in one of which the signals of the isomers **14*ll*** and **14*uu*** may be coincidentally overlapped, and the other can be assigned to the signal of the isomer **14*ul***. The methyl protons also appear on the chiral silicon atom (H-3) at δ 0.67, 0.70, 0.74, and 0.76 in the ratio of 1:1:1:1, due to the methyl groups in **14*ll*** and **14*uu*** and non-equivalence of the two methyl groups in **14*ul***. The ^{29}Si-NMR spectrum (Fig. 2(b)) shows signals of the silicon atom of the Me_3Si group (Si-1) at δ −78.07, −77.87, and −77.79 in the ratio of 1:2:1, which is consistent with the ^{1}H-NMR spectrum. Two signals of the branched silicon atoms (Si-2) appear at δ −11.64 and −11.51 in the ratio of 1:3, where the former is assigned to the signal of **14*ll*** (or **14*uu***) and the latter is assigned to the coincidentally overlapped signals of **14*ul*** and **14*uu*** (or **14*ll***). Signals for the chiral silicon atoms (Si-3) appear at δ 18.42, 18.57, 18.75, and 18.90 in the ratio of 1:1:1:1, which is consistent with the ^{1}H-NMR spectrum.

The ^{1}H-NMR spectrum of **18**, obtained from **14** and purified by medium-pressure liquid chromatography, displays several peaks due to the methyl protons attributed to the isomers, as shown in Fig. 3, but the assignment of these peaks was difficult at this stage. Fortunately, the major isomer could be isolated using reverse-phase liquid chromatography, which allowed us to make an assignment of the ^{1}H and ^{29}Si peaks, as shown in Fig. 4.

The ^{1}H-NMR spectrum of the major isomer (Fig. 4(a)) displays a singlet for the methyl protons on the Me_3Si group (H-1) at δ −0.010 and a singlet for the methyl protons on the branched silicon atom (H-2) at δ −0.28. A pair of signals for the methyl protons on the chiral silicon atom (H-3) appears at δ 0.41 and 0.51 in the ratio of 1:1. The non-equivalence of the methyl groups is the expected pattern of the isomer **18*ul***. The methyl protons on the terminal silicon atoms (H-4) also

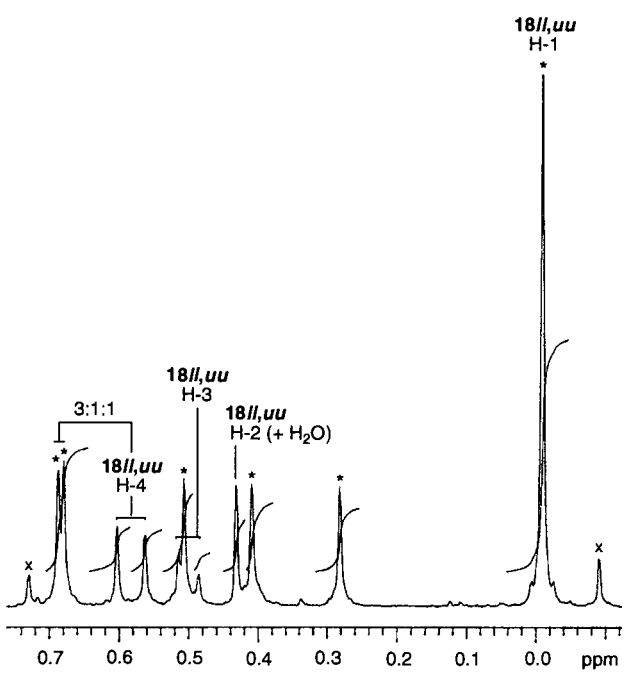


Fig. 3. ^{1}H-NMR spectrum of **18**. The peaks marked with an asterisk (*) belong to **18*ul***. The marked (×) peaks are due to impurities.

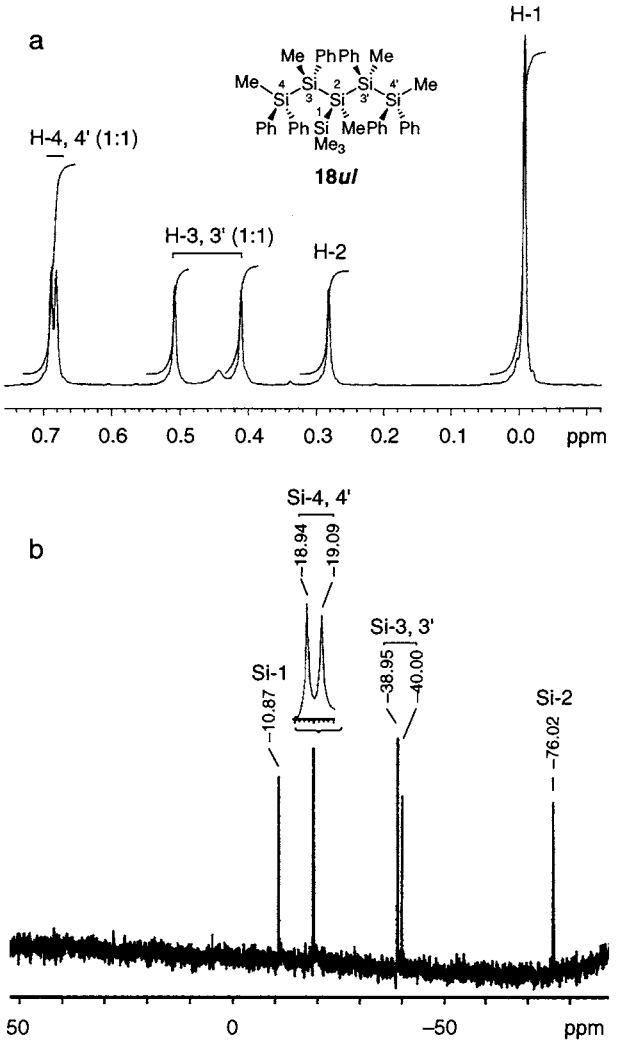


Fig. 4. ^{1}H- and ^{29}Si-NMR spectrum of **18*ul***. (a) ^{1}H-NMR, and (b) ^{29}Si-NMR.

appear as a pair of signals at δ 0.68 and 0.69 in the ratio of 1:1. The ^{29}Si-NMR spectrum (Fig. 4(b)) displays a single peak for the branched silicon atom (Si-2) at δ −76.02. A pair of signals for the chiral silicon atoms (Si-3) appears at δ −40.00 and −38.95 in the ratio of 1:1, and also a pair of signals for the terminal silicon atoms (Si-4) at δ −19.09 and −18.94 in the ratio of 1:1, which is consistent with the ^{1}H-NMR spectrum. A single peak for the silicon atom of the Me_3Si group (Si-1) appears at δ −10.87. Thus the major isomer formed is assigned to **18*ul***.

Based on the assignment of **18*ul***, other peaks in the ^{1}H-NMR spectrum shown in Fig. 3 can be tentatively assigned. Thus, the ratio of the isomers **18*ll***, **18*ul***, and **18*uu*** is roughly estimated to be 1:3:1, based on the integral ratio of the methyl protons on the terminal silicon atoms (H-4) [14]. The estimated ratio is different from the statistical distribution of the three isomers (1:2:1). It is plausible that the formation of **18*ll*** and **18*uu*** is less favorable than **18*ul*** due to the steric repulsion between the phenyl groups on Si-3.

3. Experimental

3.1. General

The ^{1}H(200 MHz)-, ^{13}C(50.29 MHz)-, and ^{29}Si(39.73 MHz)-NMR spectra were recorded on a Varian VXR-200 spectrometer or the ^{1}H(270 MHz)-, ^{13}C(67.94 MHz)-, and ^{29}Si(53.67 MHz)-NMR spectra were recorded on a JEOL EX-270 spectrometer. The ^{1}H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^{1}H δ 7.200 and ^{13}C δ 128.00). Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected to a JEOL LGC-20K gas chromatograph equipped with a 1 m glass column packed with OV-17 (3%) on Chromosorb. The elemental analyses were performed at the Microanalysis Center of Kyoto University or at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Analytical samples were purified by preparative GLC, preparative medium-pressure liquid chromatography (MPLC), or recycling reverse-phase liquid chromatography. The GLC analysis was performed on a Shimadzu GC-4B gas chromatograph equipped with a 3 or 1 m column packed with 30% Silicone DC550 on Celite 545. Preparative MPLC was performed with a silica gel prepacked C.I.G. column (Kusano, Si-10). Recycling reverse-phase liquid chromatography was performed with a JAI LC-908 equipped with JAIGEL-ODS S-343-15 and P-15 columns. Column chromatography was performed by using Kieselgel 60 (Merck, 70–230 mesh). Thin-layer chromatography (TLC) was performed on plates of silica gel 60F-254 (Merck).

The lithium dispersion (25 or 30 wt.% in mineral oil) was purchased from Aldrich. Lithium granules were purchased from Chemetall Gesellshaft. Methylmagnesium bromide in diethyl ether was purchased from Tokyo Chemical Industry Co. Ethylmagnesium bromide in diethyl ether and isopropylmagnesium bromide in diethyl ether were prepared from magnesium with ethylbromide and isopropylbromide, respectively, and titrated prior to use [15]. Phenyldimethylchlorosilane was distilled under reduced pressure before use. 1,1-Dichlorotetramethyldisilane **8** was prepared by the literature method [10]. Ether and THF were distilled under a nitrogen atmosphere from sodium–benzophenone. Hexane was dried over sodium wire and distilled under a nitrogen atmosphere. All reactions were carried out under a nitrogen or argon atmosphere.

The (aminosilyl)lithiums **1**–**3** were prepared by reaction of the corresponding (amino)chlorosilanes with lithium metal in THF as previously reported [4].

3.2. A typical procedure for preparation of the mixed reagent (aminosilyl)lithiums/*i*-PrMgBr: preparation of **2**/*i*-PrMgBr and trapping as 1,1-bis(diethylamino)-1,2-diphenyl-2,2-dimethyldisilane (**6**)

To a solution of **2**, prepared from bis(diethylamino)phenylchlorosilane (2.0 mmol) and lithium dispersion (11 mg atom) in THF (4.0 ml) [4], was added *i*-PrMgBr in Et_2O (1.5 ml, 2.0 mmol) at 0°C. The solution was stirred at the same temperature for 30 min to afford a dark brown solution **6**. To the solution was added phenyldimethylchlorosilane (0.36 ml, 2.2 mmol) at 0°C. The reaction mixture was stirred at the same temperature for 30 min and at room temperature (r.t.) overnight. The reaction mixture was then diluted with hexane (20 ml), stirred vigorously, and filtered. The filtrate was concentrated and the residue was subjected to bulb-to-bulb distillation to give **6** (543 mg, 72% yield) as a pale yellow oil. B.p. 185–205°C/0.55 mmHg (bath temperature). ^{1}H-NMR (C_6D_6): δ 0.53 (s, 6H), 1.01 (t, $J = 7.0$ Hz, 12H), 3.02 (q, $J = 7.0$ Hz, 8H), 7.18–7.22 (m, 3H), 7.29–7.33 (m, 3H), 7.46–7.50 (m, 2H), 7.71–7.75 (m, 2H). ^{13}C-NMR (C_6D_6): δ −1.28, 15.03, 40.24, 127.82, 127.95, 128.60, 129.15, 134.72, 135.52, 139.51, 140.23. MS: *m*/*e* 384 [M^+]. Anal. Calc. for $C_{22}H_{36}N_2Si_2$: C, 68.69; H, 9.43. Found: C, 68.60; H, 9.26%.

3.3. 1-Diethylamino-1,1,2-triphenyl-2,2-trimethyldisilane (**4**)

B.p. 225–255°C/1.0 mmHg (bath temperature). ^{1}H-NMR (C_6D_6): δ 0.25 (s, 9H), 1.00 (t, $J = 7.0$ Hz, 6H), 3.03 (q, $J = 7.0$ Hz, 4H), 7.26–7.30 (m, 3H), 7.71–7.76 (m, 2H). ^{13}C-NMR (C_6D_6): δ −1.99, 15.28, 41.86, 127.93, 128.07, 128.85, 129.28, 134.74, 135.71, 138.12, 139.21. MS: *m*/*e* 389 [M^+]. Anal. Calc. for $C_{24}H_{31}NSi_2$: C, 73.77; H, 8.01. Found: C, 73.54; H, 8.10%.

3.4. 1-Diethylamino-1,2-diphenyl-1,2,2-trimethyldisilane (**7**)

B.p. 160–180°C/1.0 mmHg (bath temperature). ^{1}H-NMR (C_6D_6): δ 0.42 (s, 3H), 0.44 (s, 3H), 0.52 (s, 3H), 0.92 (t, $J = 7.0$ Hz, 6H), 2.87 (q, $J = 7.0$ Hz, 4H), 7.23–7.29 (m, 6H), 7.47–7.52 (m, 2H), 7.58–7.62 (m, 2H). ^{13}C-NMR (C_6D_6): δ −2.91, −1.72, 15.71, 41.69, 128.00, 128.07, 128.74, 128.99, 134.42, 134.54, 139.54, 140.35. MS: *m*/*e* 327 [M^+]. Anal. Calc. for $C_{19}H_{29}NSi_2$: C, 69.66; H, 8.92. Found: C, 69.36; H, 9.19%.

3.5. Reaction of the mixed reagent **1**/*i*-PrMgBr with 1,1-dichlorotetramethyldisilane (**8**): synthesis of 2-trimethylsilyl-1,3-bis(diethylamino)-1,1,3,3-tetraphenyl-2-methyltrisilane (**9**)

To a solution of **1**, prepared from (diethylamino)-diphenylchlorosilane (5.6 mmol) and granular lithium (26 mg-atom) in THF (10 ml) [4], was added *i*-PrMgBr in Et_2O (4.3 ml, 5.6 mmol) over 4 min at 0°C. The reaction solution was then stirred at 0°C for 30 min. To the solution was added a solution of **8** (546 mg, 2.8 mmol) in THF (1.0 ml) at 0°C over 1 min. The reaction mixture was stirred at 0°C for 2 h and at r.t. overnight. To the reaction mixture was slowly added a 1 M NaOH aq. solution (0.3 ml) at 0°C and stirred for ca. 10 min. The mixture was filtered and the filtrate was evaporated. The residue was diluted with hexane (10 ml), dried over K_2CO_3 and concentrated in vacuo to give a 1.49 g of mixture of **9** and **10**: ^{1}H-NMR analysis of the mixture showed that the ratio of **9**:**10** was $\geq 95:\leq 5$. **9**: ^{1}H-NMR (C_6D_6): δ 0.14 (s, 9H), 0.66 (s, 3H), 0.94 (t, $J = 7.0$ Hz, 12H), 3.00 (q, $J = 7.0$ Hz, 8H), 7.23–7.27 (m, 12H), 7.60–7.64 (m, 4H), 7.69–7.74 (m, 4H). **10**: ^{1}H-NMR (C_6D_6): δ 0.25 (s, 9H), 1.00 (t, $J = 7.0$ Hz, 6H), 3.03 (q, $J = 7.0$ Hz, 4H), 7.26–7.30 (m, 6H), 7.71–7.75 (m, 4H).

3.6. Transformation of **9**: synthesis of 2-trimethylsilyl-1,1,3,3-tetraphenyl-1,2,3-trimethyltrisilane (**12**)

1. Through a solution of crude **9** (1.49 g) in Et_2O (20 ml) as prepared above, was bubbled dry hydrogen chloride, generated from ammonium chloride (7.8 g, 148 mmol) and concentrated sulfuric acid (6.3 ml, 113 mmol), at r.t. for 30 min with stirring. The mixture was diluted with hexane (20 ml) and filtered. The filtrate was concentrated to afford crude **11** (1.27 g) as an oil, which was used in the next step without purification. ^{1}H-NMR (C_6D_6): δ 0.16 (s, 9H), 0.66 (s, 3H), 7.07–7.13 (m, 12H), 7.60–7.66 (m, 8H). ^{13}C-NMR (C_6D_6): (The phenyl carbons of the $ClPh_2Si$– groups are diastereotopic.) δ −9.92, 0.13, 128.34, 128.38, 130.38, 130.43, 134.87, 135.01, 135.07, 135.41. ^{29}Si-NMR (C_6D_6): δ −76.32, −10.42, 10.35.
2. To a solution of **11** in Et_2O (5.0 ml) was added MeMgBr in Et_2O (3.9 ml, 11.1 mmol) at r.t. over 10 min and the reaction mixture was refluxed for 5 h. After being cooled to 0°C, the reaction mixture was hydrolyzed with 1 M hydrochloric acid (10 ml) and extracted with Et_2O (2 × 20 ml). The combined organic layer was washed with brine (20 ml), water (20 ml), dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel (60 ml) eluted with 70:1 hexane–AcOEt to give **12** (892 mg, overall 63% yield) ($R_f = 0.20$) as an oil. **12**: ^{1}H-NMR (C_6D_6): δ 0.029 (s, 9H), 0.52 (s, 3H), 0.62 (s, 6H), 7.15–7.22 (m, 12H), 7.45–7.57 (m, 8H). ^{13}C-NMR ($CDCl_3$) (The phenyl carbons of

the $MePh_2Si$– groups are diastereotopic.): δ −10.29, −2.75, 0.15, 127.67, 127.75, 128.63, 128.75, 134.86, 134.97, 137.81, 137.93. ^{29}Si-NMR (C_6D_6): δ −85.29, −16.06, −11.50. MS: *m/e* 510 [M^+, 50], 495 [$M^+ - Me$, 4], 437 [$M^+ - SiMe_3$, 10], 360 (19), 313 [$M^+ - SiPh_2Me$, 22], 298 (44), 236 (49), 197 [$MePh_2Si^+$, 100]. Anal. Calc. for $C_{30}H_{38}Si_4$: C, 70.52; H, 7.50. Found: C, 70.43; H, 7.39%.

3.7. Reaction of **1** with **8**

To a solution of **1**, prepared from (diethylamino)diphenylchlorosilane (2.2 mmol) and granular lithium (10 mg-atom) in THF (3.0 ml) [4], was added Et_2O (1.6 ml), and then a solution of **8** (252 mg, 0.97 mmol) in Et_2O (1.0 ml) was added at 0°C. This reaction mixture was stirred at 0°C for 2 h and at r.t. overnight. The reaction mixture was evaporated and the residue was diluted with hexane (10 ml) and filtered. The filtrate was concentrated in vacuo to give an 820 mg mixture of **9** and **10**: ^{1}H-NMR analysis of the mixture showed that the ratio of **9**:**10** was 86:14.

3.8. Synthesis of 2-trimethylsilyl-1,3-diphenyl-1,1,2,3,3-pentamethyltrisilane (**15**)

1. To a solution of **3**, prepared from (diethylamino)phenylmethylchlorosilane (2.9 mmol) and a lithium dispersion (18 mg-atom) in THF (3 ml), was added *i*-PrMgBr in Et_2O (2.2 ml, 2.9 mmol) over 3 min at 0°C. The solution was stirred for 30 min to afford a dark-brown solution of the mixed reagent. To the solution was added **8** (217 mg, 1.1 mmol) in THF (1.0 ml) at 0°C. The reaction mixture was then stirred at 0°C for 2 h and at r.t. overnight. The reaction mixture was diluted with hexane (20 ml), stirred vigorously, and filtered. The filtrate was concentrated in vacuo to give crude **13** (600 mg) as a colorless oil, which was used in the next step without purification.
2. Through a solution of **13** (600 mg) in Et_2O (10 ml) was bubbled dry hydrogen chloride, generated from ammonium chloride (4.1 g, 75 mmol) and concentrated sulfuric acid (3.2 ml, 58 mmol), at 0°C for 20 min with stirring. The mixture was diluted with hexane (10 ml) and filtered. The filtrate was concentrated to afford crude **14** (455 mg) as an oil, which was used in the next step without purification. ^{1}H-NMR (C_6D_6): δ 0.096; 0.15; 0.18 (1:2:1), 0.34; 0.36 (1:1), 0.67; 0.70; 0.74; 0.76 (1:1:1:1). ^{29}Si-NMR (C_6D_6): δ 18.90; 18.75; 18.57; 18.42 (1:1:1:1), −11.51; −11.64 (3:1), −77.79; −77.87; −78.07 (1:2:1).
3. To a solution of **14** in Et_2O (7.0 ml) was added MeMgBr in Et_2O (2.0 ml, 5.8 mmol) at r.t. over 7 min and the reaction mixture was refluxed for 4 h. After being cooled to 0°C, the reaction mixture was hydrolyzed with 1 M hydrochloric acid (12 ml) and extracted with Et_2O (2 × 20 ml). The combined organic layer was washed with brine (10 ml), water (10 ml), dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel (30 ml) eluted with hexane to give **15** (255 mg, overall 59% yield based on **8**) ($R_f = 0.40$) as an oil. **15**: ^{1}H-NMR (C_6D_6) (the methyl protons of the Me_2PhSi– groups are diastereotopic): δ 0.072 (s, 9H), 0.25 (s, 3H), 0.38 (s, 6H), 0.42 (s, 6H), 7.20–7.24 (m, 6H), 7.43–7.48 (m, 4H). ^{13}C-NMR (C_6D_6) (The methyl carbons of Me_2PhSi– groups are diastereotopic.): δ −12.07, −1.41 and −1.36, 0.24, 128.05, 128.74, 134.07, 140.56. ^{29}Si-NMR (C_6D_6): δ −86.4, −15.5, −11.9. MS: *m/e* 386 [M^+, 46], 371 [$M^+ - Me$, 18], 313 [$M^+ - SiMe_3$, 15], 298 (3), 251 [$M^+ - SiMe_2Ph$], 236 (72), 221 (22), 191 (39), 177 (57), 174 (68), 135 [Me_2PhSi^+, 100]. Anal. Calc. for $C_{20}H_{34}Si_4$: C, 62.10; H, 8.86. Found: C, 62.02; H, 8.67%.

3.9. Synthesis of 3-trimethylsilyl-1,1,2,4,5,5-hexaphenyl-1,2,3,4,5-pentamethylpentasilane (**18**)

1. A solution of the mixed reagent prepared from **1** (2.1 mmol) in THF (3.5 ml) and *i*-PrMgBr in Et_2O (1.6 ml, 2.1 mmol) was added to a solution of the crude **14** (382 mg, ca. 0.89 mmol), prepared as above from **8** (4.4 mmol), in THF (5.0 ml) at 0°C over 20 min. The reaction mixture was stirred at 0°C for 12 h and at r.t. overnight. To the reaction mixture was added 1 M NaOH aq. solution (0.11 ml) at 0°C and the mixture was stirred at 0°C for 5 min. The mixture was dried over K_2CO_3 and concentrated to give crude **16** (832 mg) as an oil, which was used in the next step without purification.
2. Through a solution of **16** (832 mg) in Et_2O (10 ml) was bubbled dry hydrogen chloride, generated from ammonium chloride (7.25 g, 134 mmol) and concentrated sulfuric acid (6.00 ml, 108 mmol), at 0°C for 40 min with stirring. The mixture was diluted with hexane (20 ml) and filtered. The filtrate was concentrated to afford crude **17** as an oil, which was used in the next step without purification.
3. To a solution of **17** in Et_2O (4.0 ml) was added MeMgBr in Et_2O (1.5 ml, 4.1 mmol) at r.t. over 5 min and the reaction mixture was stirred at r.t. for 30 min and refluxed for 6 h. After being cooled to 0°C, the reaction mixture was hydrolyzed with 1 M hydrochloric acid (10 ml) and extracted with Et_2O (2 × 20 ml). The combined organic layer was washed with brine (10 ml), water (10 ml), and dried over $MgSO_4$, and concentrated. The residue was subjected to column chromatography on silica gel

(30 ml) eluted with 40:1 hexane–AcOEt ($R_f = 0.28$) and MPLC eluted with 40:1 hexane–AcOEt, which afforded a mixture of the configurational isomers of **18** (303 mg) as an oil in an overall 43% yield based on **8**. The ratio of the isomers ***18ll*–*18ul*–*18uu*** was roughly estimated to be 1:3:1. An analytical sample of the major isomer ***18ul*** was obtained by the recycling reverse-phase liquid chromatography eluted with CH_3CN. ***18ul***: ^{1}H-NMR (C_6D_6): δ −0.01 (s, 9H), 0.28 (s, 3H), 0.41 (s, 3H), 0.51 (s, 3H), 0.68 (s, 3H), 0.69 (s, 3H), 7.08–7.22 (m, 18H), 7.26–7.29 (m, 2H), 7.34–7.43 (m, 6H), 7.48–7.57 (m, 4H). ^{13}C-NMR ($CDCl_3$) (the phenyl carbons of the $MePh_2Si$– groups are diastereotopic): δ −8.55, −5.39, −5.01, −3.50, −3.30, 0.49, 127.42 (2C), 127.49, 127.53, 127.62, 127.67, 127.87, 128.10, 128.48 (2C), 128.77, 128.82, 134.91 (2C), 135.11, 135.18, 135.27, 135.42, 136.68, 136.73, 137.16, 137.41 (2C), 137.52. ^{29}Si-NMR (C_6D_6): δ −76.0, −40.0, −39.0, −19.1, −18.9, −10.9. MS: *m/e* 750 [M^+, 6], 553 [$M^+ - Ph$, 80], 476 [$M^+ - SiPh_2Me$, 35], 433 [$M^+ - SiPhMeSiPh_2Me$, 34], 197 (100). Anal. Calc. for $C_{44}H_{54}Si_6$: C, 70.33; H, 7.24. Found: C, 70.22; H, 7.14%.

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