Regioselective Synthesis of Polyfunctionalized Alkyltrisilanes and -tetrasilanes via Reductive Cross-Coupling Reaction of Aminoalkylsilyl Chlorides with Lithium

Kohei Tamao,* Guang-Ri Sun, Atsushi Kawachi, and Shigehiro Yamaguchi

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

Received November 12, 1996[⊗]

Highly selective cross-coupling reactions promoted by lithium metal have been achieved between aminodichloromonosilanes $R(Et_2N)SiCl_2$ (R = Me, Et, Ph, Et_2N) and 2 equiv of Me_3SiCl (**1**) or $(Et_2N)Me_2SiCl$ (**2**) and between aminochlorodisilanes $(Et_2N)_nMe_{3-n}SiSiMe(NEt_2)Cl$ (n = 1, 2) and 1 equiv of **1**, **2**, or $(Me_2N)_nR_{3-n}SiCl$ (n = 1, R = Et; n = 2, R = Me, Et) in THF at room temperature to form the corresponding symmetrical and unsymmetrical diamino- to pentaaminotrisilanes in high yields, which are transformed into alkoxy and fluoro derivatives under mild conditions. A tetraaminotetrasilane has also been prepared by reductive homocoupling of $(Et_2N)Me_2SiSiMe(NEt_2)Cl$ and converted into the alkoxytetrasilane. Some special experimental procedures have been employed for the selective coupling reactions.

Introduction

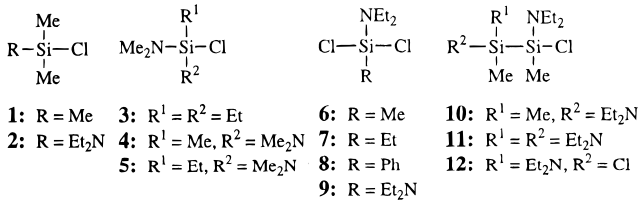
We have recently reported the synthesis of symmetrical di- and tetrafunctionalized disilanes via reductive *homo*coupling reactions of the corresponding aminoalkylsilyl chlorides with lithium.[1] Now we report the synthesis of a variety of polyfunctionalized tri- and tetrasilanes via reductive *cross*-coupling reactions of the corresponding aminoalkylsilyl chlorides with lithium. It is essential to employ an appropriate combination of two aminochlorosilanes and special experimental procedures for highly selective cross-coupling: the matched pair of aminochlorosilanes has been predicted mainly by simple semiempirical MO calculations. In view of the ready availability of aminoalkylsilyl chlorides and facile functional group transformations under mild conditions, the present method may afford the most convenient access to the structurally well-defined polyfunctionalized oligosilanes, since the synthesis of such compounds by traditional methods has been an extremely tedious task.[2]

Results and Discussion

I. Cross-Coupling Reactions between Two Kinds of Aminoalkylsilyl Chlorides with Lithium: Synthesis of Aminooligosilanes. Cholosilanes used in this study are listed in Chart 1. These chlorosilanes are monochloromonosilanes **1**−**5**, dichloromonosilanes **6**−**9**, monochlorodisilanes **10** and **11**, and dichlorodisilane **12**. In order to achieve highly selective cross-coupling reactions between two components of these chlorosilanes, we have first estimated the electron affinity of these compounds, i.e., the lowest unoccupied molecular orbital (LUMO) levels, by semiempirical PM3 calculations[3] on some model compounds which contain NMe_2 group(s) in place of the actual NEt_2. The results are summarized in Table 1. There are some distinct tendencies. The LUMO levels become lower and lower in the order monochloromonosilane (0 to +0.1 eV) > dichloromonosilane (−0.5 to −0.7 eV) > chlorodisilane (−1.4 to −1.7 eV). While in the first two the LUMO lies on the Si−Cl bond, in the last the LUMO lies on the Si−Si bond and the LUMO + 1 on the Si−Cl bond. The electron affinity thus increases in the reverse order monochloromonosilane < dichloromonosilane < chlorodisilane. In view of the energy differences in the LUMO levels, if the absolute values are not accurate on the present semiempirical level of calculation, the last two, dichloromonosilane and chlorodisilane, must be converted into the corresponding "silyllithium" species much faster than the first, monochloromonosilane, upon treatment with lithium metal. Thus, a selective cross-coupling reaction could be realized by reduction of the reactive dichloromonosilane or chlorodisilane in the presence of the least reactive monochloromonosilane, since the last can act as the trapping agent for the transient silyllithium species.

Although there has been no direct evidence for the formation of silyllithium as a stable species in the present reaction systems, we will describe the reduced active species derivable from the reactive chlorosilane to be a transient silyllithium throughout this paper for the sake of ready understanding from a synthetic view point, apart from the mechanistic details.

Chart 1



1: R = Me
2: R = Et_2N
3: $R^1 = R^2$ = Et
4: R^1 = Me, $R^2 = Me_2N$
5: R^1 = Et, $R^2 = Me_2N$
6: R = Me
7: R = Et
8: R = Ph
9: R = Et_2N
10: R^1 = Me, $R^2 = Et_2N$
11: $R^1 = R^2 = Et_2N$
12: $R^1 = Et_2N$, R^2 = Cl

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

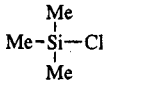
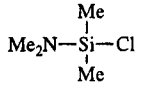
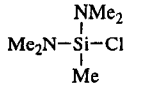
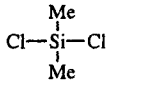
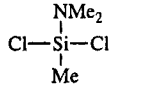
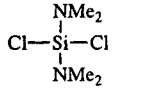
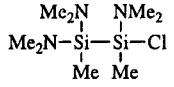
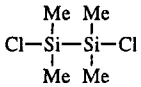
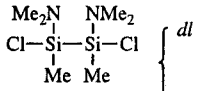
(1) Tamao, K.; Kawachi, A.; Ito, Y. *Organometallics* **1993**, *12*, 580.

(2) Reviews: (a) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19. (b) West, R. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 2, p 365. For a compilation of pertinent references, see ref 1.

(3) MOPAC version 6.0 program: Stewart, J. J. P. *J. Comput.-Aided Mol. Des.* **1990**, *4*, 1.

S0276-7333(96)00978-8 CCC: $14.00

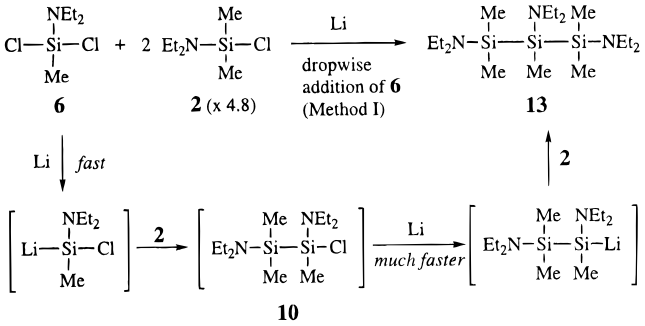
Table 1. LUMO and/or LUMO+1 Levels of Chlorosilanes Estimated by Semiempirical PM3 Calculations

chlorosilane	LUMO and/or LUMO+1 (eV)
 **1**	+0.12 (Si-Cl)
 **2'**	+0.10 (Si-Cl)
 **4'**	+0.02 (Si-Cl)
	−0.52 (Si-Cl)
 **6'**	−0.60 (Si-Cl)
 **9'**	−0.72 (Si-Cl)
 **11'**	+0.16 (LUMO+1, Si-Cl) −1.45 (LUMO, Si-Si)
	−0.16 (LUMO+1, Si-Cl) −1.57 (LUMO, Si-Si)
 **12'**	*dl*: −0.10 (LUMO+1, Si-Cl); −1.69 (LUMO, Si-Si) *meso*: −0.13 (LUMO+1, Si-Cl); −1.66 (LUMO, Si-Si)

Of course, the idea has long been used for the synthesis of permethylated linear oligosilanes[4] and branched oligosilanes.[5] In the present cases, the electronic and steric effects of the amino group(s) should be considered additionally. The calculation results in Table 1 indicate that the amino group on chlorosilane may act as a weak electron-withdrawing group. Within dichloromonosilanes, for example, diaminodichlorosilane **6′** may react faster than monoaminodichlorosilane **9′**. Rather large steric effects have been observed experimentally, as will be mentioned later.

Synthesis of Trisilanes. Representative results for the cross-coupling reaction are summarized in Table 2.

Scheme 1



Some symmetrical 1,2,3-triaminotrisilanes **13**−**15**, 2,2-diaminotrisilane **16**, and 1,2,2,3-tetraaminotrisilane **17** have been prepared by appropriate combinations between aminodichlorosilanes **6**−**9** (category A in Table 2) and monochlorosilanes **1** and **2** (category B), the latter being used in quantities of 2.3−4.8 molar equiv (entries 1−5). Unsymmetrical 1,2-diaminotrisilanes **18**, 1,1,2,3-tetraaminotrisilanes **19** and **20**, and 1,1,2,3,3-pentaaminotrisilanes **21** and **22** have been synthesized by combinations of aminochlorodisilanes **10** and **11** with monochlorosilanes **1**−**5**, the latter again being used in quantities of 1.5−2.2 molar equiv (entries 6−10). Two kinds of experimental procedures have been used. The choice of the procedure simply depends on the combination of two components, i.e., the reactivity differences toward lithium.

Method I. In method I, to a mixture of 20−30% monochlorosilane (category B), lithium powder, and THF is added dropwise a mixture of the remaining monochlorosilane and the more reactive dichlorosilane (category A) at room temperature (entries 1−5).

Typically, the coupling of **6** with **2** (entry 1) gave trisilane **13**, tetrasilanes, and other unknown products in the ratio of 1:0.1:0.1, respectively, as determined by GLC. While the formation of higher homologs was minimized to only trace amounts by this method, the formation of disilane arising from the homocoupling of monochlorosilane **2** used in excess could not be avoided of course: the disilane, however, could be readily removed by simple distillation under reduced pressure. The desired trisilane **13** was isolated in ca. 60% yield based on dichlorosilane **6**.

For comparison, it has been confirmed that method II (vide infra) is not suitable for the selective synthesis of trisilane. Thus, a mixture of **6**, **2** (4.8 equiv), Li (26 equiv), and THF (10 mL) was stirred at room temperature for 2 days to give trisilane, tetrasilane, and other unknown products (except disilane) with much lower selectivity for trisilane in the ratio of 1:0.5:0.3, respectively, as determined by GLC analysis.

The preferential formation of trisilane **13** by method I may be visualized as shown in Scheme 1. Thus, the more reactive dichlorosilane **6** is readily converted into the corresponding monolithio species, which as formed can be trapped by the less reactive monochlorosilane **2** present in a large excess amount. The resulting chlorodisilane **10** is much more reactive toward lithium and must be converted into disilanyllithium, which is trapped again by **2** to form trisilane **13**.

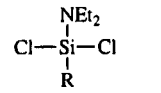
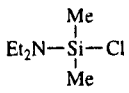
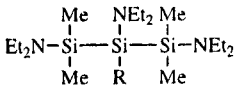
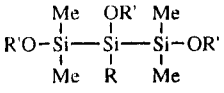
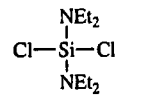
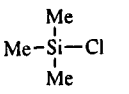
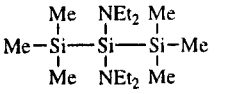
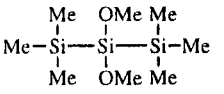
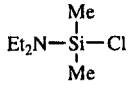
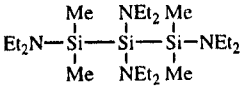
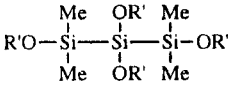
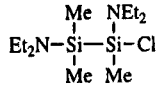
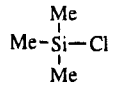
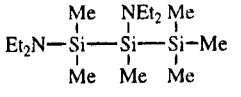
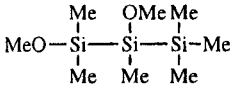
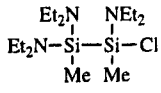
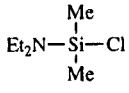
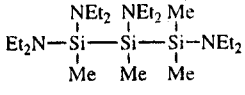
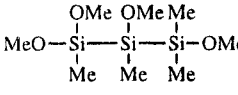
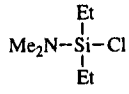
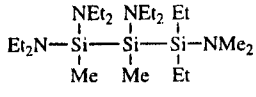
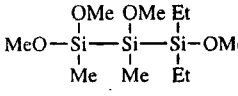
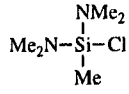
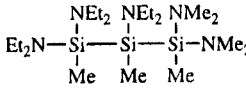
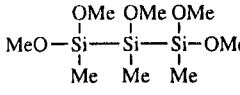
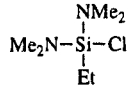
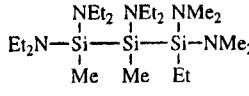
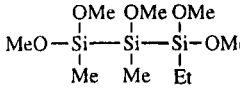
Similarly, trisilanes **14**−**17** were obtained in 60−84% isolated yields.

Method II. The selective cross-coupling reactions of the highly reactive chlorodisilanes **10** and **11** with the

(4) (a) Kumada, M.; Ishikawa, M. *J. Organomet. Chem.* **1963**, *1*, 153. (b) Kumada, M.; Ishikawa, M.; Maeda, S. *J. Organomet. Chem.* **1966**, *5*, 120. (c) Gilman, H.; Harrell, R. L. *J. Organomet. Chem.* **1966**, *5*, 199. (d) Ruehl, K. E.; Davis, M. E.; Matyjaszewski, K. *Organometallics* **1992**, *11*, 788.

(5) Dickhaut, J.; Giese, B. *Org. Synth.* **1991**, *70*, 164 and references cited therein.

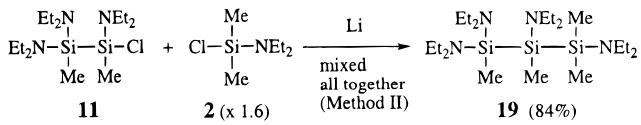
Table 2. Coupling Reactions of Aminochlorosilanes and Subsequent Alcoholysis

Entry	(amino)chlorosilanes A	(ratio)	B	reaction conditions [a]	coupling products: (amino)oligosilanes (yield, %) [b]	alcoholysis products (alkoxy)oligosilanes (yield, %) [c]
						
1	**6**: R = Me	(1 : 4.8)	**2**	Method I	**13**: R = Me (58)	**26**: R = Me; R'O = MeO (77)
2	**7**: R = Et	(1 : 2.7)		Method I	**14**: R = Et (58)	**27**: R = Et; R'O = MeO (65)
3	**8**: R = Ph	(1 : 2.3)		Method I	**15**: R = Ph (84)	**28**: R = Ph; R'O = EtO (78)
4	 **9**	(1 : 3)	 **1**	Method I	 **16** (70)	 **29** (56)
5	**9**	(1 : 3)	 **2**	Method I	 **17** (67)	 **30**: R'O = MeO (79) **31**: R'O = EtO (92) **32**: R'O = *i*-PrO (59)
6	 **10**	(1 : 1.5)	 **1**	Method II	 **18** (86)	 **33** (69)
7	 **11**	(1 : 1.6)	 **2**	Method II	 **19** (84)	 **34** (56)
8	**11**	(1 : 2.2)	 **3**	Method II	 **20** (94)	 **35** (86)
9	**11**	(1 : 1.4)	 **4**	Method II	 **21** (76)	 **36** (67)
10	**11**	(1 : 2.2)	 **5**	Method II	 **22** (54)	 **37** (78)

[a] Carried out in THF in the presence of lithium powder, unless otherwise stated, under the following conditions. Condition I: To a mixture of 20-30% of chlorosilane B, lithium and THF was added dropwise a solution of chlorosilane A and the remaining chlorosilane B in THF at room temperature. Condition II: A mixture of both chlorosilanes A and B, lithium, and THF was stirred at room temperature. [b] Isolated yields based on chlorosilane A. [c] An (amino)oligosilane was mixed with a large excess amount of the corresponding alcohol in the presence of NH_4Cl as catalyst at room temperature. Isolated yields are given.

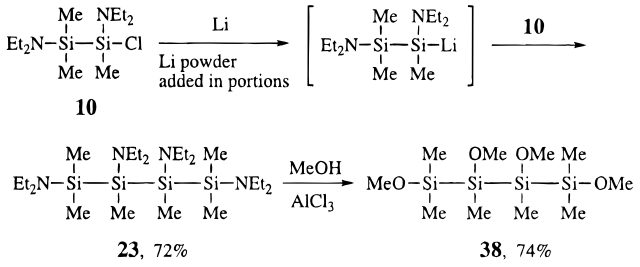
least reactive chloromonosilanes **1**−**5** can be achieved by just mixing them all together with lithium in THF to form trisilanes **18**−**22** in 54−94% isolated yields (entries 6−10). As shown in Scheme 2 for a typical case, by this simple method, the chlorodisilane **11** is first converted into the disilanyllithium species, which reacts faster with the sterically less hindered chloromonosilane **2** used in excess than with the remaining, sterically hindered chlorodisilane, resulting in the highly selective formation of trisilane **19**, together with disilanes result-

Scheme 2

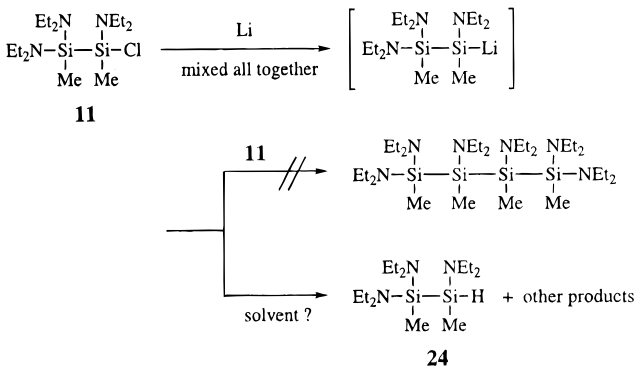


11 **2** (x 1.6) **19** (84%)

Scheme 3



Scheme 4



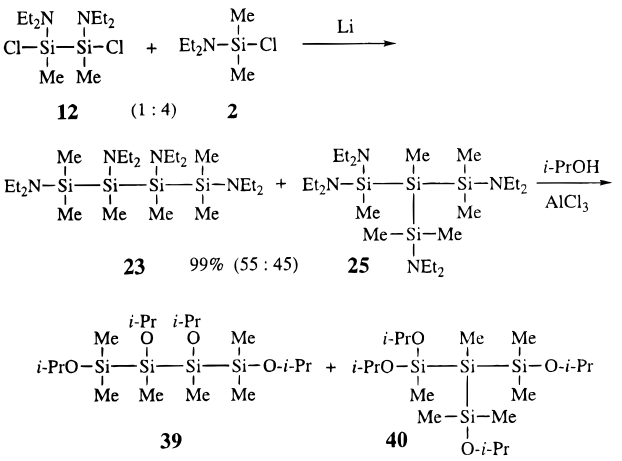
ing from the homocoupling of the chloromonosilane and only a trace amount of hydrodisilane (cf. Scheme 4, vide infra).

For the selective cross-coupling reactions, less bulky chloromonosilanes should be used. Thus, in entries 8−10, Me_2N derivatives **3**−**5** have been used instead of Et_2N derivatives. With more bulky, less reactive chlorosilanes, the coupling reaction is accompanied by the formation of hydrodisilanes in 5−10% yields, arising from decomposition of the disilanyllithium species (cf., Scheme 4; vide infra).

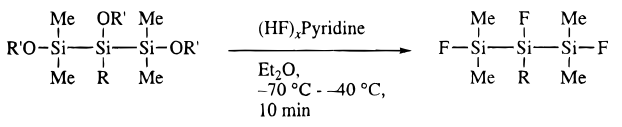
Synthesis of Tetrasilanes. As shown in Scheme 3, homocoupling of 1,2-diaminochlorodisilane **10** was attained by addition of lithium powder suspended in THF in several portions intermittently to a solution of **10** over 12 h, the 1,2,3,4-tetraaminotetrasilane **23** being obtained in high yield. By this technique, the highly reactive chlorodisilane is converted into the disilanyllithium species little by little only when lithium is added, and hence, the relative ratio of chlorodisilane to lithiodisilane can be maintained to be very large until the final stage of the reaction, favoring the smooth cross-coupling reaction.

This technique was based on the following observation shown in Scheme 4. Thus, a similar 1,2,2-triamino-1-chlorodisilane **11** was mixed with an excess amount of lithium *all together* in THF to form not the homocoupling product tetrasilane but a rather complex mixture of products in which the reduction product hydrodisilane **24** was the major product. This may be ascribed to the fact that the highly reactive chlorodisilane **11** has been entirely transformed into the disilanyllithium species much faster than the expected coupling reaction can occur with the rather sterically hindered chlorodisilane. The resulting disilanyllithium thus cannot find the coupling partner in the reaction mixture and may decompose into the hydrodisilane and other species: attempted trapping of the "disilanyllithium" species with trimethylchlorosilane failed, resulting in the formation of the same mixture of product as given above.

Scheme 5



Scheme 6



26: R = Me; R'O = MeO
27: R = Et; R'O = MeO
28: R = Ph; R'O = EtO

41: R = Me, 91%
42: R = Et, 86%
43: R = Ph, 68%

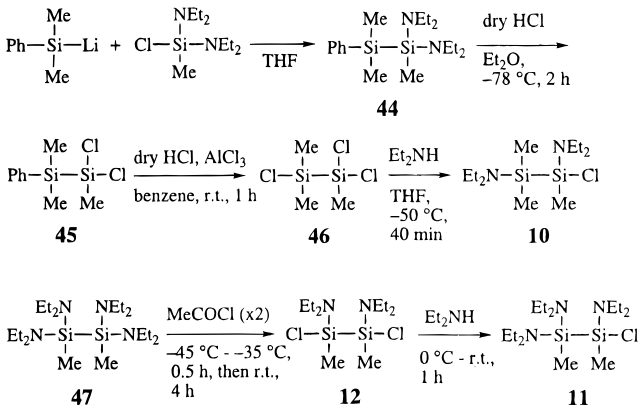
A cross-coupling reaction of 1,2-diamino-1,2-dichlorodisilane **12** with aminochlorosilane **2** has also been carried out to obtain the tetrasilane **23** by addition of the former to the latter (method I), as shown in Scheme 5. The reaction, however, gave a mixture of **23** and the branched isomer **25** in the ratio of 55:45 in almost quantitative yield; the structures were characterized after conversion into the alkoxy derivatives. The isomerization mechanism has not been clarified.

II. Transformations of Aminooligosilanes to Alkoxyoligosilanes and Fluorooligosilanes. The aminotrisilanes **13**−**22** were readily converted into the corresponding alkoxytrisilanes **26**−**37** in high yields by treating with excess dry alcohol in the presence of a catalytic amount of anhydrous aluminum chloride, as summarized in Table 1. Alkoxytetrasilanes **38**−**40** have also been obtained from the corresponding aminotetrasilanes **23** and **25**, as shown in Schemes 3 and 5. As representative examples for the synthesis of fluorotrisilanes, 1,2,3-trialkoxytrisilanes **26**−**28** have been transformed into 1,2,3-trifluorotrisilanes **41**−**43** by treatment with hydrogen fluoride−pyridine, as shown in Scheme 6.

III. Preparation of the Starting Materials, Aminochlorosilanes. Aminochloromonosilanes have been prepared by selective partial amination of the corresponding chlorosilanes as reported previously.[1,6] Aminochlorodisilanes **10**−**12** have been prepared also from the corresponding polychlorodisilanes, obtainable from polyaminodisilanes, as summarized in Scheme 7. Thus, **10** was obtained from the known 1,1,2-trichlorotrimethyldisilane (**46**)[7] by partial amination: we have developed a new convenient method for the synthesis of **46**, which involves a selective cross-coupling reaction

(6) Tamao, K.; Nakajo, E.; Ito, Y. *Tetrahedron* **1988**, *44*, 3997.
(7) (a) Sakurai, H.; Tominaga, K.; Watanabe, T.; Kumada, M. *Tetrahedron Lett.* **1966**, 5493. (b) Kumada, M.; Watanabe, T.; Sakurai, H. *J. Organomet. Chem.* **1967**, *7*, P15.

Scheme 7



of phenylchlorosilane with aminochlorosilane under conditions similar to those described above, as shown in Scheme 7. The resulting phenyldiaminodisilane **44** was readily transformed into **46** via **45** in two steps. Traditionally, pure **46** has been prepared by chlorodemethylation or dephenylation of hexamethyldisilane or 1,1,2-triphenyldisilane.[7] The ready availability of the starting material makes the present method more convenient than the traditional methods.

1,1,2,2-Tetraaminodisilane **47**[1] could be transformed into the 1,2-dichloro-1,2-diaminodisilane **12** via selective monochlorodeamination on each silicon atom with acetyl chloride, which was subsequently converted into 1,2,2-triamino-1-chlorodisilane **11** via selective monoamination, as shown in Scheme 7.

Experimental Section

General Comments. ^{1}H (200 MHz or 270 MHz), ^{13}C (50 MHz or 67.94 MHz), ^{19}F (254.5 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded in C_6D_6 on a Varian VXR-200 spectrometer equipped with a VX-4000 computer and/or on a JEOL EX-270 spectrometer. ^{1}H and ^{13}C chemical shifts are referenced to external benzene-d_6 (^{1}H δ 7.200 ppm and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts are referenced to internal tetramethylsilane (0 ppm). ^{19}F chemical shifts are referenced to external fluorotrichloromethane (0 ppm). Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Analytical and preparative GLC measurements were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3 or 1 m glass column packed with 30% silicone DC550 on Celite 545. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University: since aminosilanes, however, gave no satisfactory analytical data even after many trials owing to their moisture sensitivity, they were analyzed by high-resolution mass spectrometry.

The starting materials aminochloromonosilanes **2**−**9** were prepared by partial amination of the corresponding chlorosilanes in essentially the same manner reported previously:[1,6,8] a typical procedure is given below for the synthesis of the new compound **7**. Trimethylchlorosilane (**1**) was treated with several pieces of sodium under nitrogen to remove the dissolved HCl, and the supernatant was used. Lithium dispersion (30 wt % in mineral oil) and hydrogen fluoride−pyridine ($(HF)_x$py) were purchased from Aldrich. Ether and THF were distilled under nitrogen from sodium benzophenone ketyl. Hexane was dried over sodium wire and distilled under nitrogen. Diethylamine was distilled from calcium hydride. Dry dimethylamine was generated from a 50% aqueous solution of dimethylamine and potassium hydroxide[9] and kept as a THF solution. Methanol and ethanol were distilled from magnesium methoxide and ethoxide, respectively. Isopropyl alcohol was distilled from calcium hydride. All reactions were carried out under a nitrogen or an argon atmosphere. The purity of the product was checked by ^{1}H NMR and/or GLC analysis.

Reductive Coupling Reaction of Aminochlorosilanes with Lithium. 1,2,3-Tris(diethylamino)-1,1,2,3,3-pentamethyltrisilane (13). To a mixture of $(Et_2N)Me_2SiCl$ (**2**; 5.67 g, 34 mmol), Li (2.32 g, 331 mmol) and THF (35 mL) was added dropwise a solution of additional **2** (17 g, 103 mmol) and $(Et_2N)MeSiCl_2$ (**6**; 5.3 g, 28.5 mmol) in THF (10 mL) at room temperature over 9 h. The mixture was stirred for 12 h. The resulting mixture was condensed under reduced pressure, followed by addition of dry hexane (20 mL), and filtered. The filtrate was concentrated, and the residue was analyzed by GLC to show the ratio of trisilane **13** to the higher homologs tetrasilane and other unknown products (except disilane) to be about 1:0.1:0.1, respectively. The residue was distilled to give the product **13** (6.2 g, 58% yield based on **6**): bp 109−125 °C/0.2 mmHg, purity 92% on GLC. ^{1}H NMR (200 MHz, C_6D_6): terminal methyl groups are diastereotopic, δ 0.362 (s, 6H), 0.395 (s, 6H), 0.540 (s, 3H), 1.069 (t, J = 7.0 Hz, 12H), 1.085 (t, J = 7.0 Hz, 6H), 2.921 (q, J = 7.0 Hz, 8H), 2.951 (q, J = 7.0 Hz, 4H). ^{13}C NMR (50 MHz, C_6D_6): δ −0.89, 1.39, 1.59, 16.04, 16.36, 41.58, 42.59. ^{29}Si NMR (54 MHz, C_6D_6): δ −17.88, −3.91. HRMS: calcd for $C_{17}H_{45}N_3Si_3$, *m/e* 375.291 99; found, *m/e* 375.288 89.

For comparison, a similar reaction was carried out under the conditions of method II. A mixture of $(Et_2N)Me_2SiCl_2$ (**2**; 2.6 g, 15.7 mmol), $(Et_2N)MeSiCl_2$ (**6**; 610 mg, 3.3 mmol), Li (600 mg, 86 mmol), and THF (10 mL) was stirred at room temperature for 2 days. The resulting mixture was found by GLC to contain trisilane, tetrasilane, and other unknown products (except disilane) in the ratio of 1:0.5:0.3, respectively.

1,2,3-Tris(diethylamino)-2-ethyl-1,1,3,3-tetramethyltrisilane (14). To a mixture of **2** (2.43 g, 14.7 mmol), Li (518 mg, 74 mmol), and THF (20 mL) was added dropwise a solution of **2** (4.23 g, 25.6 mmol) and $(Et_2N)EtSiCl_2$ (**7**) (2.94 g, 14.7 mmol) in THF (15 mL) at room temperature over 8 h. The mixture was stirred for 10 h. Workup similar to the above gave **14** (3.3 g, 58% yield based on **7**): bp 141−143 °C/0.8 mmHg, purity 99% on ^{1}H NMR. ^{1}H NMR (270 MHz, C_6D_6): terminal methyl groups are diastereotopic, δ 0.412 (s, 6H), 0.418 (s, 6H), 1.061−1.121 (m, 20H), 1.291 (t, J = 7.3 Hz, 3H), 2.936 (q, J = 7.0 Hz, 8H), 2.961 q, J = 7.3 Hz, 4H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 2.43, 2.57, 9.06, 9.96, 15.50, 16.36, 41.62, 42.79. ^{29}Si NMR (54 MHz, C_6D_6): δ −12.07, −3.71. HRMS: calcd for $C_{18}H_{47}N_3Si_3$, *m/e* 389.307 69; found, *m/e* 389.304 99.

1,2,3-Tris(diethylamino)-2-phenyl-1,1,3,3-tetramethyltrisilane (15). To a mixture of **2** (0.4 g, 2.4 mmol), Li (303 mg, 43 mmol), and THF (15 mL) was added dropwise a solution of **2** (3.6 g, 22 mmol) and $(Et_2N)PhSiCl_2$ (**8**; 3.47 g, 14 mmol) in THF (10 mL) at room temperature over 8 h. The mixture was stirred for 6 h. Workup similar to the above gave product **15** (3.5 g, 84% yield based on **8**): bp 210−230 °C (bath temperature)/1 mmHg, purity 90% on ^{1}H NMR. ^{1}H NMR (200 MHz, C_6D_6): terminal methyl groups are diastereotopic, δ 0.417 (s, 6H), 0.477 (s, 6H), 0.958 (t, J = 7.0 Hz, 12H), 1.184 (t, J = 7.0 Hz, 6H), 2.849 (q, J = 7.0 Hz, 8H), 3.207 (q, J = 7.0 Hz, 4H), 7.322 (m, 3H), 7.797 (m, 2H). ^{13}C NMR (50 MHz, C_6D_6): δ 2.00, 2.27, 15.25, 15.97, 41.45, 43.03, 127.66, 127.82, 134.44, 135.33. ^{29}Si NMR (54 MHz, C_6D_6): δ −18.94, −3.56. HRMS: calcd for $C_{22}H_{47}N_3Si_3$, *m/e* 437.312 80; found, *m/e* 437.310 30.

2,2-Bis(diethylamino)-1,1,1,3,3,3-hexamethyltrisilane (16). To a mixture of Me_3SiCl (**1**; 1.1 g, 10 mmol), Li (600 mg, 86 mmol), and THF (10 mL) was added dropwise a solution of

(8) (a) Issleib, K.; Kuehne, U.; Krech, F. *Phosphorus Sulfur* **1985**, *21*, 367. (b) Uhlig, W.; Tretner, C. *J. Organomet. Chem.* **1994**, *467*, 31.

(9) Overberger, C. G.; Kogon, I. C.; Minin, R. *Organic Syntheses;* Wiley: New York, 1963; Collect. Vol. 4, p 336.

1 (2.17 g, 20 mmol) and $(Et_2N)_2SiCl_2$ (**9**; 2.3 g, 9.4 mmol) in THF (15 mL) at room temperature over 7 h. The mixture was stirred for 10 h. Workup similar to the above gave **16** (2.1 g, 70% yield based on **9**): bp 140−160 °C (bath temperature)/0.6 mmHg, purity 93% on ^{1}H NMR. ^{1}H NMR (270 MHz, C_6D_6): δ 0.315 (s, 18H), 1.056 (t, J = 7.0 Hz, 12H), 2.985 (q, J = 7.0 Hz, 8H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 0.71, 15.28, 41.32. ^{29}Si NMR (54 MHz, C_6D_6): δ −22.74, −2.83. HRMS: calcd for $C_{14}H_{38}N_2Si_3$, *m/e* 318.234 15; found, *m/e* 318.233 05.

1,2,2,3-Tetrakis(diethylamino)-1,1,3,3-tetramethyltrisilane (17). To a mixture of **2** (0.6 g, 3.6 mmol), Li (250 mg, 36 mmol), and THF (5 mL) was added dropwise a solution of **2** (2.48 g, 15 mmol) and **9** (1.46 g, 6.0 mmol) in THF (13 mL) at room temperature over 12 h. The mixture was stirred for 12 h. The usual workup, similar to that above, gave **17** (1.74 g, 67% yield based on **9**): bp 180−200 °C (bath temperature)/0.2 mmHg, purity 93% on ^{1}H NMR. ^{1}H NMR (200 MHz, C_6D_6): δ 0.464 (s, 12H), 1.088 (t, J = 7.0 Hz, 12H), 1.129 (t, J = 7.0 Hz, 12H), 2.973 (q, J = 7.0 Hz, 8H), 3.170 (q, J = 7.0 Hz, 8H). ^{13}C NMR (50 MHz, C_6D_6): δ 2.69, 14.83, 16.22, 40.83, 41.48. ^{29}Si NMR (54 MHz, C_6D_6): δ −7.16, −6.66. HRMS: calcd for $C_{20}H_{52}N_4Si_3$, *m/e* 432.349 99; found, *m/e* 432.350 39.

1,2-Bis(diethylamino)-1,1,2,3,3,3-hexamethyltrisilane (18). A mixture of $(Et_2N)Me_2SiSiMe(NEt_2)Cl$ (**10**; 660 mg, 2.4 mmol), Me_3SiCl (385 mg, 3.6 mmol), Li (182 mg, 26 mmol), and THF (10 mL) was stirred at room temperature for 12 h. Workup similar to that given for the preparation of **13** gave **18** (641 mg, 86% yield based on **10**): bp 155−175 °C (bath temperature)/1.8 mmHg, purity 90% on GLC. ^{1}H NMR (270 MHz, C_6D_6): δ 0.272 (s, 9H), diastereotopic methyls 0.316 (s, 3H), 0.355 (s, 3H), 0.458 (s, 3H), 1.043 (t, J = 7.0 Hz, 6H), 1.051 (t, J = 7.0 Hz, 6H), 2.899 (q, J = 7.0 Hz, 4H), 2.899 (q, J = 7.0 Hz, 4H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −2.44, −0.32, 1.26, 1.55, 16.02, 16.25, 41.44, 42.81. ^{29}Si NMR (54 MHz, C_6D_6): δ −19.76, −15.73, −3.83. HRMS: calcd for $C_{14}H_{38}N_2Si_3$, *m/e* 318.234 28; found, *m/e* 318.235 48.

1,1,2,3-Tetrakis(diethylamino)-1,2,3,3-tetramethyltrisilane (19). A mixture of $(Et_2N)_2MeSiSiMe(NEt_2)Cl$ (**11**; 570 mg, 1.7 mmol), **2** (450 mg, 2.7 mmol), Li (210 mg, 30 mmol), and THF (5 mL) was stirred at room temperature for 11 h. After the usual workup, GLC analysis showed the product ratio of **19** to hydrodisilane **24** to be 94:6. Bulb-to-bulb distillation gave **19** (618 mg, 84% yield based on **11**): bp 190−230 °C (bath temperature)/0.3 mmHg, purity 97% on GLC. ^{1}H NMR (200 MHz, C_6D_6): there are two diastereotopic methyl and Et_2N groups, δ 0.403 (s, 3H), 0.409 (s, 3H), 0.434 (s, 3H), 0.616 (s, 3H), 1.139−1.025 (m, 24H), 3.059−2.880 (m, 16H). ^{13}C NMR (50 MHz, C_6D_6): δ −0.55, 1.25, 1.66, 1.80, 15.35, 15.82, 16.09, 16.66, 40.20, 40.42, 41.89, 42.72. ^{29}Si NMR (54 MHz, C_6D_6): δ −19.26, −7.39, −3.48. HRMS: calcd for $C_{20}H_{52}N_4Si_3$, *m/e* 432.349 93; found, *m/e* 432.350 13.

1,1,2-Tris(diethylamino)-3-(dimethylamino)-3,3-diethyl-1,2-dimethyltrisilane (20). A mixture of **11** (680 mg, 2 mmol), $(Me_2N)Et_2SiCl$ (**3**; 730 mg, 4.4 mmol), Li (175 mg, 25 mmol), and THF (5 mL) was stirred at room temperature for 10 h. Workup similar to that above gave **20** (812 mg, 94% yield based on **11**): bp 210−240 °C (bath temperature)/0.75 mmHg; purity 98% on GLC. ^{1}H NMR (270 MHz, C_6D_6): there are two diastereotopic Et and Et_2N groups, δ 0.400 (s, 3H), 0.613 (s, 3H), 0.76−1.07 (m, 4H), 1.076−1.27 (m, 24H), 2.596 (s, 6H), 2.942−3.022 (m, 12H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 0.15, 1.12, 7.12, 7.19, 8.09, 15.41, 15.66, 16.00, 39.65, 40.10, 40.33, 42.75. ^{29}Si NMR (54 MHz, C_6D_6): δ −19.36, −7.36, −3.08. HRMS: calcd for $C_{20}H_{52}N_4Si_3$, *m/e* 432.349 91; found, *m/e* 432.349 01.

1,1,2-Tris(diethylamino)-3,3-bis(dimethylamino)-1,2,3-trimethyltrisilane (21). A mixture of **11** (977 mg, 2.9 mmol), $(Me_2N)_2MeSiCl$ (**4**; 696 mg, 4.2 mmol), Li (210 mg, 30 mmol), and THF (5 mL) was stirred at room temperature for 16 h. After the usual workup, GLC analysis showed the product ratio of **21** to hydrodisilane **24** to be 87:13. Bulb-to-bulb distillation gave the product **21** (957 mg, 76% yield based on **11**): bp 200−220 °C (bath temperature)/0.6 mmHg, purity 98% on GLC. ^{1}H NMR (200 MHz, C_6D_6): there are two diastereotopic Me_2N and Et_2N groups, δ 0.384 (s, 3H), 0.421 (s, 3H), 0.672 (s, 3H), 1.106 (t, J = 7.0 Hz, 6H), 1.117 (t, J = 7.0 Hz, 12H), 2.606 (s, 6H), 2.642 (s, 6H), 3.000 (q, J = 7.0 Hz, 4H), 3.012 (q, J = 7.0 Hz, 8H). ^{13}C NMR (50 MHz, C_6D_6): δ −0.46, 0.33, 1.17, 15.62, 15.75, 38.86, 38.93, 40.37, 40.42, 42.59. ^{29}Si NMR (54 MHz, C_6D_6): δ −20.64, −7.46, −4.63. HRMS: calcd for $C_{19}H_{51}N_5Si_3$, *m/e* 433.329 01; found, *m/e* 433.347 01.

1,1,2-Tris(diethylamino)-3,3-bis(dimethylamino)-3-ethyl-1,2-dimethyltrisilane (22). A mixture of **11** (697 mg, 2.1 mmol), $(Me_2N)_2EtSiCl$ (**5**; 821 mg, 4.5 mmol), Li (175 mg, 25 mmol), and THF (6 mL) was stirred at room temperature for 12 h. The usual workup gave **22** (500 mg, 54% yield based on **11**): bp 220−260 °C (bath temperature)/0.7 mmHg, purity 95% on GLC. ^{1}H NMR (270 MHz, C_6D_6): there are two diastereotopic Me_2N and Et_2N groups, δ 0.429 (s, 3H), 0.674 (s, 3H), 0.928 (q, J = 8.1 Hz, 2H), 1.082−1.145 (m, 18H), 1.180 (t, J = 8.1 Hz, 3H), 2.633 (s, 6H), 2.651 (s, 6H), 2.960−3.077 (m, 12H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 0.56, 1.21, 8.04, 9.91, 15.57, 15.73, 39.05, 40.29, 40.44, 42.56. ^{29}Si NMR (54 MHz, C_6D_6): δ −20.54, −7.46, −2.20. HRMS: calcd for $C_{20}H_{53}N_5Si_3$, *m/e* 447.360 78; found, *m/e* 447.360 08.

1,2,3,4-Tetrakis(diethylamino)-1,1,2,3,4,4-hexamethyltetrasilane (23). To a solution of $(Et_2N)Me_2SiSiMe(NEt_2)Cl$ (**10**; 886 mg, 3.2 mmol) in THF (8 mL) was added a suspension of Li powder (182 mg, 26 mmol) and THF (5 mL) at room temperature in several parts intermittently over 12 h. The mixture was stirred for 2 h. The usual workup gave the product **23** (556 mg, 72% yield): bp 220−250 °C (bath temperature)/0.5 mmHg, purity ca. 90% on ^{1}H NMR. ^{1}H NMR (270 MHz, C_6D_6): a mixture of two diastereomers, each having two diastereotopic methyl groups, δ 0.418, 0.458, 0.462 (s, 12H), 0.574, 0.675 (s, 6H), 1.065−1.144 (m, 24H), 2.934−3.008 (m, 16H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −0.50, −0.25, 1.70, 1.91, 2.09, 15.98, 16.14, 16.45, 16.50, 41.69, 41.75, 43.04, 43.11. ^{29}Si NMR (54 MHz, C_6D_6): δ −14.88, −14.03, −3.08. HRMS: calcd for $C_{22}H_{58}N_4Si_4$, *m/e* 490.373 82; found, *m/e* 490.375 52.

Attempted Homocoupling of 11 with Li Metal: Formation of Hydrodisilane 24. A mixture of **11** (300 mg, 0.8 mmol), Li (120 mg, 17 mmol), and THF (6 mL) was stirred at room temperature for 13 h. The resulting mixture was checked by GLC to show the formation of $(Et_2N)_2MeSiSiMe(NEt_2)H$ (**24**), $(Et_2N)_2MeSiSiMe(NEt_2)_2$, and unknown product in the ratio of 70:25:5. The usual workup gave a mixture of products (170 mg) boiling at bp 180−200 °C (bath temperature)/0.2 mmHg. Preparative GLC afforded a pure sample of **24**. ^{1}H NMR (270 MHz, C_6D_6): two Et_2N groups are diastereotopic, δ 0.366 (s, 3H), 0.448 (d, J = 4.3 Hz, 3H), 1.023−1.112 (m, 18H), 2.922−3.010 (m, 12H), 4.980 (q, J = 4.3 Hz, 1H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −1.59, 0.02, 16.05, 16.14, 40.56, 43.33, 44.62.

Reaction of $Cl(Et_2N)MeSiSiMe(NEt_2)Cl$ (12) with 2 and Subsequent Alkoxylation. (1) To a mixture of **2** (1.36 g, 8 mmol), Li (990 mg, 140 mmol), and THF (12 mL) was added dropwise a solution of **2** (5 g, 30 mmol) and **12** (2.87 g, 9.5 mmol) in THF (20 mL) at room temperature over 7 h. The mixture was stirred for 14 h. The usual workup gave an isomeric mixture of the tetraaminotetrasilanes, linear **23** (see above) and branched **25** in a ca. 1:1 ratio (4.6 g, 99% yield based on **12**): bp 200−240 °C (bath temperature)/0.7 mmHg, purity 94% on GLC, which could not be separated pure. ^{1}H NMR (270 MHz, C_6D_6) of a mixture of **23** and **25**: in **25** there are two diastereotopic Et_2N and $(Et_2N)Me_2Si$ groups, δ 0.418, 0.440, 0.446, 0.458, 0.462, 0.489, 0.491, 0.572, 0.674 (nine singlets, total 18H), 1.055−1.150 (m, 24H), 2.88−3.08 (m, 16H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −7.90, −0.48, −0.25, 1.70, 1.91, 2.05, 2.09, 2.85, 2.90, 15.90, 15.98, 16.12, 16.45, 16.50, 16.66, 40.60, 41.66, 41.79, 42.02, 43.01, 43.08. HRMS: calcd for $C_{22}H_{58}N_4Si_4$, *m/e* 490.373 82; found, *m/e* 490.375 52.

(2) The isomer mixture of **23** and **25** (1.2 g, 2.5 mmol) obtained from the above experiment was added to a mixture

of *i*-PrOH (8 mL) and solid $AlCl_3$ (66 mg, 0.5 mmol) at room temperature. After being stirred for 11 h, the resulting mixture was condensed under reduced pressure, followed by addition of hexane and filtration. The filtrate was concentrated and distilled to give a mixture of the isomeric tetraisopropoxytetrasilanes **39** and **40** (771 mg, 72% yield): bp 144−180 °C (bath temperature)/0.4 mmHg, the linear to branched ratio was 55:45 by GLC. Each structural isomer was isolated by preparative GLC. Linear (*meso*, *dl* mixture in the ratio of 1:1.6, not identified each) **39**: ^{1}H NMR (270 MHz, C_6D_6) of a mixture of diastereomers δ 0.486, 0.503 (two singlets, total 12H), 0.628, 0.725 (two singlets, total 6H), 1.202−1.292 (m, 24H), 4.049−4.20 (m, 4H); ^{13}C NMR (67.8 MHz, C_6D_6) δ −0.91, −0.61, 1.41, 1.53, 26.12, 26.21, 65.76, 67.89, 68.02. Branched **40**: ^{1}H NMR (270 MHz, C_6D_6) δ 0.431 (s, 3H), 0.490 (s, 3H), 0.556 (s, 12H), 1.181−1.283 (m, 24H), 4.064 (sep, J = 8.6 Hz, 2H), 4.253 (sep, J = 8.6 Hz, 2H); ^{13}C NMR (67.8 MHz, C_6D_6) δ −12.36, 1.62, 2.58, 2.67, 26.21, 26.24, 65.50, 65.68. Anal. Calcd for $C_{18}H_{46}O_4Si_4$: C, 49.14; H, 10.56. Found: C, 48.83; H, 10.61.

Transformation of Aminooligosilanes into Alkoxyoligosilanes. Typical Procedure: Synthesis of 1,2,3-Trimethoxy-1,1,2,3,3-pentamethyltrisilane (26). To a mixture of MeOH (20 mL) and solid $AlCl_3$ (0.4 g, 3 mmol) was added **13** (4.1 g, 11 mmol) at 0 °C. After it was stirred for 30 min at 0 °C, the mixture was condensed under reduced pressure, followed by addition of dry hexane (30 mL) and filtration. The filtrate was concentrated and distilled bulb-to-bulb to give **26** (2.13 g, 77% yield): bp 110−120 °C (bath temperature)/15 mmHg (lit.[10] bp 74 °C/5 mmHg). ^{1}H NMR (200 MHz, C_6D_6): there are two diastereotopic methyls, δ 0.375 (s, 6H), 0.385 (s, 6H), 0.531 (s, 3H), 3.394 (s, 6H), 3.424 (s, 3H). ^{13}C NMR (50 MHz, C_6D_6): δ −2.68, −0.18, 50.83, 52.93. ^{29}Si NMR (54 MHz, C_6D_6): δ 5.59, 14.18. HRMS: calcd for $C_8H_{24}O_3Si_3$, *m/e* 252.096 64; found, *m/e* 252.102 64. Anal. Calcd for $C_8H_{24}O_3Si_3$: H, 9.58; C, 38.05. Found: H, 9.83; C, 37.46.

1,2,3-Trimethoxy-2-ethyl-1,1,3,3-tetramethyltrisilane (27). In a similar manner, **14** (1.15 g, 3 mmol), $AlCl_3$ (127 mg, 1 mmol), and MeOH (8 mL) gave **27** (514 mg, 65% yield): bp 135−142 °C (bath temperature)/18 mmHg. ^{1}H NMR (270 MHz, C_6D_6): there are two diastereotopic methyls, δ 0.404 (s, 6H), 0.412 (s, 6H), 1.059 (q, J = 8.1 Hz, 2H), 1.252 (t, J = 8.1 Hz, 3H), 3.394 (s, 6H), 3.456 (s, 3H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 0.47, 0.51, 7.59, 8.56, 50.72, 53.34. ^{29}Si NMR (54 MHz, C_6D_6): δ 8.53, 14.43. HRMS: calcd for $C_9H_{26}O_3Si_3$, *m/e* 266.119 02; found, *m/e* 266.119 82. Anal. Calcd for $C_9H_{26}O_3Si_3$: H, 9.83; C, 40.55. Found: H, 10.09; C, 40.89.

1,2,3-Triethoxy-2-phenyl-1,1,3,3-tetramethyltrisilane (28). A mixture of **15** (502 mg, 1.15 mmol), $AlCl_3$ (53 mg, 0.4 mmol), and EtOH (10 mL) was stirred at room temperature for 9 h. The usual workup gave **28** (319 mg, 78% yield): bp 160−170 °C (bath temperature)/0.6 mmHg. ^{1}H NMR (200 MHz, C_6D_6): there are two diastereotopic methyls, δ 0.452 (s, 6H), 0.470 (s, 6H), 1.153 (t, J = 6.8 Hz, 6H), 1.272 (t, J = 6.8 Hz, 3H), 3.662 (q, J = 6.8 Hz, 4H), 3.869 (q, J = 6.8 Hz, 2H), 7.280−7.350 (m, 3H), 7.860−7.910 (m, 2H). ^{13}C NMR (50 MHz, C_6D_6): δ 0.68, 0.80, 18.80, 18.96, 59.25, 62.21, 128.30, 129.00, 133.92, 138.51. ^{29}Si NMR (54 MHz, C_6D_6): δ −5.34, 11.15. HRMS: calcd for $C_{16}H_{32}O_3Si_3$, *m/e* 456.170 50; found, *m/e* 356.168 20. Anal. Calcd for $C_{16}H_{32}O_3Si_3$: H, 9.04; C, 53.87. Found: H, 9.08; C, 53.09.

2,2-Dimethoxy-1,1,1,3,3,3-hexamethyltrisilane (29).[11] In a manner similar to the procedure for the synthesis of **26**, **16** (1.7 g, 5.3 mmol), $AlCl_3$ (60 mg, 0.45 mmol), and MeOH (5 mL) gave **29** (632 mg, 50% yield): bp 140−150 °C (bath temperature)/26 mmHg. ^{1}H NMR (270 MHz, C_6D_6): δ 0.276 (s, 18H), 3.516 (s, 6H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −1.07, 52.42. ^{29}Si NMR (54 MHz, C_6D_6): δ −22.54, 11.82. HRMS: calcd for $C_8H_{24}O_2Si_3$, *m/e* 236.111 64; found, *m/e* 236.109 64.

For the purpose of elemental analysis, the isoproxy analog was prepared in a similar manner. Thus, **16** was treated with *i*-PrOH and $AlCl_3$, followed by column chromatography on silica gel (hexane/AcOEt 20:1, R_f 0.3) to give 2,2-diisopropoxy-1,1,1,3,3,3-hexamethyltrisilane. ^{1}H NMR (270 MHz, C_6D_6): δ 0.311 (s, 18H), 1.237 (d, J = 5.94 Hz, 12H), 4.146 (hepta, J = 5.94 Hz, 2H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −0.86, 26.26, 67.66. ^{29}Si NMR (54 MHz, C_6D_6): δ −22.92, 2.30. Anal. Calcd for $C_{12}H_{32}O_2Si_3$: H, 11.02; C, 49.25. Found: H, 11.10; C, 49.13.

1,2,2,3-Tetramethoxy-1,1,3,3-tetramethyltrisilane (30). Similarly, **17** (3.75 g, 8.7 mmol), $AlCl_3$ (156 mg, 1.2 mmol), and MeOH (20 mL) gave **30** (1.85 g, 79% yield): bp 180−200 °C (bath temperature)/17 mmHg. ^{1}H NMR (200 MHz, C_6D_6): δ 0.431 (s, 12H), 3.443 (s, 6H), 3.577 (s, 6H). ^{13}C NMR (50 MHz, C_6D_6): δ 0.11, 50.90, 52.59. ^{29}Si NMR (54 MHz, C_6D_6): δ 2.19, 10.08. HRMS: calcd for $C_8H_{24}O_4Si_3$, *m/e* 268.098 17; found, *m/e* 268.093 97. Anal. Calcd for $C_8H_{24}O_4Si_3$: H, 9.01; C, 35.78. Found: H, 9.15; C, 36.05.

1,2,2,3-Tetraethoxy-1,1,3,3-tetramethyltrisilane (31). A mixture of **17** (1.11 g, 2.56 mmol), $AlCl_3$ (54 mg, 0.4 mmol), and EtOH (10 mL) was stirred at room temperature for 2.5 h. The usual workup gave **31** (676 mg, 82% yield): bp 120−130 °C (bath temperature)/0.95 mmHg. ^{1}H NMR (200 MHz, C_6D_6): δ 0.480 (s, 12H), 1.220 (t, J = 7.0 Hz, 6H), 1.258 (t, J = 7.0 Hz, 6H), 3.758 (q, J = 7.0 Hz, 4H), 3.923 (q, J = 7.0 Hz, 4H). ^{13}C NMR (50 MHz, C_6D_6): δ 0.61, 18.86, 18.94, 59.21, 61.12. ^{29}Si NMR (54 MHz, C_6D_6): δ −2.53, 7.31. HRMS: calcd for $C_{12}H_{32}O_4Si_3$, *m/e* 324.160 73; found, *m/e* 324.159 33. Anal. Calcd for $C_{12}H_{32}O_4Si_3$: H, 9.94; C, 44.39. Found: H, 10.03; C, 44.20.

1,2,2,3-Tetraisopropoxy-1,1,3,3-tetramethyltrisilane (32). A mixture of **17** (1.25 g, 2.9 mmol), $AlCl_3$ (54 mg, 0.4 mmol), and *i*-PrOH (10 mL) was stirred at room temperature for 19 h. The usual workup gave **32** (626 mg, 57% yield): bp 140−150 °C (bath temperature)/0.28 mmHg. ^{1}H NMR (200 MHz, C_6D_6): δ 0.495 (s, 12H), 1.250 (d, J = 6.0 Hz, 12H), 1.311 (d, J = 6.0 Hz, 12H), 4.116 (sep, J = 6.0 Hz, 2H), 4.337 (sep, J = 6.0 Hz, 2H). ^{13}C NMR (50 MHz, C_6D_6): δ 1.41, 26.19, 26.21, 65.84, 67.92. ^{29}Si NMR (54 MHz, C_6D_6): δ −7.54, 4.63. HRMS: calcd for $C_{16}H_{24}O_4Si_3$, *m/e* 380.223 42. Found: *m/e* 380.223 63. Anal. Calcd for $C_{16}H_{24}O_4Si_3$: H, 10.59; C, 50.47. Found: H, 10.55; C, 50.53.

1,2-Dimethoxy-1,1,2,3,3,3-hexamethyltrisilane (33). In a manner similar to the procedure for the synthesis of **26**, **18** (361 mg, 1.13 mmol), $AlCl_3$ (61 mg, 0.45 mmol), and MeOH (7 mL) gave **33** (185 mg, 69% yield): bp 120−140 °C (bath temperature)/32 mmHg. ^{1}H NMR (270 MHz, C_6D_6): there are two diastereotopic methyls, δ 0.256 (s, 9H), 0.342 (s, 3H), 0.356 (s, 3H), 0.484 (s, 3H), 3.375 (3H), 3.383 (s, 3H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −3.09, −1.45, 0.02, 50.79, 52.87. ^{29}Si NMR (54 MHz, C_6D_6): δ −1.55, 3.73. HRMS: calcd for $C_8H_{24}O_2Si_3$, *m/e* 236.108 34; found, *m/e* 236.106 54.

1,1,2,3-Tetramethoxy-1,2,3,3-tetramethyltrisilane (34). In a similar manner, **19** (464 mg, 1.1 mmol), $AlCl_3$ (45 mg, 0.34 mmol), and MeOH (5 mL) gave **34** (161 mg, 56% yield): bp 190−210 °C (bath temperature)/22 mmHg. ^{1}H NMR (200 MHz, C_6D_6): there are two diastereotopic methyl and MeO groups, δ 0.361 (s, 3H), 0.417 (s, 6H), 0.595 (s, 3H), 3.427 (s, 3H), 3.465 (s, 3H), 3.487 (s, 3H), 3.498 (s, 3H). ^{13}C NMR (50 MHz, C_6D_6): δ −2.35, −1.54, −0.42, 50.30, 50.89, 52.94. ^{29}Si NMR (54 MHz, C_6D_6): δ −1.25, 2.76, 13.90. HRMS: calcd for $C_8H_{24}O_4Si_3$, *m/e* 268.098 14; found, *m/e* 268.097 14. Anal. Calcd for $C_8H_{24}O_4Si_3$: H, 9.01; C, 35.78. Found: H, 9.14; C, 36.14.

1,1,2,3-Tetramethoxy-3,3-diethyl-1,2-dimethyltrisilane (35). In a similar manner, **20** (628 mg, 1.5 mmol), $AlCl_3$ (74 mg, 0.55 mmol), and MeOH (6 mL) gave **35** (367 mg, 83% yield): bp 130−140 °C (bath temperature)/1.5 mmHg. ^{1}H NMR (270 MHz, C_6D_6): there are two diastereotopic Et and MeO groups, δ 0.380 (s, 3H), 0.656 (s, 3H), 0.927−0.955 (m, 4H), 1.192 (t, J = 7.3 Hz, 3H), 1.196 (t, J = 8.1 Hz, 3H), 3.478 (s, 3H), 3.485 (s, 3H), 3.494 (s, 3H), 3.497 (s, 3H). ^{13}C NMR

(10) Schenzel, K.; Hassler, K. *Spectrochim. Acta* **1994**, *50A*, 127.
(11) Pitt, C. G. *J. Am. Chem. Soc.* **1969**, *91*, 6613.

(67.8 MHz, C_6D_6): δ −1.63, −1.41, 6.96, 7.14, 50.30, 51.49, 52.91. ^{29}Si NMR (54 MHz, C_6D_6): δ −19.66, 9.77, 14.73. HRMS: calcd for $C_{10}H_{28}O_4Si_3$, *m/e* 296.131 92; found, *m/e* 296.130 72. Anal. Calcd for $C_{10}H_{28}O_4Si_3$: H, 9.52; C, 40.49. Found: H, 9.56; C,40.43.

1,1,2,3,3-Pentamethoxy-1,2,3-trimethyltrisilane (36). In a similar manner, **21** (670 mg, 1.6 mmol), $AlCl_3$ (40 mg, 0.3 mmol), and MeOH (6 mL) gave **36** (294 mg, 67% yield): bp 210−230 °C (bath temperature)/21 mmHg. ^{1}H NMR (200 MHz, C_6D_6): there are two diastereotopic MeO groups, δ 0.402 (s, 6H), 0.660 (s, 3H), 3.502 (s, 3H), 3.515 (s, 6H), 3.523 (s, 6H). ^{13}C NMR (50 MHz, C_6D_6): δ −1.97, −1.65, 50.41, 53.00. ^{29}Si NMR (54 MHz, C_6D_6): δ −1.73, −0.40. HRMS: calcd for $C_8H_{24}O_5Si_3$, *m/e* 284.093 04; found, *m/e* 284.090 64. Anal. Calcd for $C_8H_{24}O_5Si_3$: H, 8.50; C, 33.77. Found: H, 8.47; C, 33.59.

1,1,2,3,3-Pentamethoxy-3-ethyl-1,2-dimethyltrisilane (37). In a similar manner, **22** (275 mg, 0.61 mmol), $AlCl_3$ (46 mg, 0.34 mmol), and MeOH (6 mL) gave **37** (142 mg, 78% yield): bp 130−140 °C (bath temperature)/2 mmHg. ^{1}H NMR (200 MHz, C_6D_6): there are four diastereotopic MeO groups, δ 0.416 (s, 3H), 0.695 (s, 3H), 0.906 (d, J = 7.8 Hz, 2H), 1.221 (t, J = 7.8 Hz, 3H), 3.500 (s, 3H), 3.519 (s, 3H), 3.524 (s, 3H), 3.544 (s, 3H), 3.557 (s, 3H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −1.68, −1.50, 6.33, 7.89, 50.39, 50.64, 50.68, 52.96. ^{29}Si NMR (54 MHz, C_6D_6): δ −2.48, −1.90, 0.10. Anal. Calcd for $C_9H_{26}O_5Si_3$: H, 8.78; C, 36.20. Found: H, 8.88; C,36.35.

1,2,3,4-Tetramethoxy-1,1,2,3,4,4-hexamethyltetrasilane (38). In a similar manner, **23** (380 mg, 0.77 mmol), $AlCl_3$ (65 mg, 0.5 mmol), and MeOH (7 mL) gave **38** (186 mg, 74% yield) as a 1:0.8 mixture of diastereomers: bp 120−130 °C (bath temperature)/0.9 mmHg. ^{1}H NMR (270 MHz, C_6D_6): δ 0.420 (s, 3H), 0.427 (s, 9H), 0.586 (s, 3H), 0.659 (s, 3H), 3.407 (s, 3H), 3.412 (s, 3H), 3.444 (s, 3H), 3.486 (s, 3H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −2.28, −1.97, −0.01, 0.04, 50.77, 53.02. ^{29}Si NMR (54 MHz, C_6D_6): δ 8.07, 8.47, 14.45, 14.50. HRMS: calcd for $C_9H_{27}O_4Si_4$, *m/e* (M−CH_3) 311.098 69; found, *m/e* (M − CH_3) 311.098 79. Anal. Calcd for $C_{10}H_{30}O_4Si_4$: H, 9.26; C, 36.76. Found: H, 9.31; C, 36.42.

Transformation into Fluorotrisilane: 1,2,3-Trifluoro-1,1,2,3,3-pentamethyltrisilane (41). 1,2,3-Trimethoxy-1,1,2,3,3-pentamethyltrisilane (**26**; 1.11 g, 4.4 mmol) was added to a saturated solution of $(HF)_x$py in ether (20 mL; large excess amount) at −70 °C with stirring. After 10 min, the mixture was condensed with a water pump at −50 to −40 °C. After the cooling bath was removed, the crude product was transferred *in vacuo* to another flask, which was cooled to −78 °C and then redistilled bulb-to-bulb to give **41** (862 mg, 91% yield): bp 130−150 °C (bath temperature)/100 mmHg, purity 90% by ^{1}H NMR (lit.[10] bp 69−70 °C/47 mmHg). ^{1}H NMR (200 MHz, C_6D_6): two terminal methyl groups are diastereotopic, δ 0.275 (d, J = 7.0 Hz, 6H), 0.319 (d, J = 7.0 Hz, 6H), 0.460 (d, J = 7.8 Hz, 3H). ^{13}C NMR (50 MHz, C_6D_6): δ −1.92 (d, J(CF) = 11 Hz, 1C), 0.15 (d, J(CF) = 11H, 2C), 0.37 (d, J(CF) = 11 Hz, 2C). ^{29}Si NMR (54 MHz, C_6D_6): δ 24.37 (dt, J(SiF) = 324.9 Hz, J(SiF) = 33.6 Hz, 1Si), 30.36 (ddd, J(SiF) = 307.9 Hz, J(SiF) = 25.5 Hz, J(SiF) = 2.7 Hz, 2Si). ^{19}F NMR (254.5 MHz, C_6D_6): δ −210.50 (tq, J(FF) = 9.9 Hz, J(FH) = 7.3 Hz, 1F), −174.34 (double septet, J(FF) = 9.9 Hz, J(FH) = 7.3 Hz, 2F). HRMS: calcd for $C_5H_{15}F_3Si_3$, *m/e* 216.043 44; found, *m/e* 216.043 54.

1,2,3-Trifluoro-2-ethyl-1,1,3,3-tetramethyltrisilane (42). In a similar manner, **27** (600 mg, 2.3 mmol) and saturated solution of $(HF)_x$py in ether (20 mL) gave **42** (450 mg, 86% yield): bp 90−110 °C (bath temperature)/110 mmHg, purity 90% on ^{1}H NMR. ^{1}H NMR (270 MHz, C_6D_6): terminal two methyl groups are diastereotopic, δ 0.309 (d, J = 8.6 Hz, 6H), 0.348 (d, J = 8.6 Hz, 6H), 0.981 (m, 2H), 1.075 (t, J = 7.3 Hz, 3H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 0.73 (d, J(CF) = 11 Hz, 2C), 0.87 (d, J(CF) = 12 Hz, 2C), 7.16 (d, J(CF) = 2.4 Hz, 1C), 7.88 (d, J(CF) = 11 Hz, 1C). ^{29}Si NMR (54 MHz, C_6D_6): δ 25.72 (dt, J(SiF) = 325.3 Hz, J(SiF) = 30.9 Hz, 1Si), 30.86 (ddd, J(SiF) = 307.9 Hz, J(SiF) = 25.5 Hz, J(SiF) = 2.7 Hz, 2Si). ^{19}F NMR (254.5 MHz, C_6D_6): δ −215.08 (tq, J(FF) = 9.9 Hz, J(FH) = 7.3 Hz, 1F), −173.17 (double septet, J(FF) = 9.9 Hz, J(FH) = 7.3 Hz, 2F).

1,2,3-Trifluoro-2-phenyl-1,1,3,3-tetramethyltrisilane (43). A mixture of **28** (800 mg, 2.3 mmol) and a saturated solution of $(HF)_x$py in ether (20 mL) was stirred at −70 °C. The resultung mixture was condensed under reduced pressure, followed by extraction with hexane (10 mL × 2). The extract was concentrated and distilled bulb-to-bulb to give **43** (435 mg, 68% yield): bp 145−155 °C (bath temperature)/15 mmHg, purity 95% on ^{1}H NMR. ^{1}H NMR (270 MHz, C_6D_6): terminal two methyl groups are diastereotopic, δ 0.287 (d, J = 8.6 Hz, 6H), 0.381 (d, J = 8.6 Hz, 6H), 7.172 (m, 3H), 7.675 (dd, J = 7.8 Hz, J = 1.9 Hz, 2H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 0.55 (d, J(CF) = 12.2 Hz, 2C), 0.33 (d, J(CF) = 12.2 Hz, 2C), 128.90, 130.39, 133.00, 133.03 (broad). ^{29}Si NMR (54 MHz, C_6D_6): δ 12.62 (dt, J(SiF) = 325.3 Hz, J(SiF) = 34.2 Hz, 1Si), 29.93 (dd, J(SiF) = 307.9 Hz, J(SiF) = 25.5 Hz, 2Si). ^{19}F NMR (254.5 MHz, C_6D_6): δ −215.33 (t, J(FF) = 7.4 Hz, 1F), −172.62 (double septet, J(FF) = 7.4 Hz, J(FH) = 8.6 Hz, 2F).

Preparation of the starting Aminochlorodisilanes. Dichloro(diethylamino)ethylsilane (7). To a solution of $EtSiCl_3$ (9.83 g, 60 mmol) and Et_3N (10 mL, 72 mmol) in THF (80 mL) was added dropwise a solution of Et_2NH (4.39 g, 60 mmol) in THF (40 mL) at −45 °C over 1 h. The mixture was gradually warmed to room temperature with stirring and was stirred for 10 h. The mixture was then condensed under reduced pressure, followed by addition of dry hexane (50 mL) and filtration. The filtrate was distilled to give the product (9.35 g, 78% yield): bp 100−102 °C/51 mmHg. ^{1}H NMR (270 MHz, C_6D_6): δ 0.87−0.92 (m, including triplet at δ 0.894, J = 7.0 Hz, 6H, total 8H), 1.009 (t, J = 7.4 Hz, 3H), 2.768 (q, J = 7.0 Hz, 4H). ^{13}C NMR (67.8 MHz, C_6D_6): δ 7.14, 12.29, 15.42, 40.06.

1,2-Bis(diethylamino)-2-chloro-1,1,2-trimethyldisilane (10). This compound was prepared in four steps.

(1) To a solution of $(Et_2N)_2MeSiCl$ (9.8 g, 44 mmol) in THF (30 mL) was added dropwise a solution of $Me_2PhSiLi$, freshly prepared from 8.5 g of $Me_2PhSiCl$, 1.2 g of Li, and 50 mL of THF, at 0 °C over 1 h. The mixture was stirred at room temperature for 16 h. Workup similar to that given for the preparation of **13** gave **1,1-bis(diethylamino)-2-phenyl-1,2,2-trimethyldisilane (44;** 10.8 g, 76% yield based on $(Et_2N)_2MeSiCl$): bp 126−127 °C/0.7 mmHg, purity 99% on GLC; ^{1}H NMR (270 MHz, C_6D_6) δ 0.294 (s, 3H), 0.513 (s, 6H), 0.977 (t, J = 7.0 Hz, 12H), 2.874 (q, J = 7.0 Hz, 4H), 7.224−7.310 (m, 3H), 2.884 (q, J = 7.0 Hz, 4H), 7.626−7.653 (m, 2H); ^{13}C NMR (67.8 MHz, C_6D_6) δ −1.85, −0.57, 15.71, 40.22, 127.96, 128.49, 134.40, 140.81; HRMS calcd for $C_{17}H_{34}N_2Si_2$ *m/e* 322.226 04, found, *m/e* 322.226 84.

(2) Through a solution of **44** (9.8 g, 30 mmol) in Et_2O (150 mL) was bubbled dry HCl (ca. 0.4 mol; generated from 24 g of NH_4Cl and 23 mL of concentrated H_2SO_4) at 0 °C over 2 h. The resulting mixture was condensed under reduced pressure, followed by addition of dry hexane (30 mL) and filtration. The filtrate was concentrated and distilled to give **1,1-dichloro-2-phenyl-1,2,2-trimethyldisilane (45**; 5.9 g, 79% yield): bp 84−85 °C/1.2 mmHg, purity 98% on GLC; ^{1}H NMR (270 MHz, C_6D_6) δ 0.379 (s, 6H), 0.530 (s, 3H), 7.169−7.197 (m, 3H), 7.414−7.449 (m, 2H); ^{13}C NMR (67.8 MHz, C_6D_6) δ −5.13, 6.53, 128.49, 130.00, 134.31 (one peak of ipso carbon was hiddened by other peaks); HRMS calcd for $C_9H_{14}Cl_2Si_2$ *m/e* 249.998 06, found, *m/e* 249.995 66.

(3) Through a mixture of **45** (5.8 g, 23 mmol), freshly sublimed $AlCl_3$ (120 mg, 0.9 mmol), and dry benzene (10 mL) was bubbled dry HCl at room temperature over 1 h. To the resulting mixture was added dry acetone (0.5 mL), followed by stirring for 15 min. The resulting solution was transferred to a 50 mL flask via syringe and distilled to give **1,1,2-trichloro-1,2,2-trimethyldisilane (46**; 4.17 g, 87% yield): bp 93−95 °C/115 mmHg (lit.[7b] bp 146−152 °C); purity 97% on GLC;

^{1}H NMR (270 MHz, C_6D_6) δ 0.324 (s, 6H), 0.591 (s, 3H); ^{13}C NMR (67.8 MHz, C_6D_6) δ 0.49, 5.43.

(4) To a solution of Et_2NH (15 mL) in THF (20 mL) was added **46** (1.87 g, 9 mmol) at −50 °C. The mixture was stirred at −50 °C for 40 min. The resulting mixture was condensed under reduced pressure, followed by addition of dry hexane (30 mL) and filtration. The filtrate was concentrated and distilled to give the final product **10** (2.08 g, 83% yield): bp 112−120 °C (bath temperature)/0.7 mmHg, purity 94% on GLC. ^{1}H NMR (270 MHz, C_6D_6): there are two diastereotopic methyl groups, δ 0.361 (s, 3H), 0.402 (s, 3H), 0.585 (s, 3H), 0.981 (t, J = 6.8 Hz, 6H), 1.036 (t, J = 6.8 Hz, 6H), 2.813 (q, J = 6.8 Hz, 4H), 2.926 (m, 4H). ^{13}C NMR (67.8 MHz, C_6D_6): δ −1.70, −0.40, 2.59, 15.26, 16.03, 41.01, 41.17. ^{29}Si NMR (54 MHz, C_6D_6): δ −6.79, 7.01. HRMS: calcd for $C_{11}H_{29}ClN_2Si_2$: *m/e* 280.155 83; found, *m/e* 280.156 63.

1,1,2-Tris(diethylamino)-2-chloro-1,2-dimethyldisilane (11). To Et_2NH (20 mL) was added **12** (4.32 g, 14.4 mmol), prepared as detailed below, at 0 °C. The mixture was stirred at room temperature for 1 h. The mixture was condensed under reduced pressure, followed by addition of dry hexane (20 mL) and filtration. The filtrate was condensed and distilled bulb-to-bulb to give **11** (4.05 g, 84% yield): bp 190−210 °C (bath temperature)/0.25 mmHg, purity 90% on ^{1}H NMR. ^{1}H NMR (200 MHz, C_6D_6): δ 0.448 (s, 3H), 0.657 (s, 3H), 1.006−1.096 (m, 18H), 2.895−3.092 (m, 12H). ^{13}C NMR (50 MHz, C_6D_6): δ −0.28, 3.72, 15.10, 15.30, 15.50, 39.95, 40.84. ^{29}Si NMR (54 MHz, C_6D_6): δ −12.52, 5.29. HRMS: calcd for $C_{14}H_{36}ClN_3Si_2$, *m/e* 337.213 53; found, *m/e* 337.213 03.

1,2-Bis(diethylamino)-1,2-dichloro-1,2-dimethyldisilane (12). To a solution of $(Et_2N)_2MeSiSiMe(NEt_2)_2$ (**47**;[1] 9.3 g, 25 mmol) in THF (10 mL) was added dropwise CH_3COCl (4.18 g, 53 mmol) in THF (5 mL) at −45 to −35 °C over 30 min. The mixture was stirred at room temperature for 4 h and condensed under reduced pressure. The residue was distilled to give the product **12** (5.32 g, 71% yield) as a *meso/dl* mixture: bp 94−95 °C / 0.5 mmHg, purity 91% on GLC. ^{1}H NMR (200 MHz, C_6D_6): δ 0.604 (s, 40% of 6H), 0.717 (s, 60% of 6H), 0.960−0.996 (m, 12H), 2.70−2.98 (m, 8H). ^{13}C NMR (50 MHz, C_6D_6): δ 1.92, 2.03, 15.10, 15.16, 40.76, 41.15. ^{29}Si NMR (54 MHz, C_6D_6): δ 0.48, 2.63. HRMS: calcd for $C_{10}H_{26}Cl_2N_2Si_2$, *m/e* 300.101 08; found, *m/e* 300.100 98.

Acknowledgment. We thank the Ministry of Education, Science, and Culture of Japan for a Grant-in-Aid (No. 05453137) and Shin-Etsu Chemical Co., Ltd., for a gift of chlorosilanes.

OM960978Y