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Different Modes of Reaction of Monoalkoxy- and Dialkoxyphenylchlorosilanes with Lithium Metal: Selective Formation of (2-Alkoxydisilanyl)lithium vs (Dialkoxysilyl)lithium

Atsushi Kawachi and Kohei Tamao*

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

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Summary: Reaction of monoalkoxychlorosilanes with lithium metal at 0 °C gives (2-alkoxydisilanyl)lithiums selectively via immediate self-condensation of the resulting (alkoxysilyl)lithiums. The (2-alkoxydisilanyl)lithiums undergo coupling with a chlorosilane and 1,4-addition to an α,β-unsaturated ester. Reaction of a dialkoxychlorosilane, however, gives the (dialkoxysilyl)lithium selectively. Decomposition modes of (2-alkoxydisilanyl)lithiums have also been studied.

Silyl anions,[1] especially functionalized silyl anions[2] and oligosilanyl anions,[3] are useful reagents for constructing silicon-silicon skeletons of oligosilanes and polysilanes and for introducing various silyl units into organic compounds.[2c,4] Since only a small number of such species have been reported so far, development of new methodologies is of interest. In particular, oligosilanyl anions are not readily available, because preparation of the required precursors, linear or cyclic oligosilanes, is often tedious.[5] We describe herein a convenient one-step synthesis of (2-alkoxydisilanyl)lithiums and of a (dialkoxysilyl)lithium from readily available monosilanes with a special emphasis on the different modes of reaction of the precursors, monoalkoxy- and dialkoxychlorosilanes, toward lithium metal.

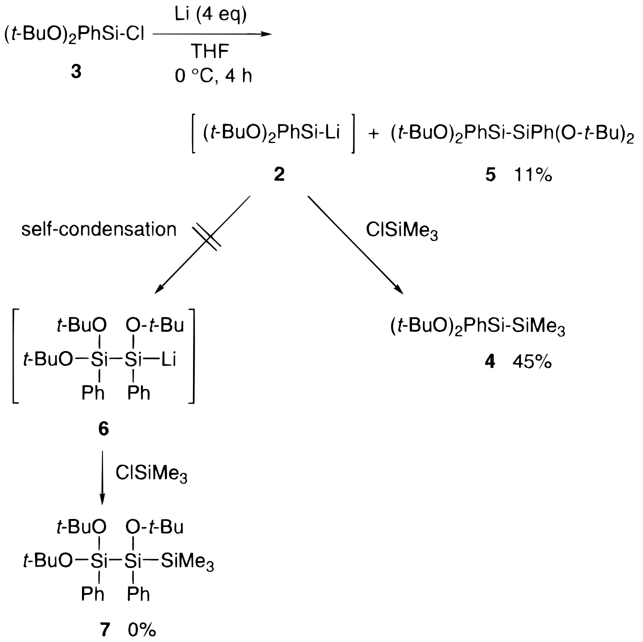
We have recently prepared (alkoxysilyl)lithiums such as **1** by a tin−lithium exchange reaction of an (alkoxysilyl)stannane with *n*-butyllithium[2a] and by reduction of alkoxychlorosilanes with lithium 1-(dimethylamino)naphthalenide[2b] at low temperature.[6] The (monoalkoxysilyl)lithiums behave as lithium alkoxysilylenoids, which undergo bimolecular self-condensation at 0 °C by nucleophilic substitution of the alkoxy group by another molecule of silyllithium to yield (2-alkoxydisilanyl)lithiums.[2a] In contrast, the (dialkoxysilyl)lithium **2** shows little silylenoid nature. These findings prompted us to investigate a direct reaction of alkoxychlorosilanes with lithium metal. Judging from the high yields of the corresponding silyllithiums, [2b] we have chosen *tert*-butoxyphenylchlorosilanes as models.

$(t\text{-BuO})Ph(R)Si\text{-}Li$ **1** $(t\text{-BuO})_2PhSi\text{-}Li$ **2**

Results and Discussion

We first examined the reaction of dialkoxychlorosilane **3** (Scheme 1). Thus, **3** was stirred with an excess of granular lithium[7] (4 equiv) in THF at 0 °C for 4 h. Addition of Me_3SiCl to the reaction mixture gave 1,1-dialkoxy-1-phenyl-2,2,2-trimethyldisilane **4** in 45% yield, together with the homocoupling product **5** in 11% yield.[8,9] This result clearly indicates the formation of

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

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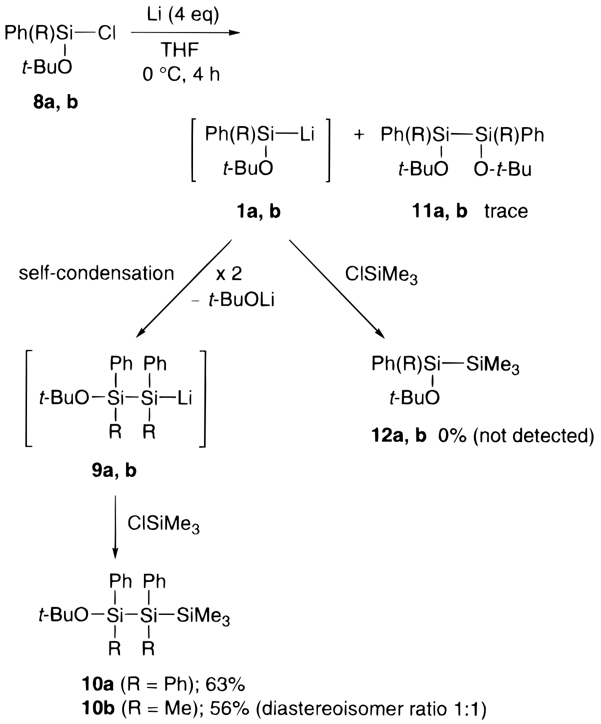
(7) Lithium dispersion gave **4** and **10** in much lower yields, together with uncharacterizable byproducts.

(8) When only an equimolar amount of lithium metal was used at room temperature, **5** was obtained selectively in 60% yield (see Experimental Section).

(9) In all cases, the chlorosilanes were consumed completely and uncharacterizable nonvolatile compounds were also obtained.

S0276-7333(96)00421-9 CCC: $12.00

Scheme 2



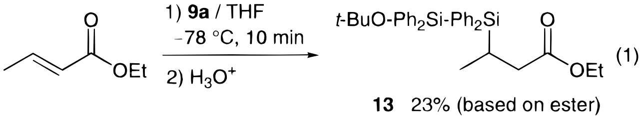
(dialkoxysilyl)lithium **2**, which, as expected from the previous results, is stable at 0 °C and gives no self-condensation product **6** (and **7**). This is the first example of the synthesis of an (alkoxysilyl)lithium by the direct reaction of an alkoxychlorosilane with lithium metal. In the ^{29}Si NMR spectrum, **2** resonates at δ 41.8.[2b]

In contrast, as shown in Scheme 2, reaction of monoalkoxychlorosilanes **8** with granular lithium[7] (4 equiv) in THF at 0 °C afforded (2-alkoxydisilanyl)lithiums **9**, which were trapped after 4 h with Me_3SiCl to give the corresponding alkoxytrisilanes **10** in about 60% yield, together with a trace amount of homocoupling product **11**.[9,10] No **12**, the trapped products of the (alkoxysilyl)lithiums **1**, were formed. It is likely that the lithium alkoxysilylenoids **1** are generated in the first step and that they undergo bimolecular self-condensation immediately, as reported previously.[2a] The diphenyl (**1a**) and the phenyl methyl (**1b**) derivatives afforded comparable results. This is the most convenient one-step synthesis of (disilanyl)lithiums **9** from the readily available monosilanes.

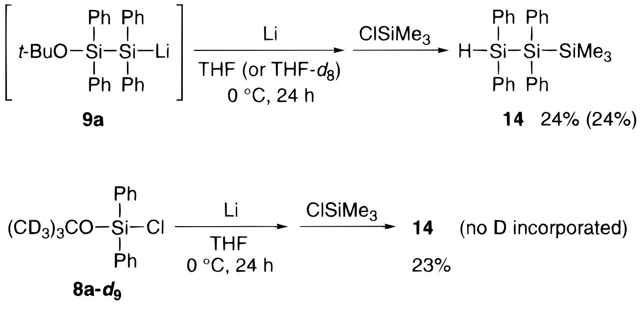
^{29}Si NMR spectroscopy showed two signals at δ −43.7 (Si−Li) and −2.3 (Si−O) for **9a** and two sets of signals at δ −64.5, −62.7 (Si−Li) and 8.1, 9.0 (Si−O) for **9b**, which are attributed to the two diastereoisomers.

The functionalized (disilanyl)lithium **9a** underwent 1,4-addition to an α,β-unsaturated ester to give the β-disilanylated ester **13** in 23% yield (eq 1), indicative of reactivity similar to that of nonfunctionalized disilanyllithiums reported earlier.[4]

No further elongation reaction of (2-alkoxydisilanyl)lithiums **9** was observed, probably due to lack of the activation of the Si−O bond by the lithium atom unlike that in the silylenoids **1**.[2a] Instead, **9a** slowly decomposed at 0 °C over 24 h in the presence of lithium metal to give, after addition of Me_3SiCl, hydrotrisilane **14** in 24% yield, together with **10a** (21% yield), as shown in Scheme 3.



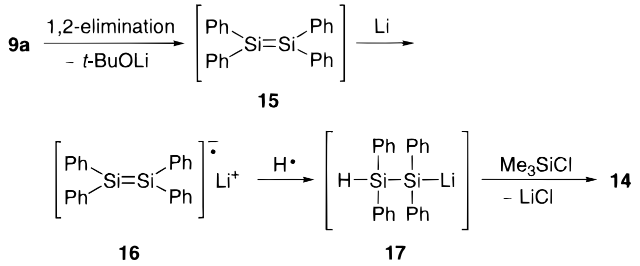
Scheme 3



It should be noted that this sort of decomposition occurred only in the presence of lithium. In the absence of lithium metal, i.e., after removal of the remaining lithium metal from the solution of **9a**, no final product **14** but only a complex mixture was obtained.

We propose one plausible mechanism of the decomposition as visualized in Scheme 4. Thus, 1,2-elimination of *t*-BuOLi from **9a** affords disilene **15**,[11] which is reduced by the remaining lithium metal to give the anion radical **16**.[12] Subsequent hydrogen abstraction affords **17**, which is finally trapped with Me_3SiCl to give **14**. The origin of the abstracted hydrogen, however, could not be determined by two deuterium experiments: (1) reaction of **8a** in THF-d_8 and (2) reaction of (*tert*-butoxy-d_9)Ph_2SiCl (**8a**-d_9) in THF (Scheme 3). Both of the experiments gave no deuteriotrisilane. Only the hydrotrisilane **14** was isolated.

Scheme 4



We have developed a new method for the preparation of (2-alkoxydisilanyl)lithiums via lithium alkoxysilylenoids, as well as of a (dialkoxysilyl)lithium, from readily available alkoxychlorosilanes by direct reaction with

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[10] Reaction of **8a** with an equimolar amount of lithium at room temperature gave **11a**[2b] in 25% yield and 1,3-di-*tert*-butoxy-1,1,2,2,3,3-hexaphenyltrisilane in 26% yield (see Experimental Section). The latter may be formed by reaction of **9a** with **8a**. The isolated disilane **11a**, however, did not react with lithium (8 equiv) even under sonication at room temperature (100% recovery of **11a**).

[11] While 1,2-elimination of lithium halides (LiX) from (α-lithioalkyl)halosilanes (XR_2Si-CR_2Li) is one of the most successful routes to silenes ($R_2Si=CR_2$), no attempt to generate disilenes ($R_2Si=SiR_2$) by a similar elimination process has been reported so far: (a) Raabe, G.; Michl, J. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, England, 1989; Chapter 17, section III. (b) Okazaki, R.; West, R. *Adv. Organomet. Chem.* **1996**, *39*, 231−273.

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lithium metal. The silylenoids have a synthetic potential for preparation of new reagents, in addition to affording a new insight into the mechanism of polysilane synthesis.[13] Much remains to be solved, however, in the decomposition process of lithium alkoxysilylenoids. Further work is underway, especially for detection of disilene species by introducing bulkier substituents on silicon.

Experimental Section

General Remarks. ^1H (270 MHz), ^{13}C (67.94 MHz), and ^{29}Si (53.67 MHz) NMR spectra were recorded on a JEOL EX-270 spectrometer. ^1H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^1H δ 7.200 ppm and ^{13}C δ 128.00 ppm) or $CDCl_3$ (^{13}C δ 77.00 ppm). ^{29}Si chemical shifts are referenced to external tetramethylsilane (0 ppm). The ^{29}Si NMR spectra were observed in an unlocked mode at 0 °C. Although the spectrometer was unlocked during the acquisition, the field was stable and no significant field shift was observed. For NMR measurements, the silyllithium **2** and disilanyllithiums **9** were prepared in THF as described in the experimental procedures and the resulting solution was transferred to an NMR sample tube via a Teflon tube under an argon atmosphere. Mass spectra were measured at 70 eV on a JEOL JMS-DX300 mass spectrometer equipped with a JMA-3500 data processing system. Melting points were measured with a Yanaco MP-S3 apparatus and were uncorrected. The elemental analyses were performed at the Microanalysis Division of the Institute for Chemical Research, Kyoto University. Analytical samples were purified by preparative GLC, preparative HPLC, recycling reverse-phase liquid chromatography, or recrystallization. Analytical and preparative GLC were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3 or 1 m column packed with 30% Silicone DC550 on Celite 545. Recycling reverse-phase liquid chromatography was performed with JAI LC-908 equipped with JAIGEL-ODS S-343-15 and P-15 columns. Reverse-phase column chromatography and thin-layer chromatography were performed by using Wakogel LP-40C18 (20−40 μm) (Wako Pure Chemical Industries) and RP-18 F_{254}s (Merck), respectively. Column chromatography and thin-layer chromatography were performed by using Kieselgel 60 (70−230 mesh) (Merck) and silica gel 60F-254 (Merck), respectively.

tert-Butoxydiphenylchlorosilane and di-*tert*-butoxyphenylchlorosilane were prepared by the same method as described in the literature.[2b] Phenylmethyldichlorosilane was distilled under reduced pressure before use. Trimethylchlorosilane was treated with small pieces of sodium under nitrogen to remove the dissolved HCl, and the supernatant was used. Triethylamine and *tert*-butyl alcohol were distilled under nitrogen from calcium hydride. 4-(Dimethylamino)pyridine was commercially available and was used without further purification. Lithium granules were purchased from Chemetall Gesellshaft. *tert*-Butyl alcohol-d_{10} (99 atom %) was purchased from Aldrich. THF was distilled under nitrogen from sodium benzophenone ketyl. All reactions were carried out under an argon atmosphere.

Synthesis of (Di-*tert*-butoxyphenylsilyl)lithium (2) and Trapping as 1,1-Di-*tert*-butoxy-1-phenyl-2,2,2-trimethyldisilane (4). To a suspension of granular lithium (32 mg, 4.6 mmol) in THF (1.0 mL) was added di-*tert*-butoxyphenylchlorosilane (**3**; 296 mg, 1.03 mmol) at room temperature. The lithium surface turned orange after about 40 min, and then the mixture was cooled to 0 °C. After being stirred for 4 h, the resulting dark red solution of **2** was added via a Teflon tube to a solution of Me_3SiCl (0.14 mL, 1.1 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min and warmed to ambient temperature. The solvent was evaporated. The residue was diluted with hexane (10 mL), filtered, and concentrated. The residue was distilled bulb to bulb (105−125 °C/0.35 mmHg, bath temperature) to give **4** (149 mg, 45% yield) as a colorless liquid. The spectral data were identical with the data reported previously.[2b] The residue was further distilled bulb to bulb (140−170 °C/0.3 mmHg, bath temperature) to give crude **5** (38 mg, 51% purity by GLC, approximately 11% yield), which was identified by comparison with the authentic compound prepared below.

1,1,2,2-Tetra-*tert*-butoxy-1,2-diphenyldisilane (5). To a suspension of granular lithium (14 mg, 2.0 mmol) in THF (2.0 mL) was added **3** (557 mg, 1.94 mmol) at room temperature. Ultrasonication was performed until the lithium surface turned orange (for about 5 min), and the mixture was stirred at room temperature for 1 day. The solvent was evaporated, the residue was diluted with hexane (10 mL), filtered, and concentrated to give crude **5** as a white solid. Recrystallization from hexane at 0 °C afforded pure **5** (294 mg, 60% yield) as colorless crystals, mp 215−216 °C (in a capillary under atmospheric pressure). Sublimation point: about 160 °C. ^1H NMR (C_6D_6): δ 1.36 (s, 36H), 7.25−7.39 (m, 6H), 8.22−8.25 (m, 4H). ^{13}C NMR (C_6D_6): δ 32.30, 73.99, 127.52, 129.49, 135.76, 140.63. MS: m/e 487 ($M^+ - Me$, 0.5), 429 ($M^+ -$ *t*-BuO, 0.7), 277 (55), 199 (4), 139 (100). Anal. Calcd for $C_{28}H_{46}O_4Si_2$: C, 66.88; H, 9.22. Found:C, 66.70; H, 9.30.

***tert*-Butoxyphenylmethylchlorosilane (8b).** This compound was prepared from phenylmethyldichlorosilane and *tert*-butyl alcohol in 68% yield by essentially the same method as described in the literature:[2b] bp 61−64 °C/1.0 mmHg. ^1H NMR (C_6D_6): δ 0.62 (s, 3H), 1.28 (s, 9H), 7.20−7.22 (m, 3H), 7.77−7.81 (m, 2H). ^{13}C NMR (C_6D_6): δ 3.96, 31.65, 75.71, 128.18, 130.59, 133.73, 136.64. MS: m/e 230 ($M^+ + 2$, 3), 228 (M^+, 7), 215 ($M^+ + 2 - Me$, 41) 213 ($M^+ - Me$, 100), 157 ($M^+ + 2 -$ *t*-BuO, 52), 155 ($M^+ -$ *t*-BuO, 68). Anal. Calcd for $C_{11}H_{17}OSiCl$: C, 57.75; H, 7.49. Found: C, 57.87; H, 7.09.

Synthesis of (2-*tert*-Butoxy-1,1,2,2-tetraphenyldisilanyl)lithium (9a) and Trapping as 1-*tert*-Butoxy-1,1,2,2-tetraphenyl-3,3,3-trimethyltrisilane (10a). To a suspension of granular lithium (29 mg, 4.2 mmol) in THF (1.0 mL) was added **8a** (309 mg, 1.06 mmol) at room temperature. The lithium surface turned orange after about 20 min, and then the mixture was cooled to 0 °C. After being stirred for 4 h, the resulting dark red solution of **9a** was added via a Teflon tube to a solution of Me_3SiCl (0.15 mL, 1.2 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min and warmed to ambient temperature. A 5% aqueous solution of NH_4Cl (10 mL) was then added. The mixture was extracted with Et_2O (10 mL × 3). The combined organic layer was washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The white solid obtained was subjected to column chromatography on silica gel eluted with hexane/AcOEt (60/1) to afford crude **9a** (236 mg, R_f 0.23) together with small amounts of impurities. The crude solid product was triturated with hexane (1 mL × 2) at 0 °C followed by filtration to give pure **9a** (170 mg, 63%) as a white solid, mp 224−225 °C (in a capillary under atmospheric pressure). Sublimation point: about 160 °C. The spectral data were identical with the reported data.[2a]

Reaction of 8a with An Equimolar Amount of Lithium. To a suspension of granular lithium (14 mg, 2.0 mmol) in THF (1.0 mL) was added a solution of **8a** (533 mg, 1.83 mmol) in THF (1.0 mL) at room temperature. Ultrasonication was performed until the lithium surface turned orange (for about 5 min), and the mixture was stirred at room temperature for 4 h. To the reaction mixture was added Me_3SiCl (1.8 mmol, 0.23 mL) at room temperature. The solvent was evaporated, the residue was diluted with hexane (10 mL), and this solution

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was filtered and concentrated to give a mixture of **11a** (25% yield) and 1,3-di-*tert*-butoxy-1,1,2,2,3,3-hexaphenyltrisilane (26% yield). The yields were estimated by means of ^{1}H NMR analysis using mesitylene as internal standard.

1,3-Di-*tert*-butoxy-1,1,2,2,3,3-hexaphenyltrisilane. The pure sample was obtained by recrystallization from hexane at 0 °C as colorless crystals in 24% yield; mp 282−283 °C (in a capillary under atmospheric pressure). Sublimation point: about 210 °C. ^{1}H NMR (C_6D_6): δ 1.24 (s, 18H), 7.12−7.17 (m, 18H), 7.71−7.75 (m, 8H), 7.82−7.85 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 31.97, 75.17, 127.01, 127.22, 128.00, 129.00, 134.36, 135.89, 137.20, 137.45. MS: *m/e* 692 (M^+, 0.5), 635 ($M^+ -$ *t*-Bu, 6), 581 (100), 503 (99), 382 (99), 303 (98), 255 ((*t*-BuO)-Ph_2Si^+, 99). Anal. Calcd for $C_{44}H_{48}O_2Si_3$: C, 76.25; H, 6.98. Found: C, 76.63; H, 7.10.

Synthesis of (2-*tert*-Butoxy-1,2-diphenyl-1,2-dimethyldisilanyl)lithium (9b) and Trapping as 1-*tert*-Butoxy-1,2-diphenyl-1,2-dimethyl-3,3,3-trimethyltrisilane (10b). To a suspension of granular lithium (31 mg, 4.4 mmol) in THF (1.0 mL) was added **8b** (236 mg, 1.03 mmol) at room temperature. The lithium surface turned orange after about 10 min, and then the mixture was cooled to 0 °C. After being stirred for 4 h, the resulting dark red solution of **9b** was added via a Teflon tube to a solution of Me_3SiCl (0.14 mL, 1.1 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 20 min and warmed to ambient temperature. The solvent was evaporated. The residue was diluted with hexane (10 mL), and this solution was filtered and concentrated. The colorless liquid obtained was subjected to column chromatography on silica gel eluted with hexane to afford **10b** (111 mg, R_f 0.20, a 1:1 mixture of diastereoisomers) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.22 (s, 9H), 0.25 (s, 9H), 0.45 (s, 3H), 0.49 (s, 3H), 0.64 (s, 3H), 0.70 (s, 3H), 1.19 (s, 9H), 1.21 (s, 9H), 7.23−7.28 (m, 6H), 7.59−7.67 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −9.04, −8.73, −1.26 (2C), 1.21, 1.33, 32.20 (2C), 73.86, 73.98, 127.42, 127.48 (2C), 127.55, 127.64, 127.67, 128.72, 128.75, 133.60, 133.69, 134.84 (2C), 137.25, 137.45, 140.97, 141.19. MS: *m/e* 386 (M^+, 0.4), 371 ($M^+ -$ Me, 1), 329 ($M^+ -$ *t*-Bu, 100), 313 ($M^+ - Me_3Si$, 7), 193 (18). Anal. Calcd for $C_{21}H_{34}OSi_3$: C, 65.22; H, 8.86. Found: C, 64.86; H, 8.90.

Reaction of 9a with Ethyl Crotonate: Synthesis of Ethyl 3-(2-*tert*-Butoxy-1,1,2,2-tetraphenyldisilanyl)butanoate (13). A solution of **9a**, prepared from **8a** (277 mg, 0.952 mmol) and granular lithium (28 mg, 4.0 mmol) in THF (1.0 mL), was added over 1 min to a solution of ethyl crotonate (**12**) in THF (1.0 mL) at −78 °C, and the mixture was stirred for 10 min. A 5% aqueous solution of NH_4Cl (5 mL) was poured into the mixture at −78 °C. After being warmed to ambient temperature, the mixture was extracted with Et_2O (10 mL × 3). The combined organic layers were washed with a 5% aqueous solution of NH_4Cl (10 mL × 1), water (10 mL × 1), and brine (10 mL × 1), dried over $MgSO_4$, and concentrated in vacuo. The residue was subjected to column chromatography on silica gel, eluted with hexane/AcOEt (20/1), to give crude **13** (124 mg, R_f 0.20). HPLC with hexane/AcOEt (7/1) gave pure **13** (59 mg, 23% yield) as a colorless oil. ^{1}H NMR (C_6D_6): δ 0.96 (t, J = 7.2 Hz, 3H), 1.27 (s, 9H), 1.36 (d, *J* = 7.0 Hz, 3H), 2.28 (dd, *J* = 14.9 and 12.2 Hz, 1H), 2.30−2.48 (m, 1H), 3.15 (dd, *J* = 14.9 and 1.6 Hz, 1H), 3.98 (q, *J* = 7.2 Hz, 2H), 7.12−7.20 (m, 12H), 7.66−7.83 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 14.25, 14.76, 15.11, 32.04, 37.25, 60.00, 75.47, 127.57 (4C), 128.88, 128.95, 129.38 (2C), 133.73, 133.78, 135.54, 135.58, 136.33, 136.39, 136.73, 136.77, 174.05. MS: *m/e* 523 ($M^+ -$ Et, 0.4), 507 ($M^+ -$ EtO, 0.7), 479 ($M^+ -$ *t*-BuO, 0.5), 451 (1), 297 ($M^+ -$ (*t*-BuO)Ph_2Si, 100). Anal. Calcd for $C_{34}H_{40}O_3Si_2$: C, 73.87; H, 7.29. Found: C, 73.55; H, 7.40.

Decomposition of 9a: Isolation of 1,1,2,2-Tetraphenyl-3,3,3-trimethyltrisilane (14). To a suspension of granular lithium (31 mg, 4.5 mmol) in THF (1.5 mL) was added **9a** (296 mg, 1.02 mmol) at room temperature. After the lithium surface turned orange, the mixture was cooled to 0 °C. After being stirred for 24 h, the resulting dark red solution was added via a Teflon tube to a solution of Me_3SiCl (0.14 mL, 1.1 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min and warmed to ambient temperature, and water (10 mL) was added. The mixture was extracted with Et_2O (20 mL × 3). The combined organic layers were washed with water (10 mL) and brine (10 mL), dried over $MgSO_4$, and concentrated in vacuo. The obtained liquid was subjected to reverse-phase column chromatography and recycling reverse-phase liquid chromatography with CH_3CN as eluent (R_f 0.45) to give **14** (53 mg, 24% yield) as a white solid, mp 63.2−64.1 °C. ^{1}H NMR (C_6D_6): δ 0.19 (s, 9H), 5.66 (s, 1H), 7.09−7.20 (m, 12H), 7.63−7.67 (m, 4H), 7.70−7.73 (m, 4H). ^{13}C NMR ($CDCl_3$): δ −0.90, 127.89, 127.92, 128.59, 129.16, 133.50, 134.50, 136.03, 136.33. MS: *m/e* 438 (M^+, 7), 423 ($M^+ -$ Me, 5), 365 ($M^+ - Me_3Si$, 74), 288 (84), 259 (100), 255 ($M^+ - HPh_2Si$), 210 (58). IR (KBr): 2110 (ν_{Si-H}) cm^{-1}. Anal. Calcd for $C_{27}H_{30}Si_3$: C, 73.91; H, 6.89. Found: C, 73.78; H, 6.88.

(*tert*-Butoxy-d_9)chlorodiphenylsilane (8a-d_9). This compound was prepared from *tert*-butyl alcohol-d_{10} and diphenyldichlorosilane by the same method as described for **8a**.[2b] ^{1}H NMR (C_6D_6): δ 7.16−7.20 (m, 6H), 7.84−7.87 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 30.62 (septet, $^1J_{C-D} = 19.5$ Hz), 76. 52, 127.85, 130.53, 134.27, 134.81.

Reaction of (*tert*-Butoxy-d_9)chlorodiphenylsilane (8a-d_9) with Lithium. To a suspension of granular lithium (27 mg, 3.9 mmol) in THF (1.0 mL) was added **8a-d_9** (291 mg, 0.970 mmol) at room temperature. After the lithium surface turned orange, the mixture was cooled to 0 °C. After being stirred for 24 h, the resulting dark red solution was added via a Teflon tube to a solution of Me_3SiCl (0.135 mL, 1.07 mmol) in THF (1.0 mL) at 0 °C. The mixture was stirred at 0 °C for 10 min and warmed to ambient temperature. The solvent was evaporated. The residue was diluted with hexane (10 mL), and this solution was filtered and concentrated to afford crude **14**. The yield was estimated by means of ^{1}H NMR analysis (23% yield) using mesitylene as internal standard.

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