

# Highly Selective Mono- and Polyallylation of Polychlorosilanes and Polychlorodisilanes<sup>1</sup>

Takanobu Sanji, Mitsuhiro Iwata, Masahiro Watanabe, Takashi Hoshi, and Hideki Sakurai\*

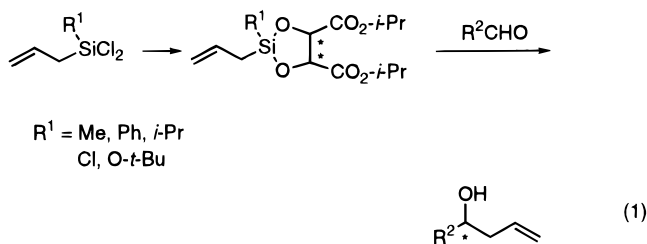
Department of Industrial Chemistry, Faculty of Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan

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The reaction of methyltrichlorosilane with an equimolar amount of allyl chloride in the presence of zinc powder proceeds quite smoothly in dimethylimidazolidinone (DMI) to give allyl(dichloro)methylsilane in high selectivity. Other  $\text{RSiCl}_3$  ( $\text{R} = \text{isopropyl, } \textit{tert}\text{-butyl, } n\text{-hexyl, phenyl, } n\text{-octyl, } n\text{-decyl}$ ) gave the corresponding allylated compounds,  $(\text{CH}_2=\text{CHCH}_2)\text{-RSiCl}_2$ , highly selectively in high yield under the same conditions. Dimethyldichlorosilane and trimethylchlorosilane are also monoallylated. The reaction of 2 equiv of allyl chloride–Zn–DMI with methyltrichlorosilane gave the diallylated compound selectively. The reaction of methyltrichlorosilane with (*E*)-1-chloro-2-butene selectively afforded 1-methyl-2-propenyl-(methyl)dichlorosilane with allylic rearrangement. The reaction was also applied successfully to the allylation of polychlorodisilanes.

## Introduction

Allylsilanes are versatile organosilicon reagents as applied to organic synthesis.<sup>2</sup> A variety of methods have been used for the preparation of allylsilanes. Allyl-trichlorosilane can be prepared quite satisfactorily by the Cu mediated reaction of allyl chloride and trichlorosilane.<sup>3</sup> Allyltrimethylsilane can be prepared easily by the Grignard reaction, but partial allylation of methylchlorosilanes, and in general partial alkylation of polychlorosilanes, with the allyl Grignard reagent usually gave mixtures of allylated products.<sup>4</sup> Partially allylated chlorosilanes such as allyl(methyl)dichlorosilane are useful precursors for modified allylsilanes such as tartaric acid ester derivatives, which can be used for enantioselective allylation of carbonyl compounds.<sup>5</sup> Allylsilanes of the types of  $\text{R}(\text{CH}_2=\text{CHCH}_2)\text{-SiCl}_2$  and  $\text{R}_2(\text{CH}_2=\text{CHCH}_2)\text{SiCl}$  may also be useful for various organosilicon transformation (eq 1).

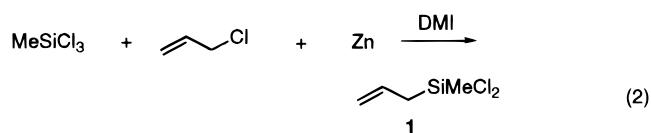


Herein we report the highly selective mono- and

diallylation of polychlorosilanes and polychlorodisilanes by an organozinc procedure.

## Results and Discussion

We have found that the reaction of methyltrichlorosilane with an equimolar amount of allyl chloride in the presence of zinc powder proceeds quite smoothly in dimethylimidazolidinone (DMI) to give allyl(methyl)dichlorosilane in high selectivity. Although the isolated yields depended on the reaction scale and the separation technique used, GLC examination of the reaction mixture showed that the reaction was virtually quantitative. No diallylated or triallylated compounds were detected (eq 2).



When 2 molar equiv of allyl chloride were used in the reaction, diallylated compounds were obtained exclusively. Correspondingly, allyl(methyl)dichlorosilane can be monoallylated selectively. Therefore, the allylation reaction proceeds in a stepwise manner quite selectively (eqs 3 and 4).

We have examined other solvents such as THF, dimethylformamide (DMF), hexamethylphosphoramide (HMPA), and acetonitrile for the Zn-mediated allylation reaction, but none of them gave satisfactory results. Only DMI gave good results among solvents we have examined. DMI was first used as an aprotic basic solvent in organometallic reactions by our hands in

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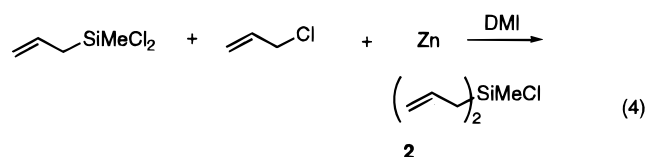
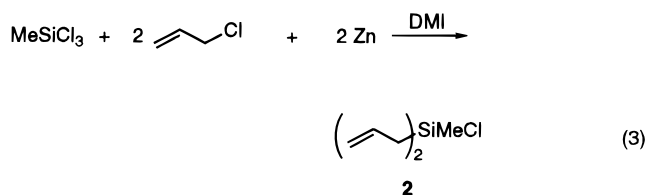
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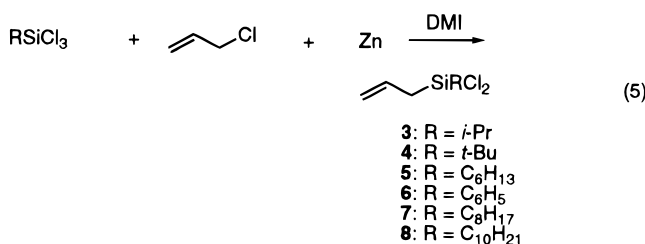
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1975.<sup>6</sup> Since then DMI has been used as an alternative for HMPA which has been disclosed to be carcinogenic. HMPA is more polar and usually better than DMI as a polar solvent, but in the present reaction, DMI was the preferred solvent.

Next, monoallylation of other alkyltrichlorosilanes,  $\text{RSiCl}_3$ , were examined. Alkyltrichlorosilanes, used in the allylation reaction, were prepared by hydrosilylation of 1-olefins with trichlorosilane. The Zn-mediated allylation reaction of the alkyltrichlorosilanes proceeds smoothly in a fashion similar to those described above (eq 5). Table 1 lists the representative results. Again,



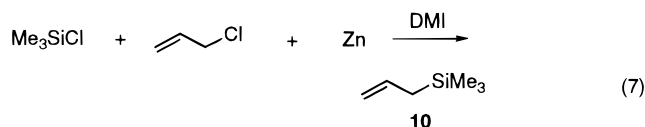
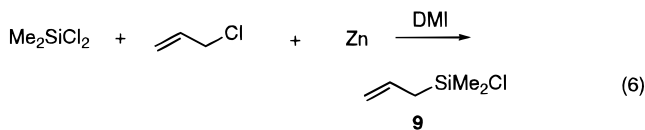
it is clear that very selective allylation took place.

For  $\text{RSiCl}_3$  with a long alkyl chain, such as decyltrichlorosilane and octyltrichlorosilane, monoallylated dichlorosilanes were obtained in high isolated yields. Isopropyltrichlorosilane gave the expected allyl(isopropyl)dichlorosilane in 71% yield, but *tert*-butyltrichlorosilane gave allyl(*tert*-butyl)dichlorosilane in only 26% yield. Apparently, steric bulkiness on the silicon center retards the reaction. In the allylation reactions of trichlorohexylsilane and trichlorophenylsilane, 2 equiv of DMI (to silanes) was used, since excess DMI was rather difficult to be separated from the product and hence the isolated yields were significantly decreased after purification. Use of less than 2 equiv of DMI (to zinc) also decreased the isolated yields. Apparently 2 equiv of DMI (to zinc) appeared to be essential for the reaction, although a small additional amount of DMI improves yields of the reaction to some extent.

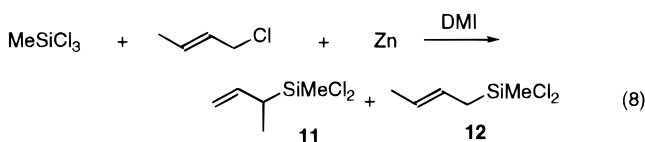
The Zn-mediated allylation reaction can be applied to dimethyldichlorosilane and trimethylchlorosilane as well. Monoallylation of dimethyldichlorosilane and trimethylchlorosilane gave allyldimethylchlorosilane and allyltrimethylsilane in 58 and 63% yield, respectively. The former reaction may be attractive to give the product highly selectively in moderate yield, since allyldimethylchlorosilane is useful for organosilicon transformation (eqs 6 and 7).

**Table 1. Monoallylation of  $\text{RSiCl}_3$**

run no.	product	R	molar ratio of DMI/ $\text{RSiCl}_3$	reaction time (h)	yield (%)
1	<b>1</b>	$\text{CH}_3$	excess	1	69
2	<b>3</b>	$(\text{CH}_3)_2\text{CH}$	excess	2	71
3	<b>4</b>	$(\text{CH}_3)_3\text{C}$	excess	4	26
4	<b>5</b>	$\text{C}_6\text{H}_{13}$	2	4	60
5	<b>6</b>	$\text{C}_6\text{H}_5$	2	4	58
6	<b>7</b>	$\text{C}_8\text{H}_{17}$	excess	4	68
7	<b>8</b>	$\text{C}_{10}\text{H}_{21}$	excess	4	74



The reaction of (*E*)-1-chloro-2-butene also proceeds smoothly to give the corresponding allylation products in 75% yield. Noteworthy is the fact that the product of the allylic rearrangement is obtained selectively. Thus, the reaction gave 1-methyl-2-propenyl(methyl)dichlorosilane (**11**) rather selectively, 3-methyl-2-propenyl(methyl)dichlorosilane (**12**) being detected only as a minor product. The ratio of **11/12** was 92/8. This is a marked contrast to the results of the Grignard reaction. The reaction of (*E*)-2-butenyl Grignard reagent with trimethylchlorosilane gave 1-methyl-2-propenyltrimethylsilane, (*E*)-2-butenyltrimethylsilane, and (*Z*)-2-butenyltrimethylsilane in a ratio of 48.4/30.1/21.5.<sup>7</sup> Therefore, the present reaction is not only selective but quite unique in the product distribution (eq 8).



The allylation reaction can also be applied to polychlorosilanes. Table 2 lists the results.

Allylation of 1-chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane gave the expected products, allylpentamethyldisilane (**13**) and 1-allyl-1,1,2,2-tetramethyl-2-chlorodisilane (**14**), in 69 and 67% yield, respectively. The reaction of 1,1-dichlorotetramethyldisilane afforded monoallylated product, 1-allyl-1,2,2,2-tetramethyl-1-chlorodisilane (**15**), selectively, but the yield was rather low (24%). The reaction of 1,1,2-trimethyl-1,2,2-trichlorodisilane provided a mixture of monoallylated products, 1-allyl-1,2,2-trimethyl-1,2-dichlorodisilane (**16**) and 1-allyl-1,1,2-trimethyl-2,2-dichlorodisilane (**17**). The reaction is, however, very selective to give a mixture of **16** and **17** in a ratio of 93/7.

Allylation of polychlorosilanes and polychlorodisilanes thus proceeds very selectively. The high selectivity originates from the large difference in the reactivities of chlorosilanes. The reactivity trend for the Zn-mediated allylation reaction is  $\text{RSiCl}_3 \gg \text{R}_2\text{SiCl}_2 \gg$

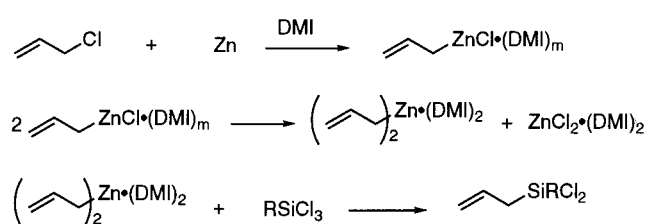
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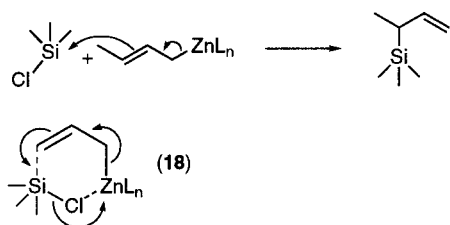
**Table 2. Allylation of Polychlorosilanes**

run no.	disilane	molar ratio of DMI/disilane	reaction time (h)	product <sup>a</sup>	yield (%)
1	ClSiMe <sub>2</sub> SiMe <sub>3</sub>	excess	2	All SiMe <sub>2</sub> SiMe <sub>3</sub>	69
2	Cl <sub>2</sub> SiMeSiMe <sub>3</sub>	2	2	All ClSiMeSiMe <sub>3</sub>	24
3	ClSiMe <sub>2</sub> SiMe <sub>2</sub> Cl	excess	2	All SiMe <sub>2</sub> SiMe <sub>2</sub> Cl	67
4	Cl <sub>2</sub> SiMeSiMe <sub>2</sub> Cl	2	2	All ClSiMeSiMe <sub>2</sub> Cl (93%) All SiMeSiMe <sub>2</sub> Cl <sub>2</sub> (7%)	22

<sup>a</sup> All = allyl (2-propenyl).

**Scheme 1**

Allylic rearrangement



R<sub>3</sub>SiCl. Due to the large difference in the reactivity between alkyltrichlorosilanes and dialkyldichlorosilanes, monoallylation proceeds highly selectively, when 1 molar equiv of the reagents is used.

It may be premature to discuss the detailed mechanism of the reaction but the evidence that the monoallylation reaction requires 2 mol of DMI and that almost complete allylic rearrangement is observed for the reaction of (*E*)-1-chloro-2-butene suggests the formation of a bulky reactive intermediate probably diallylzinc coordinated by 2 mol of DMI. The allylic rearrangement of the reagent may be slow, in contrast to the corresponding Grignard reagent which undergoes facile allylic rearrangement under the similar conditions. It is well established that the unsymmetric butenylmagnesium chloride consists mainly of the 2-butenyl isomer in mobile equilibrium with the very minor 1-methyl-2-propenyl isomer.<sup>8</sup>

The allylation reaction requires at least 2 equiv of DMI to the allyl chloride–Zn–methyltrichlorosilane system, since the use of a smaller amount of DMI than 2 equiv resulted in the sharp decrease in the yields. The exact number of coordination of DMI to zinc is not known, but the fact that after the reaction, when 2 mol of DMI was used (runs 4 and 5 in Table 1), no DMI was left suggests that 2 mol of DMI should coordinate to zinc. Because of the steric bulkiness around the zinc center, the normal S<sub>E</sub>2 type reaction with regiochemical retention may be very slow. Instead, the S<sub>E</sub>2' type reaction with allylic rearrangement becomes a major pathway to afford the observed products with allylic rearrangement. Probably a cyclic transition state (**18**)

may be involved in the reaction. Selective formation of 1-methyl-2-propenyl(methyl)dichlorosilane in the present case suggests rather slow equilibration reaction in the present butenyl-Zn reagent in contrast to the corresponding Grignard reagent. Thus Scheme 1 explains the reaction.

## Experimental Section

**General.** All reactions were run under an atmosphere of dry nitrogen. <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR were recorded at 300, 75.5, and 59.6 MHz in CDCl<sub>3</sub>, respectively. Chemical shifts are relative to internal CHCl<sub>3</sub>. Diethyl ether and THF were dried over and distilled from sodium. 1,3-Dimethyl-2-imidazolidinone (DMI) and hexane were dried over and distilled from calcium hydride. Methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, pentamethylchlorosilane, 1,1,2,2-tetramethyl-1,2-dichlorosilane, 1,2,2,2-tetramethyl-2,2-dichlorosilane, and 1,1,2-trimethyl-1,2,2-trichlorosilane were commercial products. Isopropyltrichlorosilane<sup>9</sup> and *tert*-butyltrichlorosilane<sup>10</sup> were prepared according to the literature. Hexyltrichlorosilane, octyltrichlorosilane, and decyltrichlorosilane were prepared by hydrosilylation of the corresponding 1-alkene as described in the literature.<sup>11</sup>

**Preparation of Allyl(methyl)dichlorosilane (1).**<sup>12</sup> A mixture of DMI (100 mL), 13.0 g (0.20 mol) of zinc powder, and 29.4 g (0.20 mol) of methyltrichlorosilane was placed in a 200-mL three-neck flask. The mixture was subjected to a nitrogen purge and heated to 70 °C. Then allyl chloride (15.0 g, 0.20 mol) was added to the mixture in a dropwise manner over a period of 5 min. After the addition, diethyl ether was added and precipitated salts were filtered. The mixture was then heated for another hour, and the product was distilled under reduced pressure to give **1** (21.4 g, 0.14 mol) in 69% yield.

**Preparation of Diallyl(methyl)chlorosilane (2).**<sup>13</sup> From zinc powder (5.40 g, 0.083 mol), allyl chloride (5.71 g, 0.075 mol), allyl(methyl)dichlorosilane (11.60 g, 0.075 mol), and DMI (40 mL), **2** was obtained (6.11 g, 51% yield).

**Preparation of Allyl(isopropyl)dichlorosilane (3).**<sup>5</sup> A similar procedure with zinc powder (4.09 g, 0.063 mol), isopropyltrichlorosilane (10.0 g, 0.056 mol), allyl chloride (4.20 g, 0.055 mol), and 25 mL of DMI in a 50-mL three-neck flask at 70 °C gave 7.11 g of **3** (71% yield).

**Preparation of Allyl(*t*-butyl)dichlorosilane (4).** A similar procedure with zinc powder (3.94 g, 0.060 mol), *tert*-butyltrichlorosilane (11.46 g, 0.060 mol), allyl chloride (4.74 g, 0.062 mol), and 30 mL of DMI in a 100-mL three-neck flask at 70 °C, gave 3.11 g of **4** (26% yield): colorless transparent liquid; bp 65–67 °C/16 mmHg; MS (70 eV) *m/z* (%) 198 (M<sup>+</sup> + 2, 2.9), 196 (M<sup>+</sup>, 4.4), 181 (4.5), 139 (4.9), 58 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub> δ) 1.08 (s, 9H), 2.08 (d, *J* = 7.8 Hz, 2H), 5.04–5.11 (m, 2H), 5.73–5.87 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub> δ) 23.1, 24.5, 25.1, 117.2, 130.1; <sup>29</sup>Si NMR (CDCl<sub>3</sub> δ) 31.8.

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**Preparation of Allyl(*n*-hexyl)dichlorosilane (5).**<sup>14</sup> A similar procedure with zinc powder (6.52 g, 0.10 mol), *n*-hexyltrichlorosilane (17.55 g, 0.080 mol), allyl chloride (6.56 g, 0.086 mol), and DMI (18.26 g, 0.16 mol) in a 50-mL three-neck flask at 70 °C, gave **5** (10.71 g, 60% yield).

**Preparation of Allyl(phenyl)dichlorosilane (6).**<sup>15</sup> From zinc powder (5.82 g, 0.089 mol), allyl chloride (6.14 g, 0.086 mol), phenyltrichlorosilane (17.00 g, 0.080 mol), and DMI (18.31 g, 0.16 mol), 10.14 g of **6** was obtained (58% yield).

**Preparation of Allyl(*n*-octyl)dichlorosilane (7).** From zinc powder (6.16 g, 0.094 mol), allyl chloride (6.01 g, 0.079 mol), octyltrichlorosilane (19.35 g, 0.078 mol), and DMI (40 mL), **7** was obtained (13.45 g, 68% yield): bp 60–65 °C/0.05 mmHg; colorless transparent liquid; MS (70 eV) *m/z* (%) 254 ( $M^+ + 2$ , 1.1), 252 ( $M^+$ , 1.7), 45 (100); 1.06–1.12 (m, 2H), <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.86 (t, *J* = 6.9 Hz, 3H), 1.06–1.12 (m, 2H), 1.25 (bs, 10H), 1.43–1.53 (m, 2H), 2.06 (d, *J* = 7.8 Hz, 2H), 5.02–5.10 (m, 2H), 5.69–5.83 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) 14.1, 19.5, 22.2, 22.6, 27.4, 29.0, 29.1, 32.8, 32.4, 117.4, 129.6; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ) 28.6.

**Preparation of Allyl(*n*-decyl)dichlorosilane (8).** From zinc powder (5.46 g, 0.083 mol), allyl chloride (5.38 g, 0.070 mol), *n*-decyltrichlorosilane (19.33 g, 0.070 mol), and DMI (35 mL), 14.55 g of **8** was obtained (74% yield): bp 79–84 °C/0.05 mmHg; colorless transparent liquid; MS (70 eV) *m/z* (%) 282 ( $M^+ + 2$ , 2.0), 280 ( $M^+$ , 3.0), 45 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.86 (t, *J* = 6.9 Hz, 3H), 1.06–1.12 (m, 2H), 1.25 (bs, 14H), 1.43–1.53 (m, 2H), 2.07 (d, *J* = 7.8 Hz, 2H), 5.03–5.09 (m, 2H), 5.69–5.83 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) 14.1, 19.5, 22.2, 22.7, 27.5, 29.1, 29.3, 29.4, 29.6, 31.9, 32.4, 117.4, 129.6; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ) 28.5.

**Preparation of Allyldimethylchlorosilane (9).**<sup>12</sup> Similarly from zinc powder (5.72 g, 0.087 mol), allyl chloride (6.16 g, 0.080 mol), dimethyldichlorosilane (10.36 g, 0.080 mol) and DMI (40 mL), 6.25 g of **9** was obtained (58% yield).

**Preparation of Allyltrimethylsilane (10).**<sup>16</sup> In a similar manner from zinc powder (13.75 g, 0.21 mol), allyl chloride (15.95 g, 0.21 mol), trimethylchlorosilane (21.76 g, 0.20 mol), and DMI (100 mL), 14.31 g of **10** was obtained in 63% yield.

**Preparation of 1-Methyl-2-propenyl(methyl)dichlorosilane (11).**<sup>17</sup> The similar reaction of zinc powder (5.79 g,

0.089 mol), (*E*)-crotyl chloride (7.26 g, 0.080 mol), and methylytrichlorosilane (11.98 g, 0.080 mol) in DMI (40 mL) gave 10.10 g (75%) of a 92/8 mixture of **11** and **12**.

**Preparation of Allylpentamethyldisilane (13).**<sup>18</sup> The reaction of zinc powder (15.21 g, 0.20 mol), allyl chloride (13.35 g, 0.20 mol), and pentamethylchlorodisilane (30.00 g, 0.18 mol) in DMI (100 mL) gave 21.48 g (69%) of **13**.

**Preparation of 1-Allyl-1,1,2,2-tetramethyl-2-chlorodisilane (14).** The reaction of zinc powder (2.01 g, 0.031 mol), allyl chloride (2.52 g, 0.033 mol), and tetramethyl-1,2-dichlorodisilane (5.87 g, 0.031 mol) in DMI (15 mL) gave 3.99 g (67%) of **14**: colorless transparent oil; bp 44–46 °C/7 mmHg; MS (70 eV) *m/z* (%): 194 ( $M^+ + 2$ , 0.8), 192 ( $M^+$ , 1.9), 177 (3.6), 151 (25.9), 99 (20.8), 73 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.13 (s, 6H), 0.46 (s, 6H), 1.66 (d, 8.2 Hz, 2H), 4.83–4.90 (m, 2H), 5.69–5.83 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) –4.7, 3.0, 22.2, 114.0, 126.3; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ) –17.1, 24.1.

**Preparation of 1-Allyl-1,2,2,2-tetramethyl-1-chlorodisilane (15).** The reaction of zinc powder (3.28 g, 0.050 mol), allyl chloride (3.59 g, 0.047 mol), and tetramethyl-1,1-dichlorodisilane (8.77 g, 0.047 mol) in DMI (11.42 g, 0.10 mol) gave 1.98 g (24%) of **15**: colorless transparent oil; bp 41–45 °C/7 mmHg; MS (70 eV) *m/z* (%): 194 ( $M^+ + 2$ , 0.6), 192 ( $M^+$ , 1.6), 177 (27.2), 157 (97.6), 151 (20.9), 84 (30.2), 73 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.15 (s, 9H), 0.43 (s, 3H), 1.89 (d, *J* = 8.0 Hz, 2H), 4.84–4.98 (m, 2H), 5.72–5.79 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) –2.6, –0.3, 25.8, 115.2, 132.4; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ) –17.1, 20.8.

**Preparation of 1-Allyl-1,2,2-trimethyl-1,2-dichlorodisilane (16).** The reaction of zinc powder (3.30 g, 0.050 mol), allyl chloride (3.83 g, 0.050 mol), and tetramethyl-1,1,2-trichlorodisilane (10.02 g, 0.048 mol) in DMI (11.41 g, 0.1 mol) gave 2.25 g (22%) of a 93:7 mixture of **16** and 1-allyl-1,1,2-trimethyl-2,2-dichlorodisilane (**17**): **16**: colorless transparent oil; bp 56–62 °C/7 mmHg; MS (70 eV) *m/z* (%): 214 ( $M^+ + 2$ , 5.1), 212 ( $M^+$ , 7.0), 197 (19.9), 177 (18.5), 171 (15.7), 119 (6.1), 93 (21.7), 73 (100); <sup>1</sup>H NMR (CDCl<sub>3</sub>, δ) 0.54 (s, 3H), 0.56 (s, 6H), 1.97 (td, 7.9 and 1.1 Hz, 2H), 4.92–5.04 (m, 2H), 5.72–5.83 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, δ) 1.8, 1.9, 24.7, 116.1, 131.3; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, δ) 14.9, 18.4.

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