



# Transformation of Aldehydes into (*E*)-1-Alkenylsilanes and (*E*)-1-Alkenylboronic Esters with a Catalytic Amount of a Chromium Salt

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(Diiodomethyl)trimethylsilane ( $\text{Me}_3\text{SiCHI}_2$ , **1**) is produced by treatment of iodoform with manganese in the presence of  $\text{Me}_3\text{SiCl}$ . Aldehydes are converted to (*E*)-1-trimethylsilyl-1-alkenes in a stereoselective manner with a geminal dichromium reagent generated from **1**, manganese,  $\text{Me}_3\text{SiCl}$ , and a catalytic amount of  $\text{CrCl}_3[\text{thf}]_3$  in THF. Similarly, (*E*)-1-alkenylboronic esters are prepared stereoselectively in good to excellent yields by treatment of aldehydes with a geminal dichromium reagent derived from  $\text{Cl}_2\text{CHB(OR)}_2$  [ $(\text{OR})_2 = \text{OCMe}_2\text{CMe}_2\text{O}$ ] and LiI instead of **1**.

Alkenylsilanes and -boronic esters are important synthetic intermediates for stereoselective carbon–carbon bond formation. The silanes and boronic esters having *E*-configuration are usually prepared by hydrosilylation and -boration of terminal alkynes, respectively.<sup>1,2</sup> We reported a preparative method for (*E*)-alkenylsilanes from aldehydes with a geminal dichromium reagent derived from  $\text{Me}_3\text{SiCHBr}_2$  and  $\text{CrCl}_2$  in 1987,<sup>3</sup> and a method for (*E*)-alkenylboronic esters with a reagent derived from a (dichloromethyl)boronic ester,  $\text{CrCl}_2$ , and LiI in 1995.<sup>4</sup> Although these methods provide functionalized olefins of *E*-configuration almost exclusively with one-carbon extension under mild conditions, the transformations use stoichiometric amounts of the one-electron reductant,  $\text{CrCl}_2$ . Following the report of the catalytic cycle of chromium(II) assembled by Fürstner,<sup>5</sup> we could reduce the amount of the chromium salt in the transformation of aldehydes to (*E*)-iodoalkenes using zinc as a reductant.<sup>6</sup> We disclose herein a procedure for the stereoselective preparation of (*E*)-alkenylsilanes and -boronic esters from aldehydes with geminal dichromium reagents<sup>7</sup> using a catalytic amount of the chromium salts.

## Results and Discussion

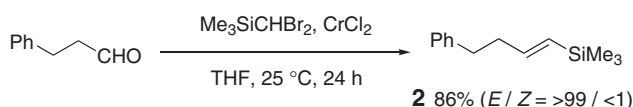
**Preparation of (*E*)-Alkenylsilanes.** Treatment of  $\text{Me}_3\text{SiCHBr}_2$  with chromium(II) chloride in THF generates a geminal dichromium reagent [ $\text{Me}_3\text{SiCH}(\text{CrX}_2)_2$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ ], which reacts with aldehydes to give (*E*)-alkenylsilanes under high stereocontrol (Scheme 1).<sup>3</sup> A typical feature of the transformation is that it can be performed under mild conditions, leaving the coexisting ketone, ester, and silyl ether groups unchanged. Thus, the method has been employed in several natural product syntheses.<sup>8</sup> However, the method still has two disadvantages: First, 6–8 equiv. of chromium(II) chloride are usually necessary to obtain reasonable yields. Second,

$\text{Me}_3\text{SiCHBr}_2$  should be prepared in advance by deprotonation and silylation from dibromomethane, which requires using a strong base at a carefully controlled low temperature.<sup>9</sup>

At first, we examined a chromium-catalyzed reaction using manganese for reduction of chromium(III) and  $\text{Me}_3\text{SiCl}$  for regeneration of chromium(II).<sup>5</sup> In contrast to the stoichiometric reaction (Table 1, entry 1), the yield of **2** decreased to 42%, and 3-phenylpropanal was recovered in only 19% yield (entry 3). Addition of LiI to the reaction mixture accelerated the transformation, and the reaction completed in 6 h to give **2** in 60% yield (entry 4). The result suggests that  $\text{Me}_3\text{SiCHI}_2$  (**1**), which could be produced in the mixture, is better suited for the catalytic reaction than  $\text{Me}_3\text{SiCHBr}_2$ . Therefore, we examined a preparative method with **1**. Treatment of 3-phenylpropanal with **1** (2 equiv.), manganese (6 equiv.),  $\text{Me}_3\text{SiCl}$  (6 equiv.), and chromium(II) chloride (0.16 equiv.) at 25 °C for 20 h afforded **2** in 87% yield (entry 5). Zinc also reduces chromium(III) to chromium(II) and can be used for a catalytic version of (*E*)-iodoalkene formation from aldehydes.<sup>6</sup> However, when zinc was used for the synthesis of **2**, the yield was somewhat lower than that obtained with manganese (entry 6). Because chromium(III) is reduced with manganese to give chromium(II), readily available chromium(III) chloride could be used for the reaction (entry 7). Handling a THF complex of chromium(III),  $\text{CrCl}_3[\text{thf}]_3$ , is easier than handling anhydrous chromium(III) chloride, especially in small-scale experiments, due to lower hygroscopicity (entry 8). In addition, slow addition of both the aldehyde and  $\text{Me}_3\text{SiCHI}_2$  to the mixture of manganese,  $\text{Me}_3\text{SiCl}$ , and a catalytic amount of  $\text{CrCl}_3[\text{thf}]_3$  in THF over 4 h improved the yield from 75% to 86% (entry 9). In contrast to the stoichiometric reactions (entries 1 and 2), the formation of a small amount of (*Z*)-alkenylsilane was observed in the catalytic reactions (entries 3–10).

The results with  $\text{Me}_3\text{SiCHI}_2$  and a catalytic amount of the chromium(III) salt are summarized in Table 2. *E*-Isomers were obtained selectively in all cases, probably due to the steric factor of the trimethylsilyl group. A ketone carbonyl remained unchanged after the reaction (Table 2, entry 5).

In 1970, Seyferth reported a procedure for  $\text{Me}_3\text{SiCHI}_2$  (**1**)



Scheme 1.

Table 1. Preparation of Trimethyl(4-phenyl-1-butenyl)silane<sup>a)</sup>

$$\text{Ph-CH}_2\text{-CH}_2\text{-CHO} \xrightarrow[\text{THF, 25 } ^\circ\text{C}]{\text{Me}_3\text{SiCHX}_2, \text{Cr(II)}} \text{Ph-CH}_2\text{-CH}_2\text{-CH=CH-SiMe}_3$$

**2**

| Entry | Me <sub>3</sub> SiCHX <sub>2</sub><br>X, equiv. | Cr salt<br>equiv.                          | Metal<br>equiv. | Me <sub>3</sub> SiCl<br>equiv. | LiI<br>equiv. | Time/h              | Yield/%          | E/Z    |
|-------|-------------------------------------------------|--------------------------------------------|-----------------|--------------------------------|---------------|---------------------|------------------|--------|
| 1     | Br, 2.0                                         | CrCl <sub>2</sub> , 8.0                    |                 |                                |               | 24                  | 86               | >99/<1 |
| 2     | I, 2.0                                          | CrCl <sub>2</sub> , 8.0                    |                 |                                |               | 4                   | 90               | >99/<1 |
| 3     | Br, 2.0                                         | CrCl <sub>2</sub> , 0.2                    | Mn, 6.0         | 6.0                            |               | 24                  | 42 <sup>c)</sup> | 95/5   |
| 4     | Br, 2.0                                         | CrCl <sub>2</sub> , 0.2                    | Mn, 6.0         | 6.0                            | 4.0           | 6                   | 60               | 97/3   |
| 5     | I, 2.0                                          | CrCl <sub>2</sub> , 0.2                    | Mn, 6.0         | 6.0                            |               | 20                  | 87               | 95/5   |
| 6     | I, 2.0                                          | CrCl <sub>2</sub> , 0.2                    | Zn, 6.0         | 6.0                            |               | 20                  | 59               | 95/5   |
| 7     | I, 2.0                                          | CrCl <sub>3</sub> , 0.2                    | Mn, 6.0         | 6.0                            |               | 20                  | 72               | 93/7   |
| 8     | I, 2.0                                          | CrCl <sub>3</sub> [thf] <sub>3</sub> , 0.2 | Mn, 6.0         | 6.0                            |               | 20                  | 75               | 94/6   |
| 9     | I, 2.0                                          | CrCl <sub>3</sub> [thf] <sub>3</sub> , 0.2 | Mn, 6.0         | 6.0                            |               | 6 (4) <sup>b)</sup> | 86               | 94/6   |

a) Reactions were conducted on a 2.0 mmol scale. Isolated yields. b) Time for adding a solution of 3-phenylpropanal and Me<sub>3</sub>SiCHI<sub>2</sub> in THF is shown in parenthesis. c) 3-Phenylpropanal was recovered in 19% yield.

Table 2. Transformation of Aldehydes into (*E*)-1-Alkenylsilanes<sup>a)</sup>

$$\text{RCHO} \xrightarrow[\text{THF, 25 } ^\circ\text{C, 6 h (slow addition, 4 h)}]{\text{Me}_3\text{SiCHI}_2, \text{Mn cat. CrCl}_3[\text{thf}]_3, \text{Me}_3\text{SiCl}} \text{R-CH=CH-SiMe}_3$$

| Entry | R                                   | Yield/% <sup>b)</sup> | E/Z  |
|-------|-------------------------------------|-----------------------|------|
| 1     | Ph(CH <sub>2</sub> ) <sub>2</sub>   | 86                    | 94/6 |
| 2     |                                     | 87 <sup>c)</sup>      | 95/5 |
| 3     | c-C <sub>6</sub> H <sub>11</sub>    | 77                    | 94/6 |
| 4     | Ph                                  | 88 <sup>d)</sup>      | 91/9 |
| 5     | MeCO(CH <sub>2</sub> ) <sub>8</sub> | 82 <sup>e)</sup>      | 95/5 |

a) Reactions were conducted on a 2.0 mmol scale. Me<sub>3</sub>SiCHI<sub>2</sub> (3.0 mol), Mn (9.0 mol), Me<sub>3</sub>SiCl (9.0 mol), and CrCl<sub>3</sub>[thf]<sub>3</sub> (0.20 mol) were used per mol of aldehyde. See the typical procedure in the experimental section. b) Isolated yields. (*E*)-Alkenylsilanes were produced exclusively. c) CrCl<sub>2</sub> was used instead of CrCl<sub>3</sub>[thf]<sub>3</sub>. A mixture of 3-phenylpropanal and iodoform in THF was added in one portion. d) GLPC yield. e) Trimethyl[(*E*)-11-methyl-1,11-dodecadienyl]silane was produced in 14% yield.

using iodine–magnesium exchange of iodoform with isopropylmagnesium chloride followed by silylation.<sup>9a</sup> Another method reported by Charreau in 1990 contained deprotonation of diiodomethane with NaN(SiMe<sub>3</sub>)<sub>2</sub>.<sup>9b</sup> Both procedures require carefully controlled temperatures below –85 °C to deal with the unstable carbenoid I<sub>2</sub>CHMtl (Mtl = MgX or Na); otherwise, 1,2-bis(trimethylsilyl)ethene (**3**) is produced smoothly. We have recently found a new preparative method for Me<sub>3</sub>SiCHI<sub>2</sub> which is conducted at ambient temperature.<sup>10</sup>

When iodoform was treated with manganese in THF in the presence of an excess amount of Me<sub>3</sub>SiCl, the desired Me<sub>3</sub>SiCHI<sub>2</sub> was produced in 21% yield (Table 3, entry 1). The formation of Me<sub>3</sub>SiCHI<sub>2</sub> suggests that selective reduction of one iodine atom of the iodoform and successive silylation occur. Such selective reduction of iodoform leading to I<sub>2</sub>CHMtl was also observed with SmI<sub>2</sub>;<sup>11</sup> however, this reduction shows a sharp contrast to the reduction with CrCl<sub>2</sub> where two of the

iodine atoms are reduced to give a geminal dichromium reagent (ICH(CrX<sub>2</sub>)<sub>2</sub>, X = I or Cl).<sup>7b</sup> The yield of **1** improved to 47% when DME was used as a solvent, and diiodomethane was obtained in 7% yield (entry 2). Although the amount of **1** increased to 52% yield when a catalytic amount of sodium iodide was added and DMF was used as a co-solvent (DME–DMF, 4:1), further reduction of **1** and silylation occurred to give (Me<sub>3</sub>Si)<sub>2</sub>CHI (**4**) in 6% yield (entry 4). Because it is difficult to remove **4** from **1** by distillation, we choose to use the reaction in only DME for large scale preparation. It is worth noting that the manganese-mediated process (entry 2) is exothermic, and it is important to keep the reaction mixture below 25 °C by using a water bath. The dimer **3** was produced as the main product when the reaction temperature was allowed to increase to 50 °C (entry 3).

**Preparation of (*E*)-Alkenylboronic Esters.** (*E*)-1-Alkenylboronic esters were prepared stereoselectively from aldehydes with one-carbon extension with a geminal dichromium reagent derived from a (dichloromethyl)boronic ester **6**,<sup>12</sup> chromium(II) chloride, and LiI under mild conditions (Scheme 2).<sup>4,13</sup> Addition of LiI was indispensable to promote the reaction; the aldehyde was recovered in 82% yield without addition of LiI (Table 4, entries 1 and 2). Treatment of **6** with LiI generated I<sub>2</sub>CHB(OCMe<sub>2</sub>)<sub>2</sub> (**8**), which is easily reduced with CrCl<sub>2</sub> to give the corresponding geminal dichromium reagent.

In order to generate chromium(II), we examined several metal reductants. Both zinc and manganese were found to be effective for assembling a catalytic cycle of the geminal dichromium reagent. For example, treatment of 3-phenylpropanal with **6** (2 equiv.), LiI (4 equiv.), manganese (6 equiv.), Me<sub>3</sub>SiCl (6 equiv.), and chromium(II) chloride (0.2 equiv.) in THF at 25 °C for 20 h gave the boronic ester **7** in 90% yield (*E*/*Z* = 95/5) (entry 3). The yield of **7** decreased to 71% (*E*/*Z* = 90/10) with zinc (6 equiv.) instead of manganese, although the yield slightly increased to 80% (*E*/*Z* = 89/11) when the amount of chromium(II) chloride was increased to 0.3 equivalent (entry 4). The less-hygroscopic chromium(III) salt CrCl<sub>3</sub>[thf]<sub>3</sub> could also be employed for the alkenylboronic

Table 3. Preparation of (Diiodomethyl)trimethylsilane<sup>a)</sup>

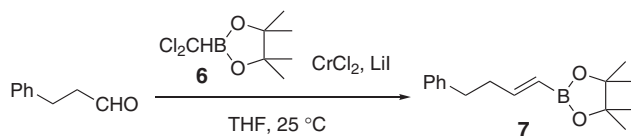
| $\text{CHI}_3 \xrightarrow[1\text{ h}]{\text{Mn, Me}_3\text{SiCl}} \text{Me}_3\text{SiCHI}_2 + \text{CH}_2\text{I}_2 + (\text{Me}_3\text{Si})_2\text{CHI}$ $+ \text{Me}_3\text{SiCH}_2\text{I} + \text{Me}_3\text{Si}-\text{CH}=\text{CH}-\text{SiMe}_3$ <div style="text-align: center;"> <span style="margin-right: 100px;"><b>1</b></span> <span><b>4</b></span> </div> <div style="text-align: center;"> <span style="margin-right: 100px;"><b>5</b></span> <span><b>3</b></span> </div> |                                 |                          |          |                                |          |          |          |                            |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------|--------------------------|----------|--------------------------------|----------|----------|----------|----------------------------|
| Entry                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | Solvent                         | Temp/°C                  | Yield/%  |                                |          |          |          | Recov.<br>CHI <sub>3</sub> |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              |                                 |                          | <b>1</b> | CH <sub>2</sub> I <sub>2</sub> | <b>4</b> | <b>5</b> | <b>3</b> |                            |
| 1                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | THF                             | 25                       | 21       | 3                              | 0        | 0        | 3        | 0                          |
| 2                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | DME                             | 25                       | 47       | 7                              | 0        | 0        | 0        | 3                          |
| 3                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | DME                             | 25 to 50<br>(exothermic) | 0        | 0                              | 0        | 0        | 34       | 0                          |
| 4                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | DME, DMF <sup>b)</sup><br>(4:1) | 25                       | 52       | 0                              | 6        | 3        | 0        | 0                          |

a) Reactions were conducted on a 20 mmol scale. Mn (3.0 mol) and Me<sub>3</sub>SiCl (3.0 mol) were used per mol of iodoform. b) NaI (0.3 mol) was added per mol of iodoform.

Table 4. Preparation of Pinacol 4-Phenyl-1-butenylboronate<sup>a)</sup>

| $\text{Ph-CH}_2\text{CH}_2\text{CHO} \xrightarrow[\text{THF, 25 } ^\circ\text{C}]{\text{Cl}_2\text{CHB}(\text{pin})_2, \text{Cr(II)}} \text{Ph-CH}_2\text{CH}_2\text{CH=CH-B}(\text{pin})_2$ <div style="text-align: center;"><b>7</b></div> |                                             |                 |                                |               |        |                 |       |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------|-----------------|--------------------------------|---------------|--------|-----------------|-------|
| Entry                                                                                                                                                                                                                                        | Cr salt<br>equiv.                           | Metal<br>equiv. | Me <sub>3</sub> SiCl<br>equiv. | LiI<br>equiv. | Time/h | Yield/%         | E/Z   |
| 1                                                                                                                                                                                                                                            | CrCl <sub>2</sub> , 8.0                     | —               | —                              | —             | 16     | 0 <sup>b)</sup> | —     |
| 2                                                                                                                                                                                                                                            | CrCl <sub>2</sub> , 8.0                     | —               | —                              | 4.0           | 16     | 91              | 98/2  |
| 3                                                                                                                                                                                                                                            | CrCl <sub>2</sub> , 0.20                    | Mn, 6.0         | 6.0                            | 4.0           | 20     | 90              | 95/5  |
| 4                                                                                                                                                                                                                                            | CrCl <sub>2</sub> , 0.30                    | Zn, 6.0         | 6.0                            | 4.0           | 20     | 80              | 89/11 |
| 5                                                                                                                                                                                                                                            | CrCl <sub>3</sub> [thf] <sub>3</sub> , 0.20 | Mn, 6.0         | 6.0                            | 4.0           | 20     | 84              | 96/4  |
| 6                                                                                                                                                                                                                                            | CrCl <sub>3</sub> [thf] <sub>3</sub> , 0.30 | Zn, 6.0         | 6.0                            | 4.0           | 20     | 77              | 90/10 |

a) Reactions were conducted on a 1.0 mmol scale. Isolated yields. b) 3-Phenylpropanal was recovered in 82% yield.



Scheme 2.

ester formation (entries 5 and 6).

Several examples of the transformation of aldehydes to the corresponding 1-alkenylboronic esters are summarized in Table 5. Reactions with manganese gave better yields and more reproducible isomeric ratios than those with zinc. Aldehyde-selective transformation of the keto aldehyde **9** was achieved (Table 5, entry 5). Under the standard reaction conditions (Table 5, entry 1, Mn), the following compounds were recovered: 1-dodecene (94%); 1-dodecyne (93%); 1-chlorododecane (95%); ethyl octanoate (95%); nonanenitrile (92%); nonanal ethylene acetal (93%).

A plausible mechanism of the alkenylsilane and boronic ester formation with manganese, Me<sub>3</sub>SiCl, and a catalytic amount

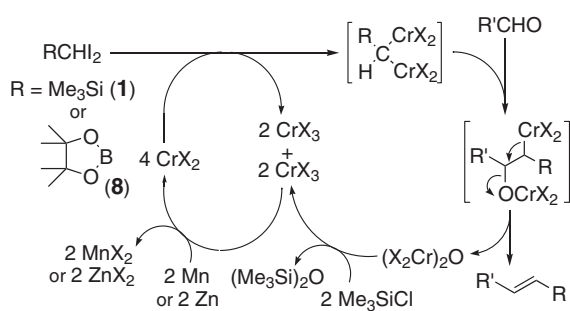
of chromium(III) salt is shown in Scheme 3. The reduction of RCHX<sub>2</sub> with 4 equiv. of chromium(II) gives a geminal dichromium reagent, which reacts with an aldehyde followed by elimination of (X<sub>2</sub>Cr)<sub>2</sub>O to afford the functionalized alkene. The produced (X<sub>2</sub>Cr)<sub>2</sub>O is converted to a chromium(III) halide with an excess amount of Me<sub>3</sub>SiCl, and the chromium(III) is then reduced with manganese to reproduce chromium(II).<sup>5</sup> Two equivalents of both manganese and Me<sub>3</sub>SiCl are necessary for this transformation. A catalytic cycle is realized, because the reduction rates of both **1** and **8** with manganese are considerably slower than that with chromium(II).

High *E*-selectivity in the formation of alkenylsilanes and -boronic esters with the *gem*-dichromium species is explained by the mechanism depicted in Scheme 4. Addition of the *gem*-dichromium species (RCH(CrL<sub>n</sub>)<sub>2</sub>) to an aldehyde (R'CHO) proceeds via a six-membered pseudo-chair transition state **10** containing two chromium ions bridged by a halogen. Both substituents R and R' possess stable equatorial positions in the transition state. *syn*-Elimination of (L<sub>n</sub>Cr)<sub>2</sub>O from the adduct **11** takes place smoothly, before rotation at the formed single bond, to give *E*-olefins. In the catalytic reactions, the coex-

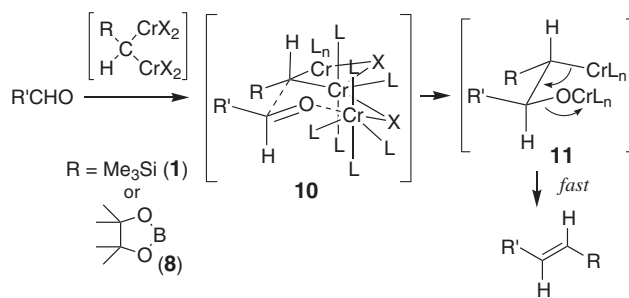
Table 5. Transformation of Aldehydes to (*E*)-1-Alkenylboronic Esters<sup>a)</sup>

| Entry | R                                                | Mn <sup>b)</sup>      |                          | Zn <sup>c)</sup>      |                          |
|-------|--------------------------------------------------|-----------------------|--------------------------|-----------------------|--------------------------|
|       |                                                  | Yield/% <sup>d)</sup> | <i>E/Z</i> <sup>e)</sup> | Yield/% <sup>d)</sup> | <i>E/Z</i> <sup>e)</sup> |
| 1     | Ph(CH <sub>2</sub> ) <sub>2</sub>                | 84                    | 96/4                     | 77                    | 90/10                    |
| 2     | <i>c</i> -C <sub>6</sub> H <sub>11</sub>         | 92                    | 97/3                     | 90                    | 94/6                     |
| 3     | <i>t</i> -Bu                                     | 93                    | 96/4                     | 88                    | 98/2                     |
| 4     | Ph                                               | 88                    | 96/4                     | 67                    | 92/8                     |
| 5     | MeCO(CH <sub>2</sub> ) <sub>8</sub> ( <b>9</b> ) | 80                    | 97/3                     | 52 <sup>f)</sup>      | 87/13                    |

a) Reactions were conducted on a 1.0 mmol scale. b) Dichloromethylboronic ester (**6**, 2 mol), LiI (4 mol), manganese (6 mol), Me<sub>3</sub>SiCl (6 mol), and CrCl<sub>3</sub>[thf]<sub>3</sub> (0.2 mol) were employed per mole of an aldehyde. See the typical procedure in the experimental section. c) The ester **6** (2 mol), LiI (4 mol), zinc (6 mol), Me<sub>3</sub>SiCl (6 mol), and CrCl<sub>3</sub>[thf]<sub>3</sub> (0.3 mol) were employed per mole of an aldehyde. d) Isolated yields. e) The *E/Z* ratios of disubstituted olefins were determined by GLPC and/or <sup>1</sup>H NMR analysis. f) The keto aldehyde **9** was recovered in 13% yield.



Scheme 3.



Scheme 4.

istent manganese (or zinc) ion generated in the reaction mixture could partially replace the chromium ion in the transition state **10**, which could cause the formation of a small amount of *Z*-olefins.<sup>7a,14</sup>

In conclusion, the amount of the chromium(II) salts needed for the selective transformations of aldehydes to (*E*)-alkenylsilanes and -alkenylboronic esters can be reduced by using a combination of manganese and Me<sub>3</sub>SiCl. Zinc can also be used as a reductant in the formation of (*E*)-alkenylboronic esters from aldehydes.

### Experimental

**General.** Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Chromium(II) chloride (99.99% purity) was purchased from Aldrich Chemical Co. The salt should be handled under an inert atmosphere. CrCl<sub>3</sub>[thf]<sub>3</sub> (97% purity) was purchased from Aldrich Chemical Co. and used without further purification. Lithium iodide was dried at 120 °C (2 Torr) for 1 day. Manganese powder was purchased from either Rare Metallic Co. (99% purity, −80 mesh) or Kojundo Chemical Laboratory (99.9% purity, −50 mesh) and was used without further activation. Zinc dust (GR grade) was purchased from E. Merck Co. (>95%), and was activated by washing several times with 5% hydrochloric acid, washing in turn with water, methanol, and ether, and drying in vacuo according to Fieser

and Fieser.<sup>15</sup> Dry, oxygen-free tetrahydrofuran (THF) and dimethoxyethane (DME) were purchased from Kanto Chemicals, Co. Dry, oxygen-free *N,N*-dimethylformamide (DMF) was purchased from Wako Pure Chemicals Co. Chlorotrimethylsilane was freshly distilled, bp 57–58 °C. Distillations of small amounts of products were performed with a Büchi Kugelrohr, and boiling points are indicated as an air bath temperature without correction. FT-IR spectra were obtained on a Bio-Rad FTS-7 or a Nicolet Protégé 460 spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined with a Varian Gemini-200 or a JEOL JNM-LA400 instrument. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane using the  $\delta$  scale. Low and high resolution of EI mass spectra were obtained with a capillary GC interfaced JEOL JMS-SX102A. Column chromatography was performed on silica gel 60 (200–400 mesh) of Merck KGaA.

**Preparation of (Diiodomethyl)trimethylsilane in Large Scale:** A dry, 500-mL three-necked, round-bottomed flask was equipped with a magnetic stirring bar, nitrogen inlet, rubber septum, and a 100-mL, graduated, pressure-equalizing addition funnel that was sealed with a rubber septum. The flask was charged with manganese powder (20 g, 0.36 mol) and dry DME (35 mL). Chlorotrimethylsilane (46 mL, 0.36 mol) was added to the suspension using a syringe at 25 °C, and the mixture was stirred at 25 °C for 30 min. The addition funnel was charged with a solution of iodoform (47 g, 0.12 mmol) in DME (120 mL), which was then added dropwise at 25 °C (water bath) to the stirring solution over a pe-

riod of 2.5 h. The addition funnel was rinsed with dry DME (5 mL). The resulting dark brown mixture was stirred at 25 °C for an additional 30 min. The magnetic stirring bar was washed with hexane (20 mL), and the whole mixture was poured into ice-cooled water (100 mL). The quenching was a slightly exothermic process. The whole mixture was passed through a short layer of Celite® on a 200-mL suction filter, using hexane (100 mL) as an eluent. The yellow organic layer that separated was washed with a sodium thiosulfate (3 × 30 mL) and sodium chloride solution (3 × 30 mL), and then dried over anhydrous MgSO<sub>4</sub>. The solvent was removed with a rotary evaporator. The crude product was distilled to give 16.7–17.3 g (41–42%) of (diiodomethyl)trimethylsilane (**1**), bp 63 °C at 1.3 Torr reduced pressure. IR (neat): 2953, 2895, 1260, 1250, 1061, 840, 758, 709, 696 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.25 (s, 9H), 4.44 (s, 1H).

**A Typical Procedure for an Alkenylsilane Using a Catalytic Amount of CrCl<sub>3</sub>[thf]<sub>3</sub> [Trimethyl[(*E*)-4-phenyl-1-butenyl]silane (**2**)]:** Under an argon atmosphere, Me<sub>3</sub>SiCl (1.5 mL, 12 mmol) was added at 25 °C to a suspension of CrCl<sub>3</sub>[thf]<sub>3</sub> (0.15 g, 0.40 mmol), and manganese (0.66 g, 12 mmol) in THF (20 mL). After the mixture was stirred at 25 °C for 30 min, a solution of 3-phenylpropanal (0.27 g, 2.0 mmol) and Me<sub>3</sub>SiCH<sub>2</sub> (**1**, 1.4 g, 4.0 mmol) in THF (10 mL) was added at 25 °C to the mixture over a period of 4 h. The color of the mixture gradually turned from gray to pale brown during the addition. The reaction mixture was poured into water (50 mL) and the organic layer was extracted with hexane (3 × 30 mL). The organic extracts were washed with brine, dried over anhydrous MgSO<sub>4</sub> and concentrated. Purification by column chromatography on silica gel (hexane) gave trimethyl(4-phenyl-1-butenyl)silane (**2**) in 86% yield (0.35 g, *E/Z* = 94/6) as a colorless oil. bp 92–94 °C (bath temp, 1.0 Torr); IR (neat): 3086, 3064, 3027, 2954, 2898, 2856, 1616, 1497, 1454, 1247, 989, 866, 838, 729, 698 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.04 (s, 9H), 2.42 (q, *J* = 7.2 Hz, 2H), 2.71 (t, *J* = 7.2 Hz, 2H), 5.67 (dd, *J* = 18.6, 1.5 Hz, 1H), 6.08 (dt, *J* = 18.6, 6.0 Hz, 1H), 7.17–7.33 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.2, 35.2, 38.5, 125.7, 128.2, 128.3, 130.4, 142.0, 146.1. Anal. Calcd for C<sub>13</sub>H<sub>20</sub>Si: C, 76.40; H, 9.86%. Found: C, 76.67; H, 9.81%.

**[(*E*)-2-Cyclohexylethenyl]trimethylsilane:**<sup>16</sup> bp 71–74 °C (bath temp, 4 Torr); IR (neat): 2952, 2922, 2848, 1614, 1449, 1247, 988, 863, 836 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.00 (s, 9H), 0.86–2.00 (m, 11H), 5.55 (dd, *J* = 18.8, 1.5 Hz, 1H), 5.96 (dd, *J* = 18.8, 6.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.1, 26.1, 26.2, 32.4, 43.8, 126.1, 152.8. HRMS (EI<sup>+</sup>) Calcd for C<sub>11</sub>H<sub>22</sub>Si: M<sup>+</sup> 182.1492. Found: *m/z* 182.1472.

**Trimethyl[(*E*)-2-phenylethenyl]silane:**<sup>16,17</sup> bp 64–67 °C (bath temp, 0.7 Torr); IR (neat): 2955, 1606, 1574, 1494, 1447, 1247, 988, 867, 843 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.15 (s, 9H), 6.48 (d, *J* = 19.2 Hz, 1H), 6.87 (d, *J* = 19.2 Hz, 1H), 7.23–7.45 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.2, 126.3, 127.9, 128.5, 129.5, 138.3, 143.5.

**Trimethyl[(*E*)-11-oxo-1-dodecenyl]silane:** bp 105 °C (bath temp, 1.5 Torr); IR (neat): 3444, 3062, 3026, 2932, 2869, 2835, 1600, 1494, 1453, 1187, 1024, 903, 721, 704, 640 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.03 (s, 9H), 1.27 (s, 10H), 1.56–1.60 (m, 2H), 2.05–2.10 (m, 2H), 2.13 (s, 3H), 2.41 (t, *J* = 7.5 Hz, 2H), 5.60 (d, *J* = 18.6 Hz, 1H), 6.01 (dt, *J* = 18.6, 6.0 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.2, 18.8, 23.7, 25.1, 29.7, 40.4, 65.8, 80.8, 127.2, 127.4, 127.9, 129.4, 133.7, 140.6. Anal. Calcd for C<sub>15</sub>H<sub>30</sub>OSi: C, 70.79; H, 11.88%. Found: C, 70.52; H, 12.09%.

**A Typical Procedure for an Alkenylboronic Ester Using a Catalytic Amount of CrCl<sub>3</sub>[thf]<sub>3</sub> [Pinacol (*E*)-4-Phenyl-1-bu-**

**tenylboronate (**7**)]:** Under an argon atmosphere, Me<sub>3</sub>SiCl (0.76 mL, 6.0 mmol) was added at 25 °C to a suspension of CrCl<sub>3</sub>[thf]<sub>3</sub> (75 mg, 0.20 mmol), manganese (0.33 g, 6.0 mmol), and LiI (0.54 g, 4.0 mmol) in THF (7 mL). After the mixture was stirred at 25 °C for 30 min, a solution of 3-phenylpropanal (0.13 g, 1.0 mmol) and (dichloromethyl)boronic ester **6** (0.42 g, 2.0 mmol) in THF (3 mL) was added at 25 °C to the mixture over a period of 4 h. The color of the mixture gradually turned from dark green to dark brown during the addition. After being stirred for an additional 2 h, the reaction mixture was filtered through a short pad of Celite®. The filtrate was poured into water (25 mL) and extracted with ether (3 × 10 mL). The combined extracts were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purification by column chromatography on silica gel (hexane) afforded 0.22 g (84%, *E/Z* = 96/4) of pinacol (*E*)-4-phenyl-1-butenylboronate **7** as a colorless oil. bp 115 °C (bath temp, 0.9 Torr); IR (neat): 3027, 2978, 2930, 1454, 1398, 1390, 1378, 1363, 1321, 1270, 1216, 1165, 1146, 973, 850 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.27 (s, 12H), 2.45–2.50 (m, 2H), 2.72–2.76 (t, *J* = 7.9 Hz, 2H), 5.50 (dt, *J* = 18.0, 1.5 Hz, 1H), 6.70 (dt, *J* = 18.0, 6.3 Hz, 1H), 7.16–7.33 (m, 5H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.7, 34.5, 37.4, 83.0, 125.8, 128.3, 141.7, 153.3. Anal. Calcd for C<sub>16</sub>H<sub>23</sub>BO<sub>2</sub>: C, 74.44; H, 8.98%. Found: C, 74.28; H, 8.94%.

**Pinacol (*E*)-2-Cyclohexylethenylboronate:**<sup>18</sup> bp 90 °C (bath temp, 1.7 Torr); IR (neat): 2978, 2926, 2852, 1636, 1397, 1389, 1371, 1349, 1321, 1147, 998, 971 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.04–1.19 (m, 4H), 1.27 (s, 12H), 1.62–1.67 (m, 2H), 1.70–1.78 (m, 4H), 1.90–2.12 (m, 1H), 5.35 (dd, *J* = 18.1, 1.2 Hz, 1H), 6.57 (dd, *J* = 18.1, 6.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.7, 25.9, 26.1, 31.8, 43.2, 82.9, 159.7.

**Pinacol (*E*)-2-Phenylethenylboronate:**<sup>19</sup> IR (neat): 3026, 2978, 2930, 1625, 1577, 1495, 1450, 1387, 1353, 1325, 1272, 1211, 1145, 998, 970, 852 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.32 (s, 12H), 6.17 (d, *J* = 18.3 Hz, 1H), 7.26–7.50 (m, 6H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.7, 83.2, 127.0, 128.5, 128.8, 137.3, 149.4.

**Pinacol (*E*)-3,3-Dimethyl-1-butenylboronate:**<sup>20</sup> bp 75 °C (bath temp, 2.0 Torr); IR (neat): 2978, 2962, 2932, 1634, 1396, 1387, 1379, 1365, 1348, 1321, 1265, 1165, 1147, 1001, 971, 851 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.04 (s, 9H), 1.27 (s, 12H), 5.35 (d, *J* = 18.3 Hz, 1H), 6.64 (d, *J* = 18.3 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.7, 28.7, 34.9, 82.9, 164.3.

**Pinacol (*E*)-11-Oxo-1-dodecenylboronate:** bp 110 °C (bath temp, 2.5 Torr); IR (neat): 2978, 2928, 2855, 1718, 1638, 1421, 1398, 1390, 1363, 1320, 1165, 1146, 971, 850 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.19–1.40 (m, 22H), 1.53–1.61 (m, 2H), 2.11–2.16 (m, 2H), 2.16 (s, 3H), 2.41 (t, *J* = 7.5 Hz, 2H), 5.42 (d, *J* = 18.0 Hz, 1H), 6.62 (dt, *J* = 18.0, 6.6 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 23.8, 24.7, 25.6, 28.1, 29.1, 29.2, 29.8, 35.7, 43.7, 67.9, 82.9, 154.7, 209.3. Anal. Calcd for C<sub>18</sub>H<sub>33</sub>BO<sub>3</sub>: C, 70.13; H, 10.79%. Found: C, 69.85; H, 10.65%.

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