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# Reactions of silanes with allylic alcohols catalyzed by titanocene derivatives: an approach to catalytic cross dehydrocoupling/co-intramolecular hydrosilation ☆

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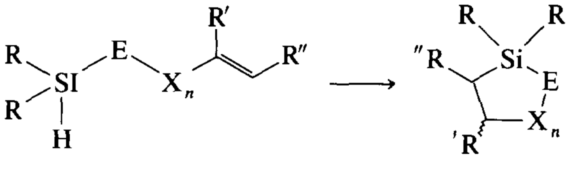
## Abstract

A preliminary study of the dimethyltitanocene, **7**, and *rac*-[ethylene-1,2-bis($\eta^5$-4,5,6,7-tetrahydroindenyl)]Ti$Me_2$, **8**, catalyzed reactions of silanes with allylic and homoallylic alcohols is described. In the presence of catalysts **7** or **8**, tertiary silanes bearing at least one phenyl group react with 2-methyl-but-1-ene-4-ol, **2a**, to produce the 4-siloxy-2-methylbut-1-ene, **3a**. Secondary silanes react with either **2a**, or 2-methylpropen-3-ol, **2b**, to give different product distributions depending on the catalyst type, concentration, and the substituents on the silicon atom. With high catalyst concentration and diphenylsilane, a redistribution reaction substantially converts the initially produced allyloxydiphenylsilane to bis(allyloxy)diphenylsilane. Low catalyst concentrations give primarily the intramolecular hydrosilation product. Under the same reaction conditions, phenylmethylsilane gives more intramolecular hydrosilation product than diphenylsilane does. Phenylsilane reacts with **2b**, to give a polymeric product, **6b** (R = Ph, R′ = H), via intermolecular hydrosilation. Under the same conditions phenylsilane reacts with **2a** to give primarily the hydrogenation product tris(3-methylbutoxy)phenylsilane, **5a** (R = Ph, R′ = $-OCH_2CH_2CH(CH_3)_2$), together with traces of oligosilane and intermolecular hydrosilation product **6a**. Some possible reaction pathways, including the observed side reactions, are discussed.

*Keywords:* Titanium; Silicon; Hydrosilation; Allylic; Titanocene; Alcohols

## 1. Introduction

Intramolecular hydrosilation involves the addition of a silicon–hydrogen bond to an unsaturated functional group in the same molecule to produce a cyclic product (Eq. (1)). These reactions are catalyzed in a number of ways, most notably by low-valent later transition metal complexes [1].



(1)

E = O, NH, $CH_2$
X = $CH_2$, $n$ = 1,2

$n$ = 1, **1a**
$n$ = 2, **1b**

The cyclic products, **1**, of reaction (1) can be readily converted to useful organic products via oxidative cleavage of the Si–C bond under appropriate conditions [2]. Thus, intramolecular hydrosilation is an efficient route to the synthesis of diols [3], aminoalcohols [4], lactones [5], etc. Asymmetric catalytic intramolecular hydrosilation also provides an efficient approach to the production of enantio-enriched (ee) organic molecules [6], and in some cases very high ees have been observed [7]. Although the synthesis of a substrate is relatively simple [8], it can require several synthetic steps. For example, the synthesis of a silyl ether usually requires initial preparation of a hydridochlorosilane [9], followed by reaction of this chlorosilane with an allylic alcohol in the presence of an organic base.

Group IV metallocenes are active catalysts for olefin hydrosilation [10] and very high regioselectivity has been observed in hydrosilation of 1-alkenes [11]. Group IV metallocenes are also very effective catalyst precursors for hydrosilane alcoholysis reactions [12]. If an

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☆ Dedicated to Professor Hideki Sakurai on the occasion of his retirement from Tohoku University.

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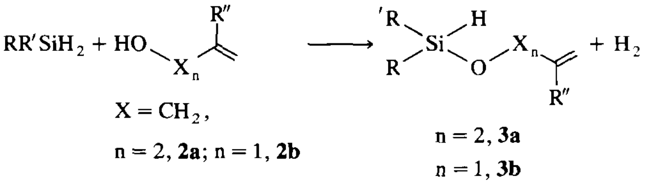
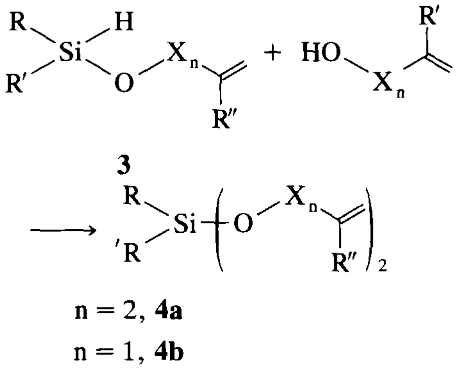
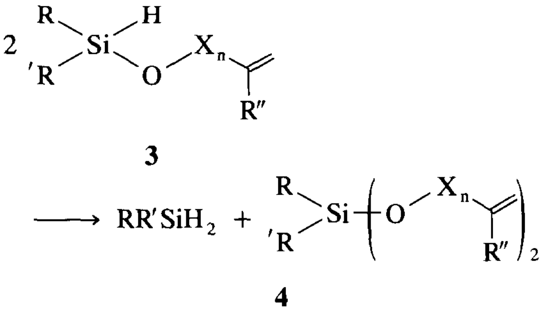
allylic, or homoallylic alcohol, **2**, and a di- or tri-hydrosilane are used as substrates, it should be possible to perform a one-pot reaction in which both processes occur without the isolation of the intermediate allyloxyhydrosilane, **3**. The first step of the reaction is expected to be the cross dehydrocoupling (or silane alcoholysis), because of the large bond energy difference between Si–H (90 kcal mol$^{-1}$) and Si–O ($\sim$ 128 kcal mol$^{-1}$) [13], and the driving force of evolution of hydrogen gas (Eq. (2)) favors the formation of an Si–O bond to give **3**. However, if **3** contains a residual Si–H bond, several other catalytic reactions may take place in the presence of an appropriate catalyst. For example, (i) alcoholysis by additional allylic alcohol molecules to form the multi-substituted product, **4** (Eq. (3)); (ii) a redistribution reaction [14] to form the multi-substituted product **4** and the dihydrosilane (Eq. (4)); (iii) hydrogenation of the olefinic group to form an alkoxysilane, **5** (Eq. (5)) (group IV metallocenes are well known hydrogenation catalysts [15]); (iv) intermolecular hydrosilation to give a polymeric product, **6** (Eq. (6)); and (v) intramolecular hydrosilation to form the cyclic product, **1** (R″ = H). If a trihydrosilane is chosen as the substrate, a competitive self dehydrocoupling of silane to form oligosilanes may also be possible [16].



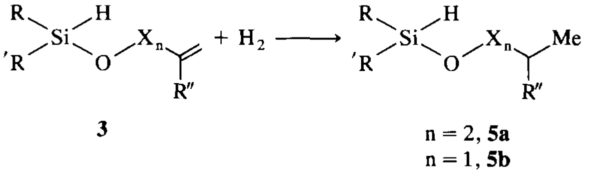
(2)



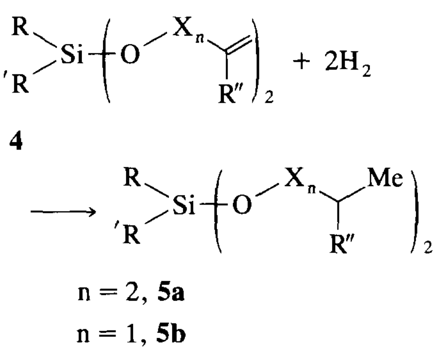
(3)



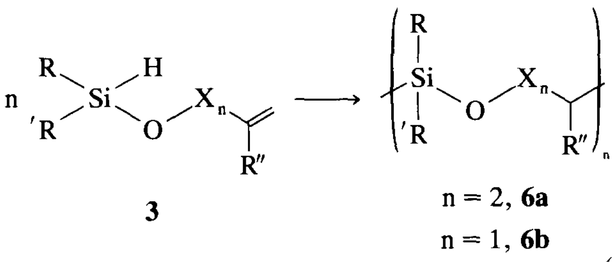
(4)



(5)

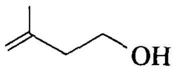


(6)

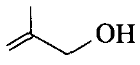


(7)

In this paper, we describe the results of a preliminary study of titanocene-catalyzed reactions of two typical allylic alcohols, 2-methylbut-1-en-4-ol, **2a**, and 2-methylprop-1-en-3-ol, **2b**, with several silanes.



**2a**



**2b**

## 2. Results and discussion

The substrates **2a** and **2b** were chosen to minimize complications arising from double-bond shifts which are known to accompany olefin hydrosilation reactions catalyzed by group IV metallocenes [17]. For these substrates migration of the double bond to the internal positions is slow compared with hydrosilation. Another criterion in the choice of substrates was that the final product be useful from the point of view of organic synthesis. Independent of whether the substrates **2a** and **2b** give the cyclization product **1**, or the polymeric product **6**, the final product, after oxidative cleavage of the Si–C bonds, will be the 1,3-, or 1,4-diol.

The key consideration in the choice of catalyst precursors was that they should be easily synthesized and transformed into the active catalyst. Cp$_2$TiMe$_2$ (Cp = $\eta^5$-cyclopentadienyl), **7**, is easy to synthesize and handle, and it can be easily converted to its active form in the presence of a hydrosilane [14,16]. The catalyst precursor *rac*-[EBTHI]TiMe$_2$ ([EBTHI] = ethylene-1,2-bis($\eta^5$-4,5,6,7-tetrahydroindenyl)), **8**, was chosen despite the fact that its synthesis is relatively challenging, because enantiomerically pure [EBTHI]TiMe$_2$, and other analogues, have been frequently used as catalyst precursors for enantioselective synthesis [18]. Hence it was of interest to investigate the activity of **8** as a catalyst for the intramolecular hydrosilation reactions.

### 2.1. Dimethyltitanocene-catalyzed reactions

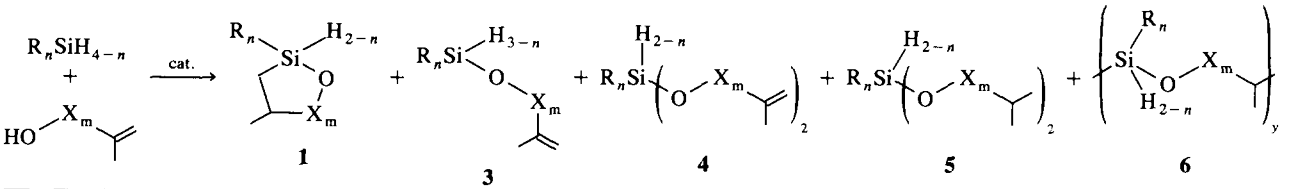
An equimolar mixture of **2a**, or **2b**, with a mono-, di-, or trihydrosilane, stirred at room temperature under argon for a week, showed no detectable reaction. In the presence of 1 mol.% of **7**, both dimethylphenylsilane (DMPS) and methyldiphenylsilane (MDPS) react slowly with **2a**. After 50 h, the reaction effectively ceased and the proton NMR spectrum showed 63% conversion for DMPS and 50% conversion for MDPS, respectively, based on the alcohol. The reaction of DMPS with **2a** also produces a considerable amount of hydrogenation product **5a**. This compound gives rise to two new signals in the $^1$H NMR spectrum of the products, a doublet at 0.83 ppm and a quartet at 1.44 ppm. In the reaction of MDPS with **2a**, the hydrogenation product cannot be detected. Under the same reaction conditions, triethylsilane showed no reaction with either **2a**, or **2b**. The product distributions for a series of reactions of silanes with **2a** and **2b**, catalyzed by **7**, are listed in Table 1. Selected $^1$H NMR and MS data for the products are listed in Table 2.

The exothermic reactions of two secondary silanes, phenylmethylsilane (PMS) and diphenylsilane (DPS), with either **2a**, or **2b**, proceed smoothly in the presence of 1.0 mol.% of **7**. Gas is evolved steadily in the first 30 min of the reaction. At this point, nearly 80% of the alcohol has been consumed. Subsequently, the rate of gas evolution declines and after a few hours essentially complete consumption of the alcohol has occurred. For PMS/**2a** and PMS/**2b** combinations, these times are 20 and 24 h respectively. The major product of the reaction of PMS with **2b** is **1b** (> 65%). The most important secondary products are the double-alcoholysis product **4b** and the hydrogenation product **5b**. The amount of **3b** accounts for less than 5% of the consumed alcohol (Table 1, entry 9).

In the reaction of PMS with **2a**, about 50% of the reacted alcohol is accounted for by the cyclic product **1a**, while significant amounts of **3a** and **4a** are also produced. An interesting point with respect to the reaction of PMS with **2a** is the production of **3a** in relatively high yield in the early stages of the reaction. Subsequently, a slow redistribution reaction converts **3a** to **4a** over long reaction times. For example, the ratios of **4a** to **3a** after reaction times of 4.5, 28, and 51 h are 1:1, 2:1, and 2.5:1, respectively. Under the same reaction conditions, **2b** gives more cyclic product, **1b**, than **2a** does, showing that the formation of the five-membered ring product is favored over the formation of a six-membered ring in reactions catalyzed by **7**. This is

Table 1

Dimethyltitanocene-catalyzed reactions of silanes with **2a** and **2b** (equimolar reactants)



| Entry | Silane | Alcohol | [7] (mol.%) | Time (h) | Conv. (%) | **1** | **3** | **4** | **5** | **6** | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | MDPS | **2a** | 1.0 | 51 | > 50 [a] | | 100 | | | | |
| 2 | DMPS | **2a** | 1.0 | 51 | ~ 63 | | 81 | | 19 | | |
| 3 | DPS | EtOH | 1.0 | 0.5 | 100 | | | 100 | | | |
| 4 | DPS | **2a** | 1.0 | 51 | 100 | > 40 | < 10 | > 48 | | | |
| 5 | DPS | **2a** | 0.5 | 51 | 100 | 58 | 8 | 31 | | | |
| 6 | DPS | **2b** | 1.0 | 49 | 100 | 29 | 24 | 35 | 10 | | TPDSO [b] |
| 7 | PMS | **2a** | 1.0 | 24 | 100 | < 50 | ~ 15 | ~ 35 | | | |
| 8 | PMS | **2a** | 0.5 | 51 | 100 | 75 | 3 | < 22 | | | |
| 9 | PMS | **2b** | 1.0 | 19 | 100 | 68 | < 5 | 20 | < 5 | | |
| 10 | PS | **2b** | 1.0 | 19 | 100 | | | | | 100 | |
| 11 | PS | **2a** | 1.0 | 4.5 | 100 | | | | > 90 | | OPS [c] |
| 12 | PS | **2a** | 0.2 | 100 | 100 | | | | > 90 | | OPS |

[a] All percentage conversions and yields are based on the alcohols used.

[b] TPDSO = tetraphenyldisiloxane. In one run of this reaction, TPDSO was yield in > 5% in the product and also some triphenylsilane (< 4%).

[c] OPS = oligophenylsilane.

Table 2
Selected $^1$H NMR and MS data

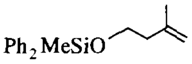
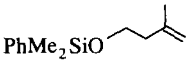
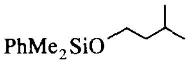
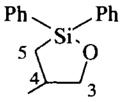
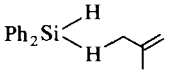
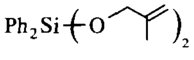
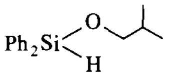
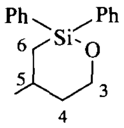
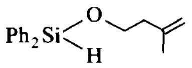
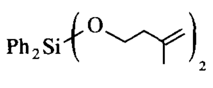
| Compound (Ref.) | $^1$H NMR ($C_6D_6$, 200 Hz) $\delta$ ppm | MS [$m/z$, Int.%] |
|---|---|---|
|  [*a*] | 7.7–7.2 (m, 10H, Si$Ph_2$),<br>0.59 (s, 3H, Si$CH_3$),<br>1.59 (s, 3H, –C($CH_3$)=$\mathrm{CH_2}$),<br>2.27 (t, $^3J_{H-H}$ = 6.98 Hz, 2H, $\mathrm{OCH_2}CH_2$–),<br>3.77 (t, $^3J_{H-H}$ = 6.88 Hz, 2H, $\mathrm{O}CH_2\mathrm{CH_2}$–),<br>4.73 (s, 2H, $\mathrm{C(CH_3)}$=$CH_2$) | |
|  [*a*] | 7.62–7.25 (m, 5H, Si$Ph$),<br>0.34 (s, 6H, Si($CH_3$)$_2$),<br>3.68 (t, $^3J_{H-H}$ = 6.82 Hz, 2H, $\mathrm{O}CH_2\mathrm{CH_2}$–),<br>2.25 (t, $^3J_{H-H}$ = 6.82 Hz, 2H, $\mathrm{OCH_2}CH_2\mathrm{C}$–),<br>1.61 (s, 3H, –C($CH_3$)=$\mathrm{CH_2}$),<br>4.72 (s, 2H, –$\mathrm{C(CH_3)}$=$CH_2$) | |
|  [*b*] | 7.62–7.25 (m, 5H, Si$Ph$),<br>0.35 (s, 6H, Si($CH_3$)$_2$),<br>3.61 (t, $^3J_{H-H}$ = 6.44 Hz, 2H, $\mathrm{O}CH_2\mathrm{CH_2}$–),<br>1.44 (q, $^3J_{H-H}$ = 6.44 Hz, 2H, $\mathrm{OCH_2}CH_2\mathrm{CH}$–),<br>1.8–1.5 (m, 1H, $\mathrm{OCH_2CH_2}CH\mathrm{(Me)_2}$),<br>0.84 (d, $^3J_{H-H}$ = 6.66 Hz, 6H, –CH($CH_3$)$_2$) | |
|  [*c*] | 8.0–7.2 (m, 10H, Si$Ph_2$),<br>3.60 (d, $^3J_{H-H}$ = 6.4 Hz, 2H *(3)*$CH_2$),<br>1.83 (m, 1H, *(4)*$CH$),<br>0.85 (d, $^3J_{H-H}$ = 6.4 Hz, 2H, *(5)*$CH_2$–Si),<br>0.89 (d, $^3J_{H-H}$ = 6.66 Hz, 3H, CH–$CH_3$) | |
|  [*c*] | 7.8–7.2 (m, 10H, Si$Ph_2$),<br>5.72 (s, 1H, Si$H$),<br>5.3–4.9 (m, 2H, $\mathrm{C(CH_3)}$=$CH_2$),<br>4.19 (s, 2H, O$CH_2$–),<br>1.57 (s, 3H, C($CH_3$)=$\mathrm{CH_2}$), | |
|  [*d*] | 8.0–7.2 (m, 10H, Si$Ph_2$),<br>4.23 (s, 4H, O$CH_2$C–),<br>1.59 (s, 6H, C($CH_3$)=$\mathrm{CH_2}$),<br>5.3–4.9 (m, 4H, $\mathrm{C(CH_3)}$=$CH_2$) | |
|  [*e*] | 7.7–7.2 (m 10 H, Si$Ph_2$)<br>5.68 (s, 1H, Si$H$),<br>3.57 (d, $^3J_{H-H}$ = 6.8 Hz, 2H, O$CH_2$–CH),<br>2.0–1.7 (m, 1H, $\mathrm{CH_2}CH\mathrm{(Me)_2}$),<br>1.02 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, CH($CH_3$)$_2$) | |
|  [*c*] | 7.9–7.1 (m, 10H, Si$Ph_2$),<br>3.93 (t, $^3J_{H-H}$ = 6.4 Hz, 2H, *(3)*$CH_2$),<br>1.56–1.46 (m, 2H, *(4)*$CH_2$),<br>1.9–1.6 (m, 1H, *(5)*$CH$),<br>0.85 (d, $^3J_{H-H}$ = 6.6 Hz, 3H, CH$CH_3$),<br>0.86 (d, $^3J_{H-H}$ = 6.6 Hz, 2H, *(6)*$CH_2$) | 268[$M^{+\cdot}$, 6.4],<br>199[$(Ph_2SiOH)^+$, 12,9]<br>191[$M^+$-$C_6H^\circ_5$, 51]<br>190[$M^+$-$C_6H_6$, 100]<br>183[$M^+$-$OC_5H_9$, 23.9], 149[29.8],<br>112[34.8], 105[$PhSi^+$, 26.9] |
|  [*c*] | 7.8–7.1 (m, 10H, Si$Ph_2$),<br>5.71 (s, 1H, Si$H$),<br>4.82 (s, 2H, $\mathrm{CH_2C(Me)}$=$CH_2$),<br>3.78 (t, $^3J_{H-H}$ = 6.5 Hz, 2H, $\mathrm{O}CH_2\mathrm{CH_2C}$–),<br>2.30 (t, $^3J_{H-H}$ = 6.5 Hz, 2H, $\mathrm{OCH_2}CH_2\mathrm{C}$–),<br>1.58 (s, 3H, $\mathrm{CH_2C}$($CH_3$)=$\mathrm{CH_2}$) | |
|  [*d*] | 7.8–7.1 (m, 10H, Si$Ph_2$),<br>4.83, (s, 4H, –$\mathrm{C(Me)}$=$CH_2$),<br>3.93 (d, $^3J_{H-H}$ = 6.8 Hz, 4H, $\mathrm{O}CH_2\mathrm{CH_2C}$–),<br>2.33 (t, $^3J_{H-H}$ = 6.8 Hz, 4H, $\mathrm{OCH_2}CH_2\mathrm{C}$–),<br>1.62 (s, 6H, $\mathrm{CH_2CH_2C}$($CH_3$)=$\mathrm{CH_2}$) | 352[$M^{+\cdot}$, 0.35],<br>337[$M^+$-$CH_3$, 0.44]<br>267[$M^+$-$OC_5H_9$, 39.2]<br>225[35.4], 189[100], 159[31],<br>131[$C_5H_9OSiH(OH)^+$, 15.9] |

Table 2 (continued)

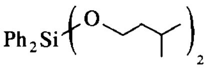
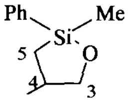
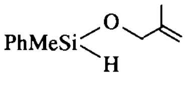
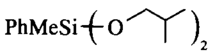
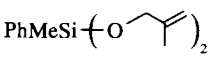
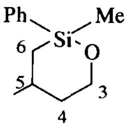
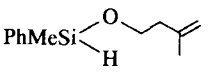
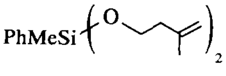
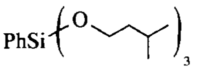
| Compound (Ref.) | $^1$H NMR ($\mathrm{C_6D_6}$, 200 Hz) δ ppm | MS [*m/z*, Int.%] |
|---|---|---|
|  [*b*] | 7.6–7.1 (m, 10H, Si$Ph_2$),<br>3.78 (t, $^3J_{\mathrm{H-H}}$ = 6.5 Hz, 2H, $\mathrm{O}CH_2\mathrm{CH_2CH}$),<br>1.45 (t, $^3J_{\mathrm{H-H}}$ = 6.5 Hz, 2H, $\mathrm{OCH_2}CH_2\mathrm{CH}$),<br>1.9–1.5 (m, 1H, -$CH$(ME)$_2$),<br>0.87 (d, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, 6H, $-\mathrm{CH}(CH_3)_2$) | 278[M$^+$-$\mathrm{C_6H_6}$],<br>269[M$^+$-$\mathrm{OC_5H_{11}}$],<br>200[$\mathrm{Ph_2Si(OH_2)^+}$, 100]<br>199[$\mathrm{Ph_2Si(OH)^+}$], 183[$\mathrm{Ph_2SiH^+}$],<br>153, 139[$\mathrm{PhSi(OH)_2^+}$] |
|  [*c*] | 7.7–7.2 (m, 5H, Si$Ph$),<br>0.39 (s, 3H, Si–$CH_3$),<br>0.91 (d, $^3J_{\mathrm{H-H}}$ = 6.66 Hz, 3H, CH–$CH_3$),<br>3.54 (d, $^3J_{\mathrm{H-H}}$ = 6.7 Hz, 3H, $(3)CH_2$),<br>2.2–1.8 (m, 1H, $(4)CH$),<br>0.87 (d, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, 2H, $(5)CH_2$), | |
|  | 7.7–7.2 (m, 5H, Si$Ph$),<br>0.37 (d, $^3J_{\mathrm{H-H}}$ = 2.86 Hz, 3H, Si–$CH_3$),<br>5.26 (q, $^3J_{\mathrm{H-H}}$ = 2.86 Hz, 1H, Si$H$),<br>5.20–4.82 (m, 2H, $\mathrm{OCH_2C(Me)}$= $CH_2$),<br>4.0 (s, 2H, $\mathrm{O}CH_2\mathrm{C(Me)}$=$\mathrm{CH_2}$),<br>1.57 (s, 3H, $\mathrm{OCH_2C}(CH_3)$=$\mathrm{CH_2}$) | 192[M$^{+\cdot}$, 10.8],<br>177[M$^+$-Me, 26.7],<br>163[M$^+$-$\mathrm{C_2H_5}$, 7.9],<br>150[M$^+$-$\mathrm{C_3H_7}$, 13.2],<br>137[M$^+$-$\mathrm{C_4H_7}$, 100],<br>123[M$^+$-$\mathrm{OC_4H_5}$, 32.7],<br>121[M$^+$-$\mathrm{OC_4H_7}$, 51.3],<br>105[12.1], 99 [24.9].<br>High resolution MS for $\mathrm{C_{11}H_{16}OSi}$ = 192.3167, (calcd. 192.3329) |
|  [*b*] | 7.6–7.2 (m, 5H, Si$Ph$),<br>0.42 (s, 3H, Si–$CH_3$),<br>3.6 (d, $^3J_{\mathrm{H-H}}$ = 6.5 Hz, 4H, $\mathrm{O}CH_2\mathrm{CH}$),<br>1.84 (m, 1H, $\mathrm{OCH_2}CH\mathrm{Me_2}$),<br>1.02 (d, $^3J_{\mathrm{H-H}}$ = 6.5 Hz, 6H, $\mathrm{OCH_2CH}(CH_3)_2$) | |
|  [*d*] | 7.5–7.1 (m, 5H, Si$Ph$),<br>0.40 (s, 3H, Si$CH_3$),<br>5.23–4.82 (m, 4H, $\mathrm{OCH_2C(Me)}$= $CH_2$),<br>4.14 (s, 4H, $\mathrm{O}CH_2\mathrm{C(Me)}$=$\mathrm{CH_2}$),<br>1.60 (s, 6H, $\mathrm{OCH_2C}(CH_3)$=$\mathrm{CH_2}$) | 262[M$^{+\cdot}$, 1.5], 247[M$^+$-$\mathrm{CH_3}$, 4.4]<br>191[M$^+$-$\mathrm{OC_4H_7}$, 14]<br>190[M$^+$-$\mathrm{OC_4H_8}$, 20]<br>177[$\mathrm{PhHSi(OC_4H_7)^+}$, 15.2]<br>137[$\mathrm{PhMeSi(OH)^+}$, 100] |
|  | 7.75–7.1 (m, 5H, Si$Ph$),<br>0.38 (s, 3H, Si–$CH_3$),<br>3.81 (t, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, 2H, $(3)CH_2$),<br>1.50 (q, $^3J_{\mathrm{H-H}}$ = 6.7 Hz, 2H, $(4)CH_2$),<br>1.76 (m, 1H, $(5)CH$),<br>0.87 (d, $^3J_{\mathrm{H-H}}$ = 6.62 Hz, 3H, CH–$CH_3$),<br>0.85 (d, $^3J_{\mathrm{H-H}}$ = 6.6 Hz, 2H, $(6)CH_2$) | 206[M$^{+\cdot}$, 2.1]<br>191[M$^+$-$\mathrm{CH_3}$, 100]<br>149[56.8],<br>137[$\mathrm{PhMeSi(OH)^+}$, 11.7]<br>129[M$^+$-$\mathrm{C_6H_5}$, 9.8]<br>128[M$^+$-$\mathrm{C_6H_6}$, 46.1]<br>121[18.7], 113[17.2], 105[19.8]<br>High resolution MS for $\mathrm{C_{12}H_{18}OSi}$ = 206.3324; (calcd. 206.3598). |
|  | 7.65–7.1 (m, 5H, Si$Ph$),<br>5.26 (q, $^3J_{\mathrm{H-H}}$ = 2.84 Hz, 1H, Si$H$),<br>0.36 (d, $^3J_{\mathrm{H-H}}$ = 2.84 Hz, 3H, Si–$CH_3$)<br>4.81 (s, 2H, -C(Me)=$CH_2$),<br>3.66 (t, $^3J_{\mathrm{H-H}}$ = 6.92 Hz, 2H, $\mathrm{O}CH_2\mathrm{CH_2C}$–),<br>2.24 (t, $^3J_{\mathrm{H-H}}$ = 6.92 Hz, 2H, $\mathrm{OCH_2}CH_2\mathrm{C}$–),<br>1.59 (s, 3H, -$\mathrm{CH_2C}(CH_3)$=$\mathrm{CH_2}$) | 206[M$^{+\cdot}$, 9.9], 191[M$^+$-Me, 50.1],<br>163[M$^+$-$\mathrm{C_3H_7}$, 7.3],<br>151[M$^+$-$\mathrm{C_4H_7}$, 55.1],<br>137[M$^+$-$\mathrm{C_5H_9}$, 21.7],<br>128[9.9], 121[M$^+$ – $\mathrm{OC_5H_9}$, 100],<br>113[9.3], 105[14.5], 91[32.5].<br>High resolution MS for $\mathrm{C_{12}H_{18}OSi}$ = 206.3216; (calcd. 206.3598). |
|  [*d*] | 7.9–7.1 (m, 5H, Si$Ph$),<br>0.40 (s, 3H, Si–$CH_3$),<br>4.83 (s, 4H, -CH(Me)=$CH_2$),<br>3.86 (t, $^3J_{\mathrm{H-H}}$ = 6.88 Hz, 4H, $\mathrm{O}CH_2\mathrm{CH_2C}$–),<br>2.31 (t, $^3J_{\mathrm{H-H}}$ = 6.88 Hz, 4H, $\mathrm{OCH_2}CH_2\mathrm{C}$–),<br>1.64 (s, 6H, -$\mathrm{CH_2C}(CH_3)$=$\mathrm{CH_2}$) | 275[M$^+$-$\mathrm{CH_3}$, 3.1]<br>205[M$^+$-$\mathrm{OC_5H_9}$, 90]<br>175[24.9], 163[73.5],<br>137[$\mathrm{PhMeSi(OH)^+}$, 34.1]<br>127[100], 121[30.3], 118[20.6],<br>105[17.2], 104[13.8] |

Table 2 (continued)2e

| Compound (Ref.) | $^1$H NMR ($C_6D_6$, 200 Hz) $\delta$ppm | MS [$m/z$, Int.%] |
|---|---|---|
| <br>[b] | 8.0–7.1 (m, 5H, Si$Ph$),<br>3.97 (t, $^3J_{H-H}$ = 6.56 Hz, 6H, O$CH_2$CH$_2$–),<br>1.80 (o, $^3J_{H-H}$ = 6.66 Hz, 3H, –CH$_2$$CH$(Me)$_2$),<br>1.57 (t, $^3J_{H-H}$ = 6.5 Hz, 6H, CH$_2$$CH_2$CH–),<br>0.89 (d, $^3J_{H-H}$ = 6.62 Hz, 18H, CH$_2$CH($CH_3$)$_2$) | 288 [$M^+$-$C_6H_6$, 65],<br>279[$M^+$-$OC_5H_{11}$, 27], 273[47],<br>231[31], 223[26], 217[34], 153[36],<br>139[$PhSi(OH)_2^+$, 100]<br>123[$PhSiH(OH)^+$, 32] |

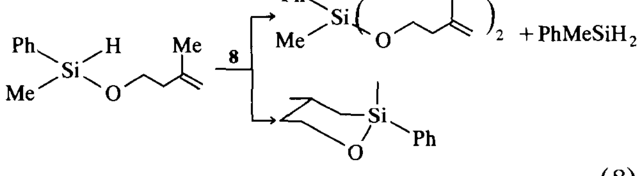
[a] (1) M. Fujita and T. Hiyama, *J. Org. Chem. 53* (1988) 5405. (2) J.J. Brunet, D. Besozzi and P. Caubère, *Synthesis*, (1982) 721. [b] Ref. [12]. [c] (1) In the supplementary materials of Ref. [7]. (2) I. Ojima and T. Kogure, *Organometallics 1* (1982) 1390. [d] I.P. Lychkin, I.A. Ososhnik and L.V. Kontsova, *Kauch Rezina 7* (1987) 32. [e] A.J. Cornish, M.F. Lappert and T.A. Nile, *J. Organomet. Chem. 132.*, (1977) 133.

probably because the expected six-membered metallacycle intermediate involved in the formation of **1b** is relatively more stable than the seven-membered metallacycle intermediate required for the formation of **1a**. In a parallel study of ketone hydrosilation in the presence of **7** [19], hex-1-ene-5-one was hydrosilated on the carbonyl group with high regioselectively while the olefinic group remained intact.

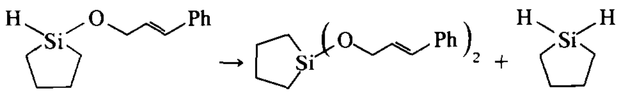
The formation of **1a** and **1b** is apparent from the $^1$H-NMR signals at 0.8–0.9 ppm (due to the methyl group on the ring overlapped with the methylene group linked to the silicon atom) and at 3.7–3.9 ppm in **1a** and 3.3–3.6 ppm in **1b** (due to the methylene group next to the oxygen atom). The methine proton is a complex multiplet in the 1.6–1.9 ppm region in both **1a** and **1b**, while the signal of the methylene group transannular to the silicon atom in **1a** is located at 1.6–1.4 ppm. All signals are relatively complicated because of the existence of a diastereoisomeric pair. The methylene proton signals are complicated by diastereotopy.

The major products from the reaction of DPS with **2b** (in order of importance) are **4b**, **1b** and **3b**. Small amounts of **5b** and of tetraphenyldisiloxane were also produced (Table 1, entry 6). The production of tetraphenyldisiloxane is surprising and may be due either to $H_2O$ contamination in the alcohol or via a C–O bond cleavage. Another minor feature of this reaction is the detection of a trace of triphenylsilane in one of the runs. The formation of triphenylsilane is presumably due to Si–Ph/Si–H redistribution, which is commonly observed in late transition metal complex catalyzed siloxane redistribution reactions [20]. It is not normally observed in the titanocene-catalyzed redistribution of alkoxy- and siloxysilanes [14]. However, such a Si–C/Si–H exchange has been observed in a study of titanocene-catalyzed hydrosilation of ketones [19]. The reaction of DPS with **2a**, under the same conditions as used with **2b**, produces two major products, bis(3-methyl-3-buten-1-oxy)diphenylsilane, **4a**, and the cyclic product, **1a**, in a 6:5 ratio, and a minor product, the mono(3-methyl-3-buten-1-oxy)diphenylsilane, **3a**, in less than 10% yield.

In the reactions of **2a** with both PMS and DPS, a significant increase in the production of **1a** is observed when a lower catalyst concentration is used. Thus, with 0.5 mol.% of **7**, the PMS/**2b** combination gave 75% of **1a**, compared with 50% with 1 mol.% of **7**. The DPS/**2b** combination gave 58% of **1b**, compared with 40% with 1 mol.% of **7**. This dependence on catalyst concentration is believed to be due to the fact that at high catalyst concentration, the competitive redistribution reaction to convert **3** to **4** is faster than the cyclization reaction to convert **3** to **1**. Support for this hypothesis is derived from the catalytic reaction of phenylmethyl(3-methylbut-3-en-1-oxy)silane under the same reaction conditions, but using 1 mol.% of **8** as the catalyst (Eq. (8)). Although the reaction rates for both the redistribution and cyclization reactions are relatively slow at room temperature, the redistribution rate was found to be at least twice as fast as the cyclization rate. Under the same reaction conditions, 1-(3-*trans*-phenylprop-2-en-1-oxy)silacyclopentane underwent a quantitative redistribution reaction (Eq. (9)) without any observable cyclization. In the cases of reactions catalyzed by **8**, the intramolecular hydrosilation is believed to be less favourable than the bimolecular redistribution reaction. This is because the organic ligand on the metal is sterically rigid and encumbered, and the olefinic group must approach the metal center with a selected face to avoid excessive steric interaction.



(8)



(9)

The reactions of both PMS and DPS with ethanol, both highly exothermic reactions, gave only the diethoxysilanes even at a silane to alcohol ratio of 1:1 and 2:1, and independent of which catalyst was used.

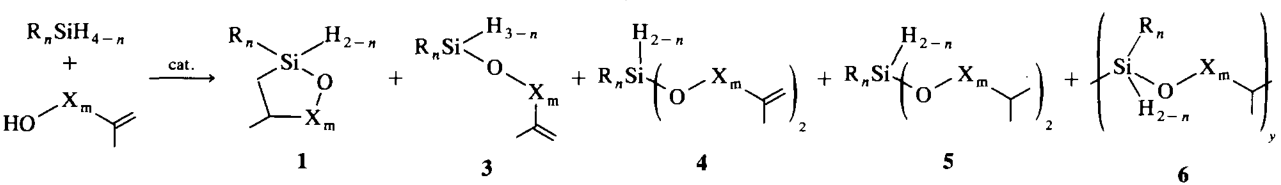
The reaction of phenylsilane (PS) with equimolar **2a**, or **2b**, catalyzed by **7**, is highly exothermic and initially quite violent. After 30 min, the reaction mixtures are noticeably viscous. After 24 h, the product of the PS/**2a** reaction is a thick oil and the PS/**2b** reaction mixture is an immobile gum which is still soluble in common organic solvents.

The product from the reaction of PS with **2a** shows a relatively clean $^1H$ NMR spectrum with resonances at 3.98 (triplet), 1.80 (multiplet), 1.55 (quartet), and 0.90 (doublet) ppm (Table 2). The ratios of these peaks are 2:1:2:6 respectively. These resonances are attributed to tris(3-methylbutoxy)phenylsilane, i.e. the completely hydrosilated and hydrogenated product, **5a** (Table 1, entries 11, 12). In addition, very broad resonances in the aromatic C–H region also suggest the presence of a significant amount of a polymeric product in the mixture. A GPC trace of the residue remaining after removal of the volatiles under high vacuum shows mainly a high molecular weight species with a bimodal distribution, with some sharp peaks, characteristic of small molecules, on the low molecular weight side. The weight average molecular weight of this residue is 31800 Dalton (polystyrene calibration) with a polydispersity index of 10.8.

The $^1H$ NMR spectrum of the PS/**2b** reaction product is dominated by a set of extremely broad signals. A sharper multiplet in the region of 4.6–4.5 ppm indicates the presence of some low molecular weight species containing Si–H bonds, but this signal overlaps a much broader peak characteristic of the Si–H signals of a mixture of oligophenylsilanes. Taken together with the complete disappearance of the $^1H$ signals due to the olefinic group of **2b**, this suggests that the product is a polymer, probably **6** (Eq. (7)) mixed with some lower molecular weight oligophenylsilanes, or a copolymer produced by a mixture of intermolecular hydrosilation and silane dehydrocoupling. A GPC trace of this material in THF solution showed a bimodel distribution, with a weight-average molecular weight of 7600 Dalton (polystyrene calibration) and a polydispersity index of 3.6.

The product distribution does not change significantly on lowering the catalyst concentration in the reactions of PS with **2a** and **2b**. For example, the PS/**2a** reaction, catalyzed by 1 mol.% of **7**, gives about 44% of non-volatile polymer, based on the total weight of the product. Similar reactions, using 0.5 mol.% and 0.2 mol.% catalyst, also give about 40% polymer. For the PS/**2a** reaction the trialkoxyphenylsilane is producd in almost quantitative yield, based on the alcohol substrate. This suggests that the alcoholysis of the Si–H bond (Eq. (2)) and the redistribution reactions of the mono- and bis-alkoxylated products (Eq. (3)) are dominant reactions in the early stages of the reaction. When all of the Si–H has been replaced by Si–O, the cyclization reaction (Eq. (1)) is precluded and the only possible reactions are intermolecular hydrosilation to produce **6** and silane dehydrocoupling to produce oligosilanes. Since the alcoholysis reaction only uses one-third of an equivalent of PS, most of the polymeric material from the reaction of PS with **2a** is likely to be oligophenylsilanes contaminated by a small amount of the intermolecular hydrosilation polymer, **6a**. Equally possible is a heteropolymer consisting mainly of an oligophenylsilane backbone with a small amount of oligomeric **6a**, either as backbone units, or as side chains. The observed results strongly suggest that the rate of silane dehydrocoupling proceeds much faster than that of intermolecular hydrosilation. The hydrogen produced by the phenylsilane dehydrocoupling reaction is consumed in hydrogenating the initially produced tris(allyl-

Table 3
*Rac*-[EBTHI]TiMe$_2$ **8**, catalyzed reaction of primary and secondary silanes with **2a** and **2b**



| Entry | Silane | Alcohol | [7] mol.% | Time (h) | Conv. (%) | 1 | 3 | 4 | 5 | 6 | Other |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | DPS | **2b** | 1.0 | 24 | 100 [a] | 26 | 28 | 28 | 30 | 14 | |
| 2 | DPS | **2a** | 1.0 | 24 | 100 | 52 | 16 | 15 | 15 | | |
| 3 | PMS | **2b** | 1.0 | 6 | 100 | | 65 | 34 | | | |
| 4 | PMS | **2a** | 1.0 | 6 | 100 | > 77 | 8 | 13 | | | |
| 5 | PS | **2b** | 1.0 | 24 | 100 | | | | | 100 | |
| 6 | PS | **2a** | 1.0 | 24 | 100 | | | | > 95 | | OPS [b] |

[a] All percentage conversions are based on the alcohols used.
[b] OPS = oligophenylsilane.

oxy)phenylsilane. Co-hydrogenation of olefins in the course of titanocene-catalyzed dehydrocoupling of silanes is well known [10a].

### 2.2. *Rac-[EBTHI]TiMe$_2$-, 8, catalyzed reactions*

The catalytic activity of **8** is slightly lower than that of **7**. However, its activity does not decline significantly, as that of **7** usually does. Although reactions catalyzed by **8** are less vigorous initially, compared with those catalyzed by **7** under the same conditions, they can eventually reach the same conversions after sufficient reaction time.

Some detailed conditions and product distributions for the reactions of **2a** and **2b** with PS, PMS, and DPS are listed in Table 3. The PMS/**2a** reaction produces two main products, the intramolecular hydrosilation product, **1a** (> 77%), and the double alcoholysis product, **4a**, along with a trace of the hydrogenation product, **5a** (Table 3). An interesting difference between the catalytic specificities of **7** and **8** is that, in the reaction of **2b** with PMS, catalyzed by **8**, the dominant products are **3b** and **4b**, while with **7** as catalyst **1b** is the major product (vide supra). Thus, the EBTHI ligand almost completely shuts down the intramolecular cyclization (Eq. (1)), while continuing to catalyze a slow redistribution, which converts **3b** to **4b**. For example, the ratio of **3b** to **4b** falls from 5.2:1 after 6 h of reaction to 2:1 after 24 h of reaction. The percentage of cyclic product **1b** is less than 4% after 24 h (Table 3). Formation of cyclic product **1b** is therefore controlled by the kinetics, not the thermodynamics of the reactions. Both electronic and steric factors may play a role in this effect. In contrast to the reactions of **2b**, the reactions of secondary silanes with **2a** catalyzed by **8** give the six-membered ring product **1b** as the main product, even at relatively high catalyst concentrations. The fact that lowering the concentration of **7** can decrease the redistribution rate and enhance the cyclization rate suggests that these two reactions may be mediated by different catalyst intermediates.

The reactions of DPS with either **2a**, or **2b**, proceed at a relatively slow rate compared with PMS. The DPS/**2a** reaction gives mainly **1a** (> 50%), with **3a**, **4a** and **5a** in lesser, roughly equal amounts (Table 3). The DPS/**2b** reaction produces mainly **1b**, **3b** and **4b**, in roughly equal amounts, along with a significant amount of hydrogenation product, **5b**.

The reactions of PS with either **2a**, or **2b**, give essentially the same products as those obtained using **7** as the catalyst.

### 2.3. *Reactions of β- and γ-hydroxyketones*

In the case of the allylic substrates described above, hydrogenation results in the loss of the olefinic functionality and prevents further intramolecular and intermolecular hydrosilation reactions. Alternative substrates, from which the organic diols can be produced yet the disadvantage of hydrogenation may be avoided, are the β-hydroxy- or γ-hydroxyketones. In these cases, after alcoholysis of the hydroxy group, both hydrogenation and intramolecular hydrosilation of the carbonyl group should give the same final product, the 2-sila-1,3-dioxanes.

To test such a concept, 2-hydroxy-4-pentanone was reacted with either PMS or DPS in the presence of 1 mol.% of **7** for 24 h. However, no reaction occurred. A similar inactivity was found for the hydrosilation of α,β- and α,γ-diketones [19]. It is assumed that in these cases the titanocene alkoxy complex is also coordinated by the free carbonyl group and that such a chelation blocks a coordination site essential to the catalytic reaction. Such behaviour favours the hypothesis that a Ti(III) species, most likely a Ti(III) hydride, is the key catalytic intermediate, since neutral titanocene(IV) complexes of the type $Cp_2TiX_2$ have little tendency to coordinate an additional ligand. Ti(III) hydrides are extremely reactive and have previously been proposed as key catalytic intermediates in many titanocene-catalyzed reactions [21]. They can be somewhat stabilized by coordination of a Lewis base [22], or by dimer formation [23].

The Ti(III) hydride dimer *rac*-{[EBTHI]Ti($\mu$-H)}$_2$ has been prepared by reaction of *rac*-[EBTHI]TiMe$_2$ with PMS, and its structure has been determined [24]. This compound can also be isolated in good yield from some of the catalytic reactions described above, strongly suggesting that most of the titanocene has been transformed into the Ti(III) hydride.

### 2.4. *Mechanistic considerations*

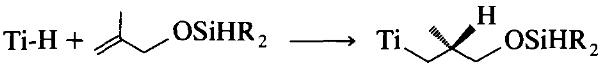
The special nature of hydrosilanes as mild reducing reagents has been extensively exploited to prepare a number of unstable and highly reactive titanocene(III) derivatives [16,22,24], especially titanocene(III) silyl hydride compounds which are usually inaccessible by other routes. Titanocene(III) hydrides have also been frequently proposed as key catalytic intermediates in many titanocene-catalyzed reactions [10a,12,14,16b, 16l,18,21]. The products obtained from the reactions of allylic and homoallylic alcohols with hydrosilanes can all be rationalized by steps involving monomeric Ti(III) species. The redistribution reactions of alkoxysilanes have previously been attributed to the action of a bimetallic Ti(III) catalytic species [14], while the catalytic dehydrocoupling of silanes is believed to involve monometallic species [10a]. Although these reactions can also be explained by sequences of insertion/σ-bond metathesis, the effects of catalyst concentration on the relative rates of redistribution and intramolecular hydrosilation, catalyzed by **7**, as described in the present paper, provide strong support for the assumption that one of these reactions (hydrosilation) is catalyzed by monometallic species, while the other (redistribution) is catalyzed by a bimetallic species.

A series of possible catalytic processes involving a Ti(III) hydride species, and which explain most of the results described above, are as follows:A. Alcoholysis

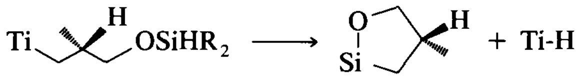
$$\text{Ti-H} + R_2SiH_2 \longrightarrow \text{Ti-Si}R_2H + H_2 \qquad (10)$$

$$\text{Ti-Si}R_2H + \text{HOR} \longrightarrow \text{Ti-H} + R_2HSi\text{-OR} \qquad (11)$$

B. Intramolecular hydrosilation

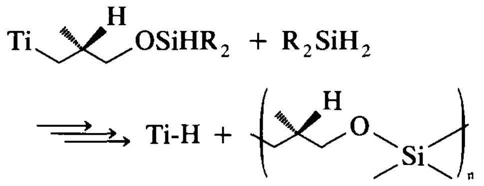


(12)



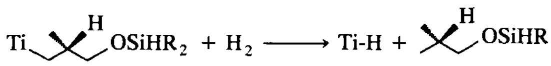
(13)

C. Intermolecular hydrosilation



(14)

D. Hydrogenation



(15)

All of the observed products of reactions (10)–(15) are expected to occur by standard sequences of insertion and $\sigma$-bond metathesis steps. However, classic oxidative addition of a substrate to a titanocene(II) species, followed by insertion/reductive elimination of the product to regenerate the titanocene(II) catalyst cannot be excluded. The relative merits of these two types of mechanism have previously been discussed with respect to the redistribution of hydrosiloxanes and alkoxyhydrosilanes [14,25,26].

Attempts to isolate titanium-containing intermediates from stoichiometric reactions of titanocenes/hydrosilane/alcohol, or aldehyde, are under investigation. It is expected that Ti(III) alkoxide species should be isolatable under appropriate conditions. We are also studying the kinetics of the competitive hydrosilation/redistribution reaction. The results of these investigations may help distinguish between the two major mechanistic possiblilities mentioned in the preceding paragraph.

## 3. Experimental

### 3.1. General remarks

All solvents were dried and degassed by standard techniques prior to use. All reactions were carried out under an atmosphere of dry argon through the use of standard Schlenk techniques. 3-methylbut-3-en-1-ol, **2a**, 2-methylprop-2-en-1-ol, **2b**, $Cp_2TiCl_2$, MeLi, and $LiAlH_4$ were purchased from Aldrich Chemical, Inc. The alcohols were dried over magnesium turnings and stored over vacuum oven-dried 4A molecular sieves. $Cp_2TiMe_2$ [27], *rac*-[EBTHI]$TiCl_2$ [28], (3-methylbut-3-en-1-oxy)phenylmethylsilane, and 1-(*trans*-3-phenylprop-2-en-1-oxy)silacyclo-pentane, were synthesized by literature procedures (this latter compound synthesized by reacting PhMeSiHCl with 3-methyl-3-buten-1-ol by following the procedures described in Ref. [7a] (yield ca. 80%)). $PhMe_2SiH$, $Ph_2MeSiH$, $Et_3SiH$, $PhSiCl_3$, $Ph_2SiCl_2$, $PhMeSiCl_2$ were purchased from Hüls American, Inc. (currently United Chemicals, Inc.). The monohydrosilanes were dried over calcium hydride to remove any chloride residue, distilled under reduced pressure and were kept over vacuum oven-dried 4A molecular sieves. The primary and secondary silanes, $PhSiH_3$ (this compound was synthesized by reacting 1-chlorosilacyclopentane with cinnamyl alcohol (from Aldrich Chemical Inc., > 97% trans isomer) by following the procedure in Ref. [7a] (yield, 76%). A similar synthesis of 1-chlorosilacyclopentane gave only 29% yield), $PhMeSiH_2$ and $Ph_2SiH_2$ were prepared by standard procedures from the reactions of chlorosilanes with $LiAlH_4$ [29,30].

NMR spectra were recorded in benzene-$d_6$ unless otherwise noted, and were measured on Varian XL-200, XL-300, or in some cases VNMR-500 spectrometers with TMS as internal reference. A long delay time ($d_1$ = 2.0–5.0 s depending on the sample to be measured) was usually used between pulses in $^1H$ NMR measurements to allow the protons on silicon atoms to be fully relaxed. Low-resolution and high-resolution mass spectra were recorded on a KRATOS MS25RFA spectrometer equipped with a KRATOS DS90 data system. GC analysis was carried out on a Shimadzu GC-8A chromatograph equipped with a DB-5 30 m capillary column (stationary phase: 95% dimethylsiloxane, 5% diphenylsiloxane copolymer, 1 $\mu$m thickness) and a hydrogen flame-ionization detector (FID). Injection port temperature 300°C, column temperature 100–300 °C, programmed at 10 °C $min^{-1}$. Carrier gas: helium, flow rate 0.5 ml $min^{-1}$.

The molecular weight distributions of polymeric samples were measured on a Varian D 5000 Liquid Chromatograph system equipped with a Waters $\mu$ Styragel column and a Varian-RI-4 detector. The mobile phase was THF with a flow rate of 1.0 ml $min^{-1}$ at a temperature of 35 °C. The column was calibrated with narrow distribution polystyrene standards (ranging from 760-400,000 Dalton). Data were collected and analyzed on a Varian DS 604 data system.

### 3.2. Dimethyltitanocene-catalyzed reactions

Dimethyltitanocene (20.4 mg; 0.1 mmol) was dissolved in ca. 0.5 ml dry benzene-$d_6$ under an atmosphere of dry argon, in a Schlenk tube equipped with magnetic stirring. The silane (10.0 mmol) was syringed into the tube. Following an induction period, whose length is characteristic of the particular silane being used, the orange–yellow solution turned to dark blue or green. At this point the alcohol (10.0 mmol) was added dropwise into the stirred solution from a syringe over a period of 5 min. Slow addition is required to prevent overheating, due to the exothermicity of the reaction. Upon completion of the addition, stirring was maintained and aliquots were periodically taken from the reaction mixture for analysis by proton NMR and GC. Sampling was continued until the product distribution remained constant. In some cases, the final reaction mixture was separated by passing through a silica-gel column ($35 \times 650$ mm$^2$) eluted with petroleum ether/$CH_2Cl_2$. After removal of the solvents, the separated compounds were characterized by $^1H$ NMR spectroscopy and GC. Some compounds were also characterized by mass spectroscopy. The elemental compositions for new compounds were established by high-resolution MS (selected $^1H$ NMR and MS data are presented in Table 2). However, silica-gel chromatography usually resulted in substantial product loss. Hence, in most cases, the true product distribution was established from the integration of the $^1H$ NMR and GC peaks of the reaction mixtures, using chemical shifts and retention times determined from isolated and purified authentic samples.

A slightly modified procedure was used for the reactions of phenylsilane. In this case, the reactor was cooled in an ice-water bath at the beginning of the reaction to prevent loss of substrate due to the violently exothermic reaction. After 30 min, the ice-water bath was removed and the mixture was then treated as above.

### 3.3. Rac-[EBTHI]TiMe$_2$-catalyzed reactions

#### 3.3.1. Synthesis of rac-[EBTHI]TiMe$_2$

*Rac*-[EBTHI]TiCl$_2$ (38.3 mg; 0.10 mmol) was suspended in 1.0 ml of dry ether, under an argon atmosphere, in a Schlenk tube equipped with a magnetic stirring bar. MeLi (0.15 ml of 1.4 M solution in diethyl ether; 0.21 mmol) was added to the suspension and the mixture was stirred for 12 h. The solvent was pumped off and the residue was extracted with dry hexanes ($5 \times 1$ ml) until colorless. The extract was cannula filtered into another Schlenk tube under argon and solvent was slowly removed under reduced pressure to yield *rac*-[EBTHI]TiMe$_2$ as a yellow crystalline material. $^1H$ NMR: $\delta$ ppm ($C_6D_6$, 500 MHz); 6.576 (d, $J = 2.93$ Hz, 2H), 4.78 (d, $J = 2.93$ Hz, 2H), 3.03–2.87 (m, 4H), 2.20–2.18 (m, 2H), 2.17 (s, 4H), 1.70–1.43 (m, 12H), 0.17 (s, 6H). $^{13}C$ NMR: ($C_6D_6$, 125.68 Hz); 126.30, 123.91, 121.85, 117.62, 107.53, 45.65, 26.45, 24.34, 23.29, 22.57, 22.51.

#### 3.3.2. Reactions of secondary silanes with alcohols

The crystalline *rac*-[EBTHI]TiMe$_2$, prepared in Section 3.3.1, was dissolved in 0.50 ml of dry benzene-$d_6$ followed by addition of the secondary silane (10.0 mmol). An immediate color change from yellow to dark green occurred and the alcohol substrate was then added over a period of 5 min. The reaction was usually less vigorous at the beginning than the reactions catalyzed by **7**, but nevertheless the mixture became quite warm due to the exothermicity of the reaction. Upon completion of the addition, the dark-brown mixture was allowed to continue reacting at room temperature and aliquots were periodically taken for analysis of the product distribution. The reaction was quenched by blowing dry air into the reactor. The catalyst was removed by passing the product through a small column of Florisil and eluting with diethyl ether. Ether was pumped off, the sample redissolved in benzene-$d_6$, and the final product distribution was established by integration of $^1H$ NMR and GC traces (see details in Section 3.2).

For the case of phenylsilane, the same modified procedure was used as described in Section 3.2.

#### 3.3.3. Reaction of (3-methylbut-3-en-1-oxy)phenylmethylsilane

(3-methylbut-3-en-1-oxy)phenylmethylsilane (10.0 mmol) was added to the catalyst solution prepared as in Section 3.3.1 and was stirred under an argon atmosphere for 53 h. At the end of this time > 50% of the starting material had been consumed. Three products were detected in the reaction mixture, $PhMeSiH_2$, $PhMeSi(OCH_2CH_2C(Me)CH_2)_2$ **4a**, and cyclization product **2a** in a 3:3:1 ratio (see Table 2 for the NMR spectra of **2a** and **4a**).

#### 3.3.4. Reaction of 1-(3-phenylprop-2-en-1-oxy)silacyclopentane

1-(3-phenylprop-2-en-1-oxy)silacyclopentane (10.0 mmol) was added to the catalyst solution prepared as in Section 3.3.1 and was stirred under an argon atmosphere for 53 h. After this time > 95% of the starting material was found to be converted to bis(*trans*-3-phenyl-2-propen-1-oxy)silacyclopentane. $^1H$ NMR; 7.3–7.0 (m, $-C_6H_5$ 10H), 6.65 (bd, $^3J_{H-H} = 15.8$ Hz [trans vinyl], $\text{-OCH}_2\text{CH=C}H\text{-Ph}$, 2H), 6.3–6.2 (dt, $^3J_{H-H}$ = 15.8 Hz [trans vinyl], $^3J_{H-H}$ = 5.2 Hz, $\text{-OCH}_2\text{C}H\text{=CH-Ph}$, 2H), 4.40–4.36 (dd, $^3J_{H-H}$ = 5.4 Hz, $\text{-OC}H_2\text{CH=CH-Ph}$, 4H), 1.7–1.55 (bm, $\text{=SiCH}_2\text{-CH}_2\text{C}H_2\text{CH}_2$, 4H), 0.85–0.6 (bm, $\text{-SiCH}_2\text{CH}_2\text{CH}_2\text{-CH}_2$, 4H) ppm.

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