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# Titanocene-catalyzed formation of allylsilanes from allyl ethers and chlorosilanes

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**Abstract**—A new method for silylation of allyl ethers with chlorosilanes has been developed by the use of $Cp_2TiCl_2$ as a catalyst. This reaction proceeds efficiently at −20 °C in THF using $^n$BuMgCl. A plausible reaction pathway via allyltitanocene intermediate was proposed.

## 1. Introduction

Allyl alcohols and their derivatives are useful synthetic intermediates as readily available reagents for introduction of allylic moieties into organic molecules.[1] There have been developed a number of catalytic reactions employing late transition metals[2] that allowed the use of a varied of allyl alcohol derivatives such as allyl ethers, acetates, carbonates, sulfonates, etc. As for early transition metal catalysts, it is known that Zr[3] and Ti[4] complexes catalyze carbon–carbon bond forming reaction of allyl ethers with ethyl Grignard reagent, however, allyl ethers are still rarely used. We have recently established new methods for regioselective silylation of alkenes and 1,3-butadienes with chlorosilanes by the combined use of Grignard reagents and titanocene[5] or zirconocene[6] catalyst. Here we disclose the transformation of allyl ethers and a thioether to the corresponding allylsilanes by the aid of titanocene catalyst using chlorosilanes and $^n$BuMgCl.

For example, to a THF solution of phenyl allyl ether (1 mmol), $^n$Pr$_3$SiCl (2.0 mmol), and $^n$BuMgCl (2.5 mmol) was added a catalytic amount of $Cp_2TiCl_2$ (0.05 mmol) at −20 °C. After stirring for 15 h, the reaction was quenched with $H_2O$. NMR analysis of the crude mixture indicated the formation of allyltripropylsilane (**1**) in 98% yield along with 94% yield of PhOSi$^n$Pr$_3$ (**2**) (Fig. 1). The product was obtained in pure form in 94% yield by HPLC.

When the reaction was carried out at 0 or 25 °C, the yields of **1** decreased in 68% or 35%, respectively. The use of EtMgCl instead of $^n$BuMgCl resulted in poor yield (28%)[7] and no reaction took place with $^t$BuMgBr or PhMgCl. When Ti(O$^i$Pr)$_4$ was used instead of $Cp_2TiCl_2$, only a 10% yield of **1** was obtained. $Cp_2ZrCl_2$ was ineffective under the same conditions.

Results obtained using some other allyl ethers and chlorosilanes are shown in Table 1. Alkyl and silyl allyl ethers also afforded **1** in 71% and 78% yields, respectively (runs 1 and 2). When cinnamyl phenyl ether **5** was used, **6** was obtained regioselectively in good yield (run 3).[8] Allyl ether **7** possessing a Ph group at the β-carbon gave the corresponding allylsilane **8** in good yield (run 4). It should be noted that **6** was also formed from allyl ether **9** (run 5). The evidence that allyl ethers **5** and **9** gave the identical product **6** implies that those reactions involve the same intermediate. Two silyl groups could be

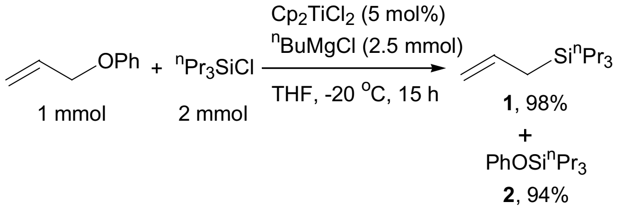

**Figure 1.** Titanocene-catalyzed formation of allylsilane.

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*Keywords*: Titanocene dichloride; Grignard reagent; Allyl ether; Chlorosilane; Allylsilane.

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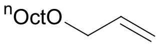
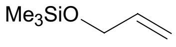
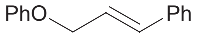
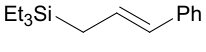
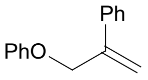
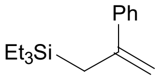
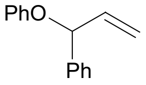
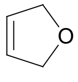
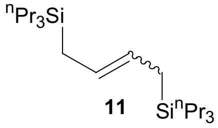
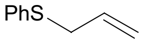
**Table 1.** Titanocene-catalyzed formation of allylsilane[a]

| Run | Substant | R in $R_3Si–Cl$ | Product | Yield (%)[b] |
|---|---|---|---|---|
| 1 |  **3** | $^n$Pr | **1** | 71 |
| 2 |  **4** | $^n$Pr | **1** | 78 |
| 3 |  **5** | Et |  **6** | 87 (83) |
| 4 |  **7** | Et |  **8** | 82 (78) |
| 5 |  **9** | Et | **6** | 94 (85) |
| 6 |  **10** | $^n$Pr |  **11** | 45 (42) [$E/Z = 78/22$] |
| 7 |  **12** | $^n$Pr | **1** | 79 |

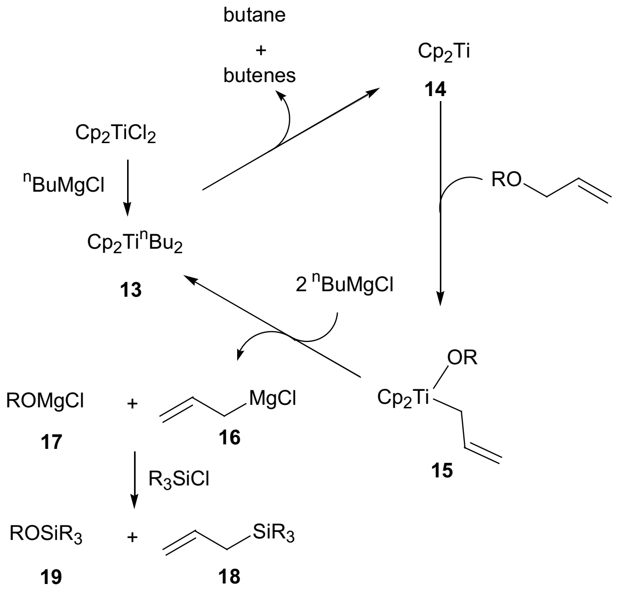
[a] Allyl ether (1.0 mmol), chlorosilane (2.0 mmol), $^n$BuMgCl (2.5 mmol), $Cp_2TiCl_2$ (0.05 mmol), −20 °C, 15 h.

[b] NMR yield. Isolated yield is given in parentheses.

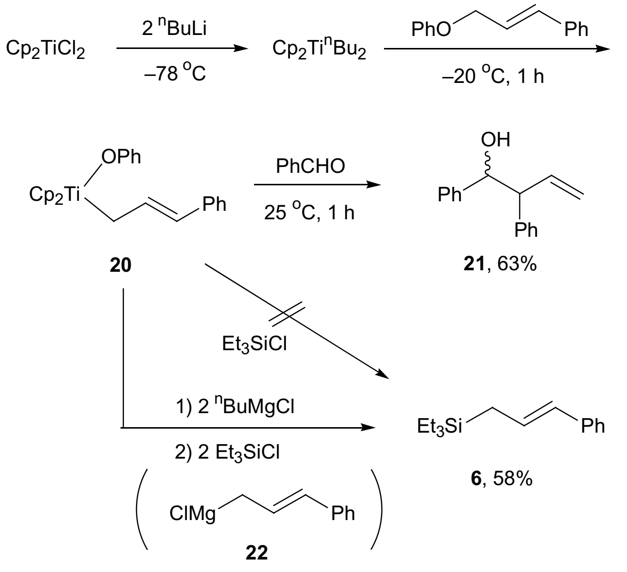
introduced at terminal carbons of the 2-butene skeleton of 2,5-dihydrofuran (**10**) (run 6). Phenylthio group could also be replaced with a silyl group to give allylsilane in 79% yield (run 7).

A plausible reaction pathway of this reaction is outlined in Scheme 1. Titanocene dichloride reacts with 2 equiv of $^n$BuMgCl at low temperatures to generate dibutyltitanocene (**13**),[9] which readily decomposes to Ti(II) complex **14** along with butane and butenes.[9b] Thus formed **14** reacts with allyl ether to afford allyltitanocene complex **15**.[10] Subsequent transmetallation of **15** with 2 equiv of $^n$BuMgCl gives allyl Grignard reagent **16**[11] and alkoxymagnesium compound (**17**) along with regeneration of **13**. Then **16** and **17** react with chlorosilane to give allylsilane **18** and alkoxysilane **19**, respectively.

In order to confirm the validity of the proposed pathway, we carried out several control experiments focusing on the active species of the C–Si bond forming process. Since it is known that $(^iPrO)_2Ti(II)$ reacts with allyl ethers to form $(^iPrO)_2TiOR(allyl)$, which react with aldehydes to give homoallyl alcohols,[10] we first examined whether a similar allyltitanocene(IV) complex can be



**Scheme 1.** A plausible reaction pathway.



**Scheme 2.** Transmetallation of allyltitanocene.

formed in our reaction system. To a THF solution of $Cp_2Ti(II)$, generated by the reaction of $Cp_2TiCl_2$ with 2 equiv of $^n$BuLi,[9] was added a stoichiometric amount of cinnamyl phenyl ether **5** at −20 °C. After stirring for 1 h benzaldehyde (1.5 equiv) was added and the solution was stirred for another 1 h at 25 °C. NMR and GC analysis indicated the formation of homoallyl alcohol in 63% yield suggesting that **20** was generated. However, similar reaction using $Et_3SiCl$ (2 equiv) instead of PhCHO under the identical conditions did not afford the expected product **6**. On the other hand, **6** was obtained in 58% yield when a reaction was performed in the presence of $^n$BuMgCl (2 equiv). These results suggest that allyltitanocene(IV) species (**20**) is generated in this reaction system but inert toward chlorosilanes and that **6** is obtained by the reaction of chlorosilane with **22** formed by transmetallation of **20** with $^n$BuMgCl (Scheme 2).[12]

In summary, a new method for preparation of allylsilanes from allyl ethers and chlorosilanes has been developed by the aid of a titanocene catalyst. The present reaction involves (i) oxidative addition of allyl ethers to $Cp_2Ti(II)$, (ii) transmetallation of allyltitanocenes with $^n$BuMgCl to afford allyl Grignard reagents, and (iii) electrophilic trapping of allyl Grignard reagents with chlorosilanes in the carbon–silicon bond forming step. There are many catalytic reactions using allyl ethers as precursors of allyl anions or their synthetic equivalents. In these reactions, the late transition metals have been employed.[2b,13] The present study provides the first example of this type catalyzed by early transition metals.

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