# Pd-catalyzed Coupling Reaction of Allyl and Propargyl Ethers with Chlorosilanes

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Pd-catalyzed synthesis of allylsilanes from chlorosilanes and allyl ethers is described. The reaction proceeds efficiently at room temperature by the use of phenyl or vinyl Grignard reagent in the presence of palladium catalysts. The present method can also be applied to synthesis of propargylsilanes by the use of propargyl ethers.

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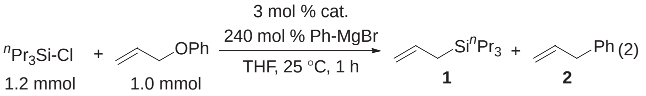
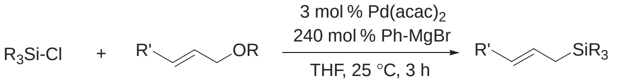
Allyl alcohols and their derivatives are useful synthetic intermediates as the versatile sources of allylic carbon units in organic synthesis. There have been developed a number of allylation reactions using allyl alcohol derivatives such as allyl ethers, acetates, carbonates, sulfonates, etc. by the aid of transition-metal catalysts.[1] We have recently developed a new method for allylation of chlorosilanes or alkyl halides with allyl ethers by the aid of $NiCl_2$ as a catalyst in the presence of vinyl Grignard reagents.[2] Here, we disclose that Pd also catalyzes reaction of chlorosilanes with allyl ethers to give allylsilanes under mild conditions in the presence of phenyl or vinyl Grignard reagents by choosing appropriate ligands (eq 1).

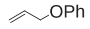
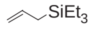
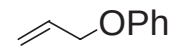
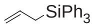
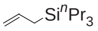
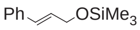
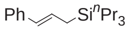
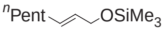
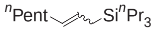
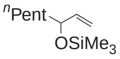
For example, chlorotripropylsilane reacted with allyl phenyl ether in the presence of PhMgBr and a catalytic amount of $Pd(acac)_2$ in THF at 25 °C for 1 h to give allyltripropylsilane **1** in quantitative yield (eq 2). In this reaction, only a trace amount of allylbenzene (<1%) was formed. $Pd(dba)_2$ and $PdCl_2(PPh_3)_2$ also afforded **1** in high yields. When $PdCl_2(dppf)$ was used, however, **1** was obtained in only a 3% yield and conventional cross-coupling between allyl ether and PhMgBr took place preferentially to form allylbenzene **2** in 70% yield.[3] It should be noted that Ni complexes, either $Ni(acac)_2$ or $NiCl_2(PPh_3)_2$, afforded **2** exclusively. In the $Pd(acac)_2$ system, vinyl Grignard reagent also promoted silylation to give **1** quantitatively (>98%). On the other hand, *n*-butyl Grignard reagent gave 42% yield of **1**.



| cat. | GC yield (%) 1 | 2 |
|---|---|---|
| $Pd(acac)_2$ | >98% | <1% |
| $Pd(dba)_2$ | 92% | 3% |
| $PdCl_2(PPh_3)_2$ | 94% | 6% |
| $PdCl_2(dppf)$ | 3% | 70% |
| $Ni(acac)_2$ | <1% | 91% |
| $NiCl_2(PPh_3)_2$ | <1% | 96% |

**Table 1.** Preparation of allylsilanes from allyl ethers[a]

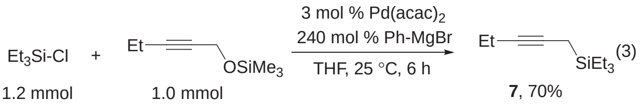


| Entry | $R_3Si$-Cl | R'~OR | Product | Yield[b]/% | [E/Z][d] |
|---|---|---|---|---|---|
| 1 | $Et_3Si$-Cl |  |  **3** | 88 | |
| 2 | $Ph_3Si$-Cl |  |  **4** | 97 | |
| 3 | $^nPr_3Si$-Cl |  |  **1** | 86 | |
| 4 | $^nPr_3Si$-Cl |  |  **5** | 96[c] | 100/0 |
| 5 | $^nPr_3Si$-Cl |  |  **6** | 76 | 76/24 |
| 6 | $^nPr_3Si$-Cl |  |  **6** | 75 | 76/24 |

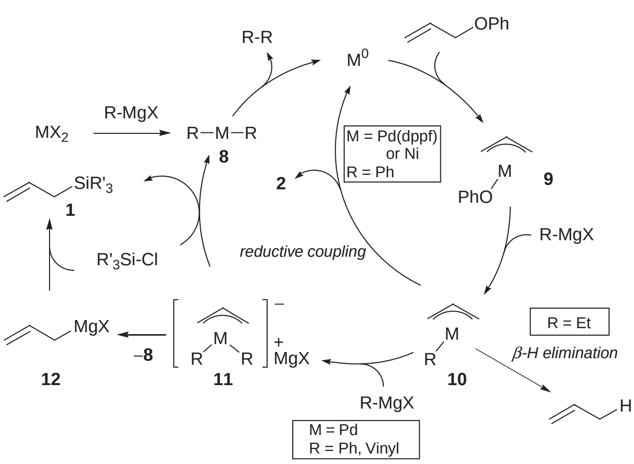
[a]Chlorosilane (1.2 mmol), allyl ether (1 mmol), $Pd(acac)_2$ (0.03 mmol), PhMgBr (2.4 mmol), THF, 25 °C, 3 h. [b]GC yield. [c]NMR yield. [d]Determined by NMR.

Results obtained using some other chlorosilanes and allyl ethers are shown in Table 1. $Et_3SiCl$ and $Ph_3SiCl$ can be employed to afford **3** and **4** in 88 and 97% yield, respectively (Entries 1 and 2). Allyl trimethylsilyl ether, easily available from the corresponding allyl alcohol, gave an allylsilane **1** in 86% yield (Entry 3). When (*E*)-cinnamyloxytrimethylsilane was used, (*E*)-cinnamylsilane **5** was obtained as a sole product (Entry 4). An allyl ether having a pentyl substituent at the $\gamma$-carbon [E/Z = 100/0] afforded the corresponding allylsilane **6** in 76% yield as a 76:24 mixture of E/Z isomers without the formation of its regioisomer (Entry 5). It should be noted that **6** was also formed from $\alpha$-pentyl-substitued allyl ether in the same regio- and stereoselectivities as Entry 5 (Entry 6), suggesting that these two reactions proceed via the same intermediate.

We next applied this procedure to propargylation of chlorosilanes. Under similar conditions as those of eq 2, reaction of $Et_3Si$–Cl with propargyl trimethylsilyl ether afforded expected propargyl silane **7** in 70% yield (eq 3).



A plausible reaction pathway is outlined in Scheme 1. $Pd(acac)_2$ is reduced by RMgX to afford $Pd^0$ via **8** (R = Ph) with the concomitant formation of biphenyl. Thus, formed $Pd^0$ undergoes oxidative addition toward allyl ether to afford ($\pi$-allyl)palladium complex **9**. Subsequent reaction of **9** with 2

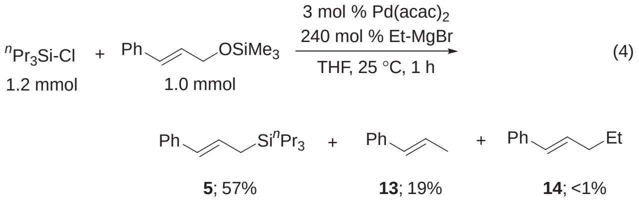


**Scheme 1.** A plausible reaction pathways.

equivalents of RMgX via ($\pi$-allyl)palladium complex **10** gives anionic ($\pi$-allyl)palladium complex **11**,[4] which react with chlorosilanes to afford **1** and $R_2Pd$ **8**. As an alternative pathway, free allyl Grignard reagent **12** formed from **11** may also react with chlorosilanes to give allylsilanes.

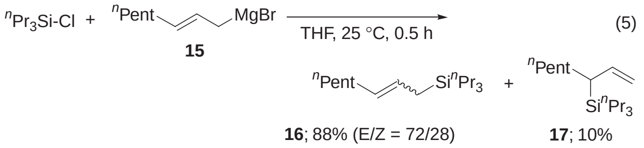
Interesting results of eq 1 that different products were obtained by changing the catalyst can be explained as follows. When $PdCl_2(dppf)$[5] and Ni complexes[6] are used instead of $Pd(acac)_2$, the reductive coupling of **10** leading to allylbenzene **2** predominates over the formation of **11** via **10**.

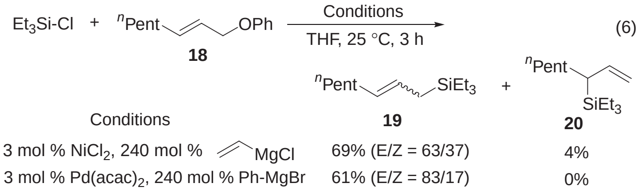
When ethylmagnesium chloride (R = Et) is employed, $\beta$-hydrogen elimination from **10** may compete with the silylation processes. In fact, a reaction of $Pr_3SiCl$ with cinnamyl trimethylsilyl ether in the presence of EtMgBr afforded 1-propenylbenzene **13** as a by-product in 19% yield along with 57% of allylsilane **5** and a trace amount of **14** (eq 4), however, **13** was not formed when PhMgBr was used (Table 1, Entry 4).



In order to shed light on an active intermediate that reacts with chlorosilanes, we compared regioselectivities of the present reaction with these of direct reaction of chlorosilane with an allyl Grignard reagent. When ($E$)-oct-2-enylmagnesium bromide **15**, generated from Rieke magnesium and the corresponding allyl ether,[7] was allowed to react with $^{n}Pr_3SiCl$, regioisomers **16** and **17** were obtained in 88 and 10% yields within 30 min, respectively (eq 5).[8] This is in large contrast to the fact that a single regioisomer **16** was obtained exclusively as shown in Table 1, Entry 5.

When we carried out the reaction of $Et_3SiCl$ with $\gamma$-pentyl-substitued allyl ether **18** in the presence of 3 mol % of $NiCl_2$ and 240 mol % of $CH_2{=}CHMgCl$, regioisomers **19** and **20** were obtained in 69 and 4% yields, respectively. On the other hand, no evidence for the formation of **20** was detected in the palladium-catalyzed system (eq 6). These results suggest that free allyl Grignard reagents may not be formed in the present reaction system.





In conclusion, carbon–silicon bond-forming reaction between allyl ethers and chlorosilanes can be achieved successfully by the combined use of Pd catalysts, such as $Pd(acac)_2$, $Pd(dba)_2$, or $PdCl_2(PPh_3)_2$, and phenyl or vinyl Grignard reagents. This reaction competes with reduction of allyl ethers when EtMgBr was employed and suppressed when Ni complexes on $PdCl_2(dppf)$ were used.

This study was supported by Industrial Technology Research Grant Program in 2006 from New Energy and Industrial Technolgy Development Organization (NEDO).

## References and Notes

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8 It is also known that crotyl Grignard reagent reacts with $Me_3SiCl$ giving rise to a mixture of (but-2-enyl)trimethylsilane and (1-methyl-2-propenyl)trimethylsilane, see: A. Hosomi, H. Iguchi, H. Sakurai, *Chem. Lett.* **1982**, 223.