Novel Nickel-Catalyzed Coupling Reaction of Allyl Ethers with Chlorosilanes, Alkyl Tosylates, or Alkyl Halides Promoted by Vinyl-Grignard Reagent Leading to Allylsilanes or Alkenes

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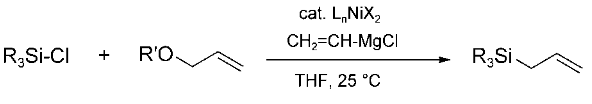
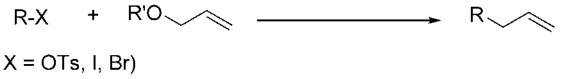
Abstract: A new method for a carbon-silicon or carbon-carbon bond forming reaction between allyl ethers and chlorosilanes, alkyl tosylates, or alkyl halides giving rise to allylsilanes or alkenes has been developed. This reaction proceeds efficiently at ambient temperature by the combined use of nickel catalysts and a vinyl-Grignard reagent. A possible reaction pathway involving the formation of allyl-Grignard reagents *via* transmetallation of π-allyl-nickel complexes with the vinyl-Grignard reagent and subsequent trapping of the thus formed allyl-Grignard reagents with electrophiles is proposed.

Keywords: alkyl tosylates; allyl ethers; carbon-carbon bond formation; carbon-silicon bond formation; chlorosilanes; Grignard reagents; nickel

Allyl ethers have been widely utilized as versatile sources of allylic carbon units in organic synthesis. A number of allylation reactions have been developed using allyl ethers catalyzed by transition metals, where palladium complexes are employed in many of these cases.[1,2] We have recently developed C–C[3] and C–Si[4] bond-forming reactions using alkyl halides and chlorosilanes, respectively, towards organometallic reagents or dienes by the combined use of nickel catalysts and Grignard reagents. During the course of these studies, we have found that Ni catalyzes the coupling reaction of allyl ethers with chlorosilanes,[5] alkyl tosylates, or alkyl halides under mild conditions in the presence of a vinyl-Grignard reagent, Eqs. (1) and (2).

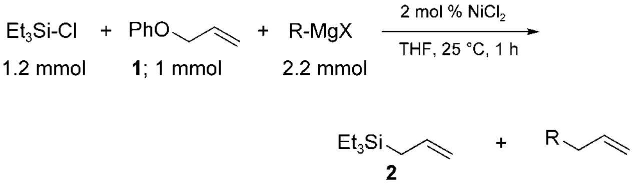


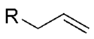
(1)



(2)

For example, chlorotriethylsilane reacted with allyl phenyl ether **1** in the presence of CH_2=CH-MgCl and a catalytic amount of $NiCl_2$ in THF at 25 °C for 1 h to give allyltriethylsilane **2** in quantitative yield based on the allyl ether **1**, Eq. (3), run 1. In this reaction, only a trace amount of $Et_3SiCH=CH_2$ (< 2%) was formed, probably through the direct reaction of Et_3SiCl with CH_2=CH-MgCl. Interestingly, when PhMgBr was used instead of CH_2=CH-MgCl, **2** was not obtained at all, but conventional cross-coupling of allyl phenyl ether with PhMgBr took place exclusively to give allylbenzene **3** in 86% yield,[6] Eq. (3), run 2. *n*-BuMgCl afforded only a 13% yield of **2** along with a trace amount of cross-coupling product **4** , Eq. (3), run 3. Under the identical conditions as run 1 in Eq. (3), $Ni(acac)_2$, $Ni(COD)_2$, and $NiCl_2(PPh_3)_2$ also afforded **2** quantitatively. When $NiCl_2$(dppp), $PdCl_2$, and Cp_2TiCl_2[7] were used, **2** was obtained in 61%, 39%, and 9% yields, respectively.



run	R-MgX	GC yield [%]	
		2	
1	CH_2=CH-MgCl	>99%	0%
2	Ph-MgBr	0%	**3**; 86%
3	*n*-Bu-MgCl	13%	**4**; <1%

(3)

In Table 1 are summarized the results of the Ni-catalyzed coupling reaction of allyl ethers with chlorosilanes using CH_2=CH-MgCl. It is noteworthy that allyl trime-

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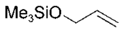
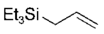
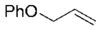
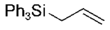
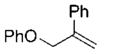
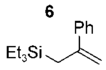
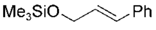
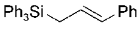
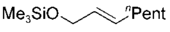
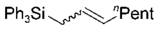
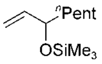
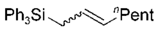
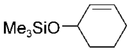
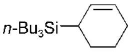
Table 1. Ni-catalyzed coupling reaction of allyl ethers with chlorosilanes using CH_2=CH-MgCl.[a]

Entry	R_3Si-Cl	Allyl ether	Product	Yield [%][b]	[*E*/*Z*][c]
1	Et_3Si-Cl	 **5**	 **2**	>99[d]	
2	Ph_3Si-Cl	 **1**	 **6**	89 (86)	
3	Et_3Si-Cl	 **7**	 **8**	77 (65)	
4[e]	Ph_3Si-Cl	 **9**	 **10**	97 (90)	100/0
5[e]	Ph_3Si-Cl	 **11**	 **12**	70	77/23
6[e]	Ph_3Si-Cl	 **13**	 **12**	81 (71)	77/23
7[e,f]	*n*-Bu_3Si-Cl	 **14**	 **15**	67 (55)	

[a] **Conditions:** R_3SiCl (1.2 mmol), allyl ether (1 mmol), CH_2=CH-MgCl (2.2 mmol), 2 mol % of $NiCl_2$, THF, 25 °C, 1 h.

[b] NMR yield. The isolated yield is given in parentheses.

[c] Determined by NMR and GC.

[d] GC yield.

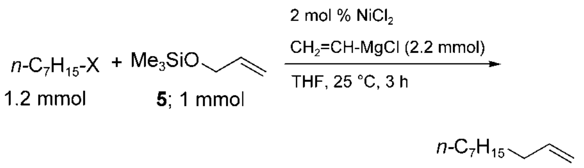
[e] 3 h.

[f] 5 mol % of $NiCl_2$ and 2 mmol of the chlorosilane were used.

thylsilyl ether **5**, easily available from the corresponding allyl alcohol, gave the allylsilane **2** in an excellent yield (entry 1). Ph_3SiCl can be employed as the silylating reagent to afford **6** in 89% yield (entry 2). Allyl ether **7** possessing a Ph group at the β-carbon gave the corresponding allylsilane **8** in 77% yield (entry 3). When (*E*)-cinnamyl trimethylsilyl ether **9** was used, (*E*)-cinnamylsilane **10** was obtained as the sole product without the formation of its regioisomer (entry 4). An allyl ether having an alkyl substituent at the γ-carbon **11** [*E*/*Z* = 100/0] afforded the corresponding allylsilane **12** in 70% yield as a 77:23 mixture of *E*/*Z* isomers (entry 5). It should be noted that the corresponding α-substituted allyl ether **13** also formed **12** (entry 6) with the same regio- and stereoselectivities as entry 5, indicating that these reaction proceed *via* the same intermediate. 2-Cyclohexenyl trimethylsilyl ether reacted with *n*-Bu_3SiCl to give the corresponding allylsilane **15** in 67% yield (entry 7).

When alkyl tosylates were used instead of chlorosilanes, the C–C bond forming reaction took place. *n*-Heptyl tosylate reacted with **5** under similar conditions as run 1 in Eq. (3) giving rise to 1-decene **16** in 78% yield, Eq. (4), run 1. *n*-Heptyl iodide and bromide also gave **16** in moderate yields, Eq. (4), runs 2 and 3, whereas the reaction of *n*-heptyl chloride was sluggish, Eq. (4), run 4.

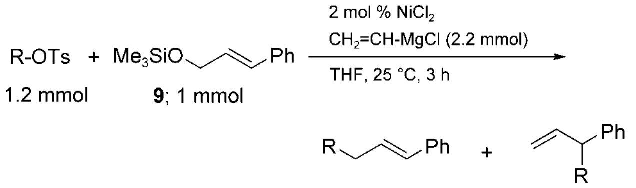
In contrast to the case of silylation reaction shown in run 4 of Table 1, alkylation of cinnamyl trimethylsilyl ether **9** with *n*-butyl tosylate took place preferentially at the benzylic carbon to yield **18** in 63% yield along with the formation of **17** as the minor product, Eq. (5). Under the same conditions, secondary alkyl tosylates can also undergo the present coupling efficiently to give a mixture of regioisomers **19** and **20** in 5% and 80% yields, respectively, Eq. (5).



16

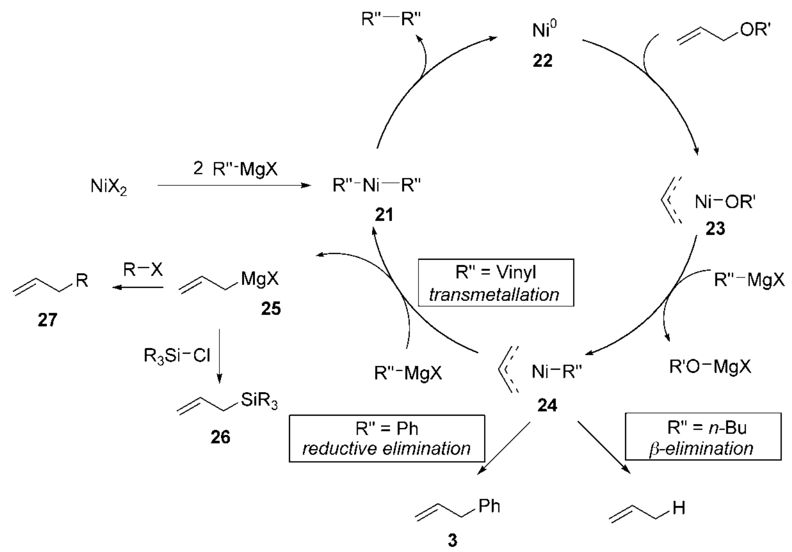
(4)

run	X	GC Yield of **16** [%]
1	OTs	78
2	I	59
3	Br	62
4	Cl	1



R = *n*-Bu	**17**; 7%	**18**; 63%
R = *s*-Bu	**19**; 5%	**20**; 80%

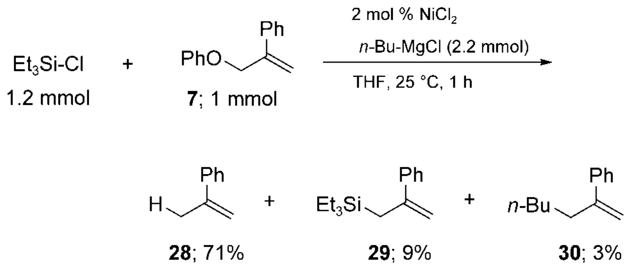
(5)



Scheme 1. A plausible reaction pathway. The other ligands are omitted for the sake of clarity.

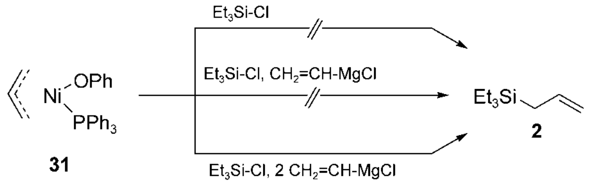
A plausible reaction pathway of this reaction is outlined in Scheme 1. NiX_2 is reduced by CH_2=CH-MgCl to afford Ni^0 *via* **21** (R″ = vinyl) with the concomitant formation of 1,3-butadiene.[8] The thus formed Ni^0 undergoes oxidative addition towards the allyl ether to afford the π-allylnickel complex **23**.[9] Subsequent transmetallation of **23** with 2 equivalents of CH_2=CH-MgCl gives the allyl-Grignard reagent **25** along with the generation of R''_2Ni **21** *via* the π-allyl(vinyl)nickel complex **24**. Then **25** reacts with electrophiles to give **26** or **27**.

The interesting result shown in Eq. (3) that different products were obtained by changing the Grignard reagents can be explained as follows. When a vinyl-Grignard reagent is used, transmetallation of **24** to give **25** predominates over the reductive elimination leading to 1,5-pentadiene. On the other hand, when R″ = phenyl, **24** might be prone to undergo reductive elimination[6] rather than transmetallation with PhMgBr [Eq. (3), run 2]. When R″ = *n*-Bu, *β*-hydrogen elimination[10] from **24** might take place. In fact, the reaction of Et_3SiCl with **7** in the presence of *n*-BuMgCl afforded isopropenylbenzene **28** as a major product along with 9% of allylsilane **29** and 3% of cross-coupling product **30**, Eq. (6).

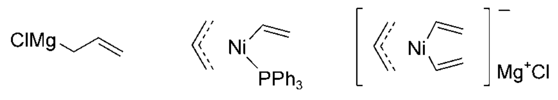


(6)

We carried out the following control experiments to examine the validity of this reaction pathway. Firstly, π-allylnickel complex **31** (corresponding to **23** in Scheme 1) was prepared by the reported procedure[9c] and its reactivity towards chlorosilanes was examined. To a THF solution of **31** was added Et_3SiCl (2.0 equivs.) and stirred at 25 °C for 1 h. The GC analysis of the reaction mixture indicated no evidence for the formation of allylsilane **2**. Then we added Et_3SiCl (2.0 equivs.) into a mixture of equimolar amounts of **31** and CH_2=CH-MgCl and the solution was stirred for 1 h, however **2** was not formed again. On the other hand, when 2 equivalents of CH_2=CH-MgCl were used, **2** was obtained in 31% yield, Eq. (7). These results may be explained by assuming that π-allylnickel complex **31** and **32** are inert towards chlorosilanes and that **2** is obtained by the reaction of Et_3SiCl with allyl-Grignard reagent **25** (X = Cl) generated by transmetallation of **32** with another molecule of CH_2=CH-MgCl *via* **33**. Although the possibility that nickelate complex **33** reacts directly with chlorosilane cannot be ruled out, the following evidence supports that transmetallation does proceed under the same conditions as a catalytic system.

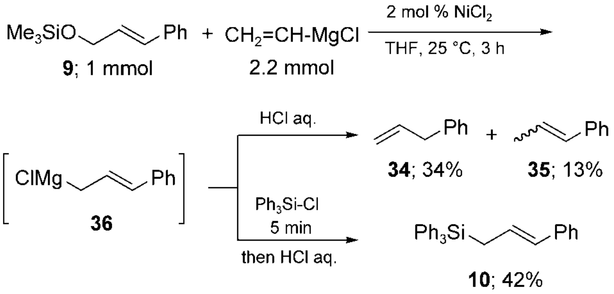


(7)



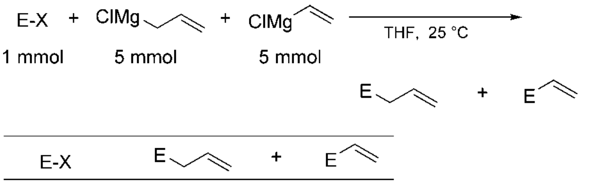
25 (X = Cl) **32** **33**

The reaction of **9** (1 mmol) with CH_2=CH-MgCl (2.2 mmol) in the presence of $NiCl_2$ (0.02 mmol) was conducted at 25 °C for 3 h in the absence of chlorosilane and then the reaction was quenched with aqueous HCl (1 N). GC analysis of the mixture indicated the formation of allylbenzene **34** and β-methylstyrene **35** in 34% and 13% yields, respectively, Eq. (8). When Ph_3SiCl was added to the reaction mixture and stirred for 5 min before addition of aqueous HCl (1 N), **10** was obtained in 42% yield along with trace amounts of **34** (2%) and **35** (3%). These results suggested that allyl-Grignard reagents **36** were formed from allyl ethers and CH_2=CH-MgCl in the presence of Ni.



(8)

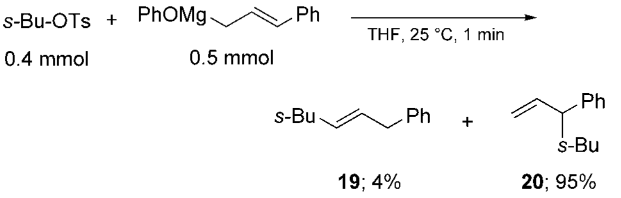
We also examined the reactivities of Grignard reagents towards chlorosilane and alkyl tosylate. To a mixture of CH_2=$CHCH_2$-MgCl (5 mmol) and CH_2=CH-MgCl (5 mmol) in THF (7.5 mL) was added Et_3SiCl (1 mmol) at 25 °C, and the reaction mixture was stirred for 1 min. After quenching the reaction mixture with aqueous HCl (1 N), the GC analysis of the resulting mixture indicated that allylsilane **2** was formed quantitatively while vinylsilane was not detected at all, Eq. (9). When *n*-octyl tosylate was used instead of Et_3SiCl, 1-undecene was also obtained quantitatively as a sole product although a longer reaction time was required. These results indicate that electrophiles react with the allyl-Grignard reagent exclusively even in the presence of a vinyl-Grignard reagent.



E-X		
Et_3Si-Cl	>99% (1 min)	0%
n-Oct-OTs	7% (1 min)	0%
	89% (30 min)	0%
	>99% (1 h)	0%

(9)

We next examined the regioselectivity of the reaction of *s*-butyl tosylate with cinnamyl-Grignard reagent, generated from Rieke magnesium and cinnamyl phenyl ether,[11] and found that **19** and **20** were obtained in 4% and 95% within 1 min, respectively, Eq. (10). This product ratio of **19** with **20** was similar to the result of Eq. (5) supporting that free cinnamyl-Grignard reagent is formed in the present Ni-catalyzed coupling reaction.



(10)

An alternative catalytic pathway involving oxidative cycloaddition of 1,3-butadiene to Ni(0) leading to a bis(π-allyl)Ni complex[3] as a catalytic intermediate might be possible since 1,3-butadiene is accumulated as the reaction proceeds following Scheme 1. In order to examine its influence, the reaction depicted in run 1 of Eq. (3) was carried out in the presence of 1,3-butadiene (400 mol % based on allyl ether **1**), however the reaction rate was not affected even at the early stage of the reaction. This may imply that 1,3-butadiene is not involved in this catalytic reaction.

In conclusion, we have developed a Ni-catalyzed coupling reaction of allyl ethers with chlorosilanes, alkyl tosylates, and alkyl halides. The present reaction would involve formation of allyl-Grignard reagents from allyl ethers and vinyl-Grignard reagents by the aid of Ni catalysts and subsequent electrophilic trapping with R_3Si-Cl or R-X to accomplish C–Si or C–C bond formation.

Although a number of Pd-catalyzed reactions have been developed to convert allyl alcohols and ethers to allyl-metal species employing different reducing agents (Zn,[2] $SnCl_2$,[2] SmI_2,[2] InI,[12] Et_2Zn[2] and Et_3B[13]), in many of these cases the resulting alkyl-metal species were trapped with carbonyl compounds as electrophiles.[14,15] The present Ni-catalyzed reaction is unique in the sense that chlorosilanes and alkyl halides or tosylates can be employed as the electrophiles and would provide a new method for the generation of allyl-Grignard reagents. Mechanistic details including the specific features of the vinyl-Grignard reagent are currently under investigation.

Experimental Section

Allyltriphenylsilane (6)

To a mixture of allyl phenyl ether **1** (132 mg, 1.0 mmol), chlorotriphenylsilane (356 mg, 1.2 mmol), and a catalytic amount of $NiCl_2$ (2.6 mg, 0.020 mmol) was added a THF solution of CH_2=CH-MgCl (1.0 M, 2.2 mL, 2.2 mmol) at 25 °C under nitrogen. After stirring the mixture for 1 h, 1 N aqueous HCl (*ca.* 1 mL) was added to the solution. Saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with diethyl ether (10 mL), dried over $MgSO_4$, and the extract evaporated to give a pale yellow crude product (89% NMR yield). Purification by recrystallization from hexane afforded **6**; yield: 254 mg (86%); mp 89–90 °C; IR (KBr): $\nu = 3059, 3045, 3007, 2991, 1427, 1111, 1102, 731, 707\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53-7.51$ (m, 6H), 7.43–7.33 (m, 9H), 5.87 (ddt, $J = 17.2, 10.0, 8.0$ Hz, 1H), 4.94 (d, $J = 17.2$ Hz, 1H), 4.88 (d, $J = 10.0$ Hz, 1H), 2.40 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.6$, 134.4, 133.6, 129.4, 127.6, 114.9, 21.3; MS (EI): *m/z* (relative intensity, %) = 300 (M^+, 0.2), 259 (100), 181 (11), 155 (3), 105 (7); HRMS: calcd. for $C_{21}H_{20}Si$: 300.1334; found: 300.1315; anal. calcd. for $C_{21}H_{20}Si$: C 83.94, H 6.71; found: C 83.75, H 6.62.

(*E*)-Cinnamyltriphenylsilane (10)

To a mixture of 3-phenylallyloxytrimethylsilane **9** (196 mg, 1.0 mmol), chlorotriphenylsilane (361 mg, 1.2 mmol), and a catalytic amount of $NiCl_2$ (2.7 mg, 0.021 mmol) was added a THF solution of $CH_2{=}CH\text{-}MgCl$ (1.1 M, 1.9 mL, 2.1 mmol) at 25 °C under nitrogen. After stirring the mixture for 3 h, 1 N aqueous HCl (*ca.* 1 mL) was added to the solution. Saturated aqueous NH_4Cl solution (10 mL) was added, and the product was extracted with ether (10 mL). The organic layer was dried over $MgSO_4$, and evaporated to give a pale yellow crude product (97% NMR yield). Purification by HPLC with $CHCl_3$ as an eluent afforded **10**; yield: 322 mg (90%); mp 93–94 °C; IR (KBr): $\nu = 3071, 3023, 1428, 1112, 968, 850, 732, 700, 522, 488, 418, 402\ cm^{-1}$; ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.55-7.08$ (m, 20H), 6.28–6.23 (m, 2H), 2.56–2.50 (br d-like m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.0$, 135.6, 134.2, 130.2, 129.4, 128.2, 127.7, 126.3, 126.0, 125.5, 20.6; MS (EI): *m/z* (relative intensity, %) = 376 (M^+, 2), 259 (100), 181 (9), 155 (3), 105 (5); HRMS: calcd. for $C_{27}H_{24}Si$: 376.1647; found: 376.1638; anal. calcd. for $C_{27}H_{24}Si$: C 86.12, H 6.42; found: C 86.04, H 6.40.

1-Decene (16)

To a mixture of allyloxytrimethylsilane **5** (118 mg, 0.9 mmol), *n*-heptyl tosylate (295 mg, 1.1 mmol), and a catalytic amount of $NiCl_2$ (2.4 mg, 0.019 mmol) was added a THF solution of $CH_2{=}CH\text{-}MgCl$ (1.3 M, 1.7 mL, 2.2 mmol) at 25 °C under nitrogen. The reaction was quenched by 1 N aqueous HCl and the organic layer was analyzed by GC using octane as an internal standard to show the formation of 1-dodecene **16** in 78% yield. The structure of **16** was confirmed by comparison with an authentic sample using GC and GC-MS.

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