Copper-Catalyzed Arylation of Chlorosilanes with Grignard Reagents

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Nucleophilic substitution reactions of chlorosilanes with aryl Grignard reagents take place efficiently in the presence of copper(I) iodide to afford tetraorganosilanes.

The reactions of chlorotriorganosilanes with organomagnesium reagents that yield tetraorganosilanes are generally slow despite the seeming simplicity.[1] We have reported that silver(I) nitrate and zinc chloride are efficient catalysts for the reaction of chlorosilanes with organomagnesium reagents.[2] We wish to report herein that copper(I) iodide is also effective for the reaction.[3]

The reactions of chlorodimethylphenylsilane (**1a**) with arylmagnesium bromides are summarized in Table 1. Treatment of **1a** with *p*-methylphenylmagnesium bromide in the presence of 5 mol % of copper(I) iodide in THF at 20 °C for 2 h afforded the corresponding tetraorganosilane **2a** in 81% yield (Table 1, Entry 1). Electron-rich arylmagnesium reagents reacted with **1a** smoothly (Entries 3 and 4). Electron-deficient *m*-trifluoromethylphenylmagnesium bromide required a prolonged reaction time due to the low nucleophilicity (Entry 6). The methyl group of the *o*-methylphenylmagnesium bromide did not retard the reaction (Entry 7). 1-Trimethylsilylethenyl-magnesium bromide as well as arylmagnesium bromide participated in the reaction (Entry 8). In the absence of copper(I) iodide, the reactions with electron-rich arylmagnesium reagents proceeded moderately (Entries 3 and 4). Without copper(I) iodide, electronically neutral, electron-deficient, and sterically demanding Grignard reagents reacted sluggishly (Entries 1, 2, and 5–8).
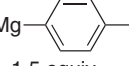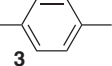
The scope of chlorosilanes is shown in Table 2. Although no arylation took place in the reactions of chloromethyldiphenyl-silane (**1b**) and chlorotriethylsilane (**1c**) in the absence of copper(I) iodide, addition of copper(I) iodide dramatically improved the yields (Entries 1 and 2). The effect of copper(I) iodide was not drastic in the reaction of allylchlorodimethyl-silane (**1d**) (Entry 3) probably because of small allyl and methyl groups. Surprisingly, the reaction of chlorodiphenyl-vinylsilane (**1e**) proceeded smoothly in the absence as well as

Table 1. Scope of Grignard Reagents

$$Me_2PhSi{-}Cl \xrightarrow[\text{THF, 20 °C}]{\substack{\text{5 mol\% CuI} \\ \text{1.5 equiv BrMg{-}Ar}}} Me_2PhSi{-}Ar$$

Entry	Ar	Time/h	2	Yield/%[a]
1	*p*-MeC$_6$H$_4$	2	**2a**	81 (13)
2	2-Naphthyl	0.5	**2b**	84 (3)
3	*p*-MeOC$_6$H$_4$	3	**2c**	81 (33)
4	*p*-(*i*-Pr$_3$SiO)C$_6$H$_4$	3	**2d**	87 (48)
5	*p*-FC$_6$H$_4$	3	**2e**	98 (9)
6	*m*-CF$_3$C$_6$H$_4$	50	**2f**	80 (21)
7	*o*-MeC$_6$H$_4$	3	**2g**	81 (0)
8	[CH$_2$=C(SiMe$_3$)]	18.5	**2h**	76 (0)

a) Isolated yield. Yields obtained in the absence of CuI are in parentheses.

Table 2. Scope of Chlorosilanes

$$Si{-}Cl + BrMg{-}\!\!\!\bigcirc\!\!\!{-}CH_3 \xrightarrow[\text{THF, 20 °C, 3 h}]{\text{5 mol\% CuI}} Si{-}\!\!\!\bigcirc\!\!\!{-}CH_3$$
1   1.5 equiv   **3**

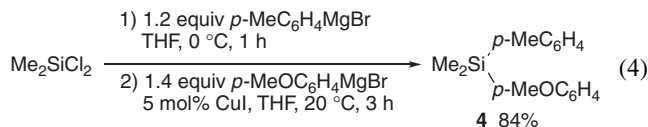| Entry	*Si*	3	Yield/%[a]
1[b]	MePh$_2$Si (**1b**)	**3b**	76 (0)
2	Et$_3$Si (**1c**)	**3c**	75 (0)
3	(CH$_2$=CHCH$_2$)Me$_2$Si (**1d**)	**3d**	70 (43)
4	(CH$_2$=CH)Ph$_2$Si (**1e**)	**3e**	85 (65)
5	(ClCH$_2$)Me$_2$Si (**1f**)	**3f**	81 (31)
6[c]	(ClCH$_2$)Me$_2$Si (**1f**)	**3f**	91 (69)
7	*i*-Pr$_3$Si (**1g**)	**3g**	0

a) Isolated yield. Yields obtained in the absence of CuI are in parentheses. b) Performed for 2 h. c) Performed for 0.5 h at reflux.

presence of the catalyst, in spite of the bulky nature of the silyl group (Entry 4). Arylation of chloro(chloromethyl)dimethyl-silane (**1f**) proceeded on silicon without loss of the chloro-methyl moiety, even at an elevated temperature (Entries 5 and 6). Bulky chlorotriisopropylsilane (**1g**) resisted the reaction (Entry 7).
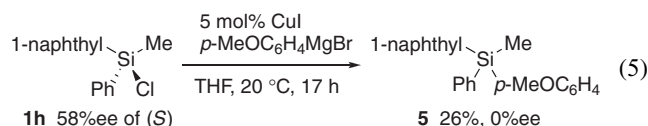
Unfortunately, the dramatic effect of copper(I) iodide in the arylation was not applicable to reactions with other Grignard reagents. An attempt to benzylate *t*-butylchlorodi-methylsilane failed, and no benzylation took place (eq 1). An attempted synthesis of allyltriisopropylsilane led to a moderate yield (eq 2). The reaction of chloromethyldiphenylsilane with butylmagnesium bromide yielded the corresponding product in 44% yield irrespective of the presence or absence of copper(I) iodide (eq 3).

$$t\text{-BuMe}_2\text{SiCl} + BrMg\!\!\diagup\!\!\diagup Ph \xrightarrow[\text{THF, 20 °C, 5 h}]{\text{5 mol\% CuI}} t\text{-BuMe}_2\text{Si}\!\!\diagup\!\!\diagup Ph \quad (1)$$
1.5 equiv   0%

$$i\text{-Pr}_3\text{SiCl} + BrMg\!\!\diagup\!\!\diagdown \xrightarrow[\text{THF, 20 °C, 5 h}]{\text{5 mol\% CuI}} i\text{-Pr}_3\text{Si}\!\!\diagup\!\!\diagdown \quad (2)$$
1.5 equiv   36%

$$Ph_2MeSiCl + BuMgBr \xrightarrow[\text{THF, 20 °C, 5 h}]{\text{(5 mol\% CuI)}} Ph_2MeSiBu \quad (3)$$
1.5 equiv   44%
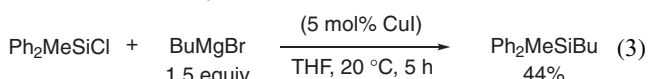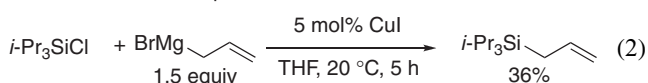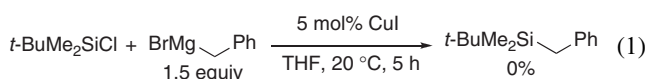
The copper-catalyzed transmetalation was applicable to the synthesis of **4** from dichlorodimethylsilane by sequential arylation (eq 4). The first arylation proceeded without copper(I) iodide. Copper(I) iodide and the second arylmagnesium reagent were then added in the same pot to yield **4** in excellent yield. The absence of copper(I) iodide for the second arylation significantly decreased the yield of **4** (<30%).

$$Me_2SiCl_2 \xrightarrow[\substack{2) \ 1.4 \ equiv \ p\text{-}MeOC_6H_4MgBr \\ 5 \ mol\% \ CuI, \ THF, \ 20\,°C, \ 3\,h}]{\substack{1) \ 1.2 \ equiv \ p\text{-}MeC_6H_4MgBr \\ THF, \ 0\,°C, \ 1\,h}} Me_2Si\substack{\nearrow p\text{-}MeC_6H_4 \\ \searrow p\text{-}MeOC_6H_4} \quad (4)$$

4 84%

The silver-catalyzed reaction of optically enriched chlorosilane **1h** resulted in the loss of chirality.[2a] This was also the case for the copper catalysis (eq 5).

$$\substack{1\text{-}naphthyl \\ Ph} Si \substack{\nearrow Me \\ \searrow Cl} \xrightarrow[\substack{THF, \ 20\,°C, \ 17\,h}]{\substack{5 \ mol\% \ CuI \\ p\text{-}MeOC_6H_4MgBr}} \substack{1\text{-}naphthyl \\ Ph} Si \substack{\nearrow Me \\ \searrow p\text{-}MeOC_6H_4} \quad (5)$$

1h 58%ee of (*S*)   **5** 26%, 0%ee

Thus, we are tempted to propose a reaction mechanism that is quite similar to the silver-catalyzed reaction[2a] (Scheme 1). Diarylcuprate[4] **6** would react with chlorosilane to form silicate **7** or **7′** bearing a Si–Cu[III] bond. Reductive elimination from **7** or **7′** would be slow enough to allow **7** or **7′** to undergo pseudorotation[5] that leads to the loss of the initial stereochemistry.[6] Reductive elimination from **7″** would then occur to yield silicate **8** and arylcopper **9**. Departure of chloride from **8** would afford tetraorganosilane. Remaining aryl Grignard reagent would convert **9** to initial cuprate **6**.

Experimental

Instrumentation and Chemicals. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were taken on a Varian Mercury 300 spectrometer and were obtained in CDCl$_3$ with tetramethylsilane as an internal standard. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Silica gel (Wakogel 200 mesh) was used for column chromatography.

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. CuI was purchased from Wako Pure Chemicals. Arylmagnesium bromide was prepared from magnesium turnings (Nacalai Tesque, Inc.) and the corresponding bromoarene in THF. THF was purchased from Kanto Chemical Co., stored under nitrogen, and used as is. Chlorosilanes were purchased from Shin-Etsu Chemical Co., Ltd. and Tokyo Chemical Industry Co., Ltd. Optically enriched **1h** was prepared according to the literature.[7]

Typical Procedure for Copper-Catalyzed Reactions. The reaction of **1a** with *p*-methylphenylmagnesium bromide (Table 1, Entry 1) is representative. CuI (9.5 mg, 0.05 mmol) was placed in a 20-mL reaction flask under argon. Chlorodimethylphenylsilane (170 mg, 1.0 mmol) in THF (5 mL) was added to the flask. Then, *p*-methylphenylmagnesium bromide (1.0 M THF solution, 1.5 mL, 1.5 mmol) was added. The mixture was stirred at 20 °C for 2 h. A saturated aqueous solution of NH$_4$Cl (2 mL) was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na$_2$SO$_4$ and concentrated in vacuo. Chromatographic purification on silica gel by using hexane as an eluent afforded dimethyl(*p*-methylphenyl)-
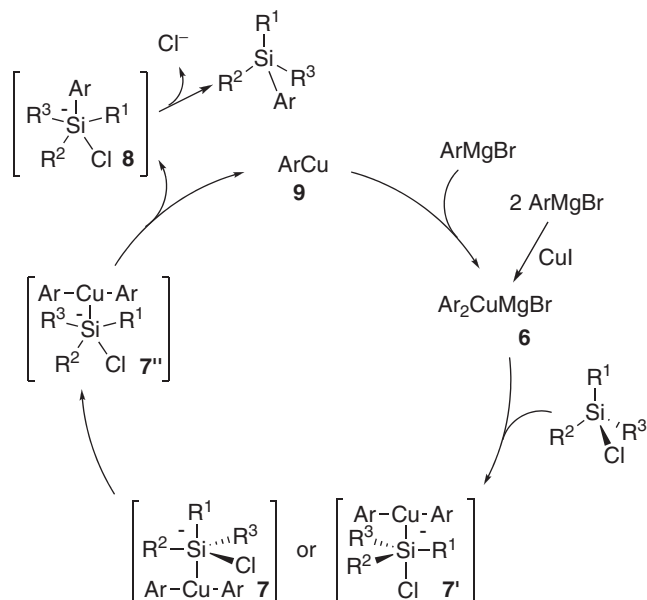
Scheme 1. Plausible reaction mechanism.

phenylsilane (**2a**, 183 mg, 0.81 mmol) in 81% yield.

Procedure for the Synthesis of Diaryldimethylsilane (eq 4). Dichlorodimethylsilane (129 mg, 1.0 mmol) was placed in a 20-mL reaction flask under argon in THF (5 mL). The flask was cooled to 0 °C. *p*-Methylphenylmagnesium bromide (1.0 M THF solution, 1.2 mL, 1.2 mmol) was slowly introduced to the flask. The reaction mixture was stirred for 1 h at 0 °C. *p*-Methoxyphenylmagnesium bromide (1.0 M THF solution, 1.4 mL, 1.4 mmol) and CuI (9.5 mg, 0.05 mmol) were sequentially added at 20 °C. The mixture was stirred for 3 h at 20 °C. A saturated aqueous solution of NH$_4$Cl (2 mL) was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na$_2$SO$_4$ and concentrated in vacuo. Silica gel column purification with hexane/ethyl acetate = 50:1 afforded (*p*-methoxyphenyl)dimethyl(*p*-methylphenyl)silane (**4**, 214 mg, 0.84 mmol) in 84% yield.

Characterization of Products. All the products showed spectra identical with those reported in the literature.[2a]

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