DOI: 10.1002/anie.200801949

Organosilver Reagents

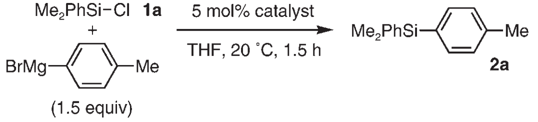
Silver-Catalyzed Transmetalation between Chlorosilanes and Aryl and Alkenyl Grignard Reagents for the Synthesis of Tetraorganosilanes**

Kei Murakami, Koji Hirano, Hideki Yorimitsu, and Koichiro Oshima**

The nucleophilic substitution reaction of chlorosilanes with organometallic reagents is a fundamental method used for forming carbon–silicon bonds.[1] The reactions of chlorotriorganosilanes with organolithium reagents generally proceed smoothly at low temperatures (−78 °C). On the other hand, reactions with the less reactive, yet readily available, organomagnesium reagents often require prolonged reaction times and high temperatures (solvent b.p.), and result in moderate yields of tetraorganosilanes.[2] Herein we report that silver salts can catalyze the reactions of chlorotriorganosilanes with organomagnesium reagents to yield a variety of tetraorganosilanes efficiently; this reveals a new aspect of silver catalysis.[3–5]

Treatment of chlorodimethylphenylsilane (**1a**) with *p*-tolylmagnesium bromide in the presence of a catalytic amount of silver nitrate in THF at 20 °C for 1.5 h provided the corresponding tetraorganosilane **2a** in 93 % yield (Table 1, entry 2).[6] The transformation is regarded as a silver-catalyzed transmetalation reaction between chlorosilane and the Grignard reagent. Notably, **2a** was obtained in only 13 % yield in the absence of silver nitrate (Table 1, entry 1). Other silver salts, such as silver halides, acetate, and triflate, accelerated the carbon–silicon bond formation (Table 1, entries 3–7). Other Group 11 metal halides, such as copper(I) bromide and gold(I) chloride, also promoted the reaction with only slightly lower efficiency (Table 1, entries 8 and 9). Nickel and palladium salts failed to catalyze the reaction (Table 1, entries 10 and 11).

Table 1: Metal-catalyzed reaction of chlorodimethylphenylsilane with *p*-tolylmagnesium bromide.

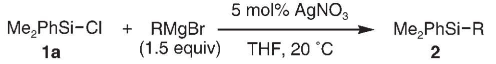


Entry	Catalyst	Yield [%][a]	Entry	Catalyst	Yield [%][a]
1	none	13	7	AgOTf	83
2	$AgNO_3$	93 (92)[b]	8	CuBr	75
3	AgCl	86	9	AuCl	78
4	AgBr	91	10	$NiCl_2$	24
5	AgI	86	11	$Pd(OAc)_2$	9
6	AgOAc	91			

[a] Yield was determined by ^{1}H NMR spectroscopy. [b] Yield of isolated product. Tf = trifluoromethanesulfonyl.

The Grignard reagent scope was studied and the results are summarized in Table 2.[7] The reactions with 2-naphthyl, *p*-fluorophenyl, *p*-methoxyphenyl, and *p*-(triisopropylsiloxy)phenyl Grignard reagents (Table 2, entries 1–4) proceeded as smoothly as those described in Table 1. Sterically hindered *o*-tolylmagnesium bromide was less reactive, and a prolonged reaction time was essential for the reaction to proceed to completion (Table 2, entry 5). An aryl Grignard reagent having an electron-withdrawing trifluoromethyl group reacted with chlorosilane **1a** slowly in the presence of silver nitrate (Table 2, entry 6). A bulky alkenylmagnesium reagent also participated in the reaction (Table 2, entry 7).[8] Unfortunately, attempts to introduce an alkyl group failed because of the instability of the alkylsilver species (Table 2, entry 8).

Table 2: Silver-catalyzed reaction of **1a** with various Grignard reagents.



$$\underset{\mathbf{1a}}{Me_2PhSi{-}Cl} + \underset{(1.5\ \text{equiv})}{RMgBr} \xrightarrow[\text{THF, 20 °C}]{5\ \text{mol\% } AgNO_3} \underset{\mathbf{2}}{Me_2PhSi{-}R}$$

Entry	R	*t* [h]	Product	Yield [%][a]
1	2-naphthyl	1.5	**2b**	71
2	*p*-FC_6H_4	1.5	**2c**	92
3	*p*-$MeOC_6H_4$	1.5	**2d**	97
4	*p*-($i$$Pr_3SiO$)$C_6H_4$	1.5	**2e**	96
5	*o*-MeC_6H_4	24	**2f**	88
6	*m*-$CF_3C_6H_4$	20	**2g**	80
7	$CH_2{=}C(SiMe_3)$	4.5	**2h**	78
8	*i*Pr	1.5	**2i**	0

[a] Yield of isolated product.

The reactions of bulkier chloromethyldiphenylsilane and chlorotriethylsilane with *p*-tolylmagnesium bromide under silver catalysis proceeded to completion after extended reaction times (Table 3, entries 1 and 2). Chlorosilanes having an olefinic moiety (Table 3, entries 3 and 4) or a chloromethyl moiety (Table 3, entry 5) reacted without any observable side reactions. Notably, the reaction could be performed on a scale as large as 50 mmol (with respect to **1f**). Sterically congested chlorotriisopropylsilane failed to react (Table 3, entry 6).

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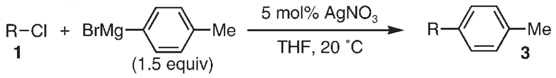
[*] K. Murakami, Dr. K. Hirano, Dr. H. Yorimitsu, Prof. Dr. K. Oshima
Department of Material Chemistry
Graduate School of Engineering, Kyoto University
Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto 615-8510 (Japan)
Fax: (+81) 75-383-2438
E-mail: yori@orgrxn.mbox.media.kyoto-u.ac.jp
oshima@orgrxn.mbox.media.kyoto-u.ac.jp

[**] This work was supported by Grants-in-Aid for Scientific Research from MEXT and JSPS. K.H. acknowledge JSPS for financial support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.200801949.

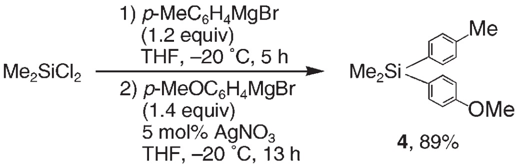
Table 3: Scope of chlorosilanes.



Entry	Chlorosilane, R	t [h]	Product	Yield [%]
1	**1b**, $MePh_2Si$	10	**3a**	87
2	**1c**, Et_3Si	9.5	**3b**	73
3	**1d**, $(CH_2{=}CHCH_2)Me_2Si$	11	**3c**	80
4	**1e**, $(CH_2{=}CH)Ph_2Si$	18	**3d**	74
5	**1f**, $(ClCH_2)Me_2Si$	3	**3e**[a]	74 (79)[b]
6	**1g**, $i\text{Pr}_3Si$	10	**3f**	trace

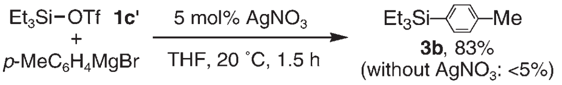
[a] PhMgBr was used instead of *p*-tolylmagnesium bromide. [b] 50 mmol scale.

We were also able to introduce two different aryl groups onto dichlorodimethylsilane in a one-pot process [Eq. (1)]. The first arylation proceeded in the absence of the silver catalyst; silver nitrate was then added along with the second Grignard reagent to yield **4** in excellent yield.



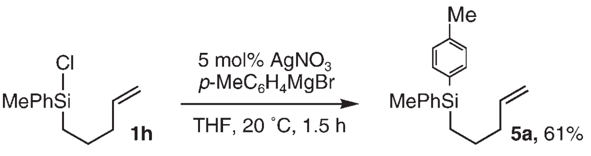
(1)

The silver-catalyzed reaction was highly effective, not only for chlorosilanes but also for the reaction of silyl triflate **1c′** [Eq. (2)]. This result suggests that silver nitrate does not serve to capture the chloride ion of **1** by precipitation of silver chloride.

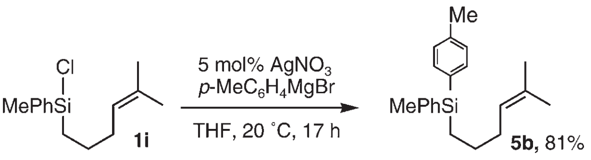


(2)

Given that the reaction mechanism would involve a silicon-centered radical intermediate or a silyl cation species, 5-*exo* or 6-*endo* cyclization might occur in the silver-catalyzed reactions of **1h** and **1i** [Eq. (3) and (4)]. However, the reactions resulted in simple arylation, and no cyclized products were observed.

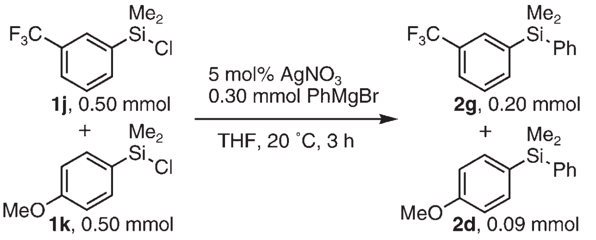


(3)



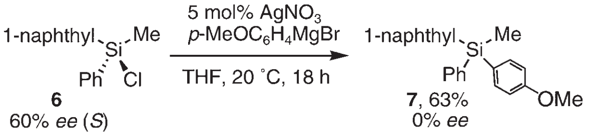
(4)

Treatment of a mixture of **1j** and **1k** with an aryl Grignard reagent under silver catalysis resulted in the predominant formation of **2g**, which is derived from **1j** [Eq. (5)]. The electron density of the silicon atom of **1j** is likely to be lower than that of **1k**. The resulting substituent effect for the aryl group of **1j** and **1k** can thus eliminate the possibility of the formation of a silyl cation or cationlike intermediate.



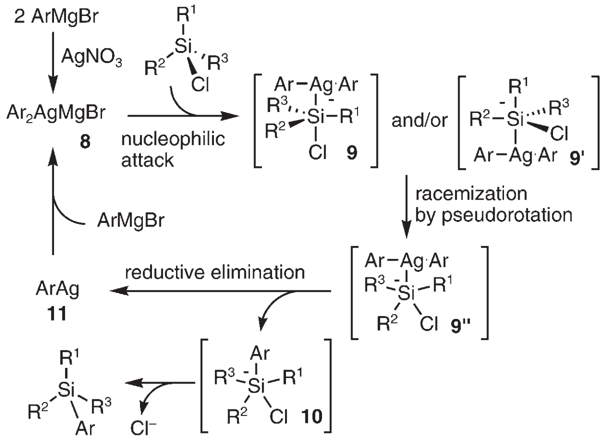
(5)

Generally, uncatalyzed nucleophilic substitution reactions of chlorosilanes proceed with either retention or inversion of configuration.[9] However, the silver-catalyzed reaction of chiral compound **6**[10] (60 % *ee*, *S* configuration) provided the corresponding product **7** in racemic form [Eq. (6)]. Such racemization upon nucleophilic substitution of chlorosilanes is rarely reported.



(6)

Based on our results [Eqs. (2)–(6)], we propose the reaction mechanism depicted in Scheme 1. Initially, diarylargentate species **8** would be generated in situ,[11] followed by nucleophilic attack of the argentate complex upon the chlorosilane to afford silicate **9** or **9′** bearing a Si–Ag^{III} bond.[12] Reductive elimination from **9** or **9′** would be



Scheme 1. A proposed mechanism. Intermediates **9″** and **10** should have trigonal-bipyramidal structures, although the position of each substituent is not clear.

slow[12] and **9** or **9′** could undergo pseudorotation,[9] resulting in the loss of the initial stereochemistry. After the scrambling, reductive elimination from **9″** would occur to afford silicate **10** with concomitant formation of arylsilver **11**. Silicate **10** would liberate a chloride ion to afford the product. By the action of the aryl Grignard reagent, **11** would be converted into the initial argentate **8**.

In summary, the protocol described here provides a mild and efficient method for the preparation of tetraorganosilanes, and will be applicable to the synthesis of organosilicon reagents and organosilicon-based advanced materials. There are many effective reactions that employ combinations of organomagnesium reagents and copper catalysts. On the other hand, little is known about the useful reactivity of organomagnesium reagents using silver catalysis.[4a,5] The present reaction will open up new possibilities for silver-catalyzed reactions with organometallic reagents.

Experimental Section

Typical procedure for silver-catalyzed reactions: Chlorodimethylphenylsilane (**1a**, 85 mg, 0.50 mmol) in THF (5 mL) was added to $AgNO_3$ (4.2 mg, 0.025 mmol) under argon, followed by 4-methylphenylmagnesium bromide (1.0 M solution in THF, 0.75 mL, 0.75 mmol). The reaction mixture was stirred at 20°C for 1.5 h before a saturated aqueous solution of NH_4Cl (2 mL) was added. The mixture was extracted with ethyl acetate and the combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. Purification of the residue by column chromatography on silica gel (*n*-hexane) afforded dimethyl(4-methylphenyl)phenylsilane (**2a**, 104 mg, 0.46 mmol) in 92% yield (Table 1, entry 2).

Received: April 25, 2008

Keywords: nucleophilic substitution · organomagnesium reagents · silanes · silver

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