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Rhodium-catalyzed silylation of *ortho*-functionalized aryl halides with hydrosilanes

Yoshinori Yamanoi* and Hiroshi Nishihara*

Department of Chemistry, School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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Abstract—The silylation of *ortho*-functionalized aryl iodide with trialkylsilanes in the presence of $RhCl(CO)(PPh_3)_2$ or $[Rh(cod)_2]BF_4$ and K_3PO_4 provides the corresponding arylalkylsilane in good to high yield. This catalytic system showed a dramatically different activity when $Pd(t\text{-}Bu_3P)_2$ was used as a catalyst.

Transition-metal-catalyzed cross-coupling reactions have become an important method for carbon–heteroatom bond formation.[1] Especially, silicon–aryl carbon bond formation has experienced a significant development, because arylsilanes are important intermediates in modern organic synthesis.[2] Traditionally, their preparation has been accomplished by the treatment of Grignard or organolithium reagents with silicon compounds having good leaving groups such as halogen or alkoxy groups.[3] The drawback of this methodology is the limited number of substrates available. Another method is the catalytic conversion of C–H bonds to C–Si bonds in the presence of transition-metal complexes.[4,5] Although the silylation of aromatic C–H bonds is one of the most straightforward and atom economical routes to arylsilane derivatives, the reaction is a little problematic with regard to the control of selectivity due to the drastic conditions required (high temperature, long reaction time, and so on).

On the other hand, Murata et al.,[6] Deshong et al.,[7] Denmark and Kallemeyn,[8] and Komuro et al.[9] independently reported on the transition-metal-catalyzed coupling reaction of aryl halides with trialkoxysilanes.[10] However, trialkylsilanes (e.g., Et_3SiH) were not suitable as silylating reagents for their catalytic system.[11] Until recently, trialkylsilanes were known to efficiently afford the reduction of aryl halides to C–H bond in the presence of a transition-metal catalyst (Eq. 1).[12,13] Kunai and Ishikawa have reported that the reaction of dialkylsilane with alkyl iodide brought out the formation of a Si–C bond (as a byproduct of the major C–H bond), indicating the potential use of hydrosilanes as silylating reagents in the presence of a palladium catalyst.[14] During the course of our studies, we have developed the $Pd(t\text{-}Bu_3P)_2$-catalyzed[15] silylation of *para*- and *meta*-functionalized aryl halides with trialkylsilanes in the presence of K_3PO_4 (Eq. 2).[16] Quite recently, similar observations have been made by Alami and co-workers using platinum oxide[17] and by Murata et al. using $Pd_2(dba)_3/P(o\text{-tol})_3$.[18] However, the trialkylsilylations of *ortho*-substituted aryl halides have been difficult even under these catalytic systems, because the reduction of the carbon–halide bond dominantly took place with *ortho*-substituted aryl halide. This decrease in reactivity can be attributed to a steric hindrance caused by the occupation of the *ortho* position (Eq. 3). To overcome this limitation, we herein report a convenient route to the preparation of *ortho*-functionalized aryltrialkylsilanes by rhodium-catalyzed silylation of *ortho*-functionalized aryl halides.

Our initial efforts were directed toward finding suitable reaction conditions using 2-iodoanisole as a model substrate. The results are listed in Table 1. As we had reported previously, $Pd(t\text{-}Bu_3P)_2$-catalyzed silylation of *ortho*-substituted aryl iodide gave a poor yield of silylated product, due to a strong tendency to produce hydrogenated product (entry 1).[16] In the light of this result, a number of transition-metal catalysts using NMP as the solvent and K_3PO_4 as the base were examined. The rhodium catalytic system is a preferred catalyst

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* Corresponding authors. Tel.: +81 3 5841 4346; fax: +81 3 5841 8063. e-mail addresses: yamanoi@chem.s.u-tokyo.ac.jp; nisihara@chem.s.u-tokyo.ac.jp

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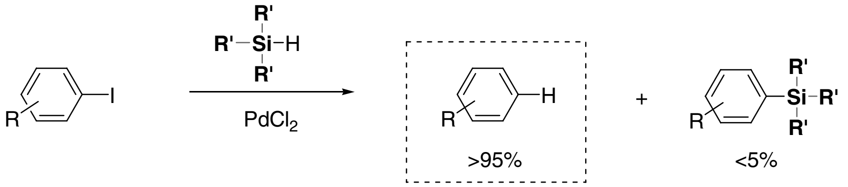
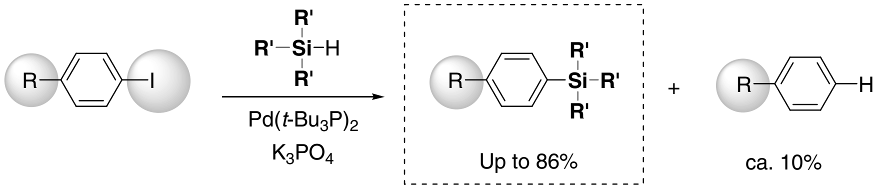


(1)



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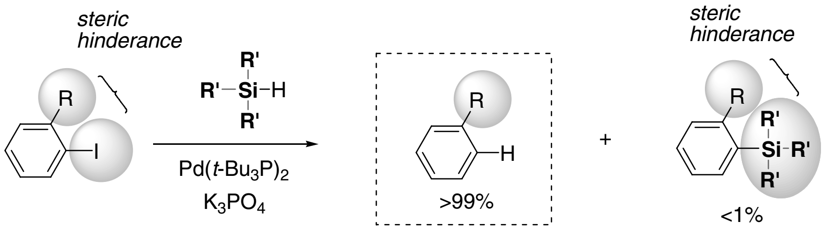
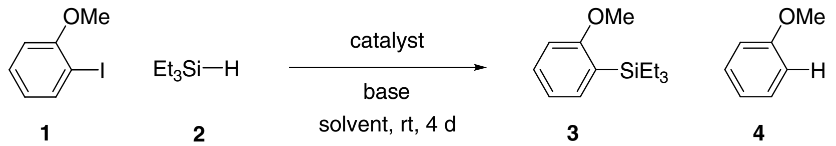


(3)

for the silylation reaction of sterically hindered aryl iodide compared to other transition metal catalytic systems (entries 1–4 vs 6–8).[19] Among the transition-metal catalysts, $RhCl(CO)(PPh_3)_2$ and $[Rh(cod)_2]BF_4$ gave reasonable conversions (entries 7 and 8). The present silylation proceeded in the presence of K_3PO_4 in a manner analogous to the palladium-catalyzed reaction.[18] In the absence of a base or in the presence of other types of bases, the reactions occurred insufficiently (entries 9–11). KOAc was also found to be effective in the coupling reaction, but the use of this base significantly increased the reaction times (entry 12). Several solvents were also tested, and it was observed that the reactions in NMP afforded silylated products in acceptable yields (entries

Table 1. Reaction of 2-iodoanisole with triethylsilane under various conditions[a]



Entry	Catalyst	Base	Solvent	Ratio[b]			Yield of **3**[c] (%)
				1	3	4	
1[d]	$Pd(t\text{-}Bu_3P)_2$	K_3PO_4	NMP[e]	—[f]	<1	>99	—[g]
2	$PdCl_2(dppf)$	K_3PO_4	NMP	52	2	46	—[g]
3	$Pd(Cy_3P)_2$	K_3PO_4	NMP	57	<1	43	—[g]
4	$IrCl(CO)(PPh_3)_2$	K_3PO_4	NMP	75	—[f]	25	—[g]
5	$RhCl(PPh_3)_3$	K_3PO_4	NMP	1	2	97	—[g]
6	$[RhCl(nbd)]_2$	K_3PO_4	NMP	—[f]	41	59	32
7	$RhCl(CO)(PPh_3)_2$	K_3PO_4	NMP	—[f]	96	4	88
8	$[Rh(cod)_2]BF_4$	K_3PO_4	NMP	—[f]	96	4	91
9	$[Rh(cod)_2]BF_4$	—[h]	NMP	28	—[f]	72	—[g]
10	$[Rh(cod)_2]BF_4$	K_2CO_3	NMP	36	59	5	40
11	$[Rh(cod)_2]BF_4$	Et_3N	NMP	25	60	15	49
12	$[Rh(cod)_2]BF_4$	KOAc	NMP	2	94	4	82
13	$[Rh(cod)_2]BF_4$	K_3PO_4	THF	3	60	37	54
14	$[Rh(cod)_2]BF_4$	K_3PO_4	Toluene	61	4	35	—[g]

[a] Reaction conditions: 2-iodoanisole (0.5 mmol), triethylsilane (1.0 mmol), catalyst (0.025 mmol), base (1.5 mmol), and solvent (1.0 mL).
[b] The ratio was determined by GC analysis.
[c] Isolated yield.
[d] The reaction was carried out in the presence of 1 mol % of catalyst and completed within 5 h.
[e] NMP: N-methylpyrrolidinone.
[f] No detection.
[g] The silylated product could not be isolated by column chromatography.
[h] The reaction was carried out without base.

7 and 8). The reactions in other kinds of solvents, such as THF or toluene, resulted in quite low yields (entries 13 and 14).

To determine the scope of this reaction, a variety of *ortho*-substituted aryl halides and a range of trialkylsilanes were used as substrates in the rhodium-catalyzed silylation.[20–22] The results are summarized in Table 2. As shown in entries 1 and 2, the coupling of **1a** with triethylsilane using $RhCl(CO)(PPh_3)_2$ or $[Rh(cod)_2]BF_4$ in NMP gave the desired arylsilane **1b** in 88% or 91% along with a small amount of the reduced form as a byproduct. In the case of aryl bromide, the silylated product was obtained in a low yield after the prolongation of reaction time (entry 3). Unfortunately, aryl chloride did not show enough reactivity, and consequently the starting materials were recovered (entry 4). Similar results were observed when triethylsilane was replaced by triphenylsilane or dimethylphenylsilane (entries 5–7 and 9). It was evident that the substituents influenced the ratio of obtained products to a certain degree. Thus, although aryl iodides having an electron-donating groups were very readily silylated with hydrosilanes (entries 1–13) in amide solvents, aryl iodides having electron-withdrawing group (e.g., $-NO_2$) had a strong tendency to give competitively reduced products (entry 15). The reaction was also effective for 1-iodonaphthalene (entry 14). In addition, it was difficult to couple di-*ortho*-substituted aryl iodide with triethylsilane because of the large steric effect (entry 16).

The exact reaction mechanism is not clear at the moment. It is difficult to account for all the observed events in a single organometallic complex, and they are probably the consequences of competing processes. Unfortunately, we have no experimental evidence to explain the reaction pathway. Therefore, at present we can only speculate on the plausible intermediates involved in the process. Scheme 1 depicts a plausible mechanism of this transformation. An oxidative addition of $R_3Si–H$ to the rhodium(I) complex **A** leads to $RhH(X)(SiR_3)$ intermediate **B**.[23] After reductive elimination of HX in the presence of a base, the (trialkylsilyl)rhodium(I) **C** is formed. An oxidative addition of Ar–X leads to intermediate **D**. Finally, the reductive elimination of intermediate **D** takes place to generate the active rhodium(I) species **A** and to give the desired silylated products (Mechanism (a)). Another mechanism via higher oxidation state, rhodium(V) intermediate, is also illustrated in Scheme 1 (Mechanism (b)). As rhodium(V) oxidation state is well precedented,[24] it is difficult to rule out the following possiblity. Triethylsilane and aryl halide would oxidatively add to rhodium catalyst **A** subsequently to form organo-rhodium(V) intermediate **E**. Then, a subsequent double reductive elimination of **E** produces arylsilane and regenerates rhodium catalyst **A**. However, no definitive proof of such a species has been obtained.

In conclusion, we have studied the metal-catalyzed trialkyl silylation of *ortho*-substituted aryl iodide. The rhodium-based catalyst leads preferentially to the

Table 2. Rhodium-catalyzed silylation of *ortho*-substituted aryl halides with $R_3Si–H$[a]

$$\underset{\mathbf{1}}{\text{Ar–X}} \quad \underset{\mathbf{2}}{\text{R}_3\text{Si–H}} \xrightarrow[\text{K}_3\text{PO}_4\text{, NMP, r.t.}]{\text{Rh cat.}} \underset{\mathbf{3}}{\text{Ar–SiR}_3} \quad \underset{\mathbf{4}}{\text{Ar–H}}$$

Entry	Ar–X	R	Product	Rh catalyst[b]	Solvent[c]	Time (d)	Ratio (**3**/**4**)[d]	Yield[e] (%)
1	o-$MeOC_6H_4I$	Et_3	o-$MeOC_6H_4SiEt_3$ (**3a**)	A	NMP	4	96/4	88
2	o-$MeOC_6H_4I$	Et_3	**3a**	B	NMP	4	96/4	91
3	o-$MeOC_6H_4Br$	Et_3	**3a**	B	NMP	20	65/35	28[f]
4	o-$MeOC_6H_4Cl$	Et_3	**3a**	B	NMP	20	<1/>99	—[g]
5	o-$MeOC_6H_4I$	Ph_3	o-$MeOC_6H_4SiPh_3$ (**3b**)	A	NMP	4	>99/<1	Quant
6	o-$MeOC_6H_4I$	Ph_3	**3b**	B	NMP	4	>99/<1	Quant
7	o-$MeOC_6H_4I$	$PhMe_2$	o-$MeOC_6H_4SiMe_2Ph$ (**3c**)	A	NMP	7	85/15	69
8	o-EtC_6H_4I	Et_3	o-$EtC_6H_4SiEt_3$ (**3d**)	A	NMP	7	92/8	79
9	o-EtC_6H_4I	Ph_3	o-$EtC_6H_4SiPh_3$ (**3e**)	B	NMP	7	>99/<1	93
10	o-$^iPrC_6H_4I$	Et_3	o-$^iPrC_6H_4SiEt_3$ (**3f**)	A	DMA	7	72/28	68
11	o-$Me_2NC_6H_4I$	Et_3	o-$Me_2NC_6H_4SiEt_3$ (**3g**)	A	DMI	30	54/46	37
12	o-$MeSC_6H_4I$	Et_3	o-$MeSC_6H_4SiEt_3$ (**3h**)	A	TMU	7	>99/<1	99
13	2,4-$Me_2C_6H_3I$	Et_3	2,4-$Me_2C_6H_3SiEt_3$ (**3j**)	B	NMP	10	89/11	76
14	1-$C_{10}H_7I$	Et_3	1-$C_{10}H_7SiEt_3$ (**3i**)	A	DMA	7	91/9	89
15[h]	o-$NO_2C_6H_4I$	Et_3	—	B	NMP	10	0/100	—
16[i]	2,4,6-$Me_3C_6H_2I$	Et_3	—	B	NMP	10	0/100	—

[a] Reaction conditions: Ar–X (0.5 mmol), $R_3Si–H$ (1.0 mmol), K_3PO_4 (1.5 mmol), Rh catalyst (0.025 mmol, 5 mol %), solvent (1.0 mL).

[b] A: $RhCl(CO)(PPh_3)_2$. B: $[Rh(cod)_2]BF_4$.

[c] NMP: *N*-methylpyrrolidinone. DMI: 1,3-dimethyl-2-imidazolidinone. DMA: *N*,*N*-dimethylacetamide. TMU: tetramethylurea.

[d] The ratio was determined by GC in the crude reaction mixture.

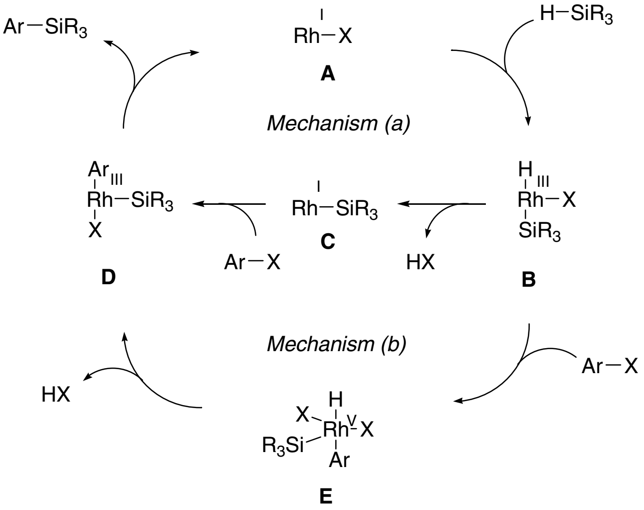
[e] Isolated yield of silylated product after column chromatography.

[f] Starting material was recovered in 7% (GC yield).

[g] Starting material was recovered in 88% (GC yield).

[h] No silylated product and no starting material were observed by GC analysis.

[i] No silylated product was obtained. GC analysis indicated a 58/42 ratio of **4**/**1**.



Scheme 1. The plausible reaction pathways.

corresponding silylated products, whereas a palladium system generally gives the hydrogenated compounds as the major products. It is also important that the complexes, $RhCl(CO)(PPh_3)_2$ and $[Rh(cod)_2]BF_4$, are commercially available, air-stable, and easily handled. The results described here should lead to new opportunities for the application of organometallic chemistry in silylation. Additional developments in this area will be reported in due course.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.08.001.

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20. *General procedure for the rhodium-catalyzed silylations of ortho-substituted aryl iodides with trialkylsilane:* An oven-dried Schlenk flask equipped with a magnetic stirring bar was charged with RhCl(CO)(PPh$_3$)$_2$ or [Rh(cod)$_2$]BF$_4$ (0.025 mmol) and K$_3$PO$_4$ (1.5 mmol) in air. Aryl iodide (0.5 mmol) and trialkylsilane (1.0 mmol) were also added at this time if they were solids. The flask was capped with a rubber septum, evacuated, and then flushed with argon. Solvent (1 mL), aryl iodide (if a liquid, 0.5 mmol), and trialkylsilane (if a liquid, 1.0 mmol) were then successively added by a syringe, and the reaction mixture was stirred at rt for several days. The reaction was quenched with water when the starting material was not observable in TLC. The aqueous layer was extracted with CH$_2$Cl$_2$ three times. The combined organic layer was washed with brine and dried over Na$_2$SO$_4$. The solvent was evaporated under reduced pressure, and column chromatography on silica gel afforded the silylated product.
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