# Arylation of Allylsilanes through Rhodium Catalysis

Haruka Omachi and Kenichiro Itami*
*Department of Chemistry, Graduate School of Science, Nagoya University, Nagoya 464-8602*
*PRESTO, Japan Science and Technology Agency, Nagoya 464-8602*

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The arylation of allylsilanes catalyzed by a rhodium complex is described. In the presence of a catalytic amount of $RhCl(CO)\{P[OCH(CF_3)_2]_3\}_2$ and $Ag_2CO_3$, allyltriisopropylsilane reacts with iodoarenes in *m*-xylene at 120 °C to furnish the corresponding C–H bond arylation products in moderate yields.

The selective transformation of ubiquitous C–H bonds not only represents an important and long-standing goal in chemistry, but also unlocks opportunities for markedly different strategies in chemical synthesis.[1] Therefore, the development of such processes has been an emerging area of extensive research. As a part of our program aimed at establishing a new biaryl coupling through C–H bond functionalization,[2–4] we recently reported that $RhCl(CO)\{P[OCH(CF_3)_2]_3\}_2$ can catalyze the C–H bond arylation of electron-rich arenes with haloarenes.[2] Although the precise mechanism remains unknown, our current approximation is shown in Figure 1. This includes (i) oxidative generation of cationic arylrhodium(III) species $ArRh^+X(L)$ by the reaction of RhX(L), ArX, and $Ag_2CO_3$, (ii) electrophilic metalation (rhodation) of arene giving diarylrhodium(III) species, and (iii) reductive elimination of biaryl product with the regeneration of RhX(L). We believe that $\pi$-acidic $P[OCH(CF_3)_2]_3$ ligand allows the key $ArRh^+X(L)$ species to be extremely electron-deficient thereby establishing a distinct nucleophile–electrophile interaction between an arene and rhodium center to promote electrophilic metalation.

On the basis of such mechanistic scenario, we surmise that a nucleophilic alkene can also be used as a nucleophilic coupling partner in this Rh-catalyzed C–H bond arylation manifold.[5] Herein we report on the C–H bond arylation of allylsilanes with iodoarenes through the agency of $Rh/P[OCH(CF_3)_2]_3/Ag_2CO_3$ system. Allylsilanes have been chosen in this study expecting the promoting effect of the $\beta$-silyl group in stabilizing the assumed carbocationic intermediate (Figure 1).[6]

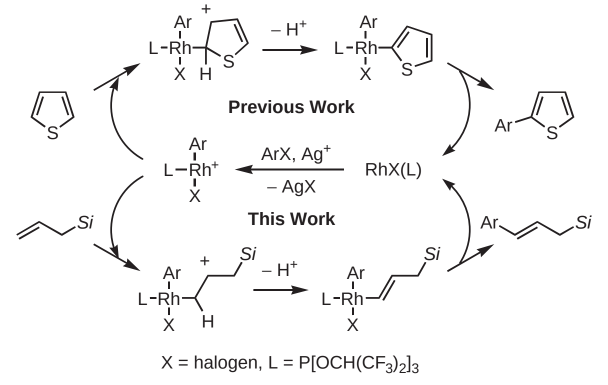
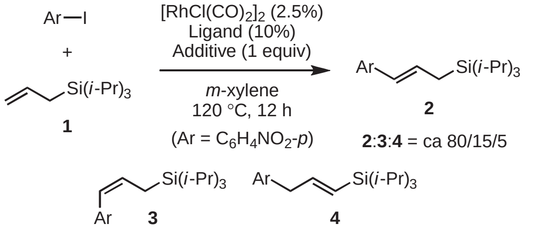


**Figure 1.** Arylation of arenes (previous work) or allylsilanes (this work) with haloarenes promoted by $Rh/P[OCH(CF_3)_2]_3/Ag_2CO_3$ system.

**Table 1.** Effect of ligand and additive[a]

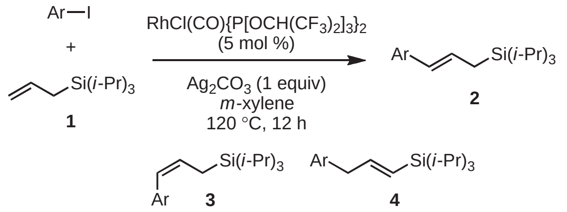


| Entry | Ligand | Additive | Yield/% (**2** + **3** + **4**) |
|---|---|---|---|
| 1[b] | $P[OCH(CF_3)_2]_3$ | $Ag_2CO_3$ | 76 |
| 2[b,c] | $P[OCH(CF_3)_2]_3$ | $Ag_2CO_3$ | 25 |
| 3 | $P[OCH(CF_3)_2]_3$ | $Ag_2CO_3$ | 20 |
| 4 | $P(OC_6H_5)_3$ | $Ag_2CO_3$ | 7 |
| 5 | $P(C_6H_5)_3$ | $Ag_2CO_3$ | 53 |
| 6 | $P(C_6H_4CF_3\text{-}p)_3$ | $Ag_2CO_3$ | 55 |
| 7 | $P(C_6F_5)_3$ | $Ag_2CO_3$ | 34 |
| 8[d] | dppe[e] | $Ag_2CO_3$ | 10 |
| 9[d] | 2,2′-bipyridyl | $Ag_2CO_3$ | <1 |
| 10[b] | $P[OCH(CF_3)_2]_3$ | AgOTf | 43 |
| 11[b] | $P[OCH(CF_3)_2]_3$ | AgOAc | 36 |
| 12[b] | $P[OCH(CF_3)_2]_3$ | $K_2CO_3$ | <1 |
| 13[b] | $P[OCH(CF_3)_2]_3$ | KO*t*-Bu | <1 |

[a]Conditions: **1** (2 equiv), $p\text{-}NO_2C_6H_4I$ (1 equiv), $[RhCl(CO)_2]_2$ (2.5 mol %), ligand (10 mol %), additive (1 equiv), *m*-xylene, 120 °C, 12 h. [b]$RhCl(CO)\{P[OCH(CF_3)_2]_3\}_2$ (5 mol %) was employed as catalyst. [c]$p\text{-}NO_2C_6H_4Br$ was employed. [d]5 mol % of ligand was employed. [e]1,2-Bis(diphenylphosphino)ethane.

In early experiments, we found that allyltriisopropylsilane (**1**) is a suitable substrate for the reaction.[7] Treatment of **1** (2 equiv), 4-nitrophenyl iodide (1 equiv), $RhCl(CO)\{P[OCH(CF_3)_2]_3\}_2$ (5 mol %) and $Ag_2CO_3$ (1 equiv) in *m*-xylene at 120 °C produced the expected C–H bond allylation product **2** (Table 1, Entry 1). Isomers such as **3** and **4** were also formed in the reaction. These isomers might be produced by abstracting the corresponding hydrogen atoms in the assumed carbocationic intermediates or by the isomerization of **2** (Figure 1). The use of 4-nitrophenyl bromide resulted in lower reaction efficiency (Entry 2). We next investigated the effects of ligand and additive in the reaction of **1** and 4-nitrophenyl iodide using $[RhCl(CO)_2]_2$ as a rhodium source. The screening of a range of ligands resulted in the finding that our original $Rh/P[OCH(CF_3)_2]_3$ is best among others (Entries 3–9). The necessity of silver-based additives is also ascertained (Entries 10–13). We believe that silver salts help generate a key cationic arylrhodium(III) species (Figure 1) by abstracting halogen from rhodium.

**Table 2.** Rh-catalyzed arylation of **1** with iodoarenes[a]



| Entry | Ar | Yield/% (**2**/**3**/**4**) |
|---|---|---|
| 1 | $C_6H_5$ | 50 (78/16/6) |
| 2 | *o*-$CH_3C_6H_4$ | 17 (65/6/29) |
| 3 | *m*-$CH_3C_6H_4$ | 54 (70/24/6) |
| 4 | *p*-$CH_3C_6H_4$ | 64 (72/14/14) |
| 5 | *p*-$CH_3OC_6H_4$ | 68 (78/13/9) |
| 6 | *m*-$NO_2C_6H_4$ | 48 (81/13/6) |
| 7 | *p*-$NO_2C_6H_4$ | 68 (82/18/0) |

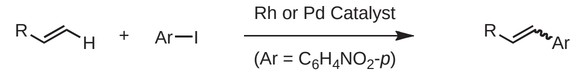
[a]Conditions: **1** (2 equiv), ArI (1 equiv), RhCl(CO){P[OCH($CF_3$)$_2$]$_3$}$_2$ (5 mol %), $Ag_2CO_3$ (1 equiv), *m*-xylene, 120 °C, 12 h.

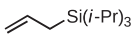
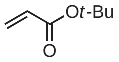
In order to roughly grasp the scope of current reactions, representative iodobenzene derivatives were subjected to the conditions established (Table 2).[8] The reactions took place with electron-neutral, -rich, and -deficient iodoarenes with reasonable efficiency. Unfortunately, ortho substitution on the benzene ring substantially decreases the yield (Entry 2).

The Mizoroki–Heck reaction represents an efficient C–H bond arylation of alkenes with haloarenes promoted by Pd catalyst and base.[9–11] A typical textbook mechanism of Mizoroki–Heck reaction includes (i) oxidative addition of ArX to Pd$^0$, (ii) carbopalladation (insertion) of the resultant ArPdX across alkene, (iii) $\beta$-hydrogen elimination, and (iv) base-mediated regeneration of Pd$^0$. This differs from our assumed carbocationic manifold, though mechanisms of Pd-catalyzed processes could vary among catalysts and alkene substrates.[9] To gain some insights into the mechanism of the Rh-catalyzed reaction, **1** and 4-nitrophenyl iodide were treated with Pd catalyst (Table 3). Under typical Mizoroki–Heck conditions [Pd(OAc)$_2$, P(*o*-Tol)$_3$, $Et_3N$, and DMF], the arylation products **2** and **3** were obtained in 48% yield with 77% stereoselectivity. The arylation reactions were also carried out with *t*-butyl acrylate, which is known to be an excellent substrate for the Mizoroki–Heck reaction under a carbometalation-based manifold. Indeed, the Pd catalyst afforded the arylation product in 86% yield with virtually complete stereoselectivity. However, under the influence of our Rh catalyst, the arylation proceeded in much lower efficiency (30%) and stereoselectivity (84% E). Although more detailed experiments are needed for elucidating the mechanism, these contrasting results clearly indicate that electrophilic Rh catalysis favors nucleophilic alkenes (allylsilanes) whereas nucleophilic Pd catalysis favors electrophilic alkenes (acrylates); the difference of Rh and Pd catalysis in the C–H bond arylation of alkenes.[10,11]

In summary, we have established a new Rh-based protocol for the C–H bond arylation of allylsilanes with iodoarenes. Although the improvement of efficiency and selectivity is necessary for this reaction to reach its full synthetic potential, the discovered reactivity might serve as a new starting point for the C–H bond functionalization of nucleophilic alkenes. Work along these lines is currently underway.

**Table 3.** Comparison of current Rh catalyst and typical Pd catalyst



| Alkene | Current Rh Cat.[a] | Typical Pd Cat.[b] |
|---|---|---|
|  | **68%**<br>(82% E) | 48%<br>(77% E) |
|  | 30%<br>(84% E) | **86%**<br>(>98% E) |

[a]RhCl(CO){P[OCH($CF_3$)$_2$]$_3$}$_2$ (5 mol %), $Ag_2CO_3$ (1 equiv), *m*-xylene, 120 °C, 12 h. [b]Pd(OAc)$_2$ (5 mol %), P(*o*-Tol)$_3$ (10 mol %), $Et_3N$ (1 equiv), DMF, 80 °C, 12 h.

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This paper is dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

## References and Notes

1 Recent reviews on catalytic C–H bond functionalization: a) F. Kakiuchi, T. Kochi, *Synthesis* **2008**, 3013. b) F. Kakiuchi, N. Chatani, *Adv. Synth. Catal.* **2003**, *345*, 1077.

2 a) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *J. Am. Chem. Soc.* **2006**, *128*, 11748. b) S. Yanagisawa, T. Sudo, R. Noyori, K. Itami, *Tetrahedron* **2008**, *64*, 6073.

3 I. Ban, T. Sudo, T. Taniguchi, K. Itami, *Org. Lett.* **2008**, *10*, 3607.

4 a) S. Yanagisawa, K. Ueda, T. Taniguchi, K. Itami, *Org. Lett.* **2008**, *10*, 4673. b) G. Deng, K. Ueda, S. Yanagisawa, K. Itami, C.-J. Li, *Chem.—Eur. J.*, in press.

5 Rh-catalyzed C–H bond arylation of alkenes: a) T. Sugihara, T. Satoh, M. Miura, M. Nomura, *Adv. Synth. Catal.* **2004**, *346*, 1765. b) A. Mori, Y. Danda, T. Fujii, K. Hirabayashi, K. Osakada, *J. Am. Chem. Soc.* **2001**, *123*, 10774.

6 I. Fleming, A. Barbero, D. Walter, *Chem. Rev.* **1997**, *97*, 2063.

7 The use of allyltrimethylsilane resulted in a complex mixture presumably due to the occurrence of competing desilylation pathways.

8 Typical procedure: A mixture of RhCl(CO){P[OCH($CF_3$)$_2$]$_3$}$_2$[2a] (25 μmol), $Ag_2CO_3$ (0.50 mmol), allyltriisopropylsilane (1.0 mmol), and *p*-nitrophenyl iodide (0.50 mmol) in dry *m*-xylene (2.0 mL) was stirred at 120 °C for 12 h under argon. After cooling to room temperature, the mixture was subjected to flash silica gel chromatography (EtOAc/hexane) to afford **2** (55%) and **3** (12%).

9 I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009.

10 Pd-catalyzed C–H bond arylation of allylsilanes: a) K. Karabelas, C. Westerlund, A. Hallberg, *J. Org. Chem.* **1985**, *50*, 3896. b) K. Olofsson, M. Larhed, A. Hallberg, *J. Org. Chem.* **1998**, *63*, 5076. c) T. Jeffery, *Tetrahedron Lett.* **2000**, *41*, 8445.

11 Under the current Rh-based conditions, other electron-rich alkenes such as vinyl ethers are not applicable. For Pd-catalyzed C–H bond arylation reaction of vinyl ethers, see Ref 9.