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Rhodium-catalyzed addition of aryldifluoromethylsilanes to *N*-sulfonylaldimines

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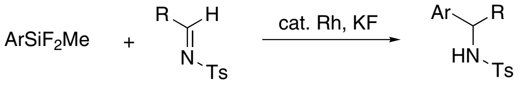
Abstract—The addition of aryldifluoromethylsilanes to *N*-sulfonylaldimines was found to be catalyzed by a rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$, in the presence of potassium fluoride to give the corresponding arylated *N*-sulfonylamines in good yield. The reaction mechanism would involve the generation of a fluoride-coordinated arylsilicate and the transmetalation between the arylsilicate and the rhodium complex to give the arylrhodium species as a key intermediate.

Transition metal-catalyzed transformations using organometallic reagents are of great importance in modern organic chemistry.[1] One of the recent topics of such transformations is the rhodium-catalyzed addition of the organometallic reagents to the carbon–heteroatom double bonds such as aldehydes or imines as well as the 1,4-addition to α,β-unsaturated carbonyl compounds.[2] These reactions commonly involve the formation organorhodium complexes as active species by the transmetalation with the organometallic reagents. In most cases, they occur chemo- and regioselectively rendering them useful in organic synthesis.

Rhodium-catalyzed addition of organometallic reagents to imines is a useful method to synthesize amines. The additions of aryl- or alkenyltin reagents,[3] arylboron reagents,[4] and alkenylzirconium reagents[5] to aldimines were reported. Organosilicon compounds are very attractive reagents due to their low cost, low toxicity, and tolerance to a variety of functional groups, however, reaction of those with aldimines has not yet been reported. We previously reported that aryldifluoromethylsilanes smoothly added to aldehydes in the presence of a catalytic amount of rhodium complex and fluoride salt, giving secondary alcohols in good yield.[6] In this letter, we report the addition of the aryldifluoromethylsilanes to *N*-sulfonylaldimines catalyzed by rhodium complexes to give arylated *N*-sulfonylamines (Eq. 1).



(1)

When the reaction of phenyldifluoromethylsilane (**1a**) with *N*-tosylbenzylideneamine (**2a**) was carried out in the presence of 2 mol% of $[Rh(cod)(MeCN)_2]BF_4$ and 3 equiv of potassium fluoride in THF at 60 °C for 20 h, *N*-tosyldiphenylmethylamine (**3a**) was obtained in a good isolated yield of 88% (Table 1, entry 1). In the reaction of **1a** with **2a**, absence of KF markedly decreased the yield to 11% (entry 2), while changing the solvent to DMF increased the yield to 99% even in the shorter reaction time of 5 h (entry 3).[7] The reaction of phenyltrimethylsilane (**1b**) and phenylfluorodimethylsilane (**1c**) in THF did not take place (entries 4 and 5), and phenyltrifluorosilane (**1d**) gave the product **3a** in a low yield of 22% (entry 6). The tendency of the reactivities of these phenylsilanes was similar to those in the reaction with aldehydes.[6]

The reactions of 2- and 4-methoxy-*N*-tosylbenzylideneamine (**2b** and **2c**) with phenyldifluoromethylsilane (**1a**) also proceeded smoothly in DMF, affording the corresponding *N*-tosyldiarylmethylamines (**3b** and **3c**) in good isolated yields of 90% and 87%, respectively

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Keywords: Arylation; Aldimines; Rhodium catalyst; Arylsilanes.

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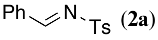
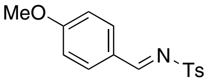
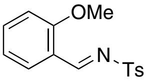
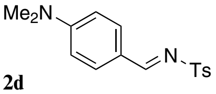
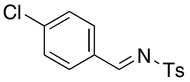
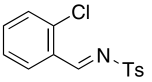
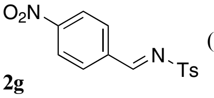
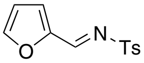
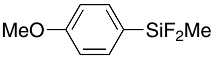
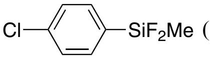
Table 1. Rhodium-catalyzed addition of arylsilanes **1** to *N*-sulfonylaldimines **2**[a]

Entry	Arylsilane **1**	Aldimine **2**	Solvent	Temp (°C)/time (h)	Product	Yield (%)[b]
1	$PhSiF_2Me$ (**1a**)	 (**2a**)	THF	60/20	**3a**	88
2[c]	**1a**	**2a**	THF	60/20	**3a**	11
3	**1a**	**2a**	DMF	60/5	**3a**	99
4	$PhSiMe_3$ (**1b**)	**2a**	THF	60/20		0
5	$PhSiFMe_2$ (**1c**)	**2a**	THF	60/20		0
6	$PhSiF_3$ (**1d**)	**2a**	THF	60/20	**3a**	22
7	**1a**	 (**2b**)	DMF	60/5	**3b**	90
8	**1a**	 (**2c**)	DMF	60/5	**3c**	87
9	**1a**	 (**2d**)	DMF	60/20	**3d**	30
10	**1a**	**2d**	THF	60/48	**3d**	66
11	**1a**	 (**2e**)	DMF	60/20	**3e**	55
12	**1a**	**2e**	THF	60/5	**3e**	96
13	**1a**	 (**2f**)	DMF	60/20	**3f**	18
14	**1a**	**2f**	THF	60/48	**3f**	42
15	**1a**	 (**2g**)	DMF	60/20	**3g**	55
16	**1a**	**2g**	THF	60/20	**3g**	93
17	**1a**	 (**2h**)	DMF	60/20	**3h**	73
18	 (**1b**)	**2a**	DMF	60/20	**3b**	98
19	 (**1c**)	**2a**	DMF	60/20	**3e**	76

[a] Common reaction conditions: **1** (1.25 mmol), **2**(0.5 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.01 mmol), KF (1.5 mmol), solvent (1.0 mL), N_2 atmosphere.

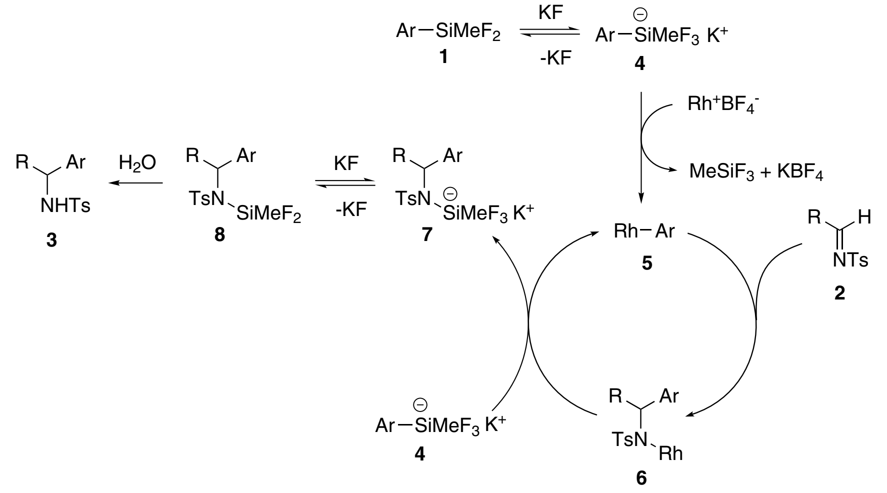
[b] Isolated yield.

[c] The reaction was carried out in the absence of KF.

(entries 7 and 8). In the case of 4-dimethylamino-*N*-tosylbenzylideneamine (**2d**), the yield of the reaction in DMF was low (entry 9), however, the reaction in THF gave the better yield of 66% (entry 10). Such solvent effect was also observed in the reaction of *N*-tosylbenzylideneamine bearing chloro or nitro group. The reaction of 4-chloro- and 4-nitro-*N*-tosylbenzylideneamine (**2e** and **2g**) with **1a** in THF gave the corresponding adducts **3e** and **3g** in good yields of 96% and 93%, respectively (entries 12 and 16), whereas the reactions in DMF gave the products in moderate yield of 55% in both cases (entries 11 and 15). Although the reaction of 2-chloro-*N*-tosylbenzylideneamine (**2f**) was sluggish, the reaction in THF also gave the better yield of 42% (entry 14). *N*-Tosylfurylideneamine (**2h**) reacted well with **1a** in DMF giving the product **3h** in 73% yield (entry 17). 4-Methoxy- and 4-chlorophenyldifluoromethylsilane (**1b** and **1c**) also reacted well with **2a** in DMF affording the corresponding adducts **3b** and **3e** in good isolated yields of 98% and 76%, respectively (entries 18 and 19).

The mechanism of the present reaction would involve the transmetalation between the arylsilicon compounds and the rhodium complex to give the arylrhodium complex as a key intermediate. In addition, a fluoride-coordinated arylsilicate would be an active species for the transmetalation with the rhodium complex, from the result that the addition of potassium fluoride is necessary for the reaction to proceed smoothly. The presumed reaction pathway is shown in Scheme 1. As the initial step, the transmetalation of the cationic rhodium complex with the silicate **4** generated from **1** and potassium fluoride produces the arylrhodium intermediate **5**. Addition of **5** to the aldimine affords the rhodium amide complex **6**, which then reacts with **4** to regenerate **5** and the aminosilicate **7**. The silicate **7** or its equilibrium partner of silylamine **8** is easily hydrolyzed during aqueous work-up to give the product **3**.

In conclusion, the addition of aryldifluoromethylsilanes to *N*-sulfonylaldimines was achieved by use of the



Scheme 1. Presumed reaction mechanism.

rhodium complex as the catalyst and potassium fluoride as the activator for the aryldifluoromethylsilanes. This process provides a new synthetic route to a wide range of arylamines from arylsilanes, which have advantages such as low cost, low toxicity, and tolerance to a variety of functional groups. Further investigation involving an asymmetric version of the reaction is now underway.

References and notes

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7. A following procedure is representative. A mixture of *N*-tosylaldimines (0.5 mmol), aryldifluoromethylsilanes (1.25 mmol), KF (87 mg, 1.5 mmol), and [Rh(cod)(MeCN)$_2$]-BF$_4$[3d] (3.8 mg, 0.01 mmol) in 1 mL of dried THF or DMF was stirred at 60 °C under N_2 atmosphere in a Schlenk tube. The reaction was quenched by adding a small amount of water and then stirred for 1 h. After the solvent was evaporated in vacuo, the residue was purified by silica gel chromatography eluting with hexane/CHCl$_3$/AcOEt (10:11:1) to give the products **3**. All products were identified by comparing the spectroscopic data with those reported before.[3d]