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Rhodium-Catalyzed Addition of Phenylmethyldifluorosilane to Aldehydes

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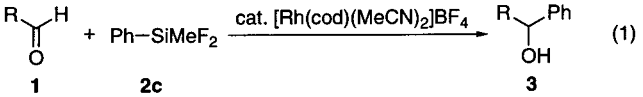
Summary: Phenylmethyldifluorosilane reacts with aldehydes in the presence of a fluoride salt and a catalytic amount of a cationic rhodium complex, [Rh(cod)-($CH_3CN)_2$]BF_4, affording the corresponding phenylated alcohols in good yield. The reaction mechanism involves the transmetalation between a fluorine-coordinated silicate and a rhodium complex to generate a phenylrhodium species.

The transmetalation between main group organometallic compounds and transition metal compounds is an important method for the generation of active organotransition metal intermediates, and many examples can be found in useful carbon−carbon bond formation reactions catalyzed by such transition metal intermediates.[1] We previously reported the novel rhodium-catalyzed addition of arylstannanes to aldehydes[2] and to aldimines[3] and the conjugate addition of arylstannanes to α,β-unsaturated carbonyl compounds.[4] Meanwhile, Miyaura and co-workers reported an analogous addition of organoboronic acids to aldehydes[5] and to enones[6] catalyzed by rhodium complexes. In these additions of organostannanes and organoboronic acids, organorhodium complexes generated by the transmetalation with the organotin or organoboron compounds are assumed to be the active species which react with the aldehydes and α,β-unsaturated carbonyl compounds. From this mechanistic consideration, it can be expected that other main group organometallic reagents could take part in such addition reactions if they undergo similar transmetalation with an appropriate rhodium complex. We have investigated the addition of phenylsilanes to aldehydes and found that phenylmethyldifluorosilane reacts with aldehydes in the presence of a fluoride salt and a catalytic amount of a cationic rhodium complex to give the corresponding phenylated alcohols in good yield (eq 1).



(1)

1a: R = Ph
1b: R = 3,4-OCH_2O-C_6H_3
1c: R = 2-MeO-C_6H_4
1d: R = 4-MeO-C_6H_4
1e: R = 4-Me_2N-C_6H_4
1f: R = 4-Me-C_6H_4
1g: R = 4-Cl-C_6H_4
1h: R = 4-MeOC(O)-C_6H_4
1i: R = 2-NO_2-C_6H_4
1j: R = 2-naphthyl
1k: R = 2-furyl
1l: R = CH_2CH_2Ph
1m: R = *c*-C_6H_{11}

Table 1. Rhodium-Catalyzed Addition of Phenylsilanes 2 to Benzaldehyde (1a)[a]

entry	phenylsilane **2**	additive	product **3**	yield (%)[b]
1	$PhSiMe_3$ (**2a**)	KF		0
2	$PhSi(OMe)_3$ (**2b**)	KF		0
3	$PhSiMeF_2$ (**2c**)	KF	**3a**	95
4	$PhSiMeF_2$ (**2c**)	KF[c]	**3a**	83
5	$PhSiMeF_2$ (**2c**)	none	**3a**	15
6	$PhSiF_3$ (**2d**)	KF	**3a**	18
7	$PhSiMe_2F$ (**2e**)	KF		0

[a] Reaction conditions: **1a** (1.0 mmol), **2** (2.0 mmol), KF (3.0 mmol), [Rh(cod)$(MeCN)_2$]BF_4 (0.02 mmol), 2 mL of THF, 60 °C, N_2 atmosphere. [b] Isolated yield. [c] 2.0 mmol of KF was added.

Initial attempts on the rhodium-catalyzed reaction of phenyltrimethylsilane (**2a**) or phenyltrimethoxysilane (**2b**) with benzaldehyde (**1a**) were unsuccessful. In both cases, the reaction did not occur at all despite the addition of KF to activate the organosilanes (Table 1, entries 1, 2). Arylfluorosilanes were reported to transmetalate to palladium complexes with the aid of fluoride ions via five-coordinate silicates in the cross-coupling reaction with aryl- or alkenylhalides.[7] Accordingly, we chose phenylmethyldifluorosilane (**2c**) as a phenylating silicon reagent. The reaction of **2c** with benzaldehyde in the presence of 2.0 mol % of the cationic rhodium(I) complex, [Rh(cod)$(MeCN)_2$]BF_4, and 3.0 molar equiv of KF in THF at 60 °C for 20 h gave diphenylmethanol **(3a)** in 95% yield (Table 1, entry 3) after a treatment with water and purification by column chromatography.[8] The addition of a smaller amount of KF (2.0 molar equiv) caused only a small decrease in the yield to 83%

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[8] A following procedure is representative. A mixture of an aldehye (1.0 mmol), phenylmethyldifluorosilane (316 mg, 2.0 mmol), KF (174 mg, 3.0 mmol), and [Rh(cod)$(MeCN)_2$]BF_4[9] (7.6 mg, 0.02 mmol) in 2 mL of dried THF was stirred at 60 °C for 20 h under a N_2 atmosphere in a sealed 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 hexanes−ethyl acetate (5:1) to give the product alcohol **3**.

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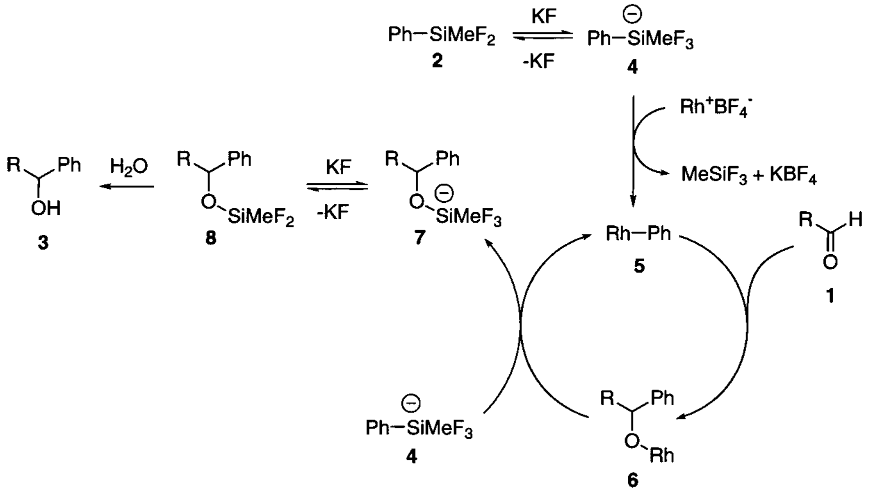
Table 2. Rhodium-Catalyzed Addition of Phenylmethyldifluorosilane (2c) to Aldehydes 1[a]

entry	aldehyde **1**	temp (°C)/time (h)	product **3**	yield (%)[b]
1	3,4-$OCH_2OC_6H_3CHO$ (**1b**)	60/18	3,4-$OCH_2OC_6H_3CH(Ph)OH$ (**3b**)	98
2	2-$MeOC_6H_4CHO$ (**1c**)	60/20	2-$MeOC_6H_4CH(Ph)OH$ (**3c**)	97
3	4-$MeOC_6H_4CHO$ (**1d**)	60/20	4-$MeOC_6H_4CH(Ph)OH$ (**3d**)	98
4	4-$Me_2NC_6H_4CHO$ (**1e**)	60/20	4-$Me_2NC_6H_4CH(Ph)OH$ (**3e**)	84
5	4-MeC_6H_4CHO (**1f**)	60/20	4-$MeC_6H_4CH(Ph)OH$ (**3f**)	97
6	4-ClC_6H_4CHO (**1g**)	60/20	4-$ClC_6H_4CH(Ph)OH$ (**3g**)	96
7	4-$MeOC(O)C_6H_4CHO$ (**1h**)	60/20	4-$MeOC(O)C_6H_4CH(Ph)OH$ (**3h**)	98
8	2-$NO_2C_6H_4CHO$ (**1i**)	60/18	2-$NO_2C_6H_4CH(Ph)OH$ (**3i**)	100
9	2-naphthyl-CHO (**1j**)	60/20	2-naphthyl-CH(Ph)OH (**3j**)	94
10	2-furyl-CHO (**1k**)	60/20	2-furyl-CH(Ph)OH (**3k**)	99
11	$PhCH_2CH_2CHO$ (**1l**)	60/20	$PhCH_2CH_2CH(Ph)OH$ (**3l**)	70
12	*c*-$C_6H_{11}CHO$ (**1m**)	60/20	*c*-$C_6H_{11}CH(Ph)OH$ (**3m**)	97

[a] Reaction conditions: **1** (1.0 mmol), **2c** (2.0 mmol), KF (3.0 mmol), $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol), 2 mL of THF, 60 °C, N_2 atmosphere. [b] Isolated yield.

Scheme 1



(entry 4), but the absence of KF markedly decreased the yield to 15% (entry 5). Although phenyltrifluorosilane (**2d**) and phenyldimethylfluorosilane (**2e**) also have fluorine atom(s) on silicon, the reaction of the former with benzaldehyde gave only an 18% yield of **3a** (entry 6) and the later did not react with benzaldehyde (entry 7). The generation of the silicate from phenyltrifluorosilane might be easier than that from phenylmethyldifluorosilane, but the increase of the electronically negative fluorine atoms on silicon would decrease the activity of the transmetalation.

The results of the reactions of various aldehydes **1** with phenylmethyldifluorosilane are summarized in Table 2.[8] The reactions proceeded smoothly with substituted benzaldehydes **1b**–**i** bearing both electron-donating and -withdrawing groups at the 2- or 4-positions, affording the product alcohols **3b**–**i** in very good yield (entries 1–8). Although the strongly coordinative dimethylamino group might inhibit the reaction, 4-dimethylaminobenzaldehyde (**1e**) gave alcohol **3e** in 84% yield (entry 4). Electrophilic functional groups in **1** such as methoxycarbonyl or nitro remained intact (entries 7, 8). Other aromatic aldehydes, 2-naphthaldehyde (**1j**) and 2-furaldehyde (**1k**), also were phenylated by phenylmethyldifluorosilane in good yield. The phenylation reaction is also applicable to aliphatic aldehydes. The reactions of 3-phenylpropanal (**1l**) and cyclohexanecarboxaldehyde (**1m**) gave alcohols **3l** and **3m** in good yield. The addition of phenyltrimethylstannane to aliphatic aldehydes gave the alcohols **3** in only moderate yields due to the side reactions,[2] whereas the addition of phenylmethyldifluorosilane gave the alcohols **3** very cleanly.

As was stated above, the addition of the fluoride salt is necessary for the reaction to proceed smoothly. This strongly suggests that a fluorine-coordinated silicate is an active species of the transmetalation between the phenylsilane and the rhodium complex. The presumed reaction pathway is shown in Scheme 1. Ligands of the rhodium complexes not concerned with the reaction are omitted in the scheme. As the initial step, the transmetalation of the cationic rhodium complex with the silicate **4** generated from **2** and KF produces the phenylrhodium intermediate **5**. Addition of **5** to the aldehyde affords the rhodium alkoxide complex **6**, which then reacts with **4** to regenerate **5** and the alkoxysilicate **7**. The silicate **7** or its equilibrium partner of silyl ether **8** is easily hydrolyzed to give the alcohol **3**.

In conclusion, the addition of phenylmethyldifluorosilane to aldehydes was achieved by use of a rhodium complex as the catalyst and KF as the activator of the phenylsilane. This process provides not only a new synthetic route to a wide range of secondary arylcarbinols but also a new method to generate a reactive phenylrhodium species. Further investigation involving an asymmetric version of the reaction is now underway.

Supporting Information Available: Characterization data for **3a**–**m**. This material is available free of charge via the Internet at http://pubs.acs.org.

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