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AgF-MEDIATED HOMOCOUPLING REACTION OF TRIALKOXY ARYL SILANES

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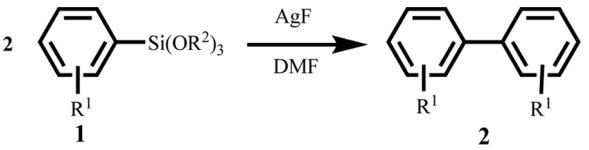
GRAPHICAL ABSTRACT



1 **2**

up to 97% yield

Abstract *In this article, we present the direct homocoupling reaction of trialkoxy aryl silanes mediated by AgF in moderate to excellent yields in very mild conditions. It is an important complement for the synthesis of symmetrical biaryls by using homocoupling of trialkoxy silanes. In this reaction, no other catalyst such as Pd or Cu was necessary.*

Supplementary materials are available for this article. Go to the publisher's online edition of Synthetic Communications® *for full experimental and spectral details.*

Keywords Ag-mediated; biaryls; homocoupling; *N,N*-dimethylformamide; phenyltrimethoxysilane

INTRODUCTION

It is well known that biaryls as a central part of organic frameworks have been found in a large number of natural products[1] and widely applied in many useful manmade compounds.[2] For more than a century, organic chemists have focused their attention on developing new and more efficient aryl–aryl bond-forming methods including cross-coupling and homocoupling.[3] Among them, the transition metal–catalyzed homocoupling reaction is one of the most efficient methods to construct symmetrical biaryls using aryl halide[4] or aryl organometallic reagents such as Mg,[5] B,[6] and Sn,[3,7] and transition metal–free oxidative homocoupling reaction has also been studied and established recently.[8] In additional to some methods for aryl–aryl cross-coupling using aryl organosilane reagents and aryl halides,[9] there are also a number of reports on the homocoupling reaction of organosilanes.[10]

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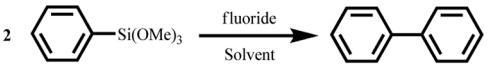
However, the substrates were limited in the scope of fluorosilane reagents in most cases. To the best of our knowledge, no report on homocoupling with trialkoxy silanes has appeared to date.

Compared with similar coupling reactions, using organostannane, Grignard, and organoboron reagents, Hiyama coupling has many advantages such as low cost, easy availability, nontoxic by-products, safe handling, and stability in many reaction conditions. Herein, we present a direct and efficient homocoupling reaction of trialkoxy aryl silane reagents mediated by AgF. Such Ag-mediated C-C bond-formation reactions are rare.[10j–k] It is an important complement for the synthesis of symmetrical biaryls through homocoupling reaction of trialkoxy aryl silanes. In this reaction, no other catalyst such as Pd or Cu was necessary.

RESULTS AND DISCUSSION

In our initial screening of various fluorides, it was gratifying to find that AgF could afford the desired homocoupling product in excellent yield using

Table 1. Optimizing the reaction conditions for the direct homocoupling of phenyltrimethoxysilane[a]



1a 2a

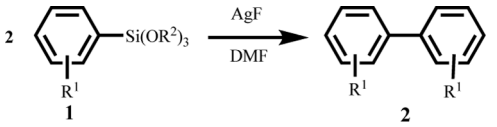
Entry	Additives	Solvent	Temp. (°C)	Yield[b] (%)
1	KF	Dioxane	80	0
2	TBAF[c]	Dioxane	80	0
3	CsF	Dioxane	80	0
4	CuF_2	Dioxane	80	0
5	$PdCl_2$ (10% mol)	DMF	80	0
6[d]	$PdCl_2$ (TBAF)	DMF	80	6
7	CuCl (1.0 equiv)	DMF	80	0
8[e]	CuI or CuBr (TBAF)	DMF	80	0
9	AgF	DCE	80	0
10	AgF	THF	60	0
11	AgF	1,4-Dioxane	80	72
12	AgF	DMF	rt	95
13	**AgF**	**DMF**	**80**	**96**
14	AgF[f]	DMF	80	48
15	AgF[g]	DMF	80	92
16	AgF[h]	DMF	80	95
17[i]	AgF	DMF	rt	61

[a]Reactions were carried out with 1.05 equiv of fluoride, 2.0 mL solvent, 8 h.
[b]Isolated yield based on phenyltrimethoxysilane.
[c]TBAF = tetra-*n*-butylammonium fluoride.
[d]10 mol% $PdCl_2$ and 2.0 equiv TBAF.
[e]10 mol% CuCl or CuI and 1.1 equiv TBAF.
[f]0.5 equiv AgF was used.
[g]1.0 equiv AgF was used.
[h]1.4 equiv AgF was used.
[i]Using phenyltriethoxysilane as substrate.

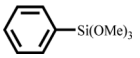
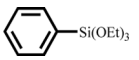
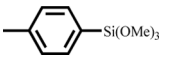
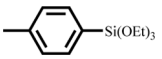
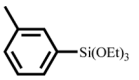
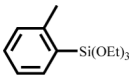
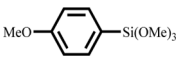
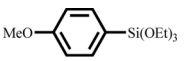
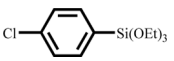
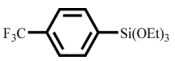
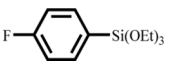
N,N-dimethylformamide (DMF) as solvent at 80 °C (Table 1, entry 13). It can be seen from Table 1 that fluorides such as KF, CsF, CuF_2, and TBAF (tetra-*n*-butyammonium fluoride) were inactive in this system (Table 1, entries 1–4). Only 6% yield was obtained by adding catalytic $PdCl_2$ (10% mol) and fluoride (Table 1, entry 6), and no desired product was obtained while only $PdCl_2$ (10% mol) was used as catalyst (Table 1, entry 5).

Even when using 1.0 equivalent of CuCl, or TBAF combined with catalytic CuBr or CuI (Table 1, entries 7, 8), no desired product was obtained. The reactions were performed in different solvents such as 1,2-dichloroethane (DCE), THF, 1,4-dioxane, and DMF (Table 1, entries 9–12). It found that DMF is the most suitable

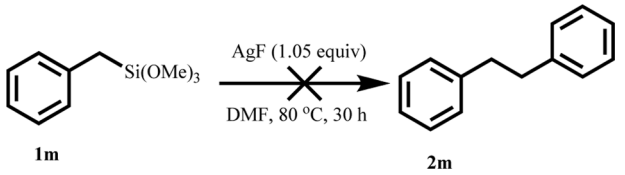
Table 2. AgF-mediated homocoupling reaction of various trialkoxy aryl silanes[a]



1 **2**

Entry	**1**	Time (h)	**2**	Yield[b]
1		4	**2a**	96
2		6	**2a**	82
3		10	**2b**	87
4		16	**2b**	69
5		12	**2c**	63
6		20	**2d**	48
7		12	**2e**	97
8		24	**2e**	88
9		12	**2f**	89
10		8	**2g**	96
11		8	**2h**	82

[a]Reactions were carried out with 1.05 equiv of silver fluoride, 2.0 mL DMF.



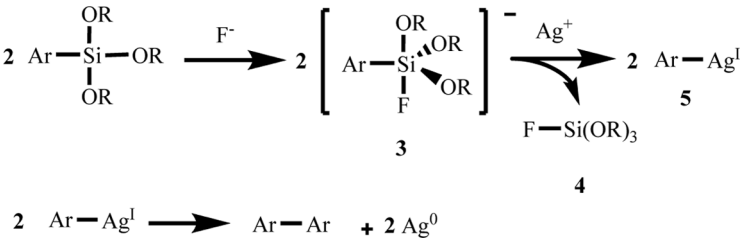
Scheme 1. AgF-mediated homocoupling reaction of trialkoxy aromatic silanes.

choice for this homocoupling reaction although 1,4-dioxane is also favored for this reaction with the desired product obtained in good yield (Table 1, entry 11). The loading of AgF could be further examined, and 1.05 equivalents of AgF was found necessary to complete the consumption of substrate (Table 1, entries 13–16). In addition, using phenyltrimethoxysilane as substrate, the reaction proceeded smoothly at room temperature in excellent yield (Table 1, entry 12). However, when phenyltriethoxysilane was tested as substrate at room temperature, the yield decreased significantly (Table 1, entry 17).

With these optimized conditions in hand, we further explored the scope of this homocoupling reaction with various trialkoxy aryl silanes in DMF at 80 °C in the presence of 1.05 equivalents of AgF. The results are summarized in Table 2. To our delight, the biaryl products were obtained in moderate to excellent yields by the homocoupling of different trialkoxy aryl silanes having electron-donating or electron-withdrawing groups on the phenyl rings. Triethoxyphenylsilane was found to be less reactive than trimethoxyphenylsilane. Notably, the yields decreased dramatically by using triethoxyphenylsilane bearing the *o*-methyl group (Table 2, entry 6), which could be due to the steric effect of the methyl substituent adjacent to the triethoxylsilyl group on the phenyl ring.

No homocoupling product was detected when benzylic silane **1m** was treated with AgF under the same condition (Scheme 1).

In correlation with Kochi's proposal for the coupling of Grignard reagents and alkyl halides,[7] we propose the possible mechanism to account for the aryl-aryl homocoupling products (Scheme 2). We envisaged that, in this coupling reaction process, AgF plays a role not only as a simple fluoride to activate the trialkoxy aryl silane but also as an oxidant to complete this aryl–aryl homocoupling reaction. The fluorinated intermediate **3** was rationally generated with the trialkoxy aryl silane activated by F^-, which underwent oxidation by Ag^+ to produce aryl-Ag^I



Scheme 2. Proposed mechanism of homocoupling of trialkoxy aryl silane mediated by AgF.

(intermediate **5**). Finally, the biaryl product of homocoupling reaction was generated along with the formation of the silver metal from the intermediate **5**.

CONCLUSION

In conclusion, we have developed a direct entry into symmetrical biaryls by homocoupling of aryl organosilane reagents mediated by AgF. It is important complement to synthesis of symmetrical biaryls using homocoupling of trialkoxy silanes. In this reaction, no other catalyst such as Pd or Cu was necessary. Futher extension of this work using catalytic silver salt is currently in progress.

EXPERIMENTAL

To an oven-dried, 10-mL, round-bottom flask equipped with a magnetic stirring bar were added AgF (67.2 mg, 0.525 mmol, 1.05 equiv) and phenyltriethoxysilane (120 mg, 0.5 mmol, 1.0 equiv) in 2 mL anhydrous DMF. Then the mixture was stirred for 6 h at 80 °C before the mixture was quenched with H_2O (5 mL). The aqueous layer was extracted with diethyl ether (10 mL × 3), and the combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash column chromatography to afford the desired pruduct **2a** (31.6 mg) as white solid. ^{1}H NMR: δ (400 MHz, $CDCl_3$) 7.59 (d, $J = 8.4$ Hz, 4H), 7.44 (t, $J = 8.0$ Hz, 4H), 7.39 (t, $J = 7.6$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 141.2, 129.9, 128.7, 127.2.

Please see the Supporting Information, available online, for complete experimental and spectral details.

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