

Copper(I) salt promoted homo-coupling reaction of organosilanes†

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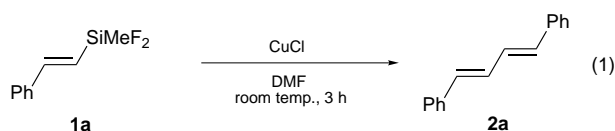
Alkenylfluorosilanes, phenylfluorosilanes or alkynylsilanes smoothly dimerize in the presence of a copper(I) salt in a polar solvent such as *N,N*-dimethylformamide (DMF) or dimethyl sulfoxide (DMSO) to give the 1,3-conjugated dienes, biphenyl or 1,3-conjugated diynes, respectively.

We have been studying the Pd-catalysed cross-coupling reaction of organosilanes in the presence of fluoride ion. The reaction has been found to proceed *via* the formation of a pentacoordinate organosilicate, which allows transmetalation of the organic group from Si to Pd *via* activation with the fluoride ion¹ or a corresponding promoter.²

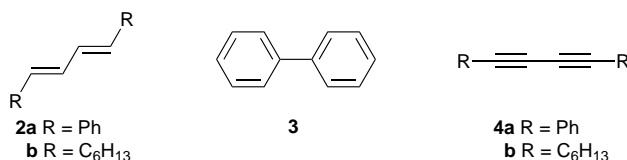
A part of our interest has thus been centred on the possibility of transmetalation by other metallic species. Kumada and co-workers documented the fact that treatment of alkenylpentafluorosilicates with a Cu^I salt³ in the solid state at 250 °C resulted in the formation of homo-coupling products (1,3-conjugated dienes). As observed in these reactions, activation by converting tetrahedral organofluorosilanes into organopentafluorosilicates is necessary to attain transmetalation from silicon to copper, although no example of the transmetalation of organosilanes to copper has been reported, to the best of our knowledge.⁴

Herein, we report our preliminary results on the transmetalation of organosilane compounds **1** to copper(I) salts, and subsequent homo-coupling reactions under extremely mild and neutral conditions. The reactions proceeded without an activator such as fluoride ion.

We first investigated the reaction of **1a** with an equimolar amount of KF in the presence of CuCl in *N,N*-dimethylformamide (DMF),⁵ and found homo-coupling product **2a** was produced in 98% yield. This observation encouraged us to study the reaction in more detail and found that it took place without KF [eqn. (1)].



DMSO, a polar solvent, also promoted the reaction, whereas none of the desired product was obtained in THF or diethyl ether. Copper cyanide (CuCN), although effective for transmetalation of organotin reagents,⁶ required a longer reaction time (72 h) and gave **2a** in 75% yield. In contrast, CuI⁷ and CuCl₂⁸ were much less reactive.



A typical procedure for the homo-coupling reaction of **1a** to **2a** is as follows. DMF (0.5 ml) and **1a** (37 mg, 0.2 mmol) were successively added to CuCl (20 mg, 0.2 mmol) placed in a

reaction tube equipped with a magnetic stirrer. The reaction mixture was stirred for 3 h at room temperature and quenched with 1 M hydrochloric acid. The aqueous layer was extracted with diethyl ether, and the organic layer was separated. The combined ethereal layer was washed with water and brine, and dried over Na₂SO₄. The homo-coupling product, (*E,E*)-1,4-diphenylbuta-2,3-diene **2a**, was obtained in 98% yield.

Results using various organosilicon compounds are summarized in Table 1. It is noteworthy that the reactivity of the silicon substrate is strongly dependent upon the number of fluorine atoms attached to silicon. Thus, the yield of **2b** from trifluoro(oct-1-enyl)silane **1b** is higher than that from difluoro(methyl)(oct-1-enyl)silane **1c** (run 2 *vs.* 3). In all cases the isomeric purity of hexadeca-7,9-diene **2b** was more than 99%, as confirmed by ¹H NMR spectroscopy. Thus, these reactions occurred with retention of configuration. The treatment of trifluorophenylsilane **1d** or ethyl(difluoro)phenylsilane **1e** with an equimolar amount of CuCl afforded biphenyl **3** (runs 4 and 5), whereas **1f** gave only a trace amount of **3**. Indeed, it has been reported that phenylcopper decomposes to produce biphenyl and copper metal.⁹ The biphenyl formation from fluoro(phenyl)silane **1d** or **1e** is ascribed to transmetalation from Si to

Table 1 CuCl promoted homo-coupling reactions of organosilanes **1**^a

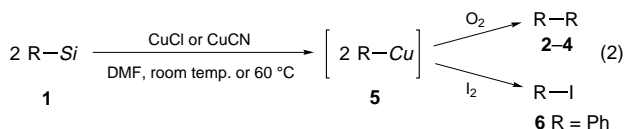
Run	Organosilane	T/°C	t/h	Product	Yield (%) ^b
1		rt	3	2a	98
2		60	24	2b	50
3 ^c		60	3	2b	38
4		60	12	3	79
5		60	12	3	75
6		60	12	3	trace
7		60	6	4a	100
8		60	3	4b	80

^a Conditions: **1** (0.2 mmol), CuCl (0.2 mmol), DMF (0.5 ml). ^b GC yield.

^c CuCl (0.4 mmol) was used.

Cu^I to give a phenylcopper intermediate. Alkynyl-trimethylsilanes **1g** and **1h** also underwent the homo-coupling reaction to give the corresponding 1,3-diyne¹⁰ in excellent yields. The results are consistent with the fact that the cross-coupling reaction of alkynylsilanes is accomplished by the use of the trimethylsilyl group.¹¹

Although the reaction mechanism of the homo-coupling remains unclear, the following results are helpful for understanding of the mechanism of the transmetalation from silicon to copper. The reaction of **1d** with CuCl in DMF under an argon atmosphere at room temperature over 3 h did not give any trace of biphenyl **3**, despite complete consumption of **1d**. However, consequent exposure to the air or treatment with iodine gave **3** in 40% yield or iodobenzene **6** in 68% yield, respectively. These results suggest that the initial step of the homo-coupling reaction promoted by a Cu^I salt is the transmetalation of organosilanes (RSi) with Cu^I salt, and that the corresponding organocopper species (RCu) **5** is actually involved as an intermediate [eqn. (2)]. The presence of air or oxygen is crucial for the formation of R–R.



In summary, the organic group of organosilanes **1** is found to transmetalate to Cu^I, and the resulting organocopper species undergo the homo-coupling reaction to give 1,3-dienes, biphenyl or 1,3-diyne. This is the first example of transmetalation of organosilanes to copper without activation of organosilanes with fluoride ion and provides the most practical and convenient method for the preparation of homo-coupling products. Details of the reaction mechanism and further synthetic applications are now under investigation.

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Footnotes

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† Note added in proof. Since submission of this manuscript a related study has appeared in which several organosilanes induce homo-coupling catalysed by CuI but a stoichiometric amount of TBAF is required: S.-K. Kong, T.-H. Kim and S. J. Pyun, *J. Chem. Soc., Perkin Trans. 1*, 1997, 797.

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