

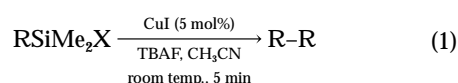
Copper(I)-catalysed homocoupling of organosilicon compounds: synthesis of biaryls, dienes and diynes

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Copper(I) iodide catalyses the homocoupling of aryl-, alkenyl- and alkynyl-substituted chloro- or fluoro-dimethylsilanes under mild conditions to afford biaryls, dienes and diynes, respectively.

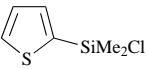
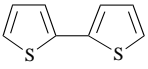
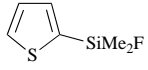
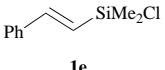
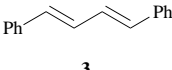
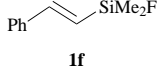
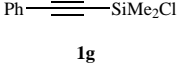
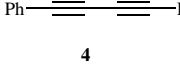
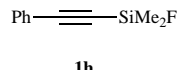
Functionalized symmetrical biaryls, dienes and diynes are able to form semiconducting complexes¹ and rigid liquid crystals² as well as ligands and precursors of optically active ligands.³ The synthesis of biaryls is usually accomplished from aryl halides catalysed by nickel or palladium complexes in the presence of a chemical reducer such as zinc powder⁴ or upon electrochemical reduction.⁵ This method is used because the reaction proceeds under mild conditions compared with the classical Ullmann coupling.⁶ The preparation of conjugated dienes utilizing organo-aluminum, -boron, -cobalt, -copper, -nickel, -lithium, -magnesium and -mercury has been described.⁷ The synthesis of diynes can be achieved by oxidative dimerization of acetylenes⁸ or lithium diaryl borates with iodine.⁹ Here we report copper(I) iodide-catalysed homocoupling of the substituted chloro- or fluoro-dimethylsilanes to afford biaryls, dienes and diynes (eqn. 1).



X = Cl, F

The results of copper-catalysed homocoupling in the presence of TBAF (tetrabutylammonium fluoride) are summarized in Table 1. When chlorodimethylphenylsilane **1a**¹⁰ or fluorodimethylphenylsilane **1b**¹⁰ was reacted with cuprous iodide (5 mol%) and TBAF in CH₃CN, biphenyl **2a** was afforded in 73 and 76% yields, respectively (entries 1 and 2 in Table 1). Of the catalysts tested (CuI, CuBr, CuCl, CuCN and CuOTf), CuI gave the best results. The presence of TBAF is essential as an accelerator for transmetalation¹¹ in this homocoupling. By the same method, chlorodimethyl(2-thienyl)silane **1c**¹⁰ was coupled to afford the thiophene dimer **2b** in 71% yield (entry 3). Alternatively, fluorodimethyl(2-thienyl)silane **1d**¹⁰ gave **2b** in 75% yield (entry 4). This method was also applied to alkenyl-substituted silanes **1e** and **1f**.¹² Treatment of chloro(styryl)-dimethylsilane with Pd(OAc)₂ (5 mol%) and TBAF produced the diene **3** in 87% yield (entry 5). Finally, this coupling was extended to alkynyl-substituted silanes **1g** and **1h**.¹⁰ The chlorosilane **1g**¹⁰ was readily coupled to give **4** in 91% yield (entry 7). The fluorosilane **1h** gave the coupled product **4** (entry 8). In considering the likely mechanism, it is presumed that oxidative addition of activated organosilane to Cu^I salts results in the formation of organo R₂CuSiMe₂X,¹³ which is then ready for transmetalation with the pentacoordinate silicate,¹⁴ formed from TBAF and organosilane, to form R₂CuI. The intermediate silicate R₂CuI then undergoes reductive elimination to afford R-R with the liberation of CuI.

Table 1 Copper(I)-catalysed homocoupling of organosilicon compounds^a

Entry	Silanes	Product	Isolated yield (%)
1	PhSiMe ₂ Cl 1a	Ph-Ph 2a	73
2	PhSiMe ₂ F 1b	2a	76
3	 1c	 2b	71
4	 1d	2b	75
5	 1e	 3	87
6	 1f	3	89
7	 1g	 4	91
8	 1h	4	94

^a All the reactions were run in the presence of TBAF in CH₃CN at room temperature for 5 min.

Experimental

Preparation of biphenyl **2a**

To a mixture of fluorosilane **1b** (350 mg, 2.27 mmol) and CuI (21.6 mg, 5 mol%) was slowly added TBAF (1.0 M in THF; 2.7 ml, 2.7 mmol) *via* a syringe pump. The reaction mixture was stirred at room temperature for 5 min and then extracted with diethyl ether (10 ml × 3). The organic layer was dried over anhydrous MgSO₄ and then evaporated *in vacuo*. The crude product was separated by SiO₂ column chromatography (eluting with hexanes, R_f 0.50) to afford the coupled product **2a** (266 mg, 76%), R_f (TLC, SiO₂, hexanes) 0.50, mp 68.5–69.5 °C

(lit.,¹⁵ 69–72 °C); δ_{H} (400 MHz, CDCl₃) 7.35 (m, 2 H), 7.45 (m, 4 H), 7.61 (m, 4 H); ν_{max} (KBr)/cm⁻¹ 3060, 1608, 1475, 832; m/z (EI) 154 (100), 152 (29), 77 (6), 76 (18), 63 (9), 51 (8).

Acknowledgements

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