

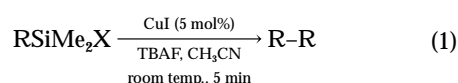
# Copper(I)-catalysed homocoupling of organosilicon compounds: synthesis of biaryls, dienes and diynes

Suk-Ku Kang,\* Tae-Hyun Kim and Sung-Jae Pyun

Department of Chemistry, Sung Kyun Kwan University, Natural Science Campus, Suwon 440-746, Korea

**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.**

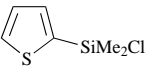
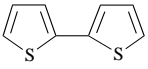
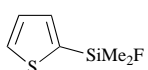
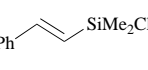
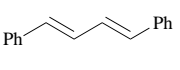
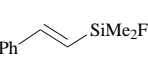
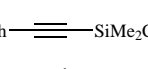
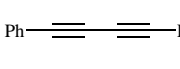
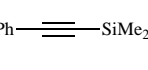
Functionalized symmetrical biaryls, dienes and diynes are able to form semiconducting complexes<sup>1</sup> and rigid liquid crystals<sup>2</sup> as well as ligands and precursors of optically active ligands.<sup>3</sup> The synthesis of biaryls is usually accomplished from aryl halides catalysed by nickel or palladium complexes in the presence of a chemical reducer such as zinc powder<sup>4</sup> or upon electrochemical reduction.<sup>5</sup> This method is used because the reaction proceeds under mild conditions compared with the classical Ullmann coupling.<sup>6</sup> The preparation of conjugated dienes utilizing organo-aluminum, -boron, -cobalt, -copper, -nickel, -lithium, -magnesium and -mercury has been described.<sup>7</sup> The synthesis of diynes can be achieved by oxidative dimerization of acetylenes<sup>8</sup> or lithium diaryl borates with iodine.<sup>9</sup> 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**<sup>10</sup> or fluorodimethylphenylsilane **1b**<sup>10</sup> was reacted with cuprous iodide (5 mol%) and TBAF in CH<sub>3</sub>CN, 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 transmetalation<sup>11</sup> in this homocoupling. By the same method, chlorodimethyl(2-thienyl)silane **1c**<sup>10</sup> was coupled to afford the thiophene dimer **2b** in 71% yield (entry 3). Alternatively, fluorodimethyl(2-thienyl)silane **1d**<sup>10</sup> gave **2b** in 75% yield (entry 4). This method was also applied to alkenyl-substituted silanes **1e** and **1f**.<sup>12</sup> Treatment of chloro(styryl)-dimethylsilane with Pd(OAc)<sub>2</sub> (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**.<sup>10</sup> The chlorosilane **1g**<sup>10</sup> 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<sup>I</sup> salts results in the formation of organo R<sub>2</sub>CuSiMe<sub>2</sub>X,<sup>13</sup> which is then ready for transmetalation with the pentacoordinate silicate,<sup>14</sup> formed from TBAF and organosilane, to form R<sub>2</sub>CuI. The intermediate silicate R<sub>2</sub>CuI then undergoes reductive elimination to afford R–R with the liberation of CuI.

**Table 1** Copper(I)-catalysed homocoupling of organosilicon compounds<sup>a</sup>

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

<sup>a</sup> All the reactions were run in the presence of TBAF in CH<sub>3</sub>CN 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 MgSO<sub>4</sub> and then evaporated *in vacuo*. The crude product was separated by SiO<sub>2</sub> column chromatography (eluting with hexanes, R<sub>f</sub> 0.50) to afford the coupled product **2a** (266 mg, 76%), R<sub>f</sub> (TLC, SiO<sub>2</sub>, hexanes) 0.50, mp 68.5–69.5 °C

(lit.,<sup>15</sup> 69–72 °C);  $\delta_{\text{H}}$ (400 MHz, CDCl<sub>3</sub>) 7.35 (m, 2 H), 7.45 (m, 4 H), 7.61 (m, 4 H);  $\nu_{\text{max}}$ (KBr)/cm<sup>-1</sup> 3060, 1608, 1475, 832;  $m/z$  (EI) 154 (100), 152 (29), 77 (6), 76 (18), 63 (9), 51 (8).

### Acknowledgements

Generous financial support by KOSEF and the Ministry of Education (BSR-96-3420) is gratefully acknowledged.

### References

- (a) U. Anton, C. Goltner and K. Mullen, *Chem. Ber.*, 1992, **125**, 2325; (b) D. S. Clelma, *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. J. Zyss, Academic Press, New York, 1983; (c) V. D. Hunstman, *The Chemistry of the Carbon–Carbon Triple Bond*, ed. S. Patai, Wiley Interscience, London, 1978, p. 553.
- (a) G. Solladie and G. Gottarelli, *Tetrahedron*, 1987, **43**, 1425; (b) A. E. Stiegman, E. Graham, K.-J. Perry, L. R. Khundkar, L.-T. Cheng and J. W. Perry, *J. Am. Chem. Soc.*, 1991, **113**, 7658; (c) C. Fouquey, J.-M. Lehn and J. Malthete, *J. Chem. Soc., Chem. Commun.*, 1987, 1424.
- (a) G. Bringmann, R. Walter and R. Weirich, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 977 and references cited therein; (b) C. Rosini, L. Franzini, A. Raffael and P. Salvadori, *Synthesis*, 1992, **6**, 503.
- (a) R. A. Kretchner and R. Glowinski, *J. Org. Chem.*, 1976, **41**, 2661; (b) M. F. Semmelhack, P. M. Helquist and L. D. Jones, *J. Am. Chem. Soc.*, 1971, **93**, 5908; (c) F. R. S. Clark, R. O. C. Norman and C. B. Thomas, *J. Chem. Soc., Perkin Trans. 1*, 1975, 121; (d) P. Banfield and P. M. Quan, *Synthesis*, 1978, 537; (e) J. Yamashita, Y. Inoue, T. Kondo and H. Hashimoto, *Chem. Lett.*, 1986, 407; (f) I. Colon and D. R. Kelsey, *J. Org. Chem.*, 1986, **51**, 2627; (g) M. Zembayashi, K. Tamao, J. Yoshida and M. Kumada, *Tetrahedron Lett.*, 1977, **47**, 4089; (h) A. Jutand and A. Mosleh, *Synlett*, 1993, 568; (i) M. Miura, H. Hashimoto, K. Itoh and M. Nomura, *Chem. Lett.*, 1990, 459; (j) M. Iyoda, H. Otsuka, K. Sato, N. Nisato and M. Oda, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 80; (k) M. Lourak, R. Vanderesse, Y. Fort and P. Caubere, *J. Org. Chem.*, 1989, **54**, 4840; (l) H. Tanaka, A. Kosaka, S. Yamashita, K. Morisaki and S. Torii, *Tetrahedron Lett.*, 1989, **30**, 1261.
- (a) S. Torii, H. Tanaka and K. Morisaki, *Tetrahedron Lett.*, 1985, **26**, 1655; (b) C. Amatore and A. Jutand, *Organometallics*, 1988, **7**, 2203; (c) A. Jutand, S. Negri and A. Mosleh, *J. Chem. Soc., Chem. Commun.*, 1992, 1729.
- P. E. Fanta, *Synthesis*, 1974, 9.
- (a) R. C. Larock, *J. Org. Chem.*, 1976, **41**, 2241 and references cited therein; (b) R. C. Larock and J. C. Bernhardt, *J. Org. Chem.*, 1977, **42**, 1680; (c) R. C. Larock and B. Riefling, *J. Org. Chem.*, 1978, **43**, 1468.
- (a) A. S. Hay, *J. Org. Chem.*, 1962, **27**, 3320; (b) E. Valent, M. A. Pericas and F. Serratos, *J. Am. Chem. Soc.*, 1990, **112**, 7405.
- A. Pelter, K. Smith and M. Tabata, *J. Chem. Soc., Chem. Commun.*, 1975, 857.
- The compounds **1a–1d** and **1g–1h** were prepared by a modified procedure reported in the literature. See, Y. Hatanaka, S. Fukushima and T. Hiyama, *Tetrahedron*, 1992, **48**, 2113.
- Y. Hatanaka, K.-I. Goda, Y. Okahara and T. Hiyama, *Tetrahedron*, 1994, **50**, 8301.
- Compounds **1e** and **1f** were prepared by the hydrosilylation of the corresponding terminal acetylene compounds with appropriate chlorosilanes followed by reaction with CuF<sub>2</sub>·2H<sub>2</sub>O. Hydrosilylation: see, (a) J. Yoshida, K. Tamao, M. Takahashi and M. Kumada, *Tetrahedron Lett.*, 1978, **25**, 2161; (b) K. Tamao, J. Yoshida, H. Yamamoto, T. Kakui, H. Matsumoto and M. Kumada, *Organometallics*, 1982, **1**, 355. Fluorination: see, (c) K. Tamao, T. Kakui, J. Yoshida and M. Kumada, *Tetrahedron*, 1983, **39**, 983.
- Oxidative addition of organic halides to Cu<sup>I</sup> salts has been described. See, (a) T. Cohen and I. Crested, *J. Org. Chem.*, 1975, **40**, 3649; (b) T. Cohen and I. Crested, *J. Am. Chem. Soc.*, 1976, **98**, 748.
- R. Damrauer and S. E. Danahey, *Organometallics*, 1986, **5**, 1490.
- The Merck Index*, ed. M. Windholz, Merck, Rahway, NJ, 11th edn., 1989, p. 3314 and references cited therein.

Paper 6/08384F

Received 13th December 1996

Accepted 17th January 1997