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## PALLADIUM-CATALYZED CROSS-COUPLING OF Cr(CO)<sub>3</sub>-COMPLEX CHLOROARENES WITH ORGANOFLUOROSILANES

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Abstract: The palladium-catalyzed cross-coupling of  $(\eta^6$ -chlorobenzene) tricarbonylchromium complexes with organofluorosilanes followed by decomplexation afforded aryl-, alkenyl-, and alkynyl-substituted arenes.

The palladium- and nickel-catalyzed cross-coupling reactions of aryl halides with organometallic reagents has developed into a powerful tool for preparing a number of valuable aromatic products.<sup>1</sup> Compared with aryl bromides and iodides, aryl chlorides are inexpensive and easily available in bulk quantities. However, aryl chlorides has been rarely used for transition-metal-catalyzed cross-coupling reaction because of the oxidative addition of aryl chlorides is too slow to

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develop the catalytic cycle.<sup>2</sup> Thus, the palladium- and nickel-catalyzed crosscoupling has been limited to activated chloroarenes such as chloropyridines,<sup>2</sup> and chloroarenes having an electron-withdrawing substituents.<sup>3</sup> In 1996, Hatanaka et al.<sup>4</sup> reported the arylation and alkenylation of palladium-catalyzed coupling of aryl electron-withdrawing chlorides containing groups with arylor alkenylchlorosilanes in the presence of a fluoride salt. The activation of the C-Cl bond of chloroarenes by coordination of a tricarbonylchromium moiety to aromatic ring has been extensively studied.<sup>5</sup> Because Cr(CO)<sub>3</sub>-activated aryl chlorides undergo facile oxidative addition of the C-Cl bond to zerovalent palladium complexes, tricarbonyl(chloroarene)chromium complexes reacted with alkyl formates or alcoholates in the presence of a catalytic amount of PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> to give esters.<sup>6</sup> We envisioned that Cr(CO)<sub>3</sub>-complexed chloroarenes can be utilized in the cross-coupling with organofluorosilanes.<sup>7</sup> Here we report the palladium-catalyzed cross-coupling of Cr(CO)3-complexed chloroarenes with organofluorosilanes.

The Cr(CO)<sub>3</sub>-complexed chlorobenzene **1a** was treated with phenyldimethylfluorosilane **2a** in the presence of  $(\eta^3-C_3H_5PdCl)_2$  (2.5 mol %) and TBAF in CH<sub>3</sub>CN at 50 °C for 6 h followed by treatment of iodine in THF for 24 h to afford biphenyl **3a** in 82% overall yield (entry 1 in Table 1). Under the same conditions the Cr(CO)<sub>3</sub>-complexed chloroarene **1a** was coupled with 2thienyldimethylfluorosilane **2b** followed by decomplexation to give 2phenylthiophene **3b**<sup>8</sup> in 67% yield (entry 2). When the compound **1a** was reacted with 1-hexenyldimethylfluorosilane **2c** followed by I<sub>2</sub> to provide (*E*)-1-phenylhexene **3c**<sup>9</sup> in 76% yield (entry 3). Similarly, (β)-(*E*)-styryldimethylfluorosilane **2d** was also coupled with **1a** followed by decomplexation to give (*E*)-stilbene **3d** (entry 4). This coupling was also applied to alkynyl-substituted organofluorosilane.

Entry <sup>C</sup>	r(CO) <sub>3</sub> -complexe Chloroarenes	d Organo- fluorosilane	es Product <sup>b</sup>	Yield(%) <sup>c</sup>
1	Čr(CO) <sub>3</sub>	SiMe <sub>2</sub> F	3a	82
2	1a 1a	SiMe <sub>2</sub> F		67
3	1a C₄	H <sub>9</sub> SiMe <sub>2</sub> 2c	FC₄H <sub>9</sub> Ph 3c	70
4	1a Pi	SiMe₂F 2d	Ph Ph 3d	76
5	<b>1a</b> Ph Cl	─ <del>──</del> ─SiMe₂F <b>2e</b>	Ph- <u></u> Ph <b>3e</b>	75
6	Cr(CO) <sub>3</sub>	2a	Ph Ph 3f	70
7	1b	2c		63
8	OMe CI Čr(CO) <sub>3</sub> 1c	2a	3g Pr OMe	61

 Table 1.
 Palladium-Catalyzed Cross-Coupling of Cr(CO)<sub>3</sub>-ComplexedChloroarenes with Organofluorosilanes<sup>a</sup>

<sup>a</sup> Reaction Conditions: Cr(CO)<sub>3</sub>-complexed chloroarene (1.1 equiv), organosilanes (1 equiv),  $[\eta^3-C_3H_5PdCI]_2(2.5 \text{ mol }\%)$ , CH<sub>3</sub>CN, TBAF (1.1 equiv), 50 °C, 6 h.; excess I<sub>2</sub>, THF, 24 h.<sup>b</sup> The decomplexed products. <sup>c</sup> The isolated yields.

successfully with The complexed compound 1a was coupled 1-(phenylethynyl)dimethylfluorosilane 2e to afford 1,2-diphenylacetylene 3e in 75% vield after decomplexation (entry 5). The Cr(CO)<sub>3</sub>-complexed dichlorobenzene 1b underwent facile coupling and decomplexation with 2a to give bis-coupled 3f in 70% vield (entry 6). Reaction of 1b with alkynyl-substituted organofluorosilane 2e gave the coupled  $3g^{10}$  in 63% yield (entry 7). Finally, the complexed ochloroanisole 1c was used in this cross-coupling with 2a followed by decomplexation to give biphenyl 3h 61% yield (entry 8). The results are summarized in Table 1.

#### **Experimental Section**

#### Typical Procedures: Preparation of Biphenyl (3a)

To a stirred solution of tricarbonyl( $\eta^6$ -chlorobenzene)chromium (1a) (200 mg, 0.805 mmol) and ( $\eta^3$ -allylPdCl)<sub>2</sub> (6.62 mg, 0.018 mmol) in CH<sub>3</sub>CN (10 mL) was added phenyl(dimethyl)fluorosilane 2a (117 mg, 0.732 mmol) and tetrabutyl-ammoniumfluoride (1 M solution in THF, 1.10 mL, 1.10 mmol). The reaction mixture was stirred at 50 °C for 6 h and then treated with excess I<sub>2</sub> (929 mg, 3.66 mmol) in THF (15 mL) for decomplexation. The reaction mixture was further stirred for 24 h and extracted with diethyl ether (20 mL x 2) and wash with saturated sodium thiosulfate solution (20 mL x 2). 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 (hexanes, R<sub>f</sub> = 0.47. mp 70-71 °C (lit.<sup>11</sup> 69-72 °C ). <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>):  $\delta$  7.35(m, 2H), 7.45(m, 4H), 7.61(m, 4H). IR(KBr) 3060, 1608, 1475, 831 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 154(M<sup>+</sup>, 100), 152(29), 77(6), 76(18), 63(9), 51(8).

2-Phenylthiophene(**3b**):<sup>8</sup> TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.52$ . <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  7.09 (dd, 1H, J = 5.1, 3.5 Hz), 7.27 (m, 2H), 7.32 (dd, 1H, J = 3.5, 1.1 Hz), 7.38 (m, 2H), 7.62 (m, 2H). IR (KBr) 3070, 1608, 1477, 832, 708 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 160 (M<sup>+</sup>, 100), 128 (13), 115 (34), 102 (5), 89 (7).

(*E*)-1-Phenylhexene(**3c**):<sup>9</sup> TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.58$ . <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  0.92(t, 3H, J = 7.2 Hz), 1.36(m, 4H), 1.63(m, 2H), 6.20(dt, 1H, J = 16, 6.0 Hz), 6.40(d, 1H, J = 16 Hz), 7.29(m, 5H). IR(neat) 3015, 1590, 1460, 1374 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 160(M<sup>+</sup>, 30), 102(100), 77(53).

*trans*-Stilbene (**3d**): TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.45$ . m.p. 121.5 - 123 °C (lit.<sup>11</sup> 122 - 124 °C). <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>):  $\delta$  7.12 (s, 2H), 7.21 (m, 2H), 7.34 (m, 4H), 7.48 (m, 4H). IR (KBr) 3019, 1597, 1496, 1072, 962, 909, 765, 693 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 180 (M<sup>+</sup>, 88), 179 (100), 178 (72), 165 (45), 89 (32), 76 (24).

Diphenylacetylene(**3e**): TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.49$ . mp 57-59 °C(lit.<sup>11</sup> 59-61 °C). <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 (m, 6H), 7.53 (m, 4H). IR (KBr) 3062, 1599, 1499, 1071, 918, 756, 689, 535, 509 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 178 (M<sup>+</sup>, 100), 176 (20), 152 (9), 89 (13), 76 (12).

o-Terphenyl(**3f**): TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.48$ . mp 58-59 °C(lit.<sup>11</sup> 58-59 °C). <sup>1</sup>H NMR(300 MHz, CDCl<sub>3</sub>)  $\delta$  7.17(m, 10H), 7.33(m, 2H), 7.45(m, 2H). IR(neat) 3015, 1590, 1460, 1374 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 230(M<sup>+</sup>, 100), 215(36), 114(44), 113(44), 108,(19), 101(33), 95(11), 88(10), 77(4).

1,2-Bis(2-phenylacetylene)benzene(**3g**):<sup>10</sup> TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.42$ . mp 49-51 °C(lit.<sup>10</sup> 51-52 °C). <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  7.33(m, 2H), 7.36(m, 6H), 7.60(m, 6H). IR(neat) 3062, 1599, 1499, 1071 cm<sup>-1</sup>. MS (EI) m/e (relative intensity) 279(M<sup>+</sup>, 23), 278(100), 276(72), 138(40), 125(16), 113(9), 87(2), 74(2).

o-Methoxybiphenyl(**3h**): TLC; SiO<sub>2</sub>, hexanes,  $R_f = 0.18$ . <sup>1</sup>H NMR(400 MHz, CDCl<sub>3</sub>)  $\delta$  3.80(s, 3H), 7.01(m, 2H), 7.34(m, 2H), 7.38(m, 3H), 7.45(m, 2H). IR(neat) 3055, 1265, 1115 cm<sup>-1</sup>. MS(EI) m/e (relative intensity) 185(13), 184(M<sup>+</sup>, 100), 169(43), 141(44), 115(34).

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