Supporting Information

Guillaume Grelaud, Ayham Tohmé, Gilles Argouarch, Thierry Roisnel, Frédéric Paul*

Stille-Type Aryl-Aryl Cross-Coupling Catalysis using Triarylphosphine Ligands with Electron-Rich Fe(II)-alkynyl Substituents

Including:

Synthesis and characterization of the Pd(II) precatalysts 8-10

General Procedure. The precatalysts **8-10** were obtained following a similar synthetic protocol; the complex **6** (1 eq) and the desired ligand among **1-4** (2.2 eq) were stirred 12 h at room temperature in THF. The solvent was removed *in vacuo* and the residue dissolved in dichloromethane. Addition of *n*-pentane and filtration afforded the corresponding palladium precatalyst **7-10** as an orange-brown powder.

***Trans-{[(dppe)(C_5Me_5)Fe-C≡C-1,4-(C_6H_4)]PPh_2}$_2PdCl_2$ (7)*:** Yield: 93%. ESI-MS(*M*/*Z*): 1924.38 [$M^{+\cdot}$]. ν_{max}(KBr)/cm^{-1} 2036 (s, C≡C). δ_P(81 MHz; C_6D_6; H_3PO_4)/ppm: 100.8 (4P, s, dppe), 23.9 (2P, s, PPh_2). δ_H(200 MHz; C_6D_6; Me_4Si)/ppm: 7.86 (16H, m, H_{ar}), 7.43-7.30 (52H, m, H_{ar}), 2.62 (4H, m, CH_2 dppe), 2.01 (4H, m, CH_2 dppe), 1.45 (30H, s, C_5Me_5).

***Trans-{[(dppe)(C_5Me_5)Fe-C≡C-1,4-(C_6H_4)]$_3$P}$_2PdCl_2$ (8)*:** Yield: 96%. ESI-MS(*M*/*Z*): 4373.1 [$M^{+\cdot}$], 2186.55 [M^{2+}], 1457.70 [M^{3+}]. ν_{max}(KBr)/cm^{-1}: 2044 (s, C≡C). δ_P(81 MHz; C_6D_6; H_3PO_4)/ppm: 101.5 (12P, s, dppe), 23.4 (2P, s, PAr_3). δ_H(200 MHz; C_6D_6; Me_4Si)/ppm: 7.97 (24H, m, H_{ar}), 7.38-7.09 (120H, m, H_{ar}), 2.62 (12H, m, CH_2 dppe), 1.80 (12H, m, CH_2 dppe), 1.56 (90H, s, C_5Me_5).

***Trans-{[(dppe)(C_5Me_5)Fe-C≡C-1,3-(C_6H_4)]PPh_2}$_2PdCl_2$ (9):** Yield: 91%. ESI-MS(*M*/*Z*): 1924.38 [$M^{+\cdot}$]. ν_{max}(KBr)/cm^{-1}: 2041 (s, C≡C). δ_P(81 MHz; C_6D_6; H_3PO_4)/ppm: 101.1 (4P, s, dppe), 25.2 (2P, s, PPh_2). δ_H(200 MHz; C_6D_6; Me_4Si)/ppm: 8.00 (16H, m, H_{ar}), 7.29-7.05 (52H, m, H_{ar}), 2.56 (4H, m, CH_2 dppe), 1.78 (4H, m, CH_2 dppe), 1.48 (30H, s, C_5Me_5).

***Trans-{[(dppe)(C_5Me_5)Fe-C≡C-1,3-(C_6H_4)]$_3$P}$_2PdCl_2$ (10)*:** Yield: 89%. ESI-MS(*M*/*Z*): 4373.10 [$M^{+\cdot}$], 2186.55 [M^{2+}], 1457.70 [M^{3+}]. ν_{max}(KBr)/cm^{-1}: 2038 (s, C≡C). δ_P(81 MHz; C_6D_6; H_3PO_4)/ppm: 101.5 (12P, s, dppe), 25.9 (2P, s, PAr_3). δ_H(200 MHz; C_6D_6; Me_4Si)/ppm: 7.98 (24H, m, H_{ar}), 7.35-7.07 (120H, m, H_{ar}), 2.64 (12H, m, CH_2 dppe), 1.81 (12H, m, CH_2 dppe), 1.54 (90H, s, C_5Me_5).

Catalytic Trials

General Procedure. In a dry Schlenk tube under argon, 1-bromo-4-methoxybenzene (0.117g, 1mmol), tributyl(*p*-tolyl)stannane (0.21g, 1.1mmol), CuI (0.019g, 0.1mmol), CsF (0.258g, 2mmol) and the appropriate palladium catalyst (0.025mmol) were suspended in DMF (2.5mL). The resulting suspension was heated at 50 °C in an oil bath for 18 h. After cooling to room temperature, solvents were cryogenically trapped and the residue was extracted with diethyl ether (50 mL) and filtered through paper to remove the black precipitate. The diethyl ether extract was washed with water (3×25 mL) and the aqueous layer was back extracted with diethyl ether (3×25 mL). The combined organic layers were dried over $MgSO_4$ and the solvent removed under reduced pressure to give a brownish solid. This solid was purified by column chromatography (silica gel, 2.5×15 cm, hexanes/dichloromethane 4/1). The first fraction gave 4,4'-dimethylbiphenyl along with tin by-products (R_f : 0.65, hexanes/dichloromethane 4/1) and the second fraction afforded the desired 4-methoxy,4'-methylbiphenyl compound as a white solid after evaporation of the solvents.

4-methoxy-4'-methylbiphenyl:[1] R_f (hexanes/dichloromethane 4/1): 0.34. ν_{max}/cm^{-1}: 2956 (m, CH_3), 2854 (m, CH_3), 1112 (m, OCH_3). δ_H(200 MHz; $CDCl_3$; Me_4Si)/ppm: 7.59 (2H, d, $J_{1,3}$ 9), 7.54 (2H, d, $J_{1,3}$ 8), 7.31 (2H, d, $J_{1,3}$ 8), 7.05 (2H, d, $J_{1,3}$ 9), 3.92 (3H, s), 2.47 (3H, s) δ_C(50 MHz; $CDCl_3$; Me_4Si)/ppm: 159.4 (s), 138.4 (s), 136.8 (s), 134.2 (s), 129.9 (s), 128.4 (s), 127.1 (s), 114.6 (s), 55.78 (s), 21.5 (s).

[1] M. Veda, A. Saitoh, S. Oh-Tani, and N. Miyaura, *Tetrahedron*, 1998, **54**, 13079