

Chloropalladated propargyl amine: a highly efficient phosphine-free catalyst precursor for the Heck reaction

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General Methods

All catalytic reactions were carried out under argon or nitrogen atmosphere in oven dried resealable Schlenk tube. All substrates were purchased from Acros and used without further purification. Butyl acrylate and styrene were purchased from Aldrich. Styrene was distilled prior to use from CaH_2 under argon. Dimethylacetamide was degassed and stored over molecular sieves. NMR spectra were recorded on a Varian Inova 300 MHz spectrometer. Infrared spectra were performed in a Bomem B-102 spectrometer. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70eV). Gas chromatography analyses were performed on a Hewlett-Packard-5890 Gas Chromatograph with a FID detector and 30 meter DB17 capillary column.

Synthesis of 3-(dimethylamino)-1-phenyl-1-propyne

Dimethylamine (40% aqueous solution, 91 mL, 0.72 mol) was added to a stirred mixture of phenylacetylene (49.0 g, 0.48 mol), paraformaldehyde (30.0 g; 0.53 mol) and cuprous iodide (0.45 g) in 250 mL dioxane. The reaction mixture was refluxed for 4 h and the solvent was removed under reduced pressure. Distillation of the residue afforded a colorless liquid of boiling point 114°C / 5 mmHg (71.8 g, 94% yield). GC-MS (m/z (%), IE, 70 eV): (159, $[\text{M}]^{+\bullet}$), (115, $[\text{M}-\text{NMe}_2]^+$). ^1H NMR (CDCl_3): δ 7.46-7.38 (m, 2H, H aromatic); 7.33-7.23 (m, 3H, H aromatic); 3.45 (s, 2H, CH_2N); 2.35 (s,

6H, NMe₂). ¹³C{¹H} NMR (CDCl₃): δ 132.1, 128.5, 128.1 (CH aromatic); 124.1 (C aromatic); 85.9, 85.1 (C≡C); 49.8 (CH₂N); 44.4 (NMe₂).

Synthesis of palladacycle {Pd[k¹-C,k¹-N-C=(C₆H₅)C(Cl)CH₂NMe₂](μ-Cl)}₂ **1**

Synthesis of **1** was reported previously.¹ A Li₂PdCl₄ solution was prepared by dissolving PdCl₂ (0.745 g, 4.20 mmol) and LiCl (0.45 g, 10.5 mmol) in hot methanol (15 mL). After dissolution of the solids, the solution was cooled to room temperature and 3-(dimethylamino)-1-phenyl-1-propyne (0.80 g, 5.00 mmol) was added. The resulting suspension was stirred for 1 h. Filtration and washing of the resulting solid with cold MeOH and drying under reduced pressure afforded a yellow solid of melting point 172-5 °C (dec.) (1.24 g, 88% yield). Anal.: (C₁₁H₁₃Cl₂NPd)₂ (673.11) Calc.: C, 39.26; H, 3.89; N, 4.16. Found: C, 39.40; H, 3.99; N, 4.15. IR (KBr, cm⁻¹): 1600 (ν_{C=C}). ¹H NMR (CDCl₃): δ 7.35-6.90 (m, 10H, H aromatic); 3.61 (s, 2H, CH₂N); 3.59 (s, 2H, CH₂N); 2.88 (s, 6H, NMe₂); 2.77 (s, 6H, NMe₂). ¹H NMR (CDCl₃ + Py-d₅): δ 6.92-6.75 (m, 5H, H aromatic); 3.67 (s, 2H, CH₂N); 3.01 (s, 6H, NMe₂). ¹³C{¹H} NMR (CDCl₃): δ 142.9, 142.7, 141.9, 141.7, 116.1, 115.7 (C aromatic and C=C); 128.1, 127.7, 127.5, 127.4, 125.9, 125.8 (CH aromatic); 74.6, 74.3 (CH₂N); 53.2, 52.9 (NMe₂).

Typical experiment for the Heck reaction

A 10 mL resealable schlenk flask was evacuated and back-filled with argon and charged with sodium acetate (1.4 mmol, 112 mg) and tetrabutylammonium bromide (0.2 mmol, 64 mg). The flask was then evacuated and back-filled with argon and then were added dimethylacetamide (5 mL), iodobenzene (1mmol, 112 μl, 204 mg), butyl acrylate (1.2 mmol, 172 μl) and methyl benzoate as internal standard (35mg). After the addition of

¹ Dupont, J.; Basso, N. R.; Meneghetti, M. R. and Konrath, R. A. *Organometallics* **1997**, *16*, 2386 -2391. Yukawa, T.; Tsutsumi, S. *Inorg. Chem.* **1968**, *7*, 1458.

the palladacycle **1** in dimethylacetamide (42 μ l of a 2.4×10^{-3} M solution, 10^{-3} mmol) the reaction mixture was stirred at 50°C for 24 h. GC analysis gave 100% yield in butyl *trans*-cinnamate. The solution was then allowed to cool to room temperature, taken up in CH_2Cl_2 (15 mL) and washed with 10 wt% aqueous sodium hydroxide (10 mL), and then dried over MgSO_4 . After filtration, solvent was evaporated to give butyl *trans*-cinnamate (150 mg, 95%) estimated to be >95% pure by ^1H NMR and GC. ^1H NMR (300 MHz, CDCl_3) δ 7.68 (d, J = 15.9 Hz, 1H, CH olefinic), 7.60-7.35(m, 5H, CH aromatic), 6.44 (d, J = 16 Hz, CH olefinic), 1.46 (m, 2H, CH_2), 1.70 (m, 2H, CH_2), 4.21 (t, 2H, CH_2), 0.96 (t, 3H, Me). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ 167.1 (CO), 144.5, 134.4, 130.1, 128.8, 128.0, 118.3 (C aromatic and CH olefinic), 64.4 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 13.7 (Me). IR (neat, cm^{-1}) 3061, 3030 (ν CH aromatic), 1713 (ν C=O), 1638 (ν C=C). GC-MS (m/z (%), IE, 70 eV): 131 (100, M + -OBu), 103 (58), 51(54), 204 (10, M +), 77 (44).

Typical experiment for the Hammett competition reaction

A 10 mL resealable schlenk flask was evacuated and back-filled with argon and charged with sodium acetate (1.4 mmol, 112 mg) and tetrabutylammonium bromide (0.2 mmol, 64 mg). The flask was then evacuated and back-filled with argon and then were added dimethylacetamide (5 mL), butyl acrylate (10 mmol, 1.5 mL), methyl benzoate as internal standard (35 mg) and 0.14 mmol of the substrates: $\text{C}_6\text{H}_5\text{Br}$, 4-MeOC $_6\text{H}_4\text{Br}$, 4-MeC $_6\text{H}_4\text{Br}$, 4-ClC $_6\text{H}_4\text{Br}$, 4-NCC $_6\text{H}_4\text{Br}$, 4-MeCOC $_6\text{H}_4\text{Br}$ and 4-NO $_2\text{C}_6\text{H}_4\text{Br}$. After the addition of the palladacycle **1** in dimethylacetamide (42 μ l of a 2.4×10^{-5} M solution) the reaction mixture was stirred at 150°C. The reaction was monitored by GC and was stopped at maximum 30% conversion of the most reactive bromoarene (4-NO $_2\text{C}_6\text{H}_4\text{Br}$). The same experiment was performing using separately the activated and deactivated bromo-arenes and the initial relative rates were used to plot Hammett correlation giving the same results.

Hg Poisoning experiment

Two identical Heck experiments consisting in butyl acrylate (1.2 mmol, 172 μ l), iodobenzene (1 mmol, 112 μ l), 5 mL of dimethylacetamide, sodium acetate (1.4 mmol, 112 mg), tetrabutylammonium bromide (0.2 mmol, 64 mg) and palladacycle **1** in dimethylacetamide (42 μ l of a 2.4×10^{-3} M solution, 10^{-3} mmol)] were stirred at 80°C.

Aliquots were taken from both reactions and analyzed by GC. After two hours, Hg (0.3 mmol, 60mg) was added to one reaction vessel.