Supporting Information for

Sulfur Containing Palladacycles as Catalyst Precursors for the Heck Reaction

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General Methods

All catalytic reactions were carried out under an argon or nitrogen atmosphere in oven dried resealable Schlenk tube. Elemental analysis were performed by Analytical Central Service of IQ-UFRGS. C_6H_5I, C_6H_5Br, 4-MeC_6H_4Br, 4-$MeOC_6H_4Br$, methyl acrylate, triethylamine, sodium acetate and dimethylacetamide were purchased from Merck. 3-$CF_3C_6H_4Br$, β-bromostyrene, butyl acrylate and styrene were purchased from Aldrich. 4-$CHOC_6H_4Br$ and 4-$NO_2C_6H_4Cl$ were purchased from Acros. Styrene was distilled prior to use from CaH_2 under argon. The thioethers were prepared according to known procedure (Hoffmann, H. M. R. *J. Chem. Soc*. **1964**, 1249). Dimethylacetamide was distilled prior to use from BaO under argon only in cases where catalyst concentration were lower then 2 x 10^{-5}. Iodobenzene was purified by distillation argon only in cases where catalyst concentration were lower then 2 x 10^{-5}. All the others chemical were used without further purification. 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 and 30 meter capillary column with a dimethylpolysiloxane stationary phase.

Synthesis of Palladacycle **1a**. To a solution of palladium acetate (295 mg, 1.3 mmol) in acetic acid (15 mL) was added t-butyl-1-methylbenzylthioether (470 mg, 1.4 mmol) at room temperature. The solution was stirred at 90°C for 20 minutes. The brown solution thus obtained was evaporated to dryness and washed with hexanes (2 x 25 mL). The remaining dark solid was suspended in acetone (25 mL), lithium chloride (80 mg, 2.0 mmol) was added and the reaction mixture stirred at room temperature for 15 minutes. Evaporation of the volatiles under reduced pressure gave a brown residue that was dissolved in dichloromethane (100 mL), filtered through a plug (4 cm) of alumina (grade I) and concentrated to *ca*. 5 mL. Addition of hexanes (50 mL) affords a yellow solid, which was collected by filtration, washed with hexanes (3 x 10 mL) and dried under reduced pressure (197 mg, 45% yield based on Pd).

Calculated for $C_{12}H_{17}ClPdS$ C= 43.00%; H= 5.11%. Found: C= 42.81%; H= 4.96%. ^{1}H NMR (300 MHz, $CDCl_3$ + εPy-d_5): δ 7.43 (s(br), 1H, CH aromatic); 6.91 and 6.84 (2m, 3H, CH aromatic); 4.00 (q, 1H, *J*= 7.1 Hz, CH); 1.76 (d, 3H, CMe); 1.44 (s, 9H, *t*-Bu). ^{13}C NMR (75 MHz, $CDCl_3$ + εPy-d_5): δ 158.0; 146.1; 136.1; 125.9; 125.4 and 122.6 (C aromatic); 52.2 (C); 51.3 (CH); 31.1 (*t*-Bu); 25.5 (Me).

The same procedure was used for the synthesis of palladacycles **1b** and **2**.

Palladacycle **1b**: (180 mg, 45% yield based on Pd). Calculated for $C_9H_{11}ClPdS$, C= 36.88%; H= 3.78%. Found: C= 37.01; H= 3.67. ^{1}H NMR (300 MHz, $CDCl_3$ + εPy-d_5) (two isomers): δ d 7.44 (t, 1H, *J*= 7.4 Hz, CH aromatic), 7.04; 6.92 and 6.83 (3m, 3H, CH aromatic), 4.44 and 4.36 (2q, 1H, CH), 2.78 and 2.49 (2s, 3H, SMe), 1.82 and 1.77 (2 d, *J*= 7.0 and 6.9 Hz, 3H, CMe). ^{13}C NMR (75 MHz, $CDCl_3$ + εPy-d_5) (major isomer): δ 152.5; 151.1; 134.6; 124.9; 124.7 and 123.4 (C aromatic); 57.1 (CH); 21.5 and 20.1 (Me).

Palladacycle **2**: (160 mg, 42% yield based on Pd). Calculated for $C_{16}H_{19}ClPdS$, C= 49.88%; H= 4.97%. Found: C= 49.67, H= 5.13. ^{1}H NMR (300 MHz, DMSO): δ 8.14 (s, 1H, CH aromatic); 7.58 (m, 2H, CH aromatic); 7.42 (s, 1H, CH aromatic); 7.27 (m, 2H, CH aromatic); 4.37 (q, 1H, *J*= 6.8 Hz, CH); 1.66 (d, 3H, Me); 1.27 (s, 9H, *t*-Bu). ^{13}C NMR (75

MHz, DMSO) δ 159.0, 148.9, 136.2, 131.7, 131.4, 127.4, 127.3, 125.1, 124.5 and 119.4 (C aromatic); 51.2 (CH); 31.2 (*t*-Bu), and 26.4 (Me).

Typical experiment for the Heck reaction (Table 1, entry 1)

Methyl acrylate (1.2 mmol, 109 μl, 103 mg) was added to a solution of iodobenzene (1 mmol, 112 μl, 204 mg) in 5 mL of dimethylacetamide followed by the addition of triethylamine (1.4 mmol, 194 μl, 142 mg) and undecane as internal standard (20 μl, 14.7 mg). After the addition of the palladacycle **1a** in dimethylacetamide (20μl of a 0.1M solution) the reaction mixture was stirred at 140°C for 1 h. GC analysis gave 94% yield in methyl *trans*-cinnamate.

The same reaction was carried out without undecane. The solution was then allowed to cool to room temperature, taken up in CH_2Cl_2 (15 mL) and washed with water (9 x 10 mL) and brine (10 mL), and then dried over $MgSO_4$. After filtration, solvent was evaporated to give methyl *trans*-cinnamate (146 mg, 90%) estimated to be >95% pure by ^{1}H NMR and capillary GC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J*= 15.9 Hz, 1H, CH olefinic), 7.52-7.35 (m, 5H, CH aromatic), 6.45 (d, *J*= 15.9 Hz, CH olefinic), 3.80 (s, 3H, CO_2Me). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 167.6 (CO), 145.1, 134.6, 130.6, 129.1, 128.3, 118.0 (C aromatic and CH olefinic) 51.9 (Me). IR (neat) ν (cm^{-1}) 3061, 3028, 2950, 2842, 1717(C=O), 1637(C=C), 1578, 1496, 1450, 1434, 1330, 1316, 1276, 1203, 1171, 980, 934, 768, 710, 684.GC-MS (IE, 70 eV) m/z (%): 131 (100, M^+-OCH_3), 103 (58), 51(54), 162 (45, M^+), 77 (44), 161 (24), 50 (17), 102 (16).