Supporting Information

Ruthenium-Catalyzed Heck-Type Olefination and Suzuki Coupling Reactions: Studies on the Nature of Catalytic Species

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Activation experiment of iodobenzene with $[\text{RuCl}_2(\text{benzene})]_2$. A mixture of $[\text{RuCl}_2(\text{benzene})]_2$ (12 mg, 0.024 mmol) and NaOAc (79 mg, 0.96 mmol) in $\text{DMF-}d_7$ (0.5 mL) was stirred at 135 °C for 2 h followed by the addition of iodobenzene (7 mg, 0.04 mmol). The ^{13}C -NMR spectrum of the reaction mixture immediately showed a set of signals in the aromatic region at $\delta = 126.0, 128.9, 129.6$, which are attributed to arise from an activated ruthenium aryl species in analogy with the Pd cases (ref. 19 in the text) and they are distinctly different from those of iodobenzene ($\delta = 94.9, 128.4, 130.4, 138.1$ ppm). But a quaternary carbon center bound to Ru was not detected by the ^{13}C NMR spectroscopy.

Figure

S1.

The ^{13}C NMR spectrum from the reaction of $[\text{RuCl}_2(\text{benzene})]_2$, NaOAc, and iodobenzene in $\text{DMF-}d_7$ at 135 °C showing a set of new signals in the aromatic region at $\delta = 129.6, 128.9, 125.9$ ppm, which are differed from those of iodobenzene ($\delta = 94.9, 128.4, 131.4, 138.1$). The peaks marked with an asterisk imply Ru-bound C atoms of the presumed aryl ruthenium species. But the quaternary carbon which is bound to Ru was not detected by ^{13}C NMR.

(c)

Figure S2. (a) $[\text{RuCl}_2(p\text{-cymene})]_2$ in $\text{DMF-}d_7$, (b) a sample of $[\text{RuCl}_2(p\text{-cymene})]_2$ in $\text{DMF-}d_7$ after treating with $\text{Hg}(0)$ for 2 h at room temperature, (c) the same experiment of (b) except the temperatures (135°C).

Figure S3. A TEM image of aggregated ruthenium nanoparticles after the second cycle (right). The left picture is a TEM image of ruthenium nanoparticles before the reaction.

(*E*)-Ethyl 3-(3,4,5,6-tetrahydro-2-pyridinyl)-2-propenoate. ^1H NMR (CDCl_3 , 300 MHz) δ 6.94 (td, 1H, $J = 15.7, 6.5$ Hz), 5.85 (d, 1H, $J = 15.7$ Hz), 4.15 (m, 4H), 2.50 (m, 2H), 1.27 (m, 7H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 172.2, 166.3, 146.4, 122.3, 60.4, 60.1, 32.5, 27.2, 14.1, 14.0; IR (neat) 2963, 1713, 1638, 1202 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_2$ 181.1103 (M^+), found 181.1097.