

# **SUPPORTING INFORMATION**

**for**

## **Hydroarylation of Unactivated Olefins Catalyzed by a Pt(II) Complex**

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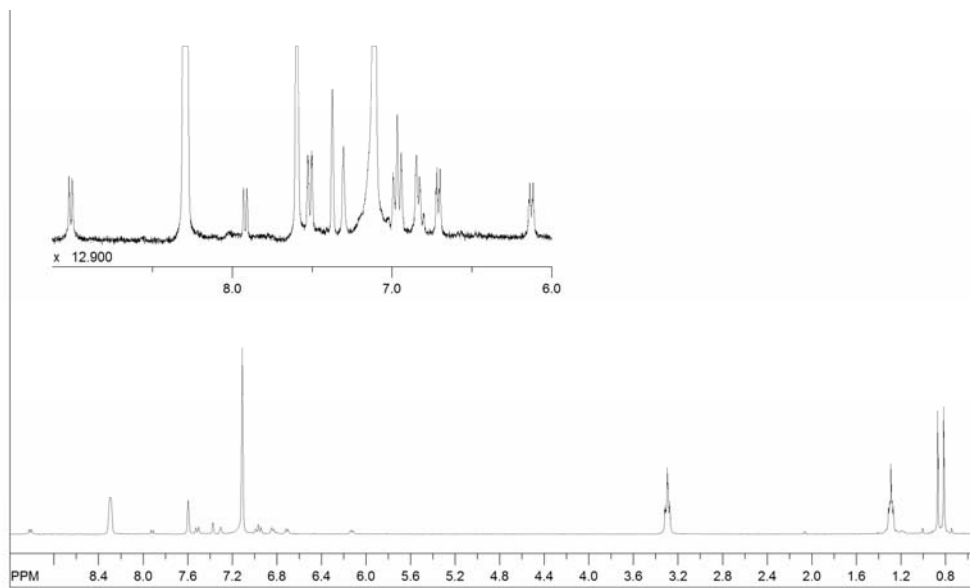
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**General Methods.** Unless otherwise noted, all synthetic procedures were performed under anaerobic conditions in a nitrogen-filled glovebox or by using standard Schlenk techniques. Glovebox purity was maintained by periodic nitrogen purges and was monitored by an oxygen analyzer  $\{\text{O}_{2(\text{g})} < 15 \text{ ppm for all reactions}\}$ . Benzene, tetrahydrofuran, and diethyl ether (stored over 4Å molecular sieves) were dried by distillation from sodium/benzophenone. Pentane was distilled over sodium. Hexanes and methylene chloride were purified by passage through a column of activated alumina. Benzene- $d_6$  was degassed with three freeze-pump-thaw cycles and stored under a  $\text{N}_2$  atmosphere over 4Å molecular sieves.  $^1\text{H}$  NMR spectra were recorded on a Varian Mercury 300 or 400 MHz spectrometer. All  $^1\text{H}$  spectra are referenced against residual proton signals of the deuterated solvents.  $^{19}\text{F}$  NMR spectra were obtained on a Varian 300 MHz spectrometer and referenced against an external standard of hexafluorobenzene ( $\delta = -164.9 \text{ ppm}$ ). Gas chromatography was performed on a Hewlett-Packard 5890 GC using a J&W DB-1701 capillary column (30 m x 0.25 mm with 0.25  $\mu\text{m}$  film thickness) with a FID detector. GC-MS was performed using a HP GCD EI system with a 30 m x 0.25 mm HP-5 column with 0.25 mm film thickness. Ethylene (99.5%) was received in a gas cylinder from MWSC High-Purity Gases and used as received. All other reagents were used as purchased from commercial sources. The preparation, isolation, and characterization of  $\text{NaBAR}'_4$   $\{\text{Ar}' = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3\}$ ,<sup>1</sup>  $(^t\text{bpy})\text{Pt(Ph)}_2$  (**1**) ( $^t\text{bpy} = 4,4'$ - di-*tert*-butyl-2,2'-bipyridine),<sup>2</sup> and  $(^t\text{bpy})\text{Pt(Cl)(Ph)}^2$  (**2**) have been previously reported.

**$[(^t\text{bpy})\text{Pt(Ph)(THF)}][\text{BAR}'_4]$  (**3**).** Complex **2** (0.079 g, 0.137 mmol) was dissolved in THF (~10 mL) and added to a solution of  $\text{NaBAR}'_4$  (0.122 g, 0.137 mmol) in THF (~15 mL). After 1 hr, the volatiles were removed *in vacuo*. The dried solid was dissolved in minimal THF and filtered through Celite. The volume of the filtrate was reduced *in vacuo* to ~1 mL, and a light yellow precipitate was formed upon addition of hexanes (~15 mL). The precipitate was collected on a fine porosity frit, washed with *n*-pentane (3 x 2 mL), and dried *in vacuo* to yield  $[(^t\text{bpy})\text{Pt(Ph)(THF)}][\text{BAR}'_4] \cdot 2 \text{ THF}$  (0.148 g,

67%).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ : 9.06 (d, 1H,  $^3J_{\text{HH}} = 6$  Hz,  $^t\text{bpy}$ ), 8.35 {br s, 8H,  $H_o(\text{BAr}')$ }, 7.97 (d, 1H,  $^3J_{\text{HH}} = 6$  Hz,  $^t\text{bpy}$ ), 7.64 {br s, 4H,  $H_p(\text{BAr}')$ }, 7.56 {d, 2H,  $^3J_{\text{HH}} = 7$  Hz,  $H_o(\text{Ph})$ }, 7.42 (s, 1H,  $^t\text{bpy}$ ), 7.35 (s, 1H,  $^t\text{bpy}$ ), 7.02 {t, 2H,  $^3J_{\text{HH}} = 7$  Hz,  $H_m(\text{Ph})$ }, 6.88 {t, 1H,  $^3J_{\text{HH}} = 7$  Hz,  $H_p(\text{Ph})$ }, 6.76 (d, 1H,  $^3J_{\text{HH}} = 6$  Hz,  $^t\text{bpy}$ ), 6.18 (d, 1H,  $^3J_{\text{HH}} = 6$  Hz,  $^t\text{bpy}$ ), 3.35 (m, 12H, THF  $\alpha\text{-CH}_2$ ), 1.34 (m, 12H, THF  $\beta\text{-CH}_2$ ), 0.92 (s, 9H,  $t\text{-butyl } ^t\text{bpy}$ ), 0.86 (s, 9H,  $t\text{-butyl } ^t\text{bpy}$ ).  $^{19}\text{F}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$ : -60.61 {s,  $\text{CF}_3$  ( $\text{BAr}'$ )}. In all cases, complex **3** is isolated with excess THF. The excess THF can be removed by multiple washings and sonication in  $n$ -pentane and diethylether; however, in the absence of a slight excess of THF, complex **3** decomposes in solution to multiple products.



**Figure S1.**  $^1\text{H}$  NMR spectrum of  $[(^t\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAr}'_4]$  in  $\text{C}_6\text{D}_6$  with the downfield region enlarged in the inset.

**Catalytic Hydroarylation Reactions.** A representative catalytic reaction is described.  $[(^t\text{bpy})\text{Pt}(\text{Ph})(\text{THF})][\text{BAr}'_4]$  (**3**) (0.026 g, 0.016 mmol) was dissolved in 1.4 mL of a stock solution of 0.1% hexamethylbenzene (HMB; internal standard) in benzene. The reaction mixture was placed in a

stainless steel pressure reactor, which was purged with ethylene, charged with 15 psi of ethylene, pressurized with dinitrogen (120 psi) and heated to 100 °C. After 4 and 16 hours, the reaction was analyzed by GC-FID, and peak areas of products were used with the internal standard to calculate product yields. Ethylbenzene production was quantified using linear regression analysis of gas chromatograms of standard samples. A set of five known standards were prepared consisting of 1:1, 2:1, 3:1, 4:1, and 5:1 molar ratios of ethylbenzene to hexamethylbenzene in benzene. A plot of the peak area ratios versus molar ratios gave a regression line. The slope and correlation coefficient for ethylbenzene were 0.66 and 0.98, respectively. Identical procedures were used to quantify 2-ethylfuran (0.23, 0.99), 1,2-diethylbenzene (0.80, 0.98), 1,3-diethylbenzene (0.47, 0.99), 1,4-diethylbenzene (0.58, 0.98), *n*-propylbenzene (0.71, 0.99), and cumene (0.75, 0.98).

## References

1. Yakelis, N. A.; Bergman, R. G. *Organometallics* **2005**, *24*, 3579-3591.
2. Ong, C. M.; Jennings, M. C.; Puddephatt, R. J. *Can. J. Chem.* **2003**, *81*, 1196-1205.