Arene C-H Bond Activation Across Pt(II)-OH Bonds: Catalyzed vs. Uncatalyzed Pathways.

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Supporting Information

General considerations.

An argon filled glove box was employed for manipulation and storage of all oxygen and moisture sensitive compounds. All reactions were performed on a double manifold high vacuum line using standard techniques.[1] Residual oxygen and moisture were removed from the argon stream by passage through an OxisorBW scrubber from Matheson Gas Products. Toluene, tetrahydrofuran, and hexanes solvents were dried and purified using the Grubbs/Dow purification system[2] and stored in evacuated 500 mL bombs over sodium- tetraglyme/benzophenone ketyl. Pentane and dichloromethane were dried, distilled, and stored in an evacuated 500 mL bombs over sodium-tetraglyme/benzophenone ketyl (pentane) and calcium hydride (dichloromethane). All solvents were distilled prior to use. Water and deuterium oxide were degassed by 3 freeze-pump-thaw cycles and stored in a glovebox designated for water usage, or in a sealed glass bomb. d_6-benzene and d_2-methylene chloride were dried over and distilled from CaH_2, and was stored in glass bomb in a glove box. Solutions of 30 mMol/L H_2O in C_6D_6 were made up in volumetric glassware in a glovebox designated for water usage and stored in a sealed glass bomb. ^1H, and ^{13}C chemical shifts were referenced to residual proton, and naturally abundant ^{13}C resonance of the deuterated solvent, respectively. Assignments of chemical shifts are based on ^1H, ^2H, ^{13}C, DQF-COSY, ^1H,^{13}C-HMQC, and NOESY NMR spectra performed on Bruker RDQ-400, DRY-400, UGI-400 and CFI-600 spectrometers. Multi-day high temperature ^1H NMR cycling experiments were performed on a CFI-600 spectrometer. NMR spectra were processed and analyzed with MestReNova (v7.0.2-8636). High-resolution mass spectra were obtained using a Bruker Esquire 3000 spectrometer operating in electrospray ionization (ESI) mode. X-ray crystallographic analyses were performed on suitable crystals coated in Paratone 8277 oil (Exxon) and mounted on a glass fibre. Measurements were collected on a Nonius KappaCCD diffractometer by Dr. Masood Parvez of this department; full details can be found in the independently deposited crystallography information files (cif). Elemental analyses were performed using a Perkin-Elmer model 2400 series II analyzer by Johnson Li of this department. Transmission Electron Microscopy (TEM) and Energy-Dispersive X-ray spectroscopy (EDX) were performed by Dr. Tobias Furstenhaupt of the University of Calgary Microscopy and Imaging Department. TEM samples were prepared by

suspending in acetone, and under protective nitrogen atmosphere a drop of the nanoparticle solution was placed on one side of a TEM mesh grid that was covered with thin continuous 40 nm formvar film and dried for several minutes. All TEM work was carried out on a Technai TF20 G2 FEG-TEM with a FEI low background double tilt holder. Bright field images were digitized on a Gatan UltraScan 4000 CCD at 2048x2048 pixels. EDX analysis was done with an EDAX CM-20T detector. Absolute ethanol and Silver(1) oxide were purchased from Aldrich and used as received. Hexamethylbenzene was purchased from Eastman Organic Chemicals, sublimed at 70°C under static vacuum and stored under argon. All NMR solvents were purchased from Cambridge Isotope Laboratories Inc. and dried according to the procedures outlined above or used as received. All air-sensitive compounds were stored in the glove box. *cis*-$[Pt(SMe_2)_2(Ph)_2]$,[3] and *cis/trans*-$[Pt(SMe_2)_2(Ph)Cl]$[4] were synthesized according to reported procedures. Compound **1** and **L** have been reported elsewhere.[5] The IR of **2** was done as a benzene film sandwiched between two NaCl plates and sealed from air in the glovebox by sealing the outer edges of the plates with black electrical tape.

Synthesis of (NN)PtCl(C_6H_5).

The bulky diimine ligand (0.178g, 0.183 mmol, 0.95 eq) and $(SMe_2)_2Pt(C_6H_5)Cl$ (0.080g, 0.185 mmol, 1eq) were added to a round bottomed flask, attached to a reflux condenser and evacuated. Dry tetrahydrofuran (50 mL) was vacuum transferred in and the solution was refluxed for 32 hrs. The tetrahydrofuran was removed on the rotovap, the solid washed with absolute ethanol (3 x 2 mL) and hexanes (2 x 5 mL) to yield an air stable dark purple powder. X-ray quality crystals were grown by slow evaporation from toluene. Yield: 0.152 g, 65%. ^{1}H NMR (400 MHz, C_6D_6, 298K): δ = 0.94 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.10 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.18 (d, $^3J_{H\text{-}H}$ = 7 Hz, 12H, CH(CH_3)$_2$), 1.29 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.30 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.30 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(CH_3)$_2$), 1.47 (d, $^3J_{H\text{-}H}$ = 7 Hz, 6H, CH(CH_3)$_2$), 2.67 (septet, $^3J_{H\text{-}H}$ = 7 Hz, 2H, CH(CH$_3$)$_2$), 2.88 (septet, $^3J_{H\text{-}H}$ = 7 Hz, 2H, CH(CH$_3$)$_2$), 3.17 (septet, $^3J_{H\text{-}H}$ = 7 Hz, 2H, CH(CH$_3$)$_2$), 3.49 (septet, $^3J_{H\text{-}H}$ = 7 Hz, 4H, CH(CH$_3$)$_2$), 6.78 (d, $^4J_{H\text{-}H}$ = 1 Hz, 2H, Ar-CH), 6.90 (d of d, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar$_{Naphth}$-CH), 6.90 (t, $^3J_{H\text{-}H}$ = 7 Hz, 1H, Pt-C_6H_5 *para*), 6.98 (d of d, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar$_{Naphth}$-CH), 7.05 (m, $^3J_{H\text{-}H}$ = 7 Hz, 2H,

Pt-C_6H_5 *meta*), 7.10 (d, 2H, Ar-CH), 7.21 (m, 3H, Ar-CH), 7.26 (d, 2H, Ar-CH), 7.28 (d, 2H, Ar-CH), 7.31 (d, 2H, Ar-CH), 7.36 (d, $^4J_{H\text{-}H}$ = 1 Hz, 2H, Ar-CH), 7.45 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar_{Naphth}-C*H*), 7.59 (d, $^3J_{H\text{-}H}$ = 7 Hz, 2H, Pt-C_6H_5 *ortho*), 7.70 (d, $^3J_{H\text{-}H}$ = 8 Hz, 1H, Ar_{Naphth}-C*H*). ^{13}C NMR (100 Mz, C_6D_6, 298K): δ = 24.71 ((CH(*C*H_3)$_2$), 24.88 ((CH(*C*H_3)$_2$), 25.02 ((CH(*C*H_3)$_2$), 25.04 ((CH(*C*H_3)$_2$), 25.21 (2 x(CH(*C*H_3)$_2$), 25.81 ((CH(*C*H_3)$_2$), 30.74 (*C*H(CH$_3$)$_2$), 31.19 (*C*H(CH$_3$)$_2$), 31.25 (*C*H(CH$_3$)$_2$), 31.59 (*C*H(CH$_3$)$_2$), 121.92 (Ar-CH), 122.63 (Ar-CH), 122.83 (Ar-CH), 123.00 (Pt-C_6H_5 *para*), 123.06 (Ar-CH_{Naphth}), 123.57 (Ar-CH_{Naphth}), 123.99 (Ar-CH), 124.07 (Ar-CH), 126.60 (Pt-C_6H_5 *meta*), 129.02, 129.12 (Ar-CH), 129.26 (Ar-CH_{Naphth}), 129.42 (Ar-CH), 129.47 (Ar-CH), 129.96 (Ar-CH_{Naphth}), 130.52, 131.14 (Ar-CH), 132.11 (Ar-CH_{Naphth}), 132.59 (Ar-C), 132.87, 138.35, 138.62 (Pt-C_6H_5 *ortho*), 139.11, 142.50, 143.05, 145.34, 146.07, 146.27, 146.82, 148.02, 148.47, 148.79, 170.91 (N=*C*-Ar), 173.39 (N=*C*-Ar). Anal Calcd for $C_{78}H_{86}N_2ClPt$: C, 73.13; H, 6.69; N, 2.19. Found: C, 73.10; H, 6.70; N, 2.05.

Preparation of C_6D_6/H_2O stock solutions:

Two stock solutions were made in 5 mL volumetric flasks containing hexamethylbenzene standard (0.007g, 8.63 mM/L). In a glovebox designated for water usage, 27 uL (30 mM/L) of degassed H_2O was added via micropipette to one flask. Dry C_6D_6 was measured into both flasks and they were stored in their retrospective gloveboxes under argon in sealed glass bombs.

*Representative procedure for monitoring conversion of **1**:*

For each run, **1** (0.0105g, 8.73 umol, 0.3 mL stock solution, 29 mMol/L) *or* (0.009g, 7.48 umol, 0.31 mL stock solution, 24.5 mMol/L) and the appropriate C_6D_6 stock solution was added to a j-young NMR tube and sealed with a Teflon screw tap. The tube was then inserted into the preheated NMR probe (353K, 600 MHz) and allowed to equilibrate for 20 minutes before beginning the cycling program. A total of 5 scans were taken each time increment with a delay time between each scan of 10 seconds to ensure proper integration.

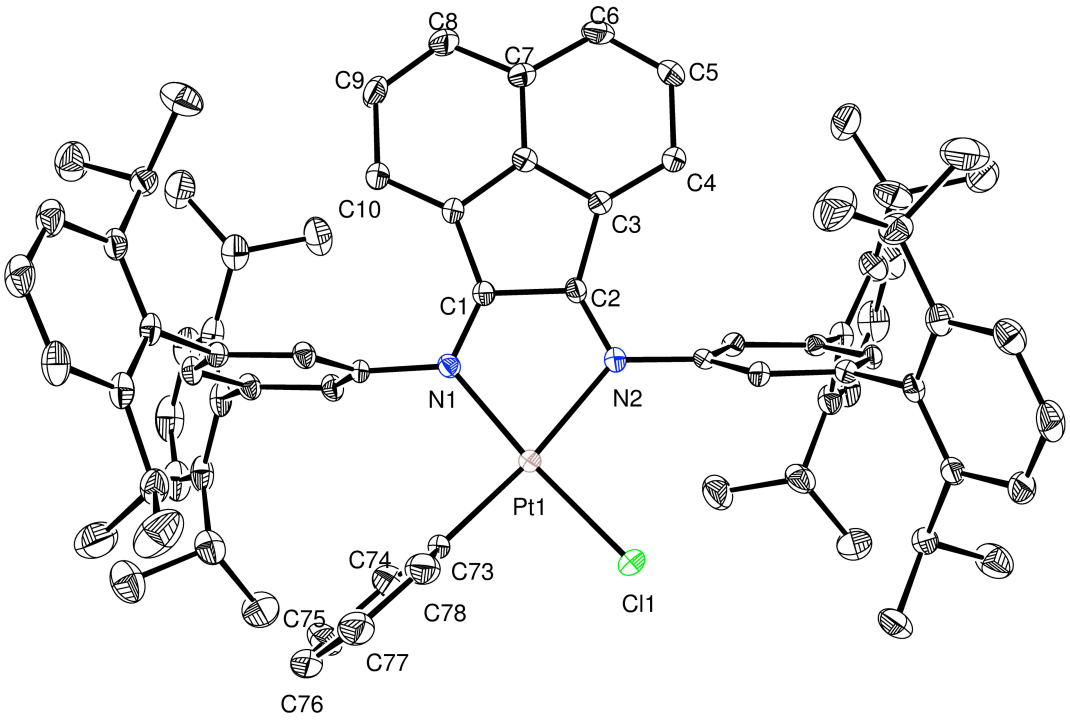

Figure S1. ORTEP plot of (NN)PtCl(C_6H_5) (30% thermal displacement ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths in Å: Pt-Cl1, 2.2785(9); Pt-C73, 2.014(5); Pt-N1, 2.014(3); Pt-N2, 2.139(4); N1-C1, 1.300(6); N2-C2: 1.283(5).

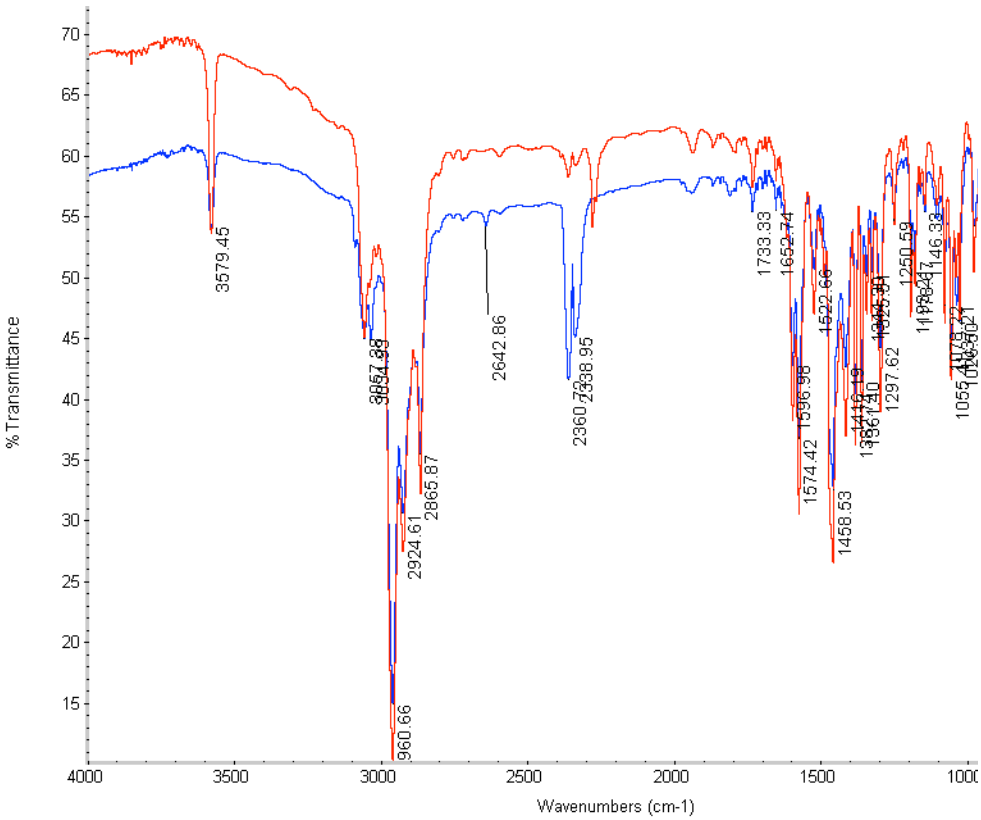

Figure S2. IR spectrum for **2**-OH (top) and **2**-OD (bottom) in the region between 1000-4000 cm^{-1}. The Pt-OD peak is significantly reduced in magnitude with resulting formation of Pt-OH due to exchange with 1 type of ^{i}Pr CH_3 groups on the ligand.

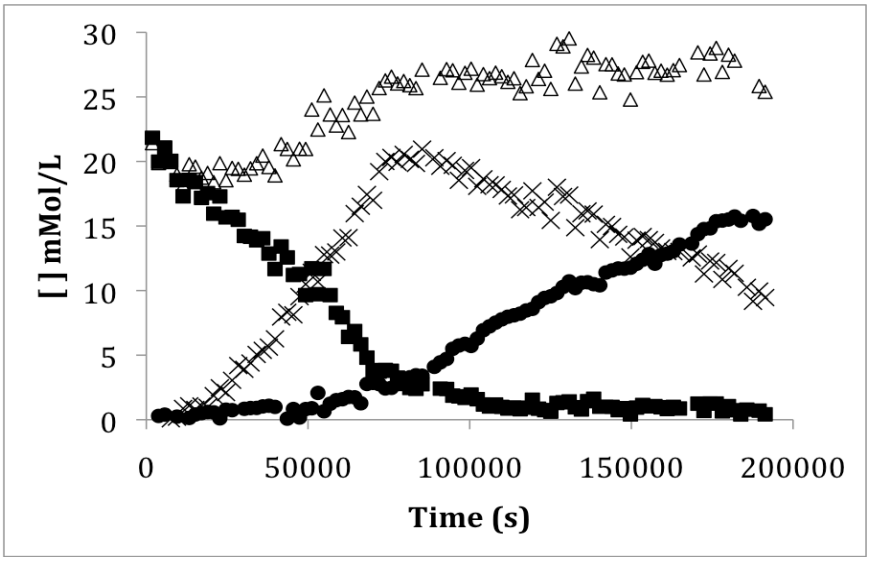

Figure S3. Concentration verses time plots for the reaction of **1** (29 mMol/L made up) in dry C_6D_6 at 353K as studied by ^{1}H NMR (**1**: ■, **2**: ✕, **3**: ●, total [Pt]: △).

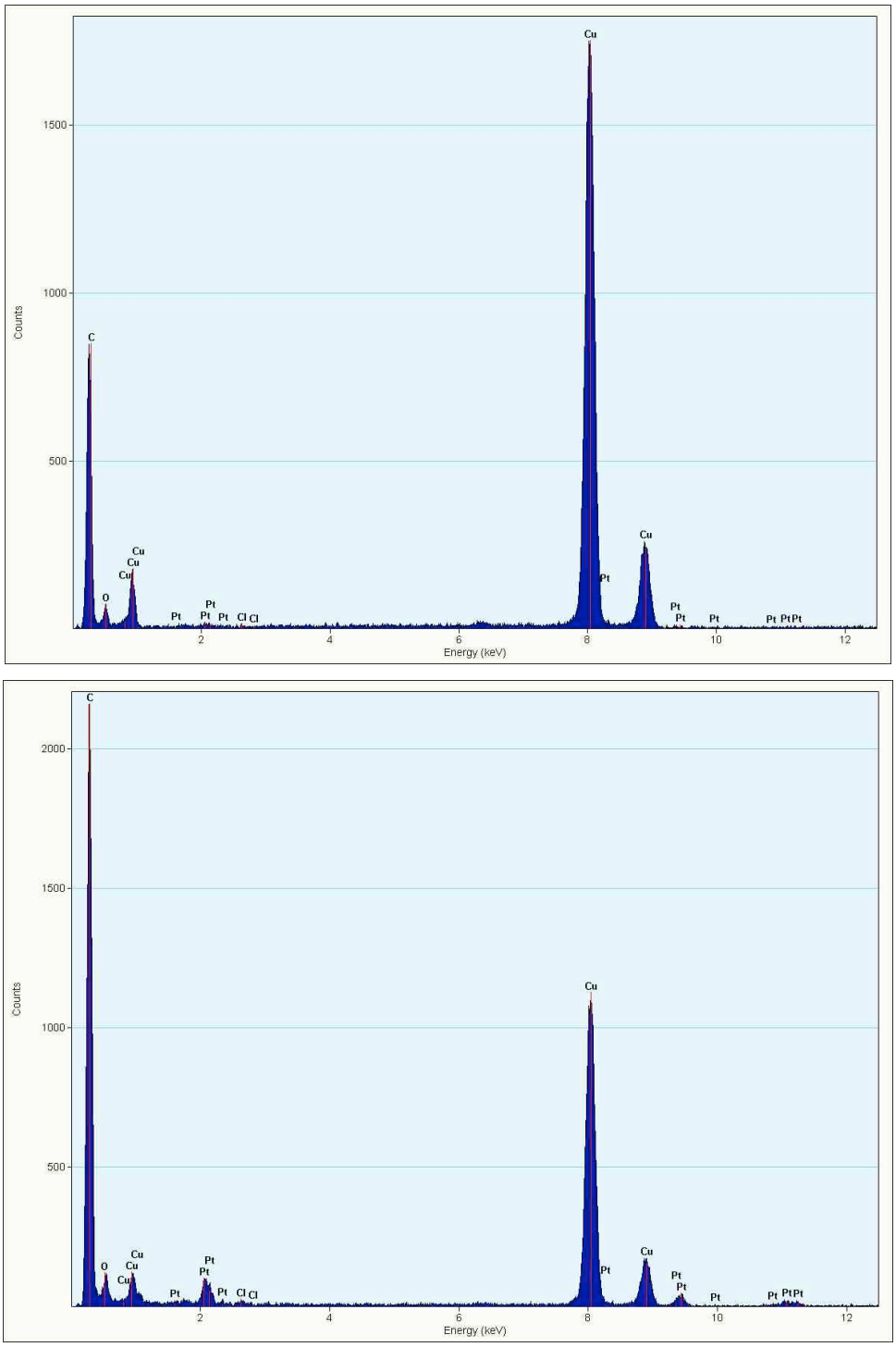

Figure S4. EDX Spectra of Nanoparticles. Top: Background spectrum in a grid area with no particles. Bottom: Spectrum in a grid area with many particles.

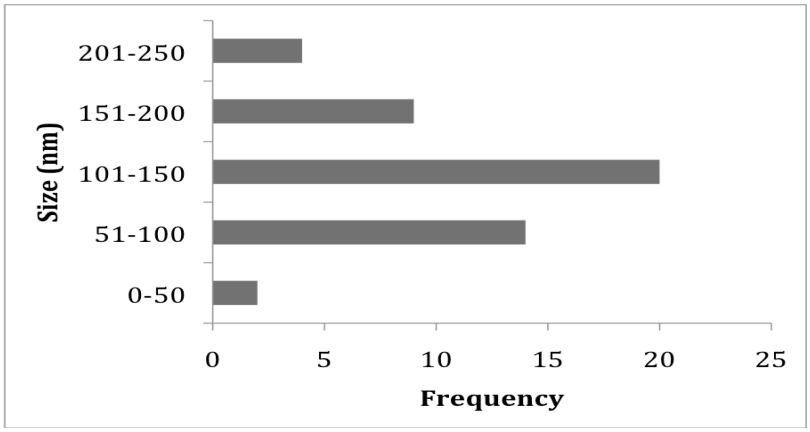

Figure S5. Size Distribution Analysis of Nanoparticles (Sample size: 50 particles)

References for Supporting Information:

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3. Hill, G. S.; Irwin, M. J.; Levy, C. J.; Rendina, L. M.; Puddephatt, R. J., *Inorg. Synth.* **1998**, *32*, 150.
4. Kapoor, P.; Kukushkin, V. Y.; Lövqvist, K.; Oskarsson, Å., *J. Organomet. Chem.* **1996**, *517*, 71-79.
5. Lohr, T. L.; Piers, W. E.; Parvez, M., *Inorg. Chem.* **2012**, *51*, 4900-4902.