

Ligand Effects on the Oxidative Addition of Halogens to (dpp-nacnac^R)Rh(phdi)

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Physical Methods. NMR spectra were collected on Bruker Avance 400, 500, and 600 MHz spectrometers in dry, degassed CDCl₃. ¹H NMR spectra were referenced to TMS using the residual proteo impurities of the solvent; ¹³C NMR spectra were referenced to TMS using the natural abundance ¹³C impurities of the solvent. All chemical shifts are reported using the standard notation in parts per million; positive chemical shifts are to a higher frequency from the given reference. Electronic absorption spectra were recorded with a Perkin-Elmer Lambda 900 UV-vis spectrophotometer.

Electrochemical Methods. Electrochemical experiments were performed on a Gamry Series G 300 Potentiostat/Galvanostat/ZRA (Gamry Instruments, Warminster, PA, USA) using a 3.0 mm glassy carbon working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode. Electrochemical experiments were performed at room temperature, either in a glovebox or under an atmosphere of pre-purified argon or nitrogen in a 1.0 mM analyte

solution in THF with 0.10 M (*n*-Bu₄N)PF₆ as supporting electrolyte. All potentials are referenced to the Fc⁺/Fc couple set at 0.00 V by using decamethylferrocene as an internal standard at –0.49 V versus ferrocene. The typical solvent system window with our configuration was 1.5 V for the oxidation limit and –2.7 V for the reduction limit (vs. the Fc⁺/Fc couple). Decamethylferrocene (Acros) was purified by sublimation under reduced pressure and tetra-*n*-butylammonium hexafluorophosphate (Acros) was recrystallized from ethanol three times and dried under vacuum. To verify that electrode processes were diffusion-controlled, forward peak currents were plotted with respect to the square root of scan rates in the range of 50 to 1600 mV/s and found to be linear.

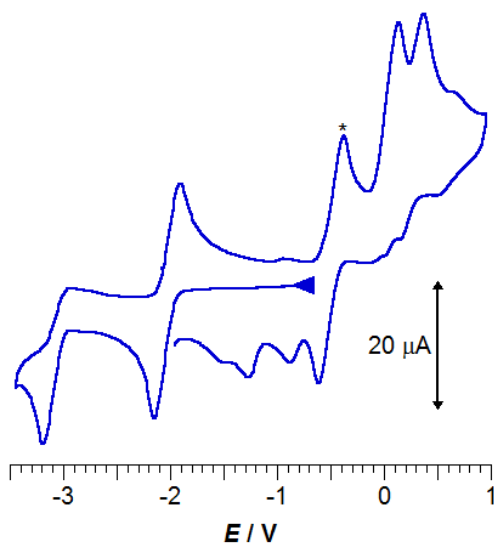


Figure S1. Cyclic voltammogram of 1 mM (dpp-nacnac^{CH₃})Rh(phdi) (**1a**) in the presence of 2 mM (*n*-Bu₄N)Cl measured at 200 mV s⁻¹. Marked with an asterisk is decamethylferrocene, which was used as an internal standard to reference potentials to (Cp₂Fe)⁺⁰. Measurements made in THF with 0.10 M (*n*-Bu₄N)PF₆ under N₂.

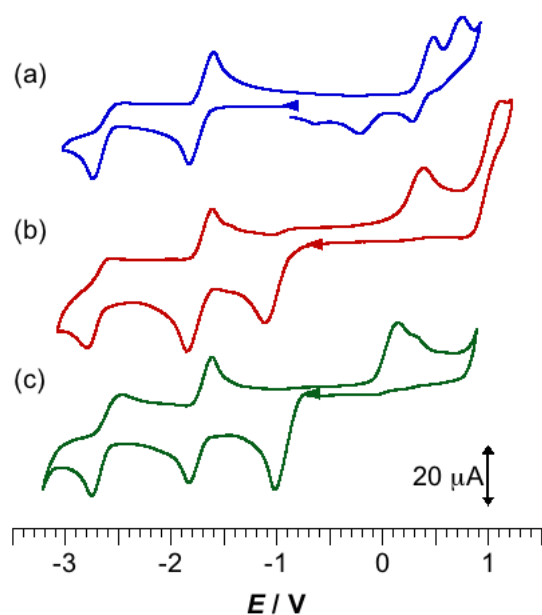


Figure S2. Cyclic voltammograms of (a) (dpp-nacnac^{CH₃})Rh(phdi) (**1b**), (b) (dpp-nacnac^{CH₃})RhCl₂(phdi) (**2b**), and (c) (dpp-nacnac^{CH₃})RhBr₂(phdi) (**3b**) measured at 200 mV s⁻¹. All measurements made in THF with 1.0 mM analyte and 0.10 M (*n*-Bu₄N)PF₆ under N₂ or Ar. Potentials referenced to (Cp₂Fe)⁺⁰.

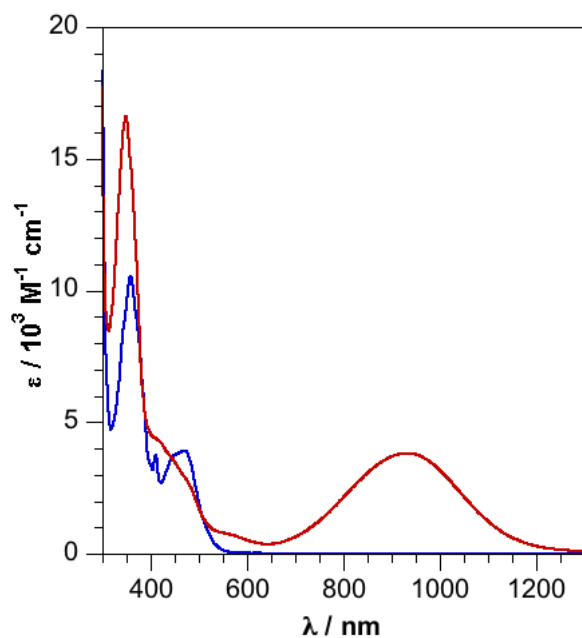


Figure S3. UV-vis-NIR absorption spectra of (dpp-nacnac^{CH₃})RhCl₂(phdi) (**2a**) (red), and [(dpp-nacnacH^{CH₃})RhCl₂(phdi)][BF₄] (**[6a][BF₄]**) (blue) in CH₂Cl₂ at 25 °C.

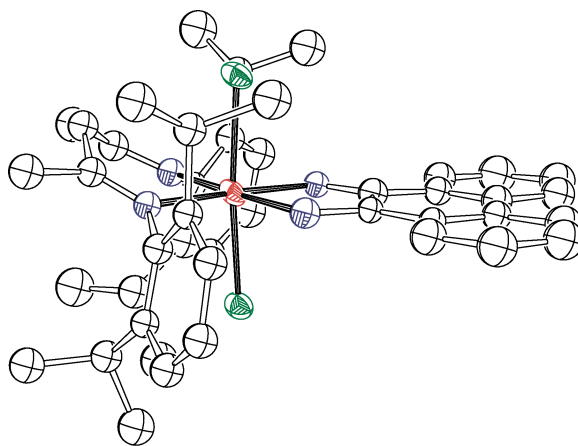


Figure S4. Molecular structure of **[6a][BF₄]**. Hydrogen atoms, solvent molecules, and anion omitted.

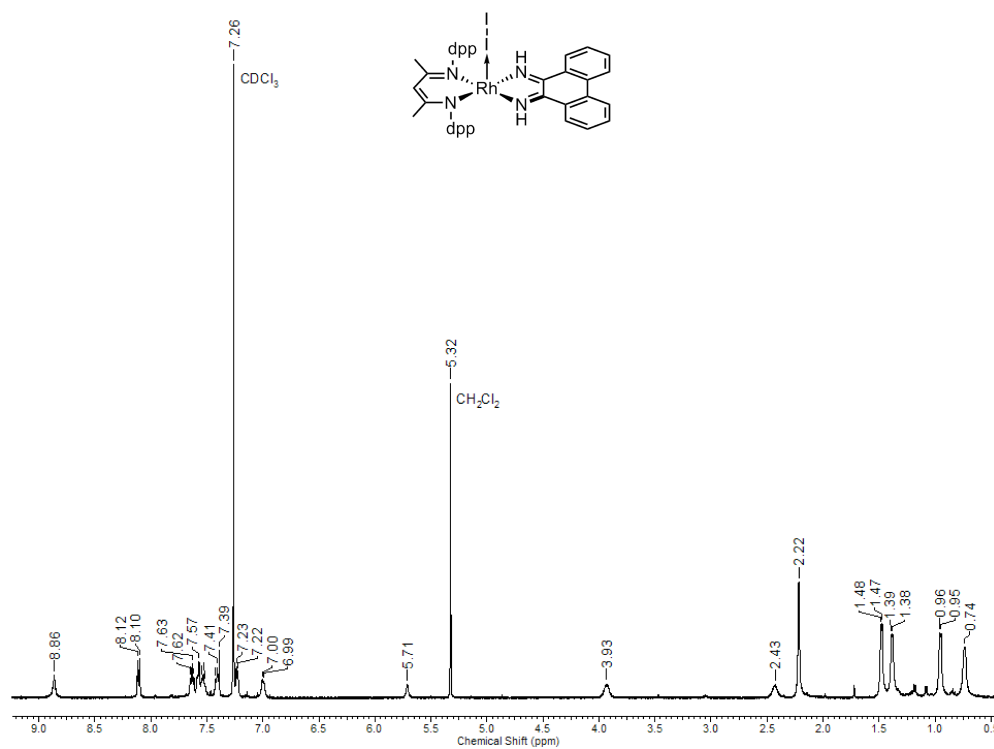


Figure S5. ¹H NMR spectrum of **4a** in CDCl₃ at 223 K.

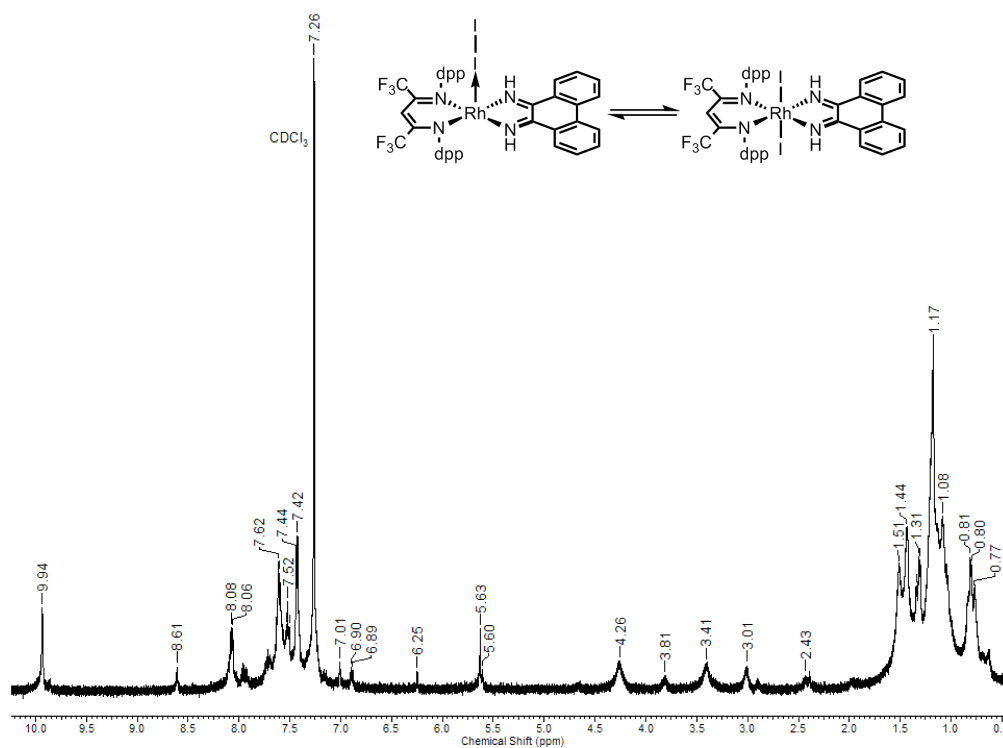


Figure S6. ¹H NMR spectrum of an equilibrium mixture of **4b** and **5b** in CDCl₃ at 223 K.

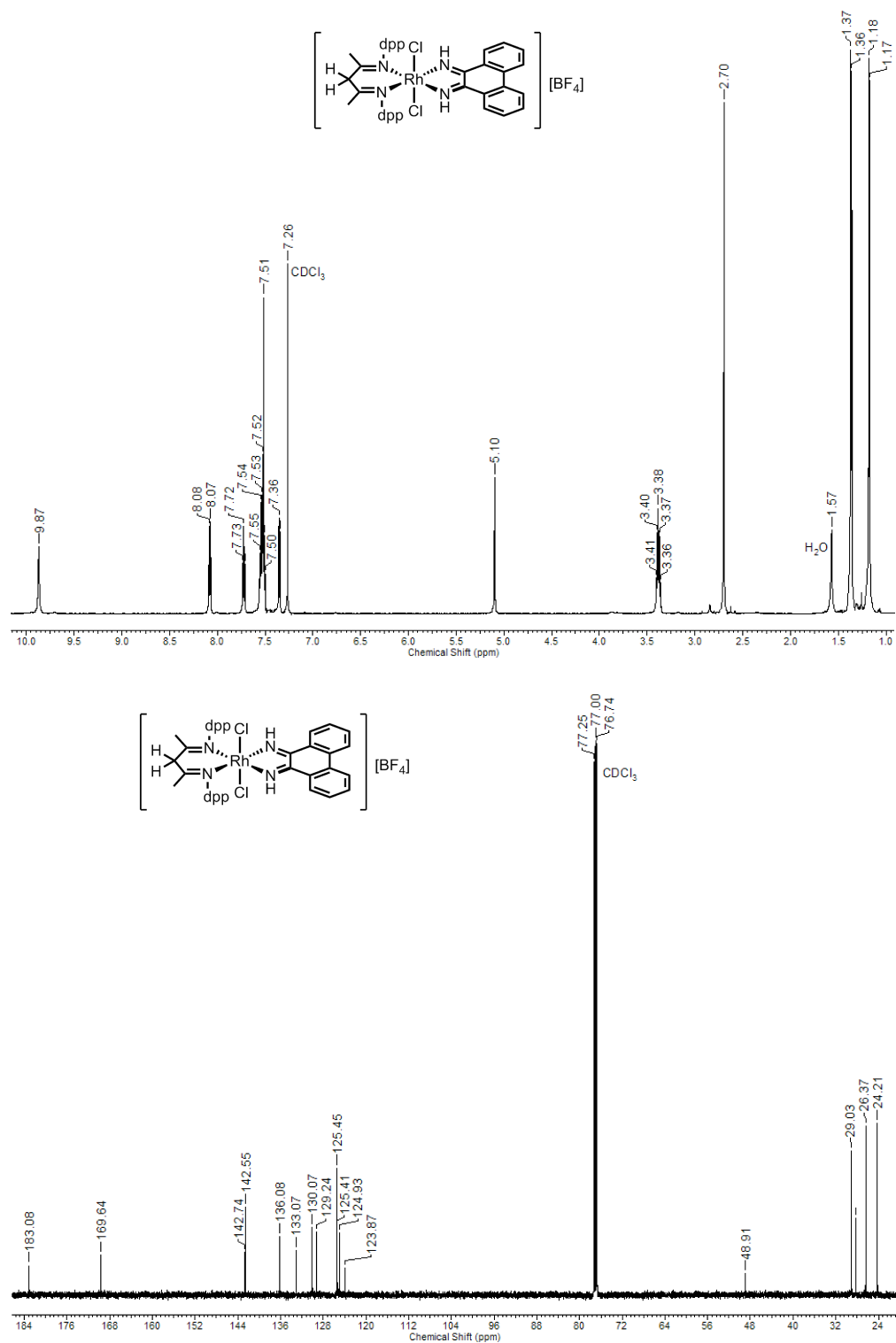


Figure S7. ^1H (top) and ^{13}C (bottom) NMR spectra of $[(\text{dpp-nacnacH}^{\text{CH}_3})\text{RhCl}_2(\text{phdi})][\text{BF}_4]$ (**[6a]**)[BF_4] in CDCl_3 at 298 K.



Figure S8. ^1H (top) and ^{13}C (bottom) NMR spectra of $[(\text{dpp-nacnacH}^{\text{CH}_3})\text{RhI}_2(\text{phdi})][\text{BF}_4]$ (**7a**) $[\text{BF}_4]$ in CDCl_3 at 298 K.