

## Supplementary Information for

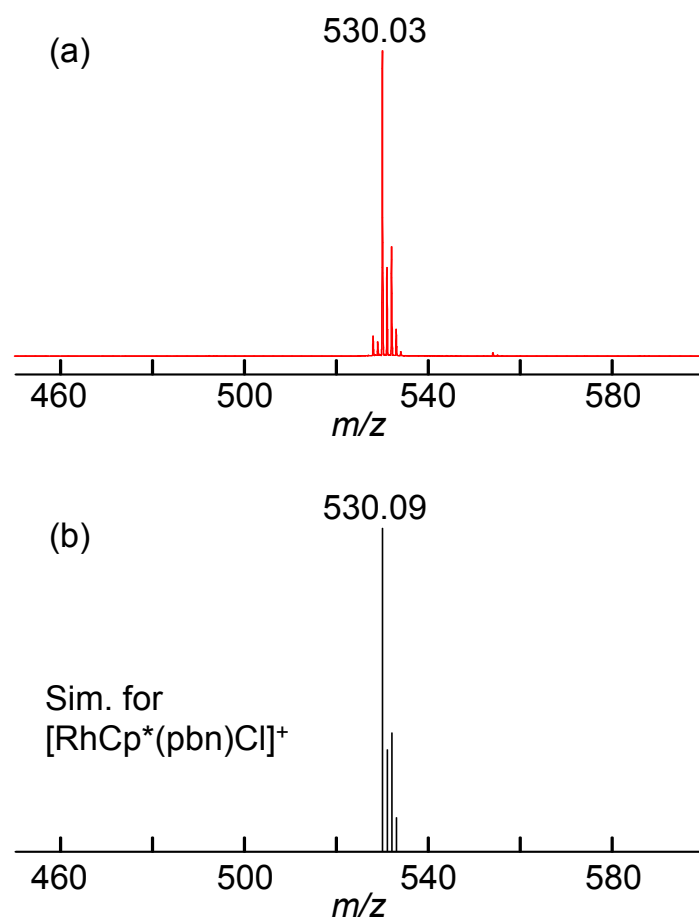
### **Electrochemical behavior of a Rh(pentamethylcyclopentadienyl) complex bearing an NAD<sup>+</sup>/NADH-functionalized ligand**

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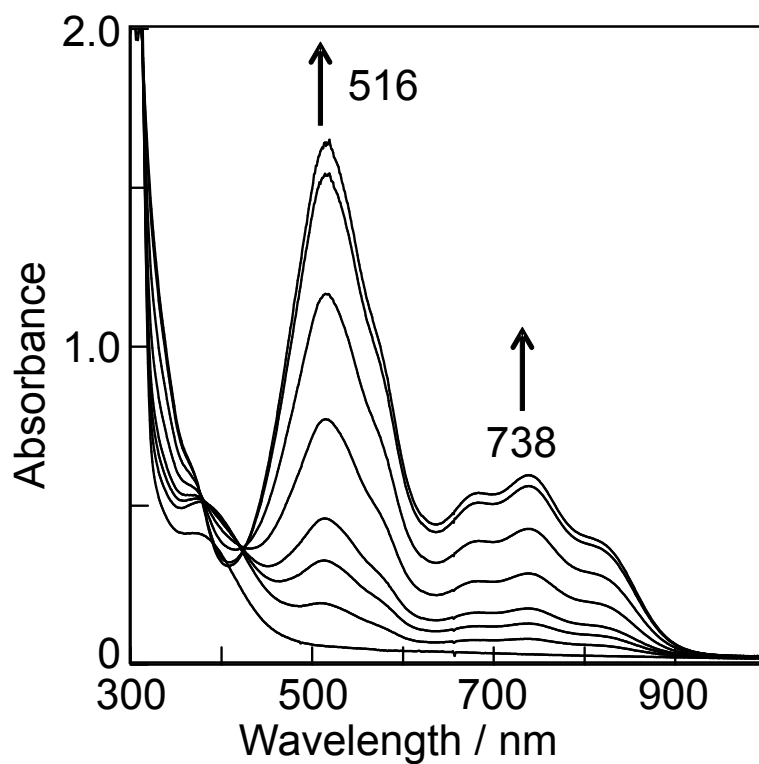
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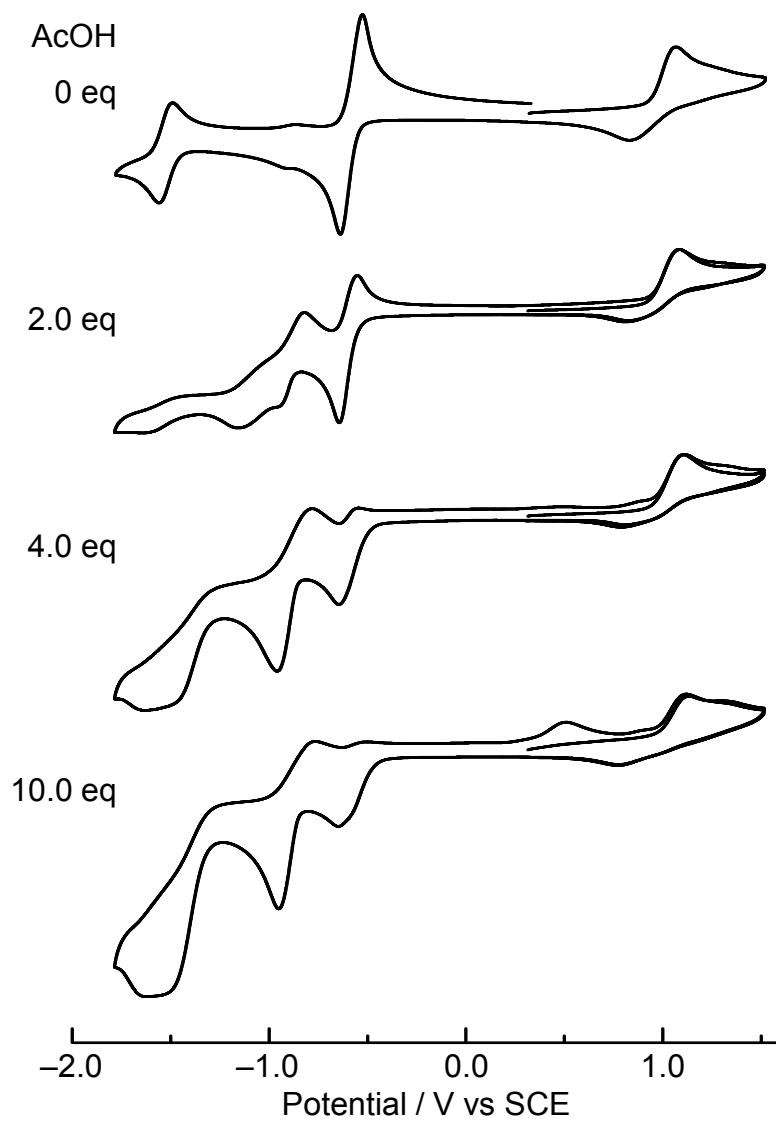
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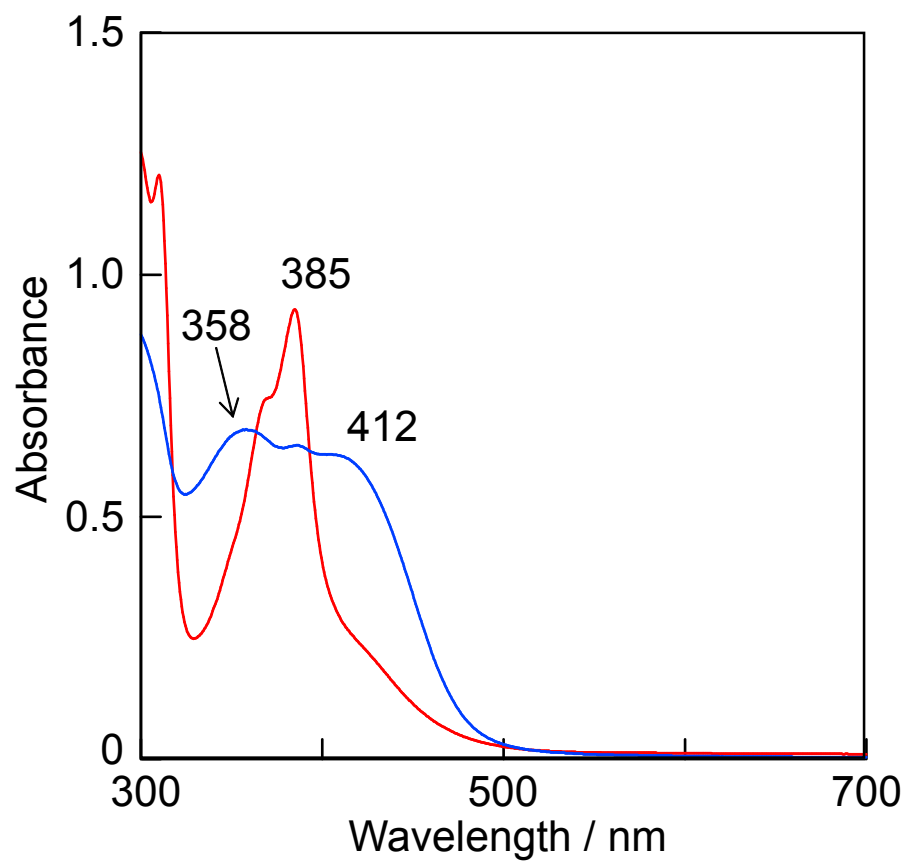
**Figure S1.** (a) ESI-MS spectrum of  $[1]Cl$  in  $CH_3CN$  containing 10% TEA and (b) simulated spectrum of  $[1]^+$ .



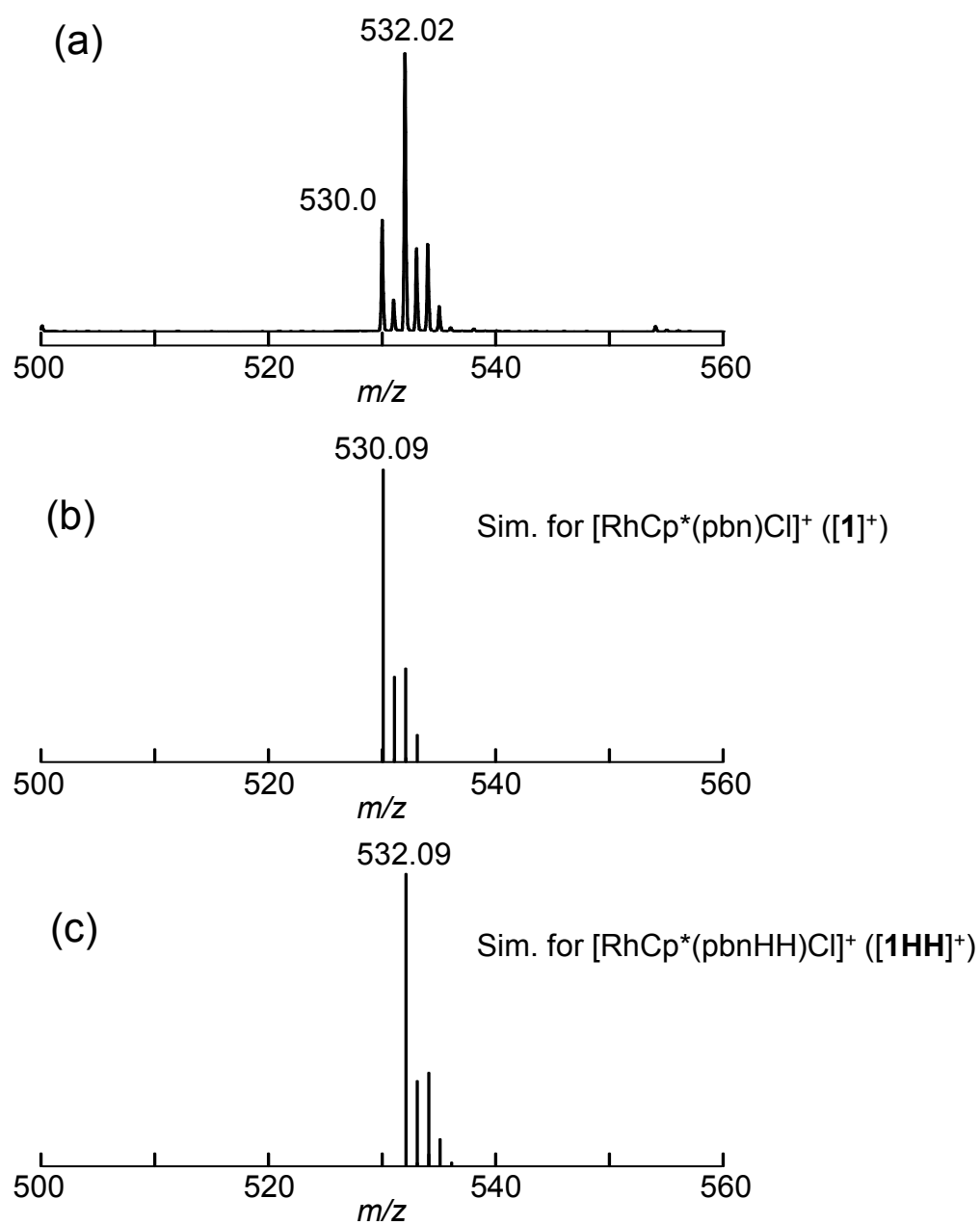
**Figure S2.** Spectral changes for [RhCp\*(bpy)Cl]Cl during reduction at  $-1.0$  V (vs. SCE) in  $\text{CH}_3\text{CN}$  with  $0.1$  M  $[\text{nBu}_4][\text{PF}_6]$  as the supporting electrolyte.



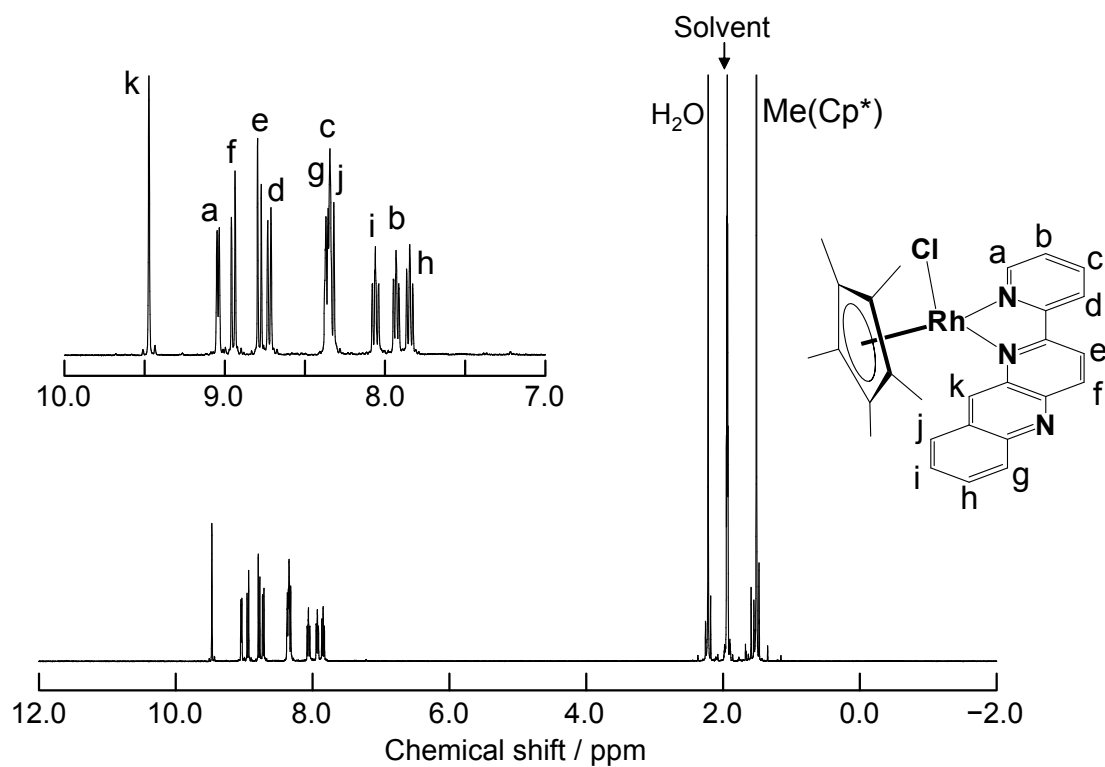
**Figure S3.** Cyclic voltammograms of [1]Cl in the presence of varying amounts of AcOH.



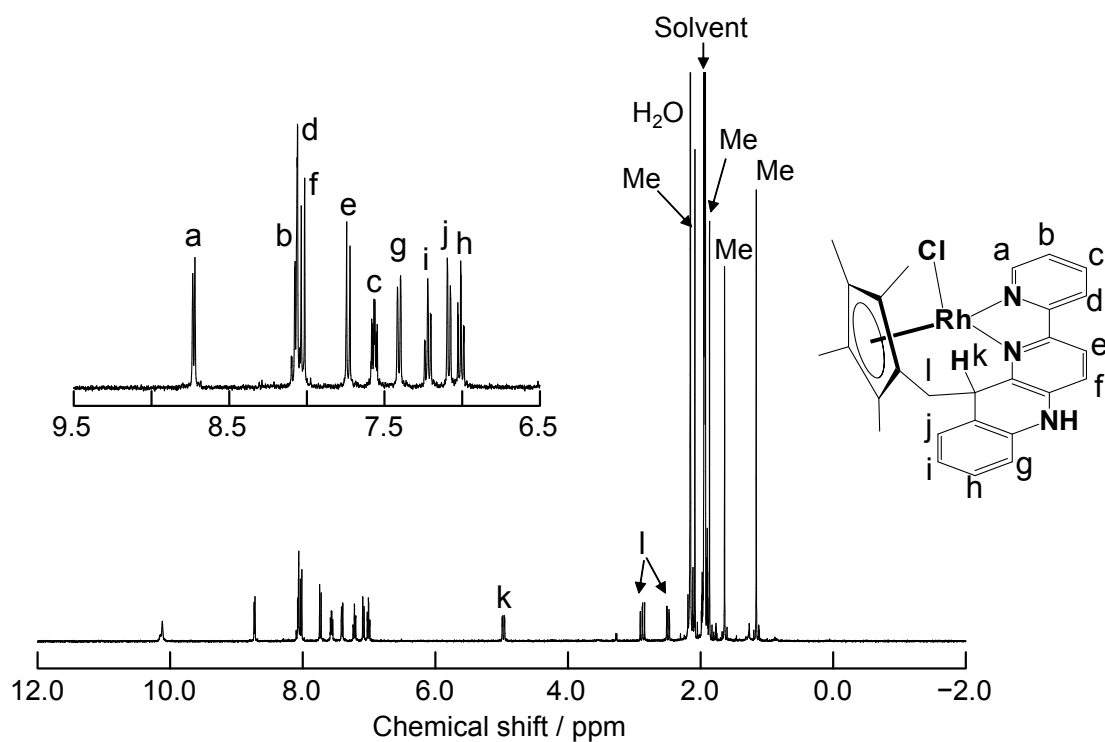
**Figure S4.** Electronic spectra of [1]Cl in the absence of CoCp<sub>2</sub> (red line) and the presence of 2 equiv. of CoCp<sub>2</sub> (blue line) in CH<sub>3</sub>CN containing 1.0% AcOH.



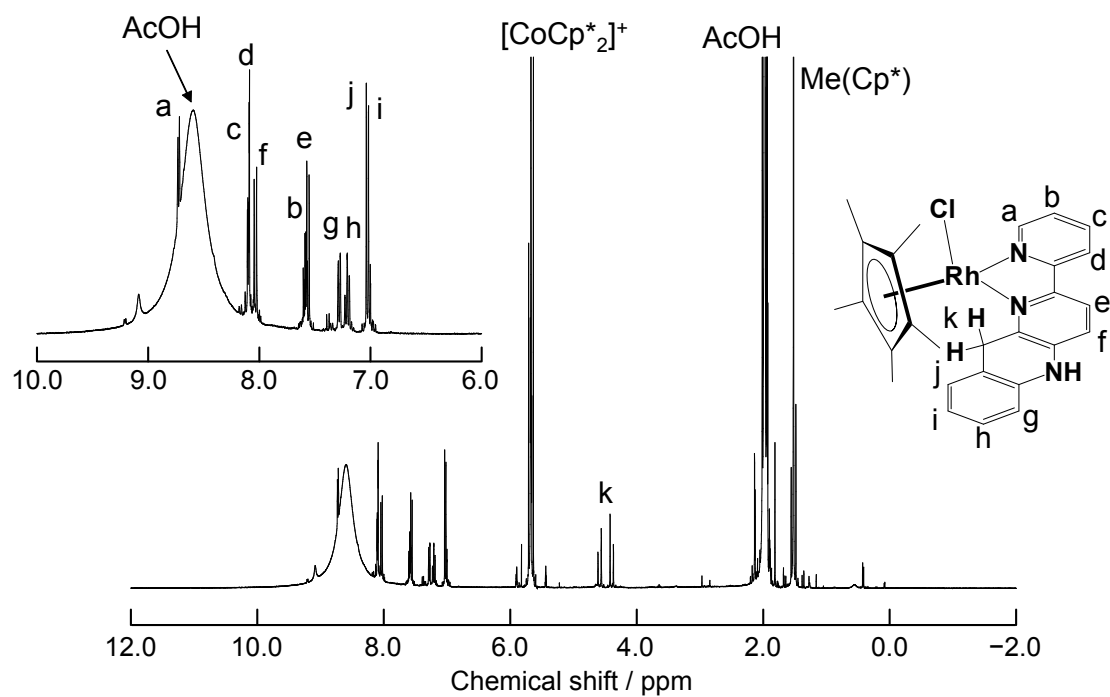
**Figure S5.** (a) ESI-MS spectrum of  $[1]Cl$  in the presence of 1.0% AcOH containing 2 equiv. of  $CoCp_2$  in  $CH_3CN$ , as well as simulated spectra of (b)  $[1]^+$  and (c)  $[1HH]^+$ .



**Figure S6.**  $^1\text{H}$  NMR spectrum (400 MHz) of  $[\mathbf{1}]\text{Cl}$  in  $\text{CD}_3\text{CN}$ .



**Figure S7.**  $^1\text{H}$  NMR spectrum (400 MHz) of  $[\mathbf{1CH}]\text{Cl}$  in  $\text{CD}_3\text{CN}$ .



**Figure S8.**  $^1\text{H}$  NMR spectrum (400 MHz) of [1]Cl containing 2 equiv. of  $\text{CoCp}_2$  in 1.0% AcOH/ $\text{CD}_3\text{CN}$ .