

Supporting Information

for

**Electrochemical and chemical routes to hydride loss
from an iridium dihydride**

Andrew G. Walden,^a Akshai Kumar,^{b,c} Nicholas Lease,^b Alan S. Goldman,^b and

Alexander J. M. Miller^{a,*}

*^aDepartment of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North
Carolina 27599-3290, United States*

*^bDepartment of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey,
New Brunswick, New Jersey 08903, United States*

*^cDepartment of Chemistry, Indian Institute of Technology Guwahati, Guwahati - 781039, Assam,
INDIA*

**ajmm@email.unc.edu*

Table of Contents

I.	General Considerations	S3
II.	Experimental Procedures	S4
III.	Electrochemical Observations	S7
IV.	References	S9

I. General Considerations

All procedures were carried out in a glovebox under an argon atmosphere, unless otherwise noted. Solvents were dried and degassed with argon using a Pure Process Technology solvent system. All deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and degassed by three freeze-pump-thaw cycles and stored over molecular sieves. The complexes (^tBu⁴PCP)Ir(H)(Cl) (**1**),¹ (^tBu⁴PCP)Ir(H)₂ (**2**),² and (^tBu⁴PCP)Ir(H)₄ (**3**)³ were synthesized according to literature procedures. All other materials were commercially available and used as received, unless otherwise noted. ¹H and ³¹P NMR spectra were recorded on a 600 MHz spectrometer at room temperature. Chemical shifts are reported with respect to residual protio solvent for ¹H.⁴ ³¹P NMR spectra were referenced to an 85% H₃PO₄ external standard (0 ppm).

II. Experimental Procedures

General Procedures for Cyclic Voltammetry Experiments

Cyclic voltammetry experiments were conducted in a single-compartment cell in a three electrode configuration. Glassy carbon disc (3 mm diameter) working electrodes, platinum wire counter electrodes, and silver wire pseudo-reference electrodes were used. Potentials are provided relative to ferrocene added as an internal reference at the conclusion of the experiment. Experiments were performed in tetrahydrofuran with $[\text{Bu}_4\text{N}][\text{PF}_6]$ (100 mM) added as supporting electrolyte. Experiments performed under argon were conducted in an argon glovebox with a Pine Instruments WaveNow potentiostat. Experiments performed under other gases were conducted on the bench with sparged solutions, and performed under positive pressure using a Pine Instruments WaveDriver potentiostat. A review on electrochemistry in THF is available.⁵

General Procedures for Bulk Electrolysis Experiments



Figure S1. Photograph of the experimental setup for bulk electrolysis in argon glove box.

Bulk electrolysis experiments were conducted in two-compartment cells (Figure S1). Reticulated vitreous carbon working electrodes, platinum wire counter electrodes and silver wire pseudo-reference electrodes were used. Experiments were performed in tetrahydrofuran with [Bu₄N][PF₆] (100 mM) added as a supporting electrolyte. Experiments were performed in an argon glovebox with a Pine Instruments WaveNow potentiostat.

The working compartment of the cell was charged with (^tBu⁴PCP)Ir(H)₂ (**2**), 0.1 M [Bu₄N][PF₆] electrolyte, a chloride source (LiCl or [Bu₄N][Cl]) as needed, and a potential of 0.2 V vs Cp₂Fe⁺⁰ was applied. After electrolysis, the anolyte was transferring to a J Young tube and analyzed by ¹H and ³¹P NMR spectroscopy. The THF solutions were then evaporated under vacuum and the residues extracted into pentane and filtered to remove the electrolyte. The pentane solutions were then evaporated under vacuum and the residues dissolved in THF-*d*₈ for additional NMR characterization.

In a characteristic experiment, 4.1 mg of a mixture of **2** and **3** (equilibrium mixtures and pure samples of **2** showed identical reactivity) was dissolved in a THF solution containing 0.1 M [Bu₄N][PF₆]. To this mixture was added 11 mg (~5 equiv) of [Bu₄N][Cl]. The solution was added to the working side of a two-compartment cell containing a reticulated vitreous carbon working electrode. The counter electrode side of the two-compartment cell was filled with 2 mL of a 0.1 M [Bu₄N][PF₆] THF solution. Controlled potential electrolysis was carried out at 0.2 V vs Cp₂Fe⁺⁰ for 2.5 hours. The reaction was analyzed by ³¹P NMR spectroscopy as described above (Figure S2).

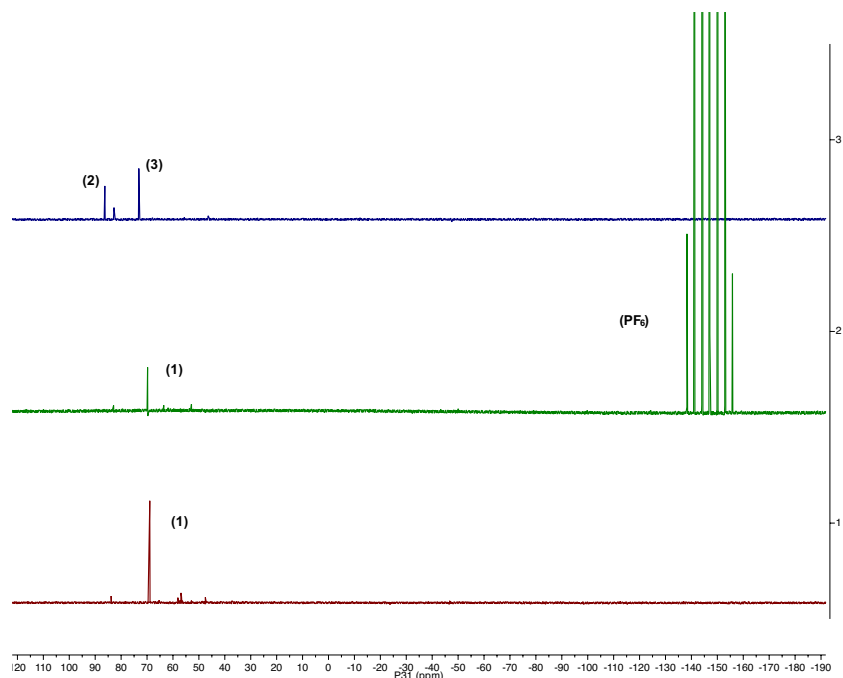


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of an equilibrium mixture of **2** and **3** before electrolysis (top blue trace) containing <5% of a small impurity, the reaction mixture following electrolysis (middle red trace), and the product distribution after removal of $[\text{Bu}_4\text{N}][\text{PF}_6]$ electrolyte showing high yield of complex **1** (bottom red trace).

General Procedures for reactions of **2** with Trityl Cation.

Hydride abstraction reactions were monitored by ^1H and ^{31}P NMR spectroscopy. In an argon glove box, an equivalent of $(^t\text{Bu}^4\text{PCP})\text{Ir}(\text{H})_2$ (**2**) was dissolved in $\text{THF-}d_8$ in a J Young tube. Five equivalents of $[\text{Bu}_4\text{N}][\text{Cl}]$ were included when desired. Initial ^1H and ^{31}P NMR spectra were taken at this point, followed by addition of one equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$. After allowing the tubes to react at room temperature for about 30 min, additional ^1H and ^{31}P NMR spectra were obtained. Interestingly, no Ph_3CCl was observed, suggesting that the $[\text{Ph}_3\text{C}]^+$ reacted selectively with Ir–H rather than Cl^- .

III. Electrochemical Observations

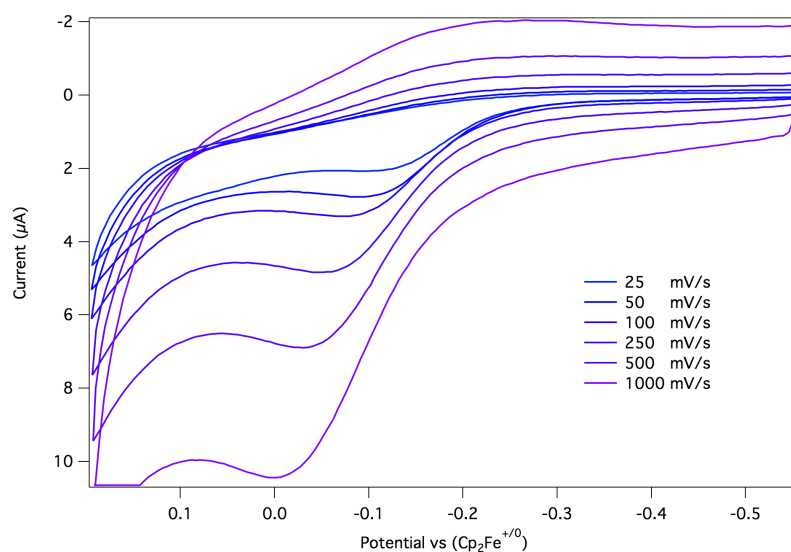


Figure S3. CV of $(t\text{Bu}^4\text{PCP})\text{Ir}(\text{H})_2$ (**2**) under argon according to the general procedure.

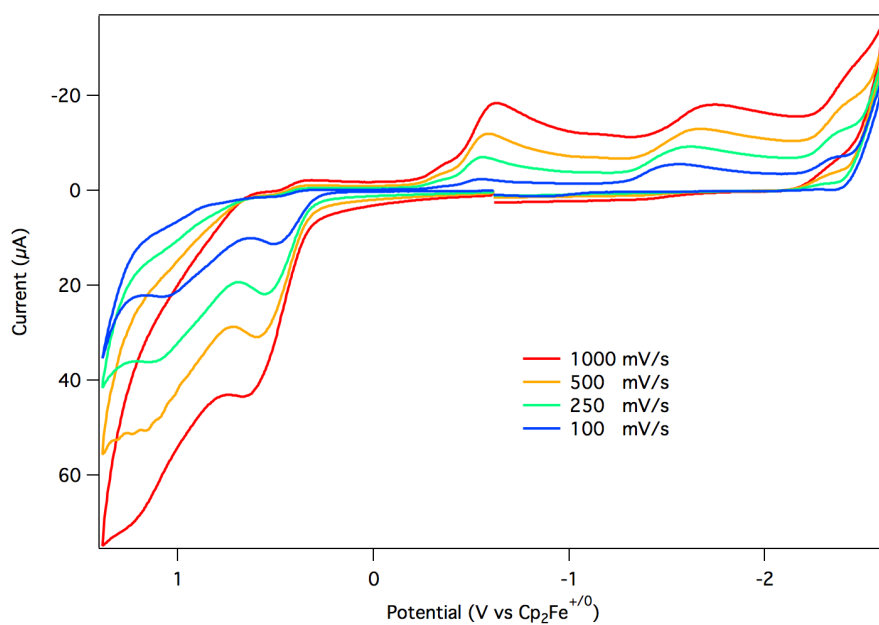


Figure S4. CV of **2** after exposure to N_2 , according to the general procedure.

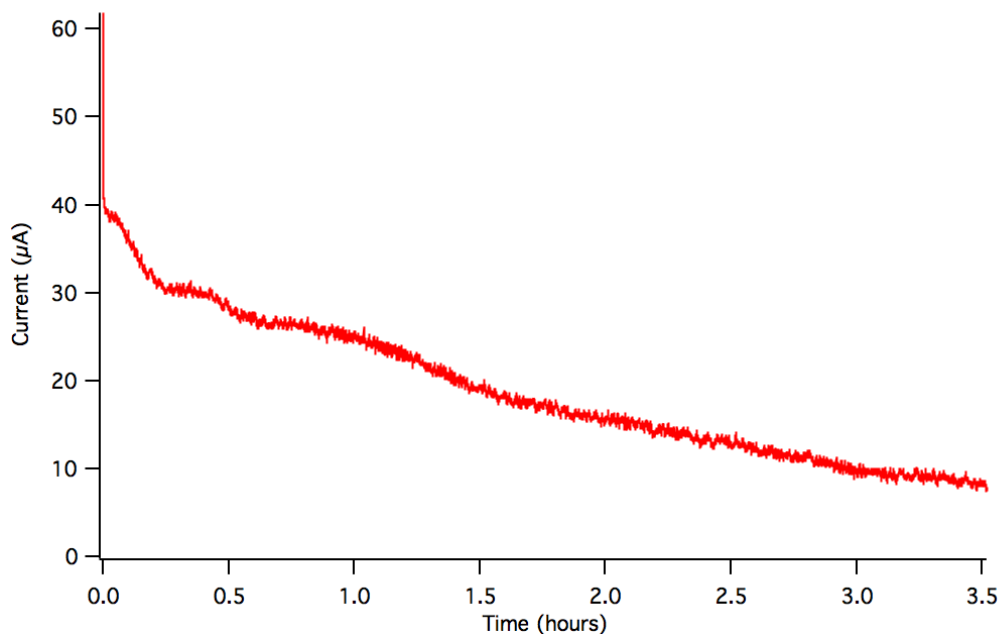


Figure S5. Controlled potential electrolysis of **2** at 0.2 V vs $\text{Cp}_2\text{Fe}^{+/0}$ (no added chloride salt). The 239 mC of charge passed corresponds to 1.9 e^- per Ir.

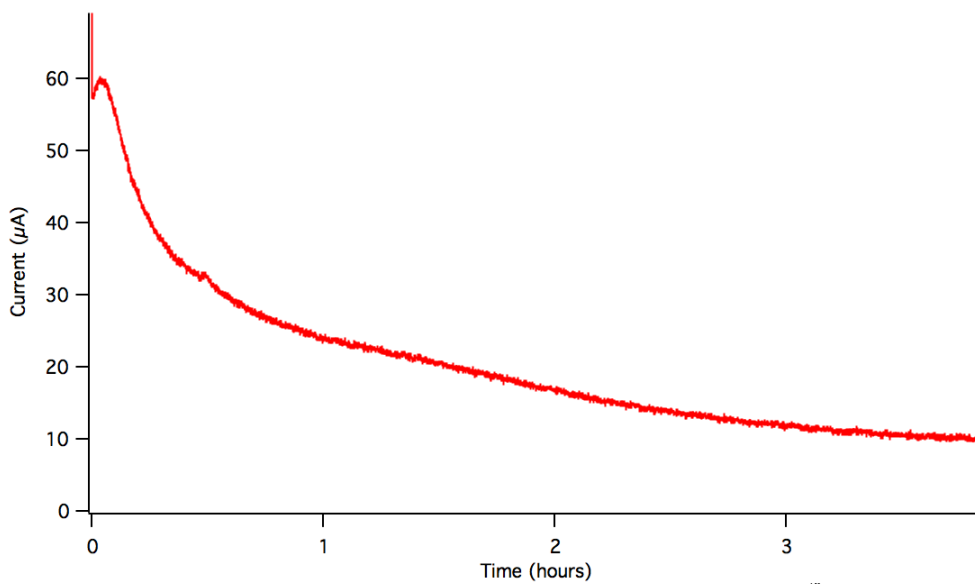


Figure S6. Controlled potential electrolysis of **2** at 0.2 V vs $\text{Cp}_2\text{Fe}^{+/0}$ in the presence of 5 equiv $[\text{Bu}_4\text{N}][\text{Cl}]$. The 283 mC of charge passed corresponds to 2.3 e^- per Ir.

VII. References

- 1) C. J. Moulton and B. L. Shaw, *J. Chem. Soc. Dalt. Trans.*, 1976, 1020–1024.
- 2) Gupta, C. Hagen, R. J. Flesher, W. C. Kaska and C. M. Jensen, *Chem. Commun.*, 1996, **36**, 2083–2084.
- 3) T. J. Hebden, K. I. Goldberg, D. M. Heinekey, X. Zhang, T. J. Emge, A. S. Goldman and K. Krogh-Jespersen, *Inorg. Chem.*, 2010, **49**, 1733–1742.
- 4) G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
- 5) R. Baron, N. M. Kershaw, T. J. Donohoe and R. G. Compton, *J. Phys. Org. Chem.*, 2009, **22**, 1136–1141.