MOLECULAR PHOTOELECTROCATALYTS FOR SOLAR FUEL PRODUCTION:
DISCOVERY, MECHANISM, AND EXPLORATION

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A dissertation submitted to the faculty at the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Department of Chemistry.

Chapel Hill
2017

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ABSTRACT

Catherine L. Pitman: Molecular Photoelectrocatalysts for Solar Fuel Production: Discovery, Mechanism, and Exploration
(Under the direction of Alexander J. M. Miller)

An exploration of the chemistry of molecular photoelectrocatalysts, beginning with the Cp*Ir(bpy) framework, is presented. Chapter 1 covers approaches to hydrogen evolution with an eye towards solar fuel production. The importance of both metal-hydride species and methods to measure metal-hydride bond strength is discussed. In Chapter 2, the central complex of this dissertation, [Cp*Ir(bpy)(H)]+, is introduced when in situ electrochemical generation permits the construction of a photoelectrocatalytic cycle. Irradiation of neutral aqueous solutions containing [Cp*Ir(bpy)(H)]+ poised at cathodic potentials produces H₂ in high Faradaic efficiency. Chapter 3 presents a general synthetic scheme whereby precipitation of Cp*Ir(bpy) and analogues from water and subsequent reaction with electrophiles enabled access to a wide range of water-soluble metal-hydride and metal-alkyl complexes. Chapter 4 explores the hydricity—the hydride donor ability—of Cp*Ir(bpy) and (arene)Ru(bpy)-based hydrides. The hydricity of [Cp*Ir(bpy-COO)(H)]⁻ is measured using a potential-pK₀ cycle, and the hydricities of the metal-hydrides accessed in Chapter 3 are measured relative to this reference complex. The thermodynamic measurements presented explain why [Cp*Ir(bpy)(H)]⁺ is stable in neutral, aqueous solutions in the dark.

Chapters 5 and 6 present results of alterations to the [Cp*Ir(bpy)(H)]⁺ structure. In Chapter 5, Rh is exchanged for Ir, resulting in an entirely unexpected activation of Cp*.
Formation of the transient [Cp*Rh(bpy)(H)][Cl] complex leads to the more stable species (Cp*H)Rh(bpy)(Cl). The implications of this structure on the reduction of NAD$^+$ are discussed. In Chapter 5, the hydride ligand is exchanged for a methyl ligand making [Cp*Ir(bpy)(CH$_3$)]$^+$. This metal-methyl complex is characterized and its photochemical reactions are explored. Kinetic order, radical traps and clocks, and isotope labelling suggest that excitation results in homolysis of the Ir–CH$_3$ bond.
ACKNOWLEDGEMENTS

I put off writing my acknowledgments section because I was sure that I was going to get it wrong. I have probably forgotten to thank someone who I should—I’m sorry—and even those I have remembered, what I say here will not capture what you have meant to me.

First, to Alexander J. M. Miller, who took a chance on a first-year graduate student with scant research experience. You took me from an unsure student to an independent scientist, and I will never be able to thank you enough for what you have done for me. It has been a privilege to watch how quickly you adapted to and thrived in being a professor and mentor. When I could see no other reason to be in graduate school, I could rest easy in the knowledge that helping you get tenure was work worth doing. I am a better person for having worked for you, and I’m so glad that I worked for someone as ridiculous about diction and figure design as I am.

To the rest of the Miller lab: to Andrew Walden and Matt Kita, who were with me there in the very beginning. There is something about starting a lab together that I can’t really put into words. To Matt Chambers, who is always happy to let me talk through my experiments. To LDoc, my job hunt and group meeting buddy, and to Seth, my desk buddy. To Kelsey Brereton, Jacob Brody Smith, Javier Grajeda, Ali Sullivan, Andrew Camp, and Brian Lindley, thank you for dogs, coffee, cupcakes, and comradery: I’m glad to be leaving the lab in such good hands. To Ann Marie, Bethany, and Quinton, good luck! It will be both better and worse than you think. To Teddy, Becca, Victoria, Ariana, and Olivia, my small
army of undergraduates, you have all been so different, and you have all taught me something unique.

To the many others in the chemistry department who have been an integral part of my time in graduate school: to Jillian Dempsey, Joe Templeton, and Brook Brookhart, you make the fourth floor of Kenan a special place to be. I hope that I will live up to the standard you have established, both as people and as scientists. To Brian McCarthy, for countless conversations, board games, and tea. To Eric Rountree, Alex Venning, Nate Romero, Meredith Zeller, and Melissa Gish, I can’t really believe how far we’ve come since our first year. I am so sure that you will all go on to do great things. To Matt Goldfolgel, thank you for always being up for a movie. To Ross Beattie, Chris Turlington, Matty J, Tom Lyons, thank you for being friends and mentors.

To Katie Lavoie, Robin Knauf, Cortnie Roberts, and Katie Michaux. I can’t really say how much better you made graduate school. When I was the only girl in my lab and in my inorganic cohort, you knew how that felt and kept me sane. Thank you for always letting me turn up at your desks and vent. Thank you for cheering me up. Thank you for being just generally awesome. Thank you for brunch and gelato martinis and being conference buddies.

To the people who keep this department running: to Peter White, Marc ter Horst, Brandie Ehrmann, and Kyle Brenneman for keeping the instruments on and for letting me pick your brains about them. To Ashley and Ann, for the tremendous amount of paperwork you do and did to keep us afloat. To Fred and Reggie, who do a lot more, for giving the friendliest hellos for five years.

To the greater UNC and Chapel Hill communities: to the Royster Society for keeping me connected to the university outside chemistry. To the Orange County Animal Shelter, for
letting me play with dogs once a week. To the Chapel Hill Library, where I write this now. To Anthony, Anthony, and Danielle, for your patience and dedication. To Kelley, Kelsey, Natalie, Paige, and all of Outdoor Fitness, for Sundays in the park. To Sarah Venning and Ribbit, for being good friends.

To the greater chemistry community: attending conferences and meeting so many of you has been one of the highlights of my graduate career. To Karen Goldberg and Melanie Sanford, for being such incredible and astounding role models. To Jim Mayer and Nilay Hazari, for lending an ear. To Mr. Nelson, Seth Brown, Olaf Wiest, Chris Timmel, Steve Davies, and John McGrady, without whom I never would have been a chemist or come to graduate school in the first place.

To my fellow chemists of the Notre Dame Class of 2011: to Andrea, Ryan, Laura, Jennifer, Jessica, Angela and on. You were always the best thing about late nights studying and long hours in labs that predictably didn’t work.

To my family: to my Dad, for always being my first call when things go wrong. To my Mom, who somehow raised four children with Dad frequently deployed. I am in awe of you. To Chris, Mary, and Claire, for all the adventures. To my Grandparents. To the Camerons.

And finally, thank you to Neskowin, Carolina North Forest, and our National Parks because “everybody needs beauty as well as bread, places to play in and pray in, where nature may heal and give strength to body and soul alike.”

"[1]"
# TABLE OF CONTENTS

LIST OF TABLES .................................................................................................................. xii

LIST OF FIGURES ............................................................................................................. xiii

LIST OF SCHEMES ........................................................................................................... xxii

LIST OF SYMBOLS AND ABBREVIATIONS ................................................................. xxiv

CHAPTER 1: MOLECULAR SOLAR FUEL PRODUCTION ........................................... 1

1.1 Introduction to Solar Fuels .......................................................................................... 1

1.2 Catalysts for Hydrogen Production .......................................................................... 3

Fuel formation from electrocatalysts ................................................................................ 4

Fuel formation from photocatalysts ................................................................................ 6

The mechanism of hydrogen evolution from \([\text{Cp}^*\text{Ir(bpy)(H)}]^{+}\) ................................ 8

1.3 Transition Metal Hydrides in Aqueous Reactions .................................................... 9

Measuring metal-hydride bond strength with hydricity .................................................. 10

1.4 Beyond Transition Metal Hydrides ........................................................................... 14

1.5 Summation .................................................................................................................. 16

CHAPTER 2: MOLECULAR PHOTOCURRENTS FOR VISIBLE LIGHT-DRIVEN HYDROGEN EVOLUTION FROM NEUTRAL WATER ........................................ 18

2.1 Introduction .................................................................................................................. 18
2.2 Results and Discussion.................................................................................................................. 19

Sustained Photoelectrocatalytic Hydrogen Evolution. ................................................................. 19

Separating the Electrochemical and Photochemical Steps. ......................................................... 24

Optimization of Photoelectrocatalytic Performance................................................................. 29

2.3 Conclusions ................................................................................................................................. 33

2.4 Experimental Section ................................................................................................................... 35

CHAPTER 3: FACILE SYNTHESIS OF (PENTAMETHYLCYCLOPENTADIENYL)-(2,2'-BIPYRIDINE)-IRIDIUM, ANALOGUES, AND REACTIONS WITH ELECTROPHILES .............................................................................................................................................. 40

3.1 Introduction .................................................................................................................................. 40

3.2 Results and Discussion.................................................................................................................. 41

\textit{In situ} generation of Cp*Ir(bpy). .............................................................................................. 41

Synthesis and Structure of Cp*Ir(bpy) and Analogues. .............................................................. 42

Functionalization via Electrophilic Attack. .................................................................................... 46

3.3 Conclusions ................................................................................................................................. 48

3.4 Experimental Section ................................................................................................................... 49

CHAPTER 4: AQUEOUS HYDRICITY OF LATE METAL CATALYSTS AS A CONTINUUM TUNED BY LIGANDS AND THE MEDIUM ........................................................................................................................... 70

4.1 Introduction .................................................................................................................................. 70

4.2 Results and Discussion.................................................................................................................. 72

Characterization of Reference Complexes. .................................................................................... 72

Establishing a Second Reference Point. ....................................................................................... 79
Building a Scale through Equilibria .................................................. 81

4.3 Conclusions .............................................................................. 88

4.4 Experimental Section .............................................................. 88

CHAPTER 5: CYCLOPENTADIENE-MEDIATED HYDRIDE TRANSFER FROM RHODIUM COMPLEXES ................................................................. 99

5.1 Introduction .............................................................................. 99

5.2 Results and Discussion .......................................................... 100

Formation of a (Cp*H)Rh complex .................................................. 100

Reactivity of diene 2 .................................................................... 106

5.3 Conclusions ............................................................................ 115

5.4 Experimental Section .............................................................. 116

CHAPTER 6: PHOTOCHEMICAL PRODUCTION OF ETHANE FROM AN IRIDIUM METHYL COMPLEX ................................................................. 120

6.1 Introduction .............................................................................. 120

6.2 Results and Discussion .......................................................... 121

Photochemical production of ethane and methane .......................... 128

Mechanistic considerations .......................................................... 130

Evidence for a radical based mechanism ....................................... 132

Differentiating mechanisms with excited state lifetime and kinetic order ...................................................... 138

Understanding the preference for homolysis ................................. 144

6.3 Conclusions ............................................................................ 146
6.4 Experimental Section ................................................................. 147

REFERENCES .................................................................................... 156
LIST OF TABLES

Table 1.1. Thermodynamic Constants for H⁺, H⁺, H⁻, and H₂ in Acetonitrile and in Water. ...................................................................................................................... 14

Table 3.1. Crystal data and structure refinement for 1.......................................................... 44

Table 3.2. Complexes synthesized by precipitation from water and literature precedent. ........................................................................................................................................ 45

Table 3.3. ¹H NMR Shifts of Metal-Hydrides in pD 7 0.1 M NaPi ........................................ 46

Table 4.1. Summary of Thermodynamics ............................................................................... 81

Table 4.2. Aquo-chloride exchange free energy and hydricity to form ligated products in kcal·mol⁻¹ ........................................................................................................... 85

Table 5.1. Crystal data and structure refinement for 2.......................................................... 102

Table 5.2. Overview of calculated change in electronic energy (ΔE), enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) for the isomerization of rhodium and iridium hydrides ......................................................................... 105

Table 6.1. Crystal data and structure refinement for [2][I] .................................................... 122

Table 6.2. Comparison of electrochemical and photophysical features of [1]+ and [2]+ ........................................................................................................................................... 127

Table 6.3. Relevant bond dissociation energies ..................................................................... 144
LIST OF FIGURES

Figure 1.1. Black box depiction of water splitting, showing the many components required to split water with light................................................................. 2

Figure 2.1. CV of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) at 5 mV·s⁻¹ illuminated (solid black) and dark (dashed black) and at 10 mV·s⁻¹ illuminated (solid red) and dark (dashed red). Glassy carbon working electrode (3 mm disc), Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode, 460 nm LED lamp. Current is scan-rate normalized: normalized current of diffusion-controlled processes is constant with changing scan rate while normalized current of catalytic waves increases as scan rate decreases.................................................. 20

Figure 2.2. A) CPE at −1 V vs. NHE of 1 mM 1 in 0.1 M phosphate buffer (pH 7) in the dark (dashed black) and under 460 nm light (solid blue). B) CPE at −0.9 V vs. NHE of 1 mM 1 in 0.1 M phosphate buffer (pH 7) with light off (gray) and on (white). Reticulated vitreous carbon working electrode, Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode. ........................................ 21

Figure 2.3. Total charge passed in the photoelectrolysis (−1.23 C, black) and charge that productively made H₂ according to the pH change (red circles) for 1 mM 1 in 50 mM sodium phosphate (initial pH = 7.8) at −0.9 V, and the charge passed in the absence of catalyst (−0.17 C, gray). Photoelectrolysis results in a seven-fold increase in total charge passed, and the pH change in the absence of catalyst was within the ±0.1 error of the probe. Faradaic efficiency drops from 100% to 90% over 90 minutes.......................................................... 22

Figure 2.4. CPE of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) at −0.9 V under 460 nm LED irradiation. After exhaustion of the buffer, addition of 100 μL 1 M H₃PO₄ restored current .................................................... 24

Figure 2.5. A) CV of 1 mM 1 in 0.1 M NaCl at a scan rate of 250 mV·s⁻¹. B) CV of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) at a scan rate of 250 mV·s⁻¹.......................................................... 25

Figure 2.6. UV–vis spectra of 0.3 mM 1 in 0.1 M phosphate buffer (solid black), after 90 min of electrolysis at −0.9 V to form 2 (solid blue), and after 90 min of 460 nm photolysis to reform 1 (dashed orange). Subsequent electrolysis reform 2 (dashed red) and photolysis reform 1 (omitted for clarity). The molar extinction coefficient (ε) of each species was calculated assuming clean conversion (see text for details). Reticulated vitreous carbon working electrode, Pt wire counter electrode, Ag/AgCl (3 M NaCl) reference electrode. ................................. 26
Figure 2.7. CV (scan rate of 250 mV·s\(^{-1}\)) performed during stepwise electrolysis (−0.9 V) and photolysis (460 nm LED) of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7)................................................................. 27

Figure 2.8. Plot showing rate dependence on lamp power. The apparent catalytic rate constants were obtained from CA experiments at different LED lamp power, each with 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) held at −0.9 V for 20 seconds. A variable power supply controlled the power of the incident light (470 nm LED strips)........................................................................................................... 30

Figure 2.9. A) Chronoamperometry of 1 mM 1 in pH 7 phosphate buffer in the dark (dashed black) and under 460 nm LED irradiation (solid blue) at −1 V vs. NHE. Inset: ratio of the two CA traces (black) and fit (dashed red) with \(k_{obs} = 0.036\ s^{-1}\). B) Apparent catalytic rate constants for 1 (black squares), 1-OMe (orange circles), and 1-COOH (blue triangles) as a function of potential. Error bars reflect two standard deviations in both directions as determined by between 3 and 7 experiments. Glassy carbon working electrode (3 mm disc), Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode. ................................................................. 31

Figure 2.10. CV of 1 mM 1-COOH\(_2\) in 0.1 M sodium phosphate buffer (pH 7) at 25 mV·s\(^{-1}\) under 460 nm LED light (solid black) and dark (dashed black) and at 50 mV·s\(^{-1}\) in the light (solid red) and dark (dashed red). Dotted line indicates thermodynamic potential for hydrogen evolution at pH 7. Current is scan-rate normalized: normalized current of diffusion-controlled processes is constant with changing scan rate while normalized current of catalytic waves increases as scan rate decreases. Glassy carbon working electrode (3 mm disc), Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode........................................................................................................... 32

Figure 2.11. Absorption spectra of electrochemically generated \([\text{Cp}^*\text{Ir}(\text{bpy})(\text{H})]^+\) (black), \([\text{Cp}^*\text{Ir}(\text{bpy}-\text{OMe})(\text{H})]^+\) (orange), and \([\text{Cp}^*\text{Ir}(\text{bpy}-\text{COOH})(\text{H})]^+\) (blue) in 0.1 M sodium phosphate buffer (pH 7) with the spectrum of the 460 nm LED lamp (green). .............................................................................................................................................. 33

Figure 3.1. A) Cyclic voltammetry of \([\text{Cp}^*\text{Ir}(\text{bpy})(\text{Cl})][\text{Cl}]\) in 0.1 M pH 7 Na\(_2\)titrated with solutions of NaOH showing the growth of the oxidation of \text{Cp}^*\text{Ir}(\text{bpy}) with increasing pH. B) Fit (dashed black) of oxidation peak area (red dots) to the Henderson-Hasselbalch equation, suggesting a \(pK_a\) of 10.6 for \([\text{Cp}^*\text{Ir}(\text{bpy})(\text{H})]^+\).................................................................................................................................. 42

Figure 3.2. Structural representation of 1 with ellipsoids drawn at the 50% probability level. Hydrogen atoms omitted. Selected distance (Å): C5-C6 1.403(5). .............................................................................................................................................. 43
Figure 3.3. $^1$H NMR spectrum of Cp*Ir(bpy) (1) in C$_6$D$_6$. .......................................................... 50

Figure 3.4. $^1$H NMR spectrum of [Cp*Ir(bpy)(H)][Cl] (1H) in 0.1 M pH 7 NaP$_7$ (referenced to dioxane). ............................................................. 51

Figure 3.5. $^1$H NMR spectrum of (cymene)Ru(bpy) (4) in C$_6$D$_6$. .......................................................... 52

Figure 3.6. $^1$H NMR spectrum of [(cymene)Ru(bpy)(H)][Cl] (4H) in 0.1 M pH 7 NaP$_7$ (referenced to dioxane). The hydride signal at -6.32 moderately underintegrates because of scrambling with D$_2$O. .......................................................... 53

Figure 3.7. $^1$H NMR spectrum of (C$_6$Me$_6$)Ru(bpy) (5) in C$_6$D$_6$. .......................................................... 54

Figure 3.8. $^1$H NMR spectrum of [(C$_6$Me$_6$)Ru(bpy)(H)][Cl] (5H) in 0.1 M pH 7 NaP$_7$ (referenced to dioxane). The hydride signal at -7.48 dramatically underintegrates because of scrambling with D$_2$O. .......................................................... 55

Figure 3.9. $^1$H NMR spectrum of Cp*Ir(bpy-Me) (6) in C$_6$D$_6$. .......................................................... 56

Figure 3.10. $^{13}$C{$_^1$H} NMR spectrum of Cp*Ir(bpy-Me) (6) in C$_6$D$_6$. .......................................................... 56

Figure 3.11. UV-Vis spectrum of Cp*Ir(bpy-Me) (6) in C$_6$H$_6$. .......................................................... 57

Figure 3.12. $^1$H NMR spectrum [Cp*Ir(bpy-Me)(H)][Cl] (6H) in 0.1 M pH 7 NaP$_7$ (referenced to dioxane). The hydride signal at -7.48 moderately underintegrates because of scrambling with D$_2$O. .......................................................... 57

Figure 3.13. $^{13}$C{$_^1$H} NMR spectrum [Cp*Ir(bpy-Me)(H)][Cl] (6H) in 0.1 M pH 7 NaP$_7$ (referenced to dioxane). .......................................................... 58

Figure 3.14. UV-Vis spectrum [Cp*Ir(bpy-Me)(H)][Cl] (6H) in 0.1 M pH 7 NaP$_7$. .......................................................... 58

Figure 3.15. $^1$H NMR spectrum of Cp*Ir(bpy-COOMe) (8) in C$_6$D$_6$. .......................................................... 59

Figure 3.16. $^{13}$C{$_^1$H} NMR spectrum of Cp*Ir(bpy-COOMe) (8) in C$_6$D$_6$. .......................................................... 60

Figure 3.17. UV-Vis spectrum of Cp*Ir(bpy-COOMe) (8) in C$_6$H$_6$. .......................................................... 60

Figure 3.18. $^1$H NMR spectrum of [Cp*Ir(bpy-COOMe)(H)][Cl] (8H) in 20 mM pH 4.3 NaOAc (referenced to dioxane). The hydride signal at -12.28 dramatically underintegrates because of scrambling with D$_2$O. .......................................................... 61

Figure 3.19. $^{13}$C{$_^1$H} NMR spectrum of [Cp*Ir(bpy-COOMe)(H)][Cl] (8H) in 20 mM pH 4.3 NaOAc (referenced to dioxane). .......................................................... 62

Figure 3.20. UV-Vis spectrum of [Cp*Ir(bpy-COOMe)(H)][Cl] (8H) in 0.1 M pH 3 NaP$_7$. .......................................................... 62
Figure 3.21. $^1$H NMR spectrum of Cp*Rh(bpy) in C$_6$D$_6$. ................................................................. 63

Figure 3.22. $^1$H NMR spectrum of [Cp*Ir(bpy)(Me)]I in CD$_3$CN. .......................................................... 64

Figure 3.23. $^{13}$C{$^1$H} NMR spectrum of [Cp*Ir(bpy)(Me)]I in CD$_3$CN. ........................................... 64

Figure 3.24. $^1$H NMR spectrum of [Cp*Rh(bpy)(Me)]I in CD$_3$CN. .......................................................... 65

Figure 3.25. $^{13}$C{$^1$H} NMR spectrum of [Cp*Rh(bpy)(Me)]I in CD$_3$CN. ........................................... 66

Figure 3.26. $^1$H NMR spectrum of [Cp*Ir(bpy)(Me)][Cl] in CD$_3$CN. ....................................................... 67

Figure 3.27. $^1$H NMR spectrum of [Cp*Ir(bpy)("Pr)]I in CD$_3$CN. .......................................................... 68

Figure 3.28. $^1$H NMR spectrum of [Cp*Ir(bpy)(CH$_2$Cl)][Cl] in CD$_3$CN. ................................................. 69

Figure 4.1. Scheme illustrating the hydricity of reference complex

[Cp*Ir(bpy-COO)(H)]$^-$ (2H) and thermochemical cycles that establish aqueous hydricity of Ir and Ru hydrides. ................................................................................................................ 71

Figure 4.2. A) Cyclic voltammetry of [Cp*Ir(bpy-COOH)(Cl)][Cl] in 0.1 M pH 7 NaP$_4$ titrated with solutions of NaOH showing the growth of the oxidation of Cp*Ir(bpy) with increasing pH and the large peak-to-peak separation between the reduction of [Cp*Ir(bpy-COO)(OH)]$^-$ (under basic conditions) and the oxidation of [Cp*Ir(bpy-COO)]$^{2-}$. B) The change in the apparent pK$_a$ with scan rate indicating a slow protonation. ......................................................... 73

Figure 4.3. (A) Spectral changes of a pH 14 solution of [Cp*Ir(bpy-COO)(OH)]$^-$ (2OH) as the solution potential is decreased by electrolysis to form [Cp*Ir(bpy-COO)]$^{2-}$ (2). (B) Absorbance at 620 nm stepping in the negative potential direction (red dots), the positive potential direction (blue dots), and the fit to the Nernst equation (dot-dashed line) giving E$^\circ$ = -0.60 V. The lack of hysteresis indicates that equilibrium was established. (C) Absorbance at 570 nm of a titration of [Cp*Ir(bpy-COO)(H)]$^-$ (2H) forming 2 (red dots) and the fit to the Henderson-Hasselbalch equation (dot-dashed line) giving pK$_a$ = 12.4. ....................... 73

Figure 4.4. (A) Summary of thermochemical values of [Cp*Ir(bpy-COO)(H)]$^-$ (2H). Free energies (kcal·mol$^{-1}$) and reduction potentials (V vs. NHE) are cited at the standard state of pH 0, 1 M reagents, and 1 atm gases, except for $\Delta G_{OH2P}$ and $\Delta G_{H2P}$ values that refer to pH 7. (B) Summary of the pH dependence of $\Delta G^\circ_{H2}(Y)$ with the H$_2$O/H$_2$ and CO$_2$/HCO$_3^-$ couples. ............................................................... 77

Figure 4.5. (A) Cyclic voltammetry of [(cymene)Ru(bpy-COOH)(OH$_2$)][OTf]$_2$ in 1 M NaOH titrated with solutions of H$_3$PO$_4$ at 50 mV/s. (B) To determine $E^\circ$, $E_{1/2}$ between pH 8 and 12 were
extrapolated to zero giving $E^\circ = -0.30$ V (assuming oxidized and reduced species have similar diffusion properties). Though at lower pH (purple trace), the oxidation is very poorly resolved as Ru$^0$ is protonated, the extrapolation is consistent with the best estimate of $E_{1/2}(pH 7.8) \sim -0.51$ V, or $-0.28$ V accounting for the deprotonation of the aquo to form the hydroxo.

**Figure 4.6.** Relative hydricity values of Ir and Ru complexes (blue). The equilibria used to determine hydricity are represented by blue arrows.

**Figure 4.7** Aqueous hydricity scale of the complexes we report along with those previously reported in the literature. Y represents the incoming ligand such that the top scale shows $\Delta G^\circ_{H-}(Cl)$ and the bottom scale shows $\Delta G^\circ_{H-}(OH_2)$. TSPP = tetra(p-sulfonatophenyl)porphyrin; TMPS = tetrakis(3,5-disulfonatomesityl)porphyrin; tpy = terpyridine; DHMPE = 1,2-bis(dihydroxymethylphosphino)ethane.

**Figure 4.8.** A) Correlation between $\sigma_p$ and $\Delta G^\circ_{H-}(Cl)$. B) Correlation between $\lambda_{\text{max}}$ of the hydride with the hydricity of that hydride.

**Figure 4.9.** $^1$H NMR spectra of the electrolytically produced $[\text{Cp}^*\text{Ir}(\text{bpy-COO})(H)]^-$ (bottom) and synthetically produced $[\text{Cp}^*\text{Ir}(\text{bpy-COO})(H)]^-$ (middle) in 0.1 M pD 7 NaP$_i$. Both contain small $[\text{Cp}^*\text{Ir}(\text{bpy-COO})(\text{Cl})]^-$ impurities. Electrolytically produced $[\text{Cp}^*\text{Ir}(\text{bpy-COO})]^2$ in 1 M NaOH in D$_2$O is shown in the top panel.

**Figure 4.10.** Molar absorptivities of $[\text{Cp}^*\text{Ir}(\text{bpy-COO})(H)]^-$ (gold) and $[\text{Cp}^*\text{Ir}(\text{bpy-COO})]^2$ (purple). Samples were prepared by electrolysis and checked for purity by $^1$H NMR before use. The Ir concentration in each sample was measured by ICP-MS.

**Figure 4.11.** $^1$H NMR spectrum of $[(\text{cymene})\text{Ru}(\text{bpy-COOH})(\text{Cl})][\text{Cl}]$ in CD$_3$OD.

**Figure 4.12.** $^1$H NMR spectra of the electrolytically produced $[(\text{cymene})\text{Ru}(\text{bpy-COO})(H)]^-$ in 0.1 M pD 7 NaP$_i$ (top) and synthetically produced $[(\text{cymene})\text{Ru}(\text{bpy-COO})]^2$ in 1 M NaOH in D$_2$O (bottom). Both are referenced to dioxane.

**Figure 4.13.** Molar absorptivities of $[(\text{cymene})\text{Ru}(\text{bpy-COO})(\text{H})]$ (red-orange) and $[(\text{cymene})\text{Ru}(\text{bpy-COO})]^2$ (purple-blue). Samples were prepared by electrolysis and checked for purity by $^1$H NMR before use. The Ru concentration in each sample was measured by ICP-MS.

**Figure 4.14.** Representative $^1$H NMR spectrum of a typical hydride equilibrium experiment. (top) Equilibrium mixture of $^1$H, $^1$Cl, $^2$H, and $^2$Cl formed from the addition of $^1$Cl to the mixture of $^2$H and $^2$Cl formed from electrolysis (bottom).
Figure 4.15. Representative $^1$H NMR spectrum of a typical hydride equilibrium experiment. (top) Equilibrium mixture of 1H, 1Cl, 6H, and 6Cl formed from the addition of 6Cl to 1H formed synthetically (bottom)........................................................................................................................................ 97

Figure 5.1. $^1$H NMR spectrum of [(Cp*H)Rh(bpy)(NCCD$_3$)][PF$_6$] in CD$_3$CN.................. 101

Figure 5.2. Structural representation of 2 with ellipsoids drawn at the 50% probability level (containing a mirror plane that bisects the Cp*H and bpy ligands). A co-crystallized CH$_2$Cl$_2$ solvent molecule and hydrogen atoms removed for clarity. Selected distances (Å) and angles (deg): C1–C2 1.517(2), C2–C3 1.440(3), Rh1–N1 2.1157(15), Rh1–Cl1 2.5440(6), C2’–C1–C2–C3 31.9(2) ........................................................................................................... 102

Figure 5.3. $^1$H NMR spectra showing the low temperature protonation of Cp*Rh(bpy) (4.8 mg, 0.012 mmol) in C$_6$D$_5$Cl (red). After injection of 5.5 μL 2.0 M HCl·Et$_2$O in an acetonitrile/dry ice bath. Spectrum recorded at 238 K (blue). After warming to 293 K (purple). A hydride resonance at –9.60 ppm at low temperatures is evidence for the intermediacy of [Cp*Rh(bpy)(H)]$^+$ in the formation of (Cp*H)Rh(bpy)(Cl).................................................................................................................. 104

Figure 5.4. The shift of the 2e$^–$ reduction of [Cp*Rh(bpy-COO)(OH)]$^–$ at 100 mV/s as the pH increases from 9.5 to 13.0 (left). $E_{1/2}$ of the reduction plotted against pH to extrapolate to pH 0 (right). .......................................................................................................................... 107

Figure 5.5 UV-vis spectra of [Cp*Rh(bpy-COO)]$^{2–}$ formed electrochemically at pH 11.2 (blue) and added to a pH 7 0.1 M sodium phosphate buffer to protonate (yellow)......................................................................................................................................... 108

Figure 5.6. Spectrophotometric titration of [Cp*Rh(bpy-COO)]$^{2–}$ with addition of acid to form [(Cp*H)Rh(bpy-COO)]$^–$ (left) and analysis of the absorbance at 610 nm to the Henderson-Hasselbalch equation giving p$K_a$ = 9.9 (right). ........................................................................................................................................ 109

Figure 5.7. (A) CV of [Cp*Rh(bpy-COOH)(Cl)][Cl] in pH 5.8 to pH 10 phosphate electrolyte at a scan rate of 100 mV/s, expanded to highlight the return wave attributed to oxidation of [Cp*Rh(bpy-COO)]$^{2–}$. In acidic water, [Cp*Rh(bpy-COO)]$^{2–}$ is protonated to form [(Cp*H)Rh(bpy-COO)]$^–$. The increasing oxidative peak current with increasing pH indicates higher concentrations of [Cp*Rh(bpy-COO)]$^{2–}$ as pH increases. (B) Plot of oxidative peak current vs. pH. At each scan rate this sigmoid was fit to the Henderson-Hasselbalch equation to determine a p$K_a$. (C) Plot of apparent p$K_a$ vs. scan rate. ................................................................. 109

Figure 5.8. $^1$H NMR spectrum of a solution of (Cp*H)Rh(bpy)(Cl) after addition of 2.7 mg NAD$^+$ (4.1 μmol) in pD 7 0.1 M NaP. The Rh species has reacted completely (best seen by the absence of any
resonance at 0.7 ppm), and NADH has appeared. The nicotinamide singlet shifts from 9.3 ppm to 6.9 ppm upon reduction and a pair of diastereotopic protons appear at 2.6 and 2.7 ppm. Assignments were made by comparison to authentic samples in the same solutions and by comparison to ref. 137.

Figure 5.9. ¹H NMR spectra showing the formation of diene products (indicated by a 6:6:3 pattern in the aliphatic region) under catalytic conditions. (top) [Cp*Rh(bpy)(OH₂)]²⁺ under an atmosphere of H₂ in pD 7 0.1 M NaPi, referenced to sodium tosylate. (middle) Product of electrolysis of [Cp*Rh(bpy)(Cl)]⁺ at −0.64 V in 80:20 pD 7:pH 7 0.1 M NaPi, referenced to dioxane. (bottom) [Cp*Rh(bpy)(Cl)]⁺ in D₂O with 10 equiv of sodium formate, referenced to formate.

Figure 5.10. ¹H NMR spectra showing an equilibrium mixture of [Cp*Ir(bpy)(H)]⁺, [Cp*Ir(bpy)(Cl)]⁺, [Cp*Ir(bpy-COO)(H)]⁻, and [Cp*Ir(bpy-COO)(H)]⁻ (formed by mixing electrochemically produced [Cp*Ir(bpy-COO)(H)]⁻ with [Cp*Ir(bpy)(Cl)](Cl))¹²⁶ shortly after equilibrium had been achieved (bottom) and 7 weeks later (top). The Cp* peaks have disappeared with no changes to the aromatics indicating per-deuteration of the Cp* protons. Deuteration was also observed by ²H NMR. [(Cp*-d₁₅)Ir(bpy)(Cl)]⁺ (m/z = 534.21 (calc), 534.33 (obs)) and [(Cp*-d₁₅)Ir(bpy-COONa)(Cl)]⁺ (m/z = 666.16 (calc), 666.20 (obs)) were also observed by mass spec.

Figure 6.1. Structural representation of [2][I] with ellipsoids drawn at the 50% probability level. Hydrogen atoms and iodide counter ion omitted for clarity. Selected distances (Å): Ir–C21 2.147(5), C5–C6 1.458(6).

Figure 6.2. A) Absorptivity (solid blue) and normalized emission (dashed red) of [2]⁺ in CH₃CN solution. Excitation at 420 nm. B) Cyclic voltammogram of 1 mM [2]⁺ in CH₃CN with 0.1 M [¹Bu₄N][PF₆] under and an atmosphere of N₂. Scan rate 0.25 V·s⁻¹. C) Orbitals from TD-DFT involved in the lowest energy transitions at 450 and 442 nm.

Figure 6.3. Instrument and background corrected emission (green) of [2][PF₆] in CH₃CN solution with excitation at 420 nm. The extrapolation of the high energy edge used to measure ΔG_ST (dashed red) intercepts the x-axis at 17300 cm⁻¹ or 50 kcal·mol⁻¹.

Figure 6.4. Representative ¹H NMR spectrum of a 6.7 mM [2][PF₆], 0.1 M CH₃I with a 3 mM mesitylene internal standard in CD₃CN after irradiation with a 443 nm light source for 3.5 hours. The iridium species has been converted to [4]⁺ while ethane, methane, and propionitrile have appeared.
Figure 6.5. $^1$H NMR spectra of 6 mM [2][PF$_6$] and 0.15 M AcOH in CD$_3$CN (bottom) photolyzed with 443 nm light for 3.5 hours (top). Methane and [Cp*Ir(bpy)(OAc)]$^+$ are the primary products. ................................................................. 132

Figure 6.6. Time course of dissolved methane and ethane during photolysis of [2]$^+$ and $^{13}$CH$_3$I in CD$_3$CN, showing that incorporation of $^{13}$C into organic products outpaces that of $^{12}$C. $^{13}$CH$_4$ and $^{13}$CH$_3$D (closed red squares), $^{12}$CH$_4$ and $^{12}$CH$_3$D (open red squares), $^{13}$C in ethane (closed blue circles), $^{12}$C in ethane (open blue circles). ........................................................ 134

Figure 6.7. Growth of $^{13}$CH$_4$, $^{13}$CH$_3$D, $^{12}$CH$_4$, and $^{12}$CH$_3$D over 443 nm 30 min of photolysis of 12.5 mM [2][PF$_6$] and 80 mM $^{13}$CH$_3$I in CD$_3$CN with a 3 mM mesitylene internal standard. The downfield satellite was used for $^{13}$C-containing methane integration. ................................................................. 135

Figure 6.8. Concentrations from $^1$H NMR spectroscopy following the irradiation at 443 nm of a solution of 5.6 mM [2][PF$_6$] (black squares), 12 mM CH$_3$I, and 24 mM TEMPO in CD$_3$CN. TEMPO-CH$_3$ (red circles) grows in at twice the rate as iodide [4]$^+$ (blue triangles). The decrease in [CH$_3$I] (not shown) accounts for half of the methyl of TEMPO-CH$_3$. Methyl [2]$^+$ is consumed at a slightly faster rate than [4]$^+$ appears: a minor iridium (open triangles, 10%) containing species grows in as evidence of a side reaction................................................................. 135

Figure 6.9. $^1$H NMR spectra of [5][Br] in CD$_3$CN (bottom) photolyzed with 443 nm light for 1 h (top). The consumption of [5]$^+$ is most clearly identified by the absence of the olefinic protons at 4.75 ppm and 5.55 ppm. The CH$_3$ doublet of methycyclopentane is at 0.95 ppm. ................................................................. 137

Figure 6.10. Self-quenching Stern-Volmer analysis for [2][PF$_6$] in CH$_3$CN at room temperature. I$_0$ is the emission extrapolated to infinite dilution. I is the corrected and normalized emission at a given concentration of [2]$^+$. The absence of upward trend indicates the absence of self-quenching. ......................................................................................................... 139

Figure 6.11. A) Photoluminescent lifetime of varying concentrations of [2][PF$_6$] in CH$_3$CN measured by time-correlated single photon counting. B) Photoluminescent lifetime of [2][PF$_6$] in CH$_3$CN with varying concentration of CH$_3$I. Laser excitation at 444.2 nm source with 73.3 ps pulse width at 2 MHz pulse rate. Emission detected at 680 nm with a 5 nm bandwidth. The independence of lifetime with concentration indicates the absence of quenching. ......................................................................................................... 139

Figure 6.12. Representative experiment following the reaction of [2][PF$_6$] with CH$_3$I in CH$_3$CN. The sample was irradiated at 443 nm (1.58 x 10$^{-6}$ moles of photons min$^{-1}$) in 30 s intervals for the first 5 min (from the red trace to the blue trace) to calculate quantum yield. Photolysis for
longer periods produces the green spectrum. The expected spectrum of $[4]^+$ is shown in the dashed black spectrum.

**Figure 6.13.** Dependence of quantum yield on $[\text{CH}_3\text{I}]$ (blue squares) and $[[2]^+]$ (red circles) in CH$_3$CN photolyzed with 443 nm light. The dashed-line marks the constant concentration of CH$_3$I and $[2]^+$ (0.1 M and 0.14 mM respectively) held while the other reagent varied. The lack of dependence in CH$_3$I indicates the reaction is zero order in substrate, while the lack of dependence on $[2]^+$ indicates an overall first order as $[2]^+$ is the chromophore.

**Figure 6.14.** Dependence of quantum yield on [AcOH] (blue squares) and $[[2]^+]$ (red circles) in CH$_3$CN photolyzed with 443 nm light. The dashed-line marks the constant concentration of AcOH and $[2]^+$ (0.1 M and 0.12 mM respectively) held while the other reagent varied. The lack of dependence in AcOH indicates the reaction is zero order in substrate, while the lack of dependence on $[2]^+$ indicates an overall first order as $[2]^+$ is the chromophore.

**Figure 6.15.** Growth of Ir-containing products on 443 nm photolysis of 1 mM (red), 2 mM (purple), 4 mM (blue), and 8 mM (green) $[2]||\text{PF}_6$ in CD$_3$CN with 10 mM AcOH. The consistent increases indicate quantum yield is not changing across this concentration range.

**Figure 6.16.** $^1$H NMR spectrum of $[2]||\text{PF}_6$ and 0.1 M CH$_3$I in 9:1 CH$_3$CN:CD$_3$CN photolyzed with 443 nm light for 3.5 hours. Methane, succinonitrile, and $[4]^+$ are formed.

**Figure 6.17.** $^1$H NMR spectrum of $[\text{Cp}^*\text{Ir(bpy)(Me)}]||\text{PF}_6$ ($[2]||\text{PF}_6$) in CD$_3$CN.

**Figure 6.18.** $^{13}$C{$^1$H} NMR spectrum of $[\text{Cp}^*\text{Ir(bpy)(Me)}]||\text{PF}_6$ ($[2]||\text{PF}_6$) in CD$_3$CN.

**Figure 6.19.** $^1$H NMR spectrum of $[\text{Cp}^*\text{Ir(bpy)(I)}]^+$ ($[4]^+$) in CD$_3$CN.

**Figure 6.20.** Absorptivity of $[\text{Cp}^*\text{Ir(bpy)(I)}]^+$ in CH$_3$CN. Sample prepared by addition of 3 equiv NaI to a solution of $[\text{Cp}^*\text{Ir(bpy)(OH}_2)]||\text{OTf}_2$. Ir concentration determined by ICP-MS.

**Figure 6.21.** $^1$H NMR spectrum of $[\text{Cp}^*\text{Ir(bpy)((CH}_2)_4\text{CHCH}_2)]||\text{Br}$ ($[5][\text{Br}]$) in CD$_3$CN.

**Figure 6.22.** $^{13}$C{$^1$H} NMR spectrum of $[\text{Cp}^*\text{Ir(bpy)((CH}_2)_4\text{CHCH}_2)]||\text{Br}$ ($[5][\text{Br}]$) in CD$_3$CN.
LIST OF SCHEMES

Scheme 1.1. Generalized representations of A) an electrocatalyst producing H₂ after reduction by a coupled photosensitizer (PS) and B) and photocatalyst producing H₂ by oxidizing a halide (X⁻), a process which typically requires two photons................................................................. 3

Scheme 1.2. Selected electrocatalysts for H₂ evolution................................................................. 5

Scheme 1.3. Ziesell’s mechanism for the photochemical water-gas shift................................. 8

Scheme 1.4. Generalized scheme for a molecular photoelectrocatalyst................................. 8

Scheme 1.5. Mechanism for H₂ production from [Cp*Ir(bpy)(H)]⁺........................................ 9

Scheme 1.6. Three LnM–H bond cleavage reactions................................................................. 11

Scheme 1.7. Determination of Hydricity by Hydride Transfer.................................................. 12

Scheme 1.8. Determination of Hydricity by Heterolysis of H₂.................................................. 12

Scheme 1.9. Determination of Hydricity from Two-Electron E° Value and a pKₐ................................................................. 13

Scheme 1.10. Tandem catalytic cycle for Rh, NAD⁺, and enzyme mediated reductions................................. 15

Scheme 2.1. Photoelectrochemical water reduction conditions.................................................. 19

Scheme 2.2. Proposed photoelectrocatalytic cycle................................................................. 28

Scheme 3.1. Synthesis of Cp*Ir(bpy) by precipitation from basic water................................ 42

Scheme 3.2. Synthesis of [Cp*Ir(bpy)(H)][Cl] by precipitation from ether............................ 45

Scheme 3.3. Reactions of Cp*Ir(bpy) with electrophiles.......................................................... 47

Scheme 4.1. Effective hydricity including ligand association.................................................... 76

Scheme 4.2. Representative hydride equilibration reaction..................................................... 95

Scheme 4.3. Representative hydride equilibration reaction..................................................... 97

Scheme 5.1. Tandem catalytic cycle for Rh, NAD⁺, and enzyme mediated reductions................................. 100

Scheme 5.2. Alternative routes to diene 2............................................................................. 103
Scheme 5.3. Relative free energies for reductive elimination of Cp*H from M–H (M = Rh, Ir) in acetonitrile solvent from DFT .......................................................... 105

Scheme 5.4. Selected hydride transfer reactions .............................................................................................................................. 111

Scheme 5.5. Proposed mechanism for the reduction of NAD⁺ through a (Cp*H)Rh(bpy) intermediate. NUN is 2,2′-bipyridine................................................................. 115

Scheme 6.1. Excited state reduction potentials .......................................................................................................................... 127

Scheme 6.2. Possible reaction pathways of metal methyls from the excited state. .............................................................................. 130

Scheme 6.3. Pathways for ethane production from [2]* ......................................................................................................................... 130

Scheme 6.4. The initial steps of isotope scrambling .......................................................................................................................... 133

Scheme 6.5. Reaction with radical trap TEMPO. ............................................................................................................................. 135

Scheme 6.6. Reaction of the radical clock complex, [5][Br].................................................................................................................... 136
## List of Symbols and Abbreviations

- • radical
- $^{13}$C{\textsuperscript{1}H} proton decoupled carbon
- \textsuperscript{1}H proton
- \textsuperscript{2}H deuterium
- A absorbance
- \(A/HA^{-}\) hydride acceptor/hydride donor
- Å Angstrom
- AcOH acetic acid
- aq aqueous
- atm atmosphere
- BH\textsubscript{4}^{-} borohydride
- bpy 2,2’-bipyridine
- bpy-X 4,4’-X-2,2’-bipyridine
- C Celsius
- C Coulomb
- CA chronoamperometry
- cal calories
- cm\textsuperscript{-1} wavenumber, inverse centimeters
- Cp\* pentamethylcyclopentadienyl
- CPE controlled potential electrolysis
- CV cyclic voltammetry
- cy cyclohexyl
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>D</td>
<td>deuterium</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>DHMPE</td>
<td>1,2-bis(dihydroxymethylphosphino)ethane</td>
</tr>
<tr>
<td>dppe</td>
<td>1,2-bis-(diphenyl-phosphino)ethane)</td>
</tr>
<tr>
<td>e⁻</td>
<td>electron</td>
</tr>
<tr>
<td>$E_{1/2}$</td>
<td>half wave potential</td>
</tr>
<tr>
<td>EC'</td>
<td>electron transfer, chemical catalysis</td>
</tr>
<tr>
<td>ECP</td>
<td>effective core potential</td>
</tr>
<tr>
<td>$E^o$</td>
<td>formal potential</td>
</tr>
<tr>
<td>eq</td>
<td>equation</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>equiv</td>
<td>equivalent</td>
</tr>
<tr>
<td>erf</td>
<td>error function</td>
</tr>
<tr>
<td>ESI</td>
<td>electrospray ionization</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>$f$</td>
<td>oscillator strength</td>
</tr>
<tr>
<td>g</td>
<td>gram</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>GW</td>
<td>gigawatt</td>
</tr>
<tr>
<td>h</td>
<td>hour</td>
</tr>
<tr>
<td>H</td>
<td>hydrogen atom</td>
</tr>
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<td>H⁻</td>
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xxv
H⁺  proton
HER  hydrogen evolution reaction
HOMO  highest occupied molecular orbital
HPLC  high performance liquid chromatography
Hz  hertz
hv  light irradiation
i_{cat}  catalytic current
i_{diff}  diffusional current
i_{p,a}  peak anodic current
i_{p,c}  peak cathodic current
i^{Pr}  isopropyl
IrOx  iridium oxide
J  joule
K  Kelvin
K_a  acid dissociation constant
k_{cat}  catalytic rate constant
K_{eq}  equilibrium constant
KIE  kinetic isotope effect
k_{obs}  observe rate constant
LED  light emitting diode
L_nM  metal with n ligands
LUMO  lowest unoccupied molecular orbital
M  molar
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>PCET</td>
<td>proton-coupled electron transfer</td>
</tr>
<tr>
<td>pD</td>
<td>-log([D&lt;sup&gt;+&lt;/sup&gt;])</td>
</tr>
<tr>
<td>pH</td>
<td>-log([H&lt;sup&gt;+&lt;/sup&gt;])</td>
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<tr>
<td>P&lt;sub&gt;i&lt;/sub&gt;</td>
<td>inorganic phosphate</td>
</tr>
<tr>
<td>pK&lt;sub&gt;a&lt;/sub&gt;</td>
<td>acidity</td>
</tr>
<tr>
<td>P&lt;sup&gt;Ph&lt;/sup&gt;&lt;sub&gt;2&lt;/sub&gt;N&lt;sup&gt;Ph&lt;/sup&gt;</td>
<td>1,3,6-triphenyl-1-aza-3,6-diphosphacycloheptane</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>PS</td>
<td>photosensitizer</td>
</tr>
<tr>
<td>ps</td>
<td>picosecond</td>
</tr>
<tr>
<td>PV</td>
<td>photovoltaic</td>
</tr>
<tr>
<td>QY</td>
<td>quantum yield</td>
</tr>
<tr>
<td>RVC</td>
<td>reticulated vitreous carbon</td>
</tr>
<tr>
<td>s</td>
<td>second</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
</tr>
<tr>
<td>TD-DFT</td>
<td>time-dependent density functional theory</td>
</tr>
<tr>
<td>TEMPO</td>
<td>(2,2,6,6-tetramethylpiperidin-1-yl)oxyl</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran</td>
</tr>
<tr>
<td>TMPS</td>
<td>tetrakis(3,5-disulfonatomesityl)porphyrin</td>
</tr>
<tr>
<td>TON</td>
<td>turnover number</td>
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<tr>
<td>tpy</td>
<td>2,2':6'2&quot;-terpyridine</td>
</tr>
<tr>
<td>TSPP</td>
<td>tetra(p-sulfonatophenyl)porphyrin</td>
</tr>
<tr>
<td>TW</td>
<td>terawatt</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
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</table>
V volts
v% volume percent
Vis visible
W watt
wt% weight percent
X- halide
δ chemical shift
ΔE electronic energy
ΔG free energy
ΔG_{ET} free energy for electron transfer
ΔG_{H-} free energy, hydricity
ΔG_{H-}(Y) effective hydricity for incoming ligand y
ΔG_{OH2→X} free energy to replace aquo ligand with x
ΔG_{ST} free energy between singlet ground state and triplet excited state
ΔH enthalpy
ΔS entropy
ΔΔG_{H-} difference in hydricity
η hapticity
λ wavelength
λ_{max} wavelength maximum
μ bridging ligand
μA microampere
μL microliter
\( \sigma \) \hspace{1cm} \text{sigma-type donor} \\
\( \sigma_{p-} \) \hspace{1cm} \text{Hammett parameter} \\
\( \varepsilon \) \hspace{1cm} \text{molar extinction coefficient}
CHAPTER 1: MOLECULAR SOLAR FUEL PRODUCTION


1.1 Introduction to Solar Fuels

Energy use is projected to increase from our current average global consumption of 18.4 TW in 2012 to 27.3 TW by 2040. Meeting this demand while limiting carbon accumulation in the atmosphere and oceans motivates exploration of alternative energy sources. The future energy portfolio will likely be comprised of a mixture of wind, solar, hydroelectric, nuclear, and petroleum sources, but of these, solar energy represents the greatest untapped potential. With an average of about 80,000 TW of solar radiation reaching the Earth’s surface, there is a strong drive to develop technologies to harness this immense energy source.

Photovoltaics (PV) and solar thermal heating have been the largest players on the solar stage. Solar PV that convert solar energy to electricity have seen a 8.3% yearly growth rate—the fastest growing renewable energy source—with global installed capacity reaching 90 GW in 2012. Solar thermal systems are primarily used in residential water heating, but have been employed for electricity generation by boiling water with concentrated light to then drive steam-powered turbines, similar to those in coal fired plants. Globally, solar thermal plants produced 3.6 GW in 2013.
Solar fuels are a third option for harnessing sunlight. Rather than transforming solar energy from sunlight into electrical or thermal energy, solar fuel systems store solar energy in the form of energy-rich chemical bonds. In order to use an intermittent energy source, like solar, as a major component of the energy economy, energy storage methods will need to be developed to level the gap between when energy is produced and when it is used. While there are a host of technologies to meet this need, from thermal storage to pumped hydroelectric to flow batteries, high energy density and low storage losses make fuels an ideal target.\(^5\)

**Figure 1.1.** Black box depiction of water splitting, showing the many components required to split water with light.

Figure 1.1 depicts a generalized solar fuels device. A collection of catalysts, photosensitizers, interfaces, and membranes are assembled into a device that absorbs light and uses that energy to split water into oxygen and hydrogen, storing the captured energy. This process is often referred to as “artificial photosynthesis” because of its similarities to biological photosynthesis: both store the energy of sunlight in chemical bonds. In order to produce low-cost fuel, devices must optimize the oxidative and reductive catalysts and integrate light absorption to efficiently manage protons, photons, and electrons. Optimization and development of each component of an artificial photosynthesis device is complex;
consequently, this work will focus on the reductive half-reaction. The reductive half-reaction leads directly to the formation of a fuel, like hydrogen, or if water is replaced with CO$_2$, a carbon-based fuel.

1.2 Catalysts for Hydrogen Production

Light-promoted evolution of hydrogen from water is as an attractive route to solar fuels, and many approaches have emerged in order to reduce protons to H$_2$ with the aid of sunlight. Two general strategies have emerged: multi-component systems which combine a photosensitizer with an electrocatalyst to form H$_2$ (Scheme 1.1A) and photocatalysts which produce H$_2$ upon photon absorption (Scheme 1.1B). Examples of these strategies are described in this section.

In these schemes, the origin of the electrons used to form the H–H bond becomes a critical consideration. To split water, these electrons must come from oxidation of water, but in optimizing the reductive half-reaction, the electrons are typically drawn from sacrificial reductant—either added reductive quenchers or oxidation of the conjugate base of the acid. Incorporating these strategies into a water-splitting solar fuel device requires electron management that does not lead to stoichiometric consumption of a sacrificial reductant.

**Scheme 1.1. Generalized representations of A) an electrocatalyst producing H$_2$ after reduction by a coupled photosensitizer (PS) and B) and photocatalyst producing H$_2$ by oxidizing a halide (X$^-$), a process which typically requires two photons.**
**Fuel formation from electrocatalysts.** Noble metals, platinum in particular, are the champion electrocatalysts for the hydrogen evolution reaction (HER). The adsorption of hydrogen to noble metals is strong enough to lower reaction barriers yet weak enough to permit product desorption, and therefore, noble metals catalyze the reaction at essentially no overpotential. With many catalysts, excess energy beyond the thermodynamic minimum is required to overcome kinetic limitations or high energy intermediates, with this excess called the overpotential. Noble metal expense and scarcity, however, have necessitated the search for cheap, abundant catalysts that mirror the activity of platinum. One strategy to accomplish this goal has been a detailed exploration and engineering of materials to maximize surface area and active sites that lead to H\(_2\). Rapid progress has been made in recent decades, particularly with sulfides (e.g. MoS\(_2\)), selenides, carbides, phosphides, and nitrides, but as a function of material surface sites, these materials are still less active than Pt.\(^6,7\)

Another strategy to replace Pt catalysis is to use highly active homogenous catalysts either freely diffusing in solution or supported on a cheaper electrode surface.\(^8\) This strategy takes inspiration from biology where hydrogenase enzymes have developed NiFe and FeFe active sites that receive electrons from cluster chains in order to make H\(_2\).\(^9,10\) Structural mimics of these active sites typically show poor activity in the absence of the surrounding protein scaffold.\(^11\)

A range of molecular electrocatalysts that are structurally unrelated to hydrogenase active sites has shown excellent HER activity. Considerable effort has been focused on the development of H\(_2\) evolution electrocatalysts in acetonitrile, which is often a convenient solvent for evaluating the electrochemistry of organometallic complexes.\(^12\) Dozens of complexes containing a variety of metals and ligand architectures have been investigated.
yielding insight into the electrocatalytic mechanism and improvement of catalytic rates and efficiency.\textsuperscript{8,13–15} The mechanism of HER from cobaloximes was investigated in detail, illustrating that additional activation of catalysts may be needed in the form of additional electrons (Scheme 1.2A).\textsuperscript{16} Systematic study of group 10 bis-diphosphine electrocatalyst led to the development of DuBois’s [Ni(P\textsubscript{Ph\textsubscript{2}}N\textsubscript{Ph})\textsubscript{2}][BF\textsubscript{4}]\textsubscript{2}, (P\textsubscript{Ph\textsubscript{2}}N\textsubscript{Ph} = 1,3,6-triphenyl-1-aza-3,6-diphosphacycloheptane, Scheme 1.2B), which catalyzes HER from protonated dimethylformamide in acetonitrile with a turnover frequency 106,000 s\textsuperscript{-1} in the presence of 1.2 M of water, a faster rate for H\textsubscript{2} evolution than hydrogenase itself.\textsuperscript{17}

\textbf{Scheme 1.2. Selected electrocatalysts for H\textsubscript{2} evolution.}

Though solar fuel generation will ideally take place in the most abundant solvent, water, aqueous media presents a unique challenge for the inorganic electrochemist. The electrochemical window is narrow: the abundance of protons in water leads to background H\textsubscript{2} evolution from the electrode at relatively positive potentials, making it difficult to study the electrocatalyst itself. Systems that can be studied under aqueous conditions are limited by their solubility and stability, which can be minimal for many organometallic complexes. Despite these challenges, many homogeneous electrocatalysts have been investigated in water.\textsuperscript{14,18} Chang, for example, has developed Mo-based catalysts that mimic the activity of
MoS$_2$ materials in water (Scheme 1.2C).$^{19,20}$ Despite these successes, matching the rates of hydrogenase in aqueous conditions remains a challenge.$^{21}$

To produce hydrogen using light as an energy input, these electrocatalysts must be coupled to a light-absorbing species, typically a molecular photosensitizer like [Ru(bpy)$_3$]$^{2+}$. Absorption of a photon produces high energy electrons and low energy holes. Quenching of the excited state with a sacrificial reductant produces a highly reducing species which can transfer an electron to the electrocatalyst and initiate H$_2$ evolution. To achieve high efficiencies, this electron transfer must be optimized, leading to the exploration of tethered systems which ensure spatial proximity of the chromophore and catalyst. Unfortunately, these linked systems have not improved efficiency, suggesting that the non-productive back-electron transfer is competitively improved by proximity.$^{22}$ The challenge with this approach is that while the catalyst and chromophore can be optimized individually, those benefits do not necessarily extend to the integrated system.

**Fuel formation from photocatalysts.** An alternative approach to light-driven hydrogen production is to merge the catalyst and the light absorber into one discrete species which collects energy from absorbed photons and then produces H$_2$. Photocatalysts of this kind have been developed which generate H$_2$ from a variety of sources. There is an extensive literature of photochemical dehydrogenations of alkanes, alcohols, and other organic substrates.$^{23}$ Several different mechanisms and photochemically active steps have appeared in the literature.$^{24}$ Many of these, like Cole-Hamilton’s Rh(P$^{\text{is}}$Pr$_3$)$_2$(CO)(H) driven decomposition of methanol$^{25}$ and Goldman’s Rh(PMe$_3$)$_2$(CO)(Cl) dehydrogenation of cyclooctane,$^{26}$ are initiated by photochemical CO dissociation. After ligand loss, the elementary steps that lead to H$_2$ production, then, are those that would be observed for any
low-coordinate organometallic fragment in the dark. In other systems, like Crabtree’s
Ir(H)₂(CF₃CO₂)(PCy₃)$_2$ dehydrogenation of cyclooctane, the photochemical step is
proposed to be H₂ reductive elimination from a dihydride intermediate.

When the substrate is an acid, many systems require two photons to close the
catalytic cycle: one to facilitate the release of H₂ and the other to assist in dissociation of the
conjugate base from the catalyst. Hexachloroiridate can photocatalytically cleave H–Cl with
one photon producing H’ and another producing Cl’ which go on to form H₂ and Cl₂. Nocera’s late-metal bimetallic H–X splitting schemes eliminate H₂ on absorbing one photon
and then Cl₂ or Br₂ equivalents upon absorbing a second photon. Often, an external halide
trap is included in functional catalytic systems to drive halogen elimination to completion.

\[
CO + H₂O \xrightarrow{hv} CO₂ + H₂
\] (1.1)

Of particular interest was a report in the literature from Ziessel of the photochemical
water-gas shift with Cp*Ir(bpy)-based (Cp* is pentamethylcyclopentadienyl, bpy is 2,2’-
bipyridine) catalysts. In this reaction (eq. 1.1), CO is oxidized to CO₂ while the protons from
water are reduced to evolve H₂. Ziessel showed that the reduction of CO with H₂O
transforms a [Cp*Ir(bpy)(Cl)]$^+$ precursor to [Cp*Ir(bpy)(H)]$^+$ with loss of CO₂ (and a proton,
Scheme 1.3). This iridium hydride intermediate was proposed to be the photoactive species
that releases H₂ on absorbing a photon.
Drawing on the mechanism of Ziessel’s photochemical water-gas shift, we envisioned a photoelectrochemical approach, in which H₂ evolution is facilitated by a single molecule acting both as light absorber and electrocatalyst, as described in Chapter 2. Unlike the water-gas shift and other multi-component hydrogen evolution strategies, no sacrificial reagent is required, enabling this half-reaction to be coupled to any favorable oxidative half-reaction, like water oxidation.

**The mechanism of hydrogen evolution from [Cp*Ir(bpy)(H)]⁺.** In the course of our lab’s investigation of [Cp*Ir(bpy)(H)]⁺ as a photoelectrocatalyst, we became interested in the photochemical mechanism that leads to H₂ release. To elucidate this mechanism,
Chambers undertook a detailed investigation of the reaction of \([\text{Cp}^*\text{Ir(bpy)(H)}]^+\) with acids in acetonitrile.\(^{29}\) From the decrease in lifetime of the excited state with increasing complex concentration, he deduced a self-quenching mechanism was operating, where electron transfer occurs between the excited state \([\text{Cp}^*\text{Ir(bpy)(H)}]^+\) and a ground state \([\text{Cp}^*\text{Ir(bpy)(H)}]^+\) (Scheme 1.5). The source of \(\text{H}_2\) was shown to be the resulting \(\text{Cp}^*\text{Ir}^{II}(\text{bpy})(\text{H})\) and \([\text{Cp}^*\text{Ir}^{IV}(\text{bpy})(\text{H})]^2+\) pair: an initial burst of \(\text{H}_2\) was observed even when deuterated acid sources where employed. Regeneration of the hydride \([\text{Cp}^*\text{Ir(bpy)(H)}]^+\) follows protonation of \(\text{Cp}^*\text{Ir(bpy)}\) which is a product of \(\text{H}_2\) release. This mechanism of self-quenching preceding bond formation had not been previously observed in the \(\text{H}_2\) photochemistry literature.

**Scheme 1.5. Mechanism for \(\text{H}_2\) production from \([\text{Cp}^*\text{Ir(bpy)(H)}]^+\).**

---

### 1.3 Transition Metal Hydrides in Aqueous Reactions

The various routes to hydrogen production have metal hydrides as a common intermediate. In nearly all of the HER reactions discussed above, there is, at some point on the catalytic cycle, a bond between a metal and a hydrogen atom. In addition to hydricity
being a useful parameter for understanding H₂ evolution from aqueous solution, transition metal hydrides are intermediates in a number of reactions in water outside of HER. Aqueous hydride transfer is an essential process in enzymatic catalysis,\textsuperscript{30,31} in CO₂ reduction,\textsuperscript{32,33} and in biphasic industrial catalysis.\textsuperscript{34,35} Demonstrating the utility of metal hydrides in aqueous conditions, an aqueous-phase Rh hydride produces \( \sim 800,000 \) tons/year \( n \)-butyaldehyde for plastics.\textsuperscript{34}

Given the prevalence of the metal-hydride bond, understanding and describing the strength and reactivity of these intermediates in order to modify and predict outcomes has become very desirable.

**Measuring metal-hydride bond strength with hydricity.** Thermochemical studies of metal hydrides provide a foundation for rational design of catalysts and for mechanistic studies of 2e⁻ proton-coupled electron transfer (PCET) reactions.\textsuperscript{36,37} In acetonitrile, DuBois and Rakowski DuBois pioneered the determination of hydricity and its use as a powerful tool for reaction development in organic solvents.\textsuperscript{38–40} DuBois’s [Ni(PPh₂NPh₂)₂][BF₄]₂ catalyst discussed above achieved its impressive rates through thermochemistry-guided catalyst design.\textsuperscript{17,41}

As shown in Scheme 1.6, the metal hydride bond can be cleaved to a proton (H⁺), a hydrogen atom (H•), or a hydride (H⁻). Thermodynamic parameters have been determined for all three M–H bond-breaking reactions. As a thermodynamic measure of the energy required to break a bond, any of the reactions in Scheme 1.6 can be considered bond strengths. The heterolytic bond cleavage with proton dissociation is the acidity of the metal hydride, reported here as a pKₐ value. *Thermodynamic hydricity*, \( \Delta G_{H^-}^{\circ} \), is defined as the free energy required to remove a hydride anion (H⁻) from a species, as shown in Scheme 1.6. Heterolytic
cleavage of a M–H bond to generate H\(^{-}\) is endergonic, and the magnitude of ∆\(G^{\circ}\)\(_{\text{H}^{-}}\) indicates how much energy is needed for bond cleavage. Species with large values of ∆\(G^{\circ}\)\(_{\text{H}^{-}}\) are therefore weak hydride donors, and species with small values of ∆\(G^{\circ}\)\(_{\text{H}^{-}}\) are strong hydride donors. Metal hydrides that are strong hydride donors can be described as being *hydridic*.

**Scheme 1.6. Three \(\text{L}_n\text{M–H} \) bond cleavage reactions.**

There are several methods that can be used to assess the hydricity of a complex. The most common of these are “hydride transfer,” “\(H_2\) heterolysis,” and “potential–p\(K_a\)” methods for determining hydricity. These methods are discussed briefly here and in more detail in reference 15.

The “hydride transfer” method determines the hydricity of a metal hydride by measuring the equilibrium constant for the reaction of a hydride donor of unknown hydricity (MH) reacting with a reference hydride acceptor (A, where HA\(^{-}\) has a known hydricity), as illustrated in Scheme 1.7. NMR spectroscopy and UV-vis spectroscopy are the two most common techniques for the measuring the equilibrium constant for eq 1.2. The free energy of eq 1.2 is combined with the free energy of eq 1.3 to yield the hydricity of MH (eq 1.4). A reliably quantifiable equilibrium constant can typically only be achieved when the two hydride donors have hydricity values within ~3 kcal/mol of each other. This difference in hydricity is based on the assumption that a 1:10 ratio of the concentrations of two species is readily quantifiable. If equimolar amounts of a hydride donor and hydride acceptor react to
form a 10:1 equilibrium mixture, then $K_{eq}$ is 100, and thereby $\Delta G^\circ = -1.364 \log(K_{eq}) \approx 2.7$ kcal/mol.

Scheme 1.7. Determination of Hydricity by Hydride Transfer.

\[
\begin{align*}
MH + A & \rightleftharpoons M^+ + HA^- \quad \Delta G^\circ = -1.364 \log(K_{eq}) \quad (1.2) \\
HA^- & \rightleftharpoons A + H^- \quad \Delta G^\circ_{H^-} \text{ of HA}^- \quad (1.3) \\
MH & \rightleftharpoons M^+ + H^- \quad \Delta G^\circ_{H^-} \text{ of MH} \quad (1.4)
\end{align*}
\]

The “$H_2$ heterolysis” method for hydricity determination relies on measuring the equilibrium constant for the reaction of a hydride acceptor, a base, and $H_2$ (eq 1.5 in Scheme 1.8) to form a metal hydride of unknown hydricity (MH). The free energy for $H_2$ heterolysis can be combined with the $pK_a$ value of the acid (reverse of eq 1.6) and the free energy for the heterolysis of $H_2$ in the same solvent (eq 1.7) to yield the hydricity of a metal hydride (eq 1.8). The $H_2$ heterolysis method is conceptually related to the relative hydricity method, in that the hydricity of a metal hydride is determined relative to the hydricity of $H_2$.

Scheme 1.8. Determination of Hydricity by Heterolysis of $H_2$.

\[
\begin{align*}
MH + H^-\text{Base}^+ & \rightleftharpoons M^+ + H_2 + \text{Base} \quad \Delta G^\circ = -1.364 \log(K_{eq}) \quad (1.5) \\
H^+ + \text{Base} & \rightleftharpoons H^-\text{Base}^+ \quad \Delta G^\circ = -1.364 pK_a \quad (1.6) \\
H_2 & \rightleftharpoons H^+ + H^- \quad \Delta G^\circ_{1.7} \quad (1.7) \\
MH & \rightleftharpoons M^+ + H^- \quad \Delta G^\circ_{H^-} \quad (1.8)
\end{align*}
\]

The “potential–$pK_a$” method for hydricity determination of a metal hydride involves measuring the $pK_a$ value of MH (eq 1.9) and the reduction potential of the conjugate hydride
acceptor (eq 1.10). Combining these experimental free energies with the free energy for the two-electron reduction potential for reduction of H\(^+\) to H\(^-\) (eq 1.11) provides the hydricity (eq 1.12). The reduction potential \(E^\circ\) is most commonly determined using cyclic voltammetry (CV), a method that can readily identify reversible reductions that reach equilibrium at the electrode surface. The \(E_{1/2}\) value from a CV experiment is a good approximation of \(E^\circ\) if the electrochemical wave is reversible.

Scheme 1.9. Determination of Hydricity from Two-Electron \(E^\circ\) Value and a \(pK_a\).

\[
\begin{align*}
MH & \rightleftharpoons M^- + H^+ & \Delta G^\circ = 1.364 \ pK_a & \quad (1.9) \\
M^- & \rightleftharpoons M^+ + 2e^- & \Delta G^\circ = 46.12 \ E^\circ & \quad (1.10) \\
H^+ + 2e^- & \rightleftharpoons H^- & \Delta G^\circ_{1.11} & \quad (1.11) \\
MH & \rightleftharpoons M^+ + H^- & \Delta G^\circ_{H^-} & \quad (1.12)
\end{align*}
\]

The “\(H_2\) heterolysis” and “potential–\(pK_a\)” methods require one or more of the thermodynamic constants that relate H\(^+\), H•, H\(^-\), and H\(_2\), shown in Table 1.1. The constants in Table 1.1 provide the basis for thermochemical cycles that can be used to quantify the favorability of each of the possible M–H bond cleavage reactions. The origins of these constants in acetonitrile\(^{43-46}\) and water\(^47\) have been previously described. Eq 1.7 is of particular importance as an expression for three different thermodynamic parameters: the free energy to heterolyze H\(_2\), the acidity of H\(_2\) (given as a free energy), and the hydricity of H\(_2\). Consistency in the implementation of these values ensures that any systematic error introduced in their formulation will not impact the prediction of reactivity trends.
Table 1.1. Thermodynamic Constants for H+, H•, H–, and H2 in Acetonitrile and in Water.ª

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔG° in MeCN (kcal·mol⁻¹)</th>
<th>ΔG° in H2O (kcal·mol⁻¹)</th>
<th>eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>2H⁺ + 2e⁻ ↔ H₂</td>
<td>3.6b</td>
<td>0.0c</td>
<td>(1.13)</td>
</tr>
<tr>
<td>H₂ ↔ 2H⁺</td>
<td>103.6</td>
<td>105.7</td>
<td>(1.14)</td>
</tr>
<tr>
<td>H⁺ + e⁻ ↔ H⁺</td>
<td>53.6b</td>
<td>52.8c</td>
<td>(1.15)</td>
</tr>
<tr>
<td>H⁺ + e⁻ ↔ H⁻</td>
<td>26.0b</td>
<td>-18.6c</td>
<td>(1.16)</td>
</tr>
<tr>
<td>H⁺ + 2e⁻ ↔ H⁻</td>
<td>79.6b</td>
<td>34.2c</td>
<td>(1.11)</td>
</tr>
<tr>
<td>H₂ ↔ H⁺ + H⁻</td>
<td>76.0</td>
<td>34.2</td>
<td>(1.7)</td>
</tr>
</tbody>
</table>

ª These values correspond to a 1 atm standard state for H₂ and a 1 M standard state for H⁺, H•, and H–. b Referenced to the FeCp₂⁺/0 couple in MeCN. c Referenced to NHE.

In light of the benefits that thermochemical understanding could have in the development of hydride-mediated catalysis in water, the aqueous hydricity of metal hydrides has been, until recently, surprisingly unexplored. Creutz’s seminal efforts relied on experimentally challenging approach-to-equilibrium kinetics under CO₂.47,48 The groups of Yang and Berben each reported the hydricity of one metal hydride based on the thermodynamics of H₂ cleavage reactions.49,50 Our interest in the aqueous reactivity of Cp*Ir-based catalysts motivated us to develop a general and expedient method for hydricity determination in water, discussed in Chapter 4.

1.4 Beyond Transition Metal Hydrides

Metal-hydride bonds are not the only intermediates for proton and electron management that have been utilized in the HER and other reactions the require PCET. For example, the mechanism for H₂ evolution from Cp*Mo(μ-S)₄MoCp* has been extensively studied and involves no metal-hydride intermediates.51 The dimolybdenum system supports a wide range of oxidation and protonation states, but protons are localized on the sulfide bridges while the electrons may be on either sulfur or molybdenum.
Biology has made extensive use of the carbon-based hydride donor NADH (the reduced form of NAD\(^+\), nicotinamide adenine dinucleotide) to manage the \(1H^+/2e^-\) transfer of a hydride. Indeed, enantioselective enzymatic reductions of carbonyls that rely on NADH as a cofactor are extremely successful. In order to take advantage of the selectivity of enzymatic catalysis without incurring the penalty of stoichiometric consumption of the expensive NADH cofactor tandem catalytic systems that regenerate NADH from NAD\(^+\) using inexpensive terminal reductants have become an area of research.\(^{52-55}\) Of the organometallic catalysts that have been shown to regenerate NADH, Cp*Rh(bpy)-based complexes have emerged as selective and efficient catalysts for reduction at the 4-position of nicotinamides, spurring innovation in tandem bio-organometallic catalysis (Scheme 1.10).\(^{53}\)

**Scheme 1.10. Tandem catalytic cycle for Rh, NAD\(^+\), and enzyme mediated reductions**

After considering the hydricity of the iridium analogues [Cp*Ir(bpy)(H)]\(^+\) in Chapter 4, we were interested in the comparison to [Cp*Rh(bpy)(H)]\(^+\), one of the best NAD\(^+\) reduction catalysts. We found, surprisingly, that rather than the expected Rh–H, the stable
hydride donor was (Cp*H)Rh(bpy)(Cl), making this species, like NADH, a carbon-based hydride donor. Our investigation of the structure and hydricity of this complex is presented in Chapter 5.

Moving farther away from metal-hydrides, for the formation of heavier fuels like propane and butane, future solar fuel systems may need to mediate C–C bond formation. Thinking of the simplest substitution for the hydride, we investigated the methyl analogue [Cp*Ir(bpy)(CH$_3$)]$^+$. Given that the Cp*Ir(bpy) scaffold exhibited an unexpected mechanism for H$_2$ evolution, we questioned whether substitution of a methyl group for the hydride would form C–C bonds through the analogous reaction to that of the hydride. Our investigation into the characterization, photochemistry, and mechanism of alkane formation from a methylated Cp*Ir(bpy) complex is discussed in Chapter 6.

1.5 Summation

Transition metal hydrides are key intermediates in many catalytic cycles, both for the formation of hydrogen and other fuels and for other reductions in biology and in industry. Designing systems that produce chemical bonds from these hydrides with the help of sunlight is a fundamental challenge for solar fuels. This work begins by integrating light absorption and electrocatalysis in a single molecule. The fundamental thermodynamics of hydride transfer were investigated to understand these reactions. With our understanding of this system, we broadened our scope to understand what happens when you perturb the catalyst by changing the metal and the ligands.

Discovering solutions to the energy needs of our planet is a multifaceted problem being approached from many different directions. By following this research path, though much
work remains, we have shed light on alternative strategies for the development of fuels from
light.
CHAPTER 2: MOLECULAR PHOTOELECTROCATALYSTS FOR VISIBLE LIGHT-DRIVEN HYDROGEN EVOLUTION FROM NEUTRAL WATER


2.1 Introduction

Light-promoted evolution of hydrogen from water is an attractive route to solar fuels. Though there are many strategies to achieve this goal, as previously discussed, most involve many components. In multi-component schemes, the catalyst is often identified and optimized using electrochemical methods before integration with a light absorber. The multi-component photoredox approach has seen widespread success in systems utilizing a molecular chromophore (e.g. Ru(bpy)$_3^{2+}$), a catalyst (e.g. Co diglyoximes), and a sacrificial reductant. A light absorbing material (e.g. Si or small band gap semiconductors) can also be employed in such systems, leading to heterogeneous photoelectrochemical cells.

We envisioned an alternative photoelectrochemical approach, in which H$_2$ evolution is facilitated by a single molecule acting both as light absorber and electrocatalyst. Such multifunctional catalysts (almost always Ru(bpy)$_3^{2+}$) have been used to produce “molecular photoelectrodes,” but this strategy has not been applied to the synthesis of a chemical fuel, as in hydrogen evolution catalysis. We report here that [Cp*Ir(bpy)(Cl)][Cl] (1) integrates light absorption and electrocatalysis in a single molecular framework. Aqueous solutions of 1 evolve negligible amounts of H$_2$ in the dark at pH 7, but illumination with visible light initiates sustained photoelectrocatalytic H$_2$ evolution with minimal applied potential (Scheme
2.1. Electron transfer occurs in the dark while H₂ release is light-triggered, consistent with previously observed reactivity pertaining to the photochemical water-gas shift reaction.\(^{61–63}\) Unlike the water-gas shift and other multi-component hydrogen evolution strategies, no sacrificial reagent is required. Tuning the electronic nature of the ligand affords photoelectrocatalysts with good activity near the thermodynamic potential for H₂ evolution.

### 2.2 Results and Discussion

**Sustained Photoelectrocatalytic Hydrogen Evolution.** A molecular photoelectrocatalyst must be capable of electrochemical hydride formation and photochemical H₂ release. Detailed electrocatalytic studies of 1 in aqueous solution are lacking,\(^{64}\) but H₂ evolution electrocatalysis in acetonitrile has been reported, albeit at very negative potentials (−1.6 V vs. Ag/Ag\(^+\)).\(^{65}\) Considering this precedent, electrochemical studies in aqueous solution, in the dark and under visible light illumination, were undertaken.

**Scheme 2.1. Photoelectrochemical water reduction conditions.**

Water-soluble chloride complex 1 was prepared according to the previously reported procedure,\(^{66}\) and cyclic voltammetry (CV) was performed as an initial probe for photoelectrocatalytic activity. In pH 7 phosphate buffer (0.1 M), protected from light, chloride complex 1 exhibited an irreversible reduction at −0.61 V on a glassy carbon working
electrode (Figure 2.1; all potentials reported vs. NHE unless otherwise noted). At scan rates of 25 mV·s\(^{-1}\) and faster, no current enhancement was observed upon illumination with a 460 nm LED lamp. At scan rates slower than 25 mV·s\(^{-1}\), however, illumination produced clear increases in current (Figure 2.1). At such slow scan rates convection can interfere with interpretation,\(^{67}\) but the current enhancement is characteristic of catalysis.

Encouraged by the current response to light in CV experiments, controlled potential electrolysis (CPE) was carried out to provide further support for photoelectrocatalysis. In CPE experiments with the potential held at \(-1\) V vs. NHE, a 1 mM solution of 1 in pH 7 phosphate buffer was irradiated at 460 nm. Sustained photocurrent around \(-600\) μA was achieved over the course of the one-hour experiment (Figure 2.2A) and bubbles evolved from solution and accumulated on the electrodes. When protected from light, the current rapidly diminished to below \(-25\) μA (Figure 2.2A). The CPE experiments confirm that while chloride 1 is an ineffective electrocatalyst in the dark, photolysis induces electrocatalytic activity. Visible light enhanced catalytic currents by a factor of roughly 25 after 60 min at \(-1\) V, suggesting efficient and sustained photoelectrocatalysis.

![Figure 2.1. CV of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) at 5 mV·s\(^{-1}\) illuminated (solid black) and dark (dashed black) and at 10 mV·s\(^{-1}\) illuminated (solid red) and dark (dashed red). Glassy carbon working electrode (3 mm disc), Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode, 460 nm LED lamp. Current is scan-rate](image-url)
normalized: normalized current of diffusion-controlled processes is constant with changing scan rate while normalized current of catalytic waves increases as scan rate decreases.

**Figure 2.2.** A) CPE at –1 V vs. NHE of 1 mM 1 in 0.1 M phosphate buffer (pH 7) in the dark (dashed black) and under 460 nm light (solid blue). B) CPE at –0.9 V vs. NHE of 1 mM 1 in 0.1 M phosphate buffer (pH 7) with light off (gray) and on (white). Reticulated vitreous carbon working electrode, Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode.

The influence of light was further established by applying a shutter to CPE experiments (Figure 2.2B). In the dark, high levels of current are initially passed before rapidly decaying, consistent with complete electrochemical reduction of all 1 in solution. In the light, the current quickly rises and remains steady as photoelectrocatalytic H₂ evolution initiates. Applying a shutter halts catalysis, and the current immediately begins to drop. The large amount of charge passed after shuttering implies that [Cp*Ir(bpy)(H)]⁺ (2), which cannot be further reduced at the potential applied, is not the dominant species in the bulk solution during catalysis. The low proportion of hydride 2 in solution suggests that the photochemical steps are not limiting the reaction in this cell configuration. As a control reaction, the same experiment was performed in the absence of catalyst: no difference in current was observed when a cell containing only aqueous phosphate buffer was toggled between dark and light conditions.
The Faradaic efficiency of photoelectrocatalysis was quantified by monitoring the solution pH change in situ during photoelectrolysis. If \( \text{H}_2 \) is produced according to Scheme 2.1, proton consumption will lead to a pH increase. Faradaic efficiency was obtained by relating the measured pH change to the expected pH change if every two electrons produced \( \text{H}_2 \).\(^\text{19}\) A weakly buffered solution (50 mM phosphate, initial pH 7.8) was irradiated while applying a potential of \(-0.9 \text{ V}\), and the pH was measured periodically. The pH increased as expected, with 100% Faradaic efficiency recorded at early times before a slight decrease to ~90% as the experiment proceeded and the pH increased (Figure 2.3).

![Figure 2.3](image)

**Figure 2.3.** Total charge passed in the photoelectrolysis (~1.23 C, black) and charge that productively made \( \text{H}_2 \) according to the pH change (red circles) for 1 mM 1 in 50 mM sodium phosphate (initial pH = 7.8) at \(-0.9 \text{ V}\), and the charge passed in the absence of catalyst (~0.17 C, gray). Photoelectrolysis results in a seven-fold increase in total charge passed, and the pH change in the absence of catalyst was within the ±0.1 error of the probe. Faradaic efficiency drops from 100% to 90% over 90 minutes.

The photon-to-hydrogen efficiency is also of great interest in photoelectrocatalytic processes. This efficiency can be measured in a number of ways; the present system, in which the specific concentration of photoactive species at any given time is unknown, is best treated by “external quantum efficiency” \((EQE = \frac{\text{moles H}_2 \text{ produced}}{\text{moles incident photons}})\). The moles of incident photons in an area ~2 mm\(^2\) greater than the electrode planar surface area were
measured using a Si photodiode. Based on the current passed and the Faradaic efficiency, 
EQE = 10(5)% in three separate controlled potential electrolysis experiments. This value is 
similar to a previous molecular photoelectrochemical cell based on photoredox quenching, and similar to the H₂ quantum yield in photochemical water-gas shift reactions involving 2. It is expected that the EQE value obtained here will be sensitive to a variety of factors such as the light source and geometric position, electrode surface area (variations in which we believe to be responsible for the relatively large uncertainty in our value), catalyst concentration, and applied potential. The EQE is useful for practical catalytic applications; the mechanistically more insightful quantum yield, which measures the efficiency of H₂ evolution based on the number of photons actually absorbed by hydride 2, will be assessed in future studies.

In prolonged photoelectrocatalysis experiments, photocurrent was relatively stable until the buffer was exhausted after 5.5 h. The total catalyst turnover number (TON) for H₂ production in this extended experiment was 16.5 (TON ~ 3.9 in a typical 1 h experiment). Photoelectrocatalytic activity was restored upon addition of acid, but steadily diminishing current over the course of 48 h suggests some catalyst degradation (Figure 2.4). In dark electrolyses under the same conditions, no H₂ was detected by GC. Similarly, when phosphate solutions (no catalyst) were subjected to photoelectrolysis, minimal charge passed (≈0.17 C without catalyst, ≈1.23 C with catalyst) and the pH change did not change.
Figure 2.4. CPE of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) at −0.9 V under 460 nm LED irradiation. After exhaustion of the buffer, addition of 100 μL 1 M H₃PO₄ restored current.

Separating the Electrochemical and Photochemical Steps. In order to establish that catalyst 1 was responsible for both the photochemical and electrochemical processes, they were studied independently. First, the electrochemical properties of 1 were probed in the absence of light. As described above, CV of 1 in pH 7 phosphate buffer (0.1 M) displays an irreversible reduction around −0.61 V that appears to be composed of multiple peaks. In contrast, solutions of 1 in pH 7 water with NaCl electrolyte (0.1 M) exhibited a single irreversible reduction feature (Figure 2.5A). The initial reduction features are assigned as 2e⁻ processes on the basis of previous reports and CPE experiments (vide infra).⁶⁴,⁶⁵ The distinct behavior observed in chloride and in phosphate electrolytes indicates partial chloride displacement in phosphate buffer to form [Cp*Ir(bpy)(H₂O)]²⁺,⁶⁴,⁶⁸ and [Cp*Ir(bpy)(H₂PO₄)]⁺,⁶⁹–⁷¹ as further evidenced by ¹H and ³¹P{¹H} NMR studies that showed two minor species (<10% of total Ir) in D₂O containing ~0.1 M pD 7 NaH₂PO₄/Na₂HPO₄. In pure D₂O, 1 was the only species observed.
Regardless of electrolyte, aqueous solutions of 1 show a second, quasi-reversible 1e\textsuperscript{-} reduction at −1.25 V (Figure 2.5B). This feature is assigned to the Ir\textsuperscript{III}–H\textsuperscript{+}/Ir\textsuperscript{II}–H couple of hydride 2, suggesting that 2e\textsuperscript{-} reduction of 1 to form Cp*Ir\textsuperscript{II}(bpy) (3) is followed by rapid protonation. Consistent with this assignment, the peak current at −1.25 V diminishes as the solution pH increases: as 3 becomes the dominant product upon reduction of 1, the feature corresponding to the reduction of 2 disappears. Above pH 10, a new oxidation feature is also observed around −0.25 V, assigned as a 2e\textsuperscript{-} oxidation of 3. At these high pH values, the voltammetric response is indicative of the neutral complex 3 adsorbing on the electrode. Similar adsorption is observed at pH < 10 when scanning beyond −1.3 V, at which point another neutral species, Cp*Ir(bpy)(H) is formed. Conditions in subsequent experiments were chosen to avoid such adsorption (see below for a discussion on homogeneity).

A stepwise electrolysis-photolysis experiment was undertaken to separately probe the role of electron transfer and photon absorption. Controlled potential electrolysis of 1 was carried out protected from light, in pH 7 phosphate buffer. The product of dark electrolysis was confirmed to be hydride 2 by \textsuperscript{1}H NMR spectroscopy and by comparison of the UV-vis spectrum to an isolated sample of 2 (Figure 2.6, \(\lambda_{\text{max}} = 410\) nm). From the electrochemically
formed 2, $\varepsilon_{410} = 2400 \text{ M}^{-1} \text{ cm}^{-1}$ which is consistent with the extinction coefficient determined from an isolated sample. The first reduction wave of 1 had also essentially disappeared, while the hydride redox couple remained. In a typical electrolysis with 2.5 mL 1 mM 1, the total charge passed during dark CPE was $-433 \text{ mC} (1.8 e^-/\text{Ir})$, consistent with $2e^-$ reduction of 1 followed by protonation to form hydride 2.

![UV–vis spectra](image.png)

**Figure 2.6.** UV–vis spectra of 0.3 mM 1 in 0.1 M phosphate buffer (solid black), after 90 min of electrolysis at $-0.9 \text{ V}$ to form 2 (solid blue), and after 90 min of 460 nm photolysis to reform 1 (dashed orange). Subsequent electrolysis reformed 2 (dashed red) and photolysis reformed 1 (omitted for clarity). The molar extinction coefficient ($\varepsilon$) of each species was calculated assuming clean conversion (see text for details). Reticulated vitreous carbon working electrode, Pt wire counter electrode, Ag/AgCl (3 M NaCl) reference electrode.
Figure 2.7. CV (scan rate of 250 mV·s⁻¹) performed during stepwise electrolysis (−0.9 V) and photolysis (460 nm LED) of 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7).

Next, the electrolysis solution containing in situ-generated hydride 2 was photolyzed. Whereas solutions of hydride 2 in neutral water are stable in the dark over several hours, irradiation with a 460 nm LED array leads to rapid consumption of 2, as judged by UV-vis (Figure 2.6) and CV (Figure 2.7). Photolysis returned the Ir-containing species to pale yellow 1. Re-subjecting the solution to CPE cleanly produced golden hydride 2, which was again consumed upon photolysis, indicating stepwise catalysis. The evolved gas, confirmed to be H₂ by GC headspace analysis, was formed with 70% Faradaic efficiency. Faint orange luminescence was apparent to the naked eye during photolysis, suggesting the involvement of the previously reported excited state of [Cp*Ir(bpy)(H)]⁺, 2*, which has been reported to have a 80 ns lifetime at 298 K in MeCN.²₂,²₃ Scheme 2.2 depicts a broad mechanism for photoelectrocatalytic H₂ evolution that is consistent with the stepwise studies. Later work
from our lab showed that the mechanism for H$_2$ evolution with 2 and acids in acetonitrile follows a bimolecular self-quenching pathway.

**Scheme 2.2. Proposed photoelectrocatalytic cycle.**

A slew of recent studies on the homogeneity of Cp*Ir-based catalysts compelled us to consider the possibility of Ir nanoparticles.$^{13,74,75}$ Without undertaking an exhaustive study, three lines of evidence suggest that a molecular catalyst is likely to be responsible for the observed behavior. First, the stepwise electrolysis/photolysis study described above shows that all of the chloride complex 1 in the bulk solution is cleanly converted to the hydride complex 2 electrochemically. If the electrochemical current was leading to deposition of nanoparticles or other decomposition, the yield of molecular species 2 should be low. Further, upon photolysis, H$_2$ gas and chloride 2 are formed in high yield; this cycle can be
repeated three times without noticeable degradation. It is noteworthy that the study was monitored by optical spectroscopy, as IrOx nanoparticles are highly colored; no absorption in the 600-800 nm range was observed. Second, a “rinse test” was performed: when the electrode was gently rinsed with water after a typical photoelectrocatalytic run and placed in a fresh phosphate solution containing no catalyst, only current attributed to glassy carbon background was observed, suggesting that adsorbed species are not the active catalyst. Finally, the kinetics of catalysis showed no induction period, with controlled potential electrolyses maintaining steady photocurrent for hours. These observations, coupled with the reductive, anaerobic conditions (as opposed to oxidizing, aerobic conditions under which Cp*Ir water oxidation catalysts have been shown to decompose), suggest that catalyst degradation to nanoparticles is not a major factor.

**Optimization of Photoelectrocatalytic Performance.** Optimization of the photoelectrocatalytic hydrogen evolution reaction was carried out with the aid of kinetic studies. As discussed above, the initial rates were too slow for reliable data to be extracted from CV experiments. Reaction rate constants were therefore measured using chronoamperometry (CA). While not commonly used to assess electrocatalysts, Delahay and Stiehl showed that CA data can provide an apparent rate constant for catalytic reactions. The model assumes that electron transfer is fast, such that the observed rate constant is a reflection of a rate-determining chemical catalytic step (EC' mechanism). While the influence of light on the reaction may complicate such analysis, we have found CA convenient for obtaining an apparent rate constant, $k_{obs}$, for comparisons. Chronoamperometry of 1 was carried out at −1.0 V for 20 seconds both in the dark and under 460 nm illumination. Irradiated samples passed significantly more current than those protected from light (Figure
The ratio of the dark and light currents was fit between 5 and 10 seconds to give \( k_{\text{obs}} = 0.037(9) \text{ s}^{-1} \). The observed rate constant varied linearly with light intensity (Figure 2.8), supporting the notion that photon fluence is a key parameter.

**Figure 2.8.** Plot showing rate dependence on lamp power. The apparent catalytic rate constants were obtained from CA experiments at different LED lamp power, each with 1 mM 1 in 0.1 M sodium phosphate buffer (pH 7) held at \(-0.9 \text{ V}\) for 20 seconds. A variable power supply controlled the power of the incident light (470 nm LED strips).

The impact of potential on photoelectrocatalysis was investigated by varying the applied CA potential between \(-0.6\) and \(-1.0 \text{ V}\) (Figure 2.9A, black squares). The observed rate constant increased with increasing overpotential,\(^{42,77}\) remaining steady with \( k_{\text{obs}} = 0.039(4) \text{ s}^{-1} \) after \(-0.8 \text{ V}\). The catalytic onset potential is consistent with the notion that the key intermediate in \( \text{H}_2 \) evolution photoelectrocatalysis is the Ir\(^{\text{III}–\text{H}^+}\) intermediate 2, which is formed electrochemically at similar potentials. Further reduction to the neutral Ir(II)–H is not required. A hydrogen evolution overpotential of only 190 mV (\(-0.60 \text{ V} \text{ vs. NHE at pH 7}\)) is required to achieve half of the maximum catalytic rate, \( k_{\text{obs}} = 0.02(1) \text{ s}^{-1} \); this potential corresponds nicely to the relevant reduction wave of 1 (\(-0.61 \text{ V}\)).\(^{77}\) In contrast, aqueous solutions of 1 protected from light do not show conclusive evidence of catalysis even upon subsequent reduction of 2 to the Ir\(^{\text{II}–\text{H}}\) intermediate. A related catalyst with pyrrole...
substituents, when electropolymerized onto an electrode surface, was reported to evolve H$_2$ via the Ir$^{II}$–H state under acidic conditions: pH 3 at $-1.31$ V, an overpotential of approximately 1.1 V.$^{65}$ When a photochemical step is harnessed, I catalyzes H$_2$ evolution at a more positive reduction potential and at neutral pH.

A variety of media were screened as supporting electrolytes for water reduction across a wide pH range. Sustained catalytic current over background was observed when 1 mM solutions of I in 0.1 M citrate buffer underwent CPE at $-0.9$ V (pH adjusted to 4, 5, and 6 in separate experiments). A phosphate solution at pH 8 and borate buffer solutions at pH 9 and 10 also showed sustained CPE photocurrents ($-1$ V).

Facile tuning by ligand substitution is a key feature of many molecular catalysts, and indeed the photoelectrocatalytic H$_2$ evolution behavior is not unique to complex I. A large variety of substituted bipyridine analogues are known, and complexes of a few of these were screened in initial studies. Sustained currents over one hour were observed when electrochemical cells containing solutions of [Cp*Ir(bpy-OMe)(Cl)][Cl] (I-OMe) and [Cp*Ir(bpy-COOH)(Cl)][Cl] (I-COOH$_2$) (bpy-X = 4,4'-X-2,2'-bipyridine, X = OMe, COOH) were held at $-1.0$ V and irradiated with a 460 nm LED in pH 7 phosphate buffer.

**Figure 2.9.** A) Chronoamperometry of 1 mM I in pH 7 phosphate buffer in the dark (dashed black) and under 460 nm LED irradiation (solid blue) at $-1$ V vs. NHE. Inset: ratio of the two CA traces (black) and fit (dashed red) with $k_{obs} = 0.036$ s$^{-1}$. B) Apparent catalytic rate...
constants for 1 (black squares), 1-OME\(_2\) (orange circles), and 1-COOH\(_2\) (blue triangles) as a function of potential. Error bars reflect two standard deviations in both directions as determined by between 3 and 7 experiments. Glassy carbon working electrode (3 mm disc), Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode.

Surprisingly, the observed rate constants obtained from chronoamperometry did not follow the trends expected for electrocatalysts. The catalyst reduced at the most negative potential, 1-OME\(_2\), gave \(k_{\text{obs}} = 0.090(5)\;\text{s}^{-1}\) at \(-1\;\text{V}\) while the catalyst reduced at the most positive potentials, 1-COOH\(_2\) (deprotonated under the experimental conditions), outperformed both catalysts, with \(k_{\text{obs}} = 0.20(1)\;\text{s}^{-1}\) at \(-0.8\;\text{V}\) (Figure 2.9B). Carboxylate-substituted catalyst 1-COOH\(_2\) also operates at lower overpotentials than 1, and CV traces show the onset of catalysis occurs just prior to the thermodynamically required potential for \(\text{H}_2\) evolution (Figure 2.10). This situation is only possible when photon energy is being utilized and suggests that further catalyst optimization may lead to significant energy storage.

Figure 2.10. CV of 1 mM 1-COOH\(_2\) in 0.1 M sodium phosphate buffer (pH 7) at 25 mV·s\(^{-1}\) under 460 nm LED light (solid black) and dark (dashed black) and at 50 mV·s\(^{-1}\) in the light (solid red) and dark (dashed red). Dotted line indicates thermodynamic potential for hydrogen evolution at pH 7. Current is scan-rate normalized: normalized current of diffusion-controlled processes is constant with changing scan rate while normalized current of catalytic
waves increases as scan rate decreases. Glassy carbon working electrode (3 mm disc), Pt wire counter electrode, Ag/AgCl (3M NaCl) reference electrode.

It is remarkable that 1-COOH₂ is both the fastest catalyst and features the lowest overpotential, in light of the general trend for molecular electrocatalysts that larger overpotentials produce faster reactivity. Inspection of the absorption spectrum reveals that [Cp*Ir(bpy-COOH)(H)]⁺ has excellent overlap with the 460 nm LED lamp used in these studies (Figure 2.11). This presumably leads to an increased external quantum efficiency, perhaps explaining the superior photoelectrochemical performance of 1-COOH₂ at low overpotential.

Figure 2.11. Absorption spectra of electrochemically generated [Cp*Ir(bpy)(H)]⁺ (black), [Cp*Ir(bpy-OMe)(H)]⁺ (orange), and [Cp*Ir(bpy-COOH)(H)]⁺ (blue) in 0.1 M sodium phosphate buffer (pH 7) with the spectrum of the 460 nm LED lamp (green).

2.3 Conclusions

A novel approach to H₂ evolution using molecular photoelectrocatalysts has been introduced. A single molecular catalyst undergoes electrochemical hydride formation followed by photochemical H₂ release. Water reduction is facilitated by three different Ir
catalysts and visible light over a wide pH range at low overpotentials. Hydrogen evolution at the thermodynamic potential was observed, with rate constants of ~0.1 s\(^{-1}\) at ~100 mV electrochemical overpotential.

Combining aspects of photocatalysis and electrocatalysis leads to a number of interesting observations. In comparison to typical hydrogen evolution electrocatalysts, visible light excitation leads to a dramatic reduction in electrochemical applied overpotential, as the required energy comes from light instead of electricity. Further, electrocatalysts typically feature trade-offs between the required potential for catalytic onset and catalytic activity. By incorporating a photochemical step, this linear correlation is broken, and the more easily reduced catalyst \(1\text{-COOH}_2\) also was found to be the most active, due to better photon absorption ability. In comparison to typical photocatalysts, the use of an electrode lifts the requirement for sacrificial reductants. Whereas a complex mixture of light absorbers, redox mediators, catalysts, and sacrificial reagents are often required for photocatalytic \(\text{H}_2\) evolution, the present system features a single component that acts as light absorber and catalyst.

Based on the approach presented here, further improvements can be envisioned: for example, the 460 nm (2.6 eV) lamp provides substantial excess photon energy that is currently not fully utilized. Future work will focus on elucidating the detailed mechanism of the reaction and developing new catalysts capable of sustaining faster hydrogen evolution rates even while absorbing lower energy light.
2.4 Experimental Section

General Considerations. Procedures were carried out under nitrogen except where noted. 2,2’-bipyridine (bpy) and 4-4’-dimethoxy-2-2’-bipyridine (bpy-OMe), 4,4’-carboxyl-2,2’-bipyridine (bpy-COOH), sodium hydroxide, phosphoric acid, and pentamethylcyclopentadiene (Cp*H) were obtained from either Alfa Aesar or Sigma-Aldrich. Sodium phosphate monobasic hydrate was obtained from Mallinckrodt. IrCl$_3$•3H$_2$O was obtained from J&J Materials Inc. Commercial HPLC-grade water was used as a solvent. Deuterium oxide was purchased from Cambridge Isotope Laboratories, Inc. Electrochemical experiments were performed on a Pine WaveNow potentiostat or Pine WaveDriver bipotentiostat controlled by Aftermath software. Details on specific electrochemical experiments are described below. Solution pH was recorded using an OrionStar A111 pH meter with a Beckman-Coulter pH probe. UV-Vis spectra were obtained using an Agilent Cary 60 spectrophotometer or an Ocean Optics USB2000+ spectrometer with a DT-MINI-2GS deuterium and tungsten halogen light source controlled by OceanView software. Photolysis was conducted using a 500 lumen blue LED lamp from Eagle Lights. The wavelength of maximum intensity was 460 nm, as measured with an Ocean Optics USB2000+ controlled by Overture software. In the power dependence experiment, a 460 nm LED light strip from Super Bright LEDs was used. An estimate of the external quantum efficiency was obtained by measuring photon flux with a Coherent LM-2VIS photodiode in conjunction with a Coherent FieldMax II Laser Power/Energy Meter. The photodiode was positioned at the same distance from the lamp as the electrode and a piece of curved glass was used to approximate the conditions of the cell.
A Varian 450-GC with a pulsed discharge helium ionization detector was used to quantify H$_2$. A calibration curve was constructed from samples of 0.5, 1.0, 3.0, and 5.0 v/v % H$_2$ in air. All gas transfers were performed with a 1.0 mL or 10 mL Vici Pressure-Lok® Precision Analytical Syringe. As much as possible, septa were pierced only once. NMR spectra were obtained on 400 or 600 MHz spectrometers. $^1$H NMR spectra were referenced to the residual solvent signals (or with acetone or sodium tosylate as an internal standard in D$_2$O).$^{78}$ Spectra were processed using the MestReNova software suite from Mestrelab Research S. L. The solution acidity in NMR experiments is reported as pD, obtained by addition of +0.4 to the reading of a pH electrode that was calibrated using H$_2$O standards.$^{79}$

**Synthesis.** The catalysts [Cp*Ir(bpy)(Cl)][Cl],$^{66}$ [Cp*Ir(bpy-OMe)(Cl)][Cl],$^{66}$ [Cp*Ir(bpy-COOH)(Cl)][Cl],$^{63}$ and [Cp*Ir(Cl)$_2$]$^{80}$ were prepared according to literature procedures. Catalyst identity and purity (>99%) was established by $^1$H NMR spectroscopy. The spectroscopic features closely matched the published data.

**Electrochemistry.** Unless otherwise noted, all electrochemical experiments were performed in a divided H-cell with a 3-electrode configuration. A carbon working electrode (specific material varied with experiment, see below) and platinum wire counter electrode were positioned on either side of the fine frit. A Ag/AgCl (3M NaCl) reference electrode was placed in the counter electrode compartment in a small glass tube fitted with a Vycor glass frit. Solutions were thoroughly degassed by sparging with nitrogen for at least 15 minutes before beginning an experiment. All potentials are reported relative to NHE, with values obtained by adding 0.21 V to the experimentally observed potential vs. Ag/AgCl.$^{81}$ Overpotentials (to achieve a certain catalytic efficiency) were calculated by subtracting the
formal potential for H₂ evolution ($E^{\circ}_{H+/H2} = 0 - 0.059 \cdot \text{pH}$) from the applied potential at which catalysis was experimentally observed.$^{82}$

Cyclic voltammetry experiments were carried out with a 3 mm diameter glassy carbon disc working electrode (polished with 0.05 micron alumina powder between scans). For experiments under irradiation, the 460 nm LED lamp was placed directly below the glass carbon electrode at a fixed distance.

Controlled potential electrolysis experiments were carried out with reticulated vitreous carbon (RVC) impaled on a graphite rod wrapped with copper wire (above the water line) as the working electrode. In the illuminated experiments, a 460 nm lamp was placed approximated one inch away from the cell. In the dark experiments, the cell was wrapped in aluminum foil. In the shutter experiment, the light was turned on and off periodically; the cell was not wrapped in aluminum foil during the dark stages.

Faradaic efficiency was determined by monitoring the pH change over the course of a CPE experiment. A solution of 1 mM [Cp*Ir(bpy)(Cl)][Cl] in 50 mM phosphate was held at $-0.9$ V while being irradiated with 460 nm LED light for 90 minutes, with the pH probe inserted into the working electrode compartment of the H-cell. For each molecule of H₂ formed, two OH⁻ ions are produced. The amount of hydroxide corresponding to the observed pH change was determined by titration of an identical sample with 0.1 M NaOH.$^{19}$ A control experiment, in which a pH 7 phosphate buffer with no catalyst was held at $-0.9$ V, showed minimal charge accumulation. Whereas the solution pH changed by 1.0 unit when the catalyst was present, without catalyst the pH changed by < 0.1 unit, suggesting little or no H₂ production at the electrode under the standard photoelectrolysis conditions.
Headspace detection of H$_2$ by gas chromatograph was performed in the same cell that was used for CV and CPE experiments. Every effort was made to configure the cell such that any leaks were minimized. After controlled potential electrolysis at –0.9 V for 30 minutes, a headspace sample was obtained before and after photolysis using a gastight 1.0 mL syringe. The volume % hydrogen was quantified by comparison to a calibration curve. Before photolysis, no H$_2$ peak was observed by GC. After photolysis, a prominent H$_2$ peak was observed in the GC trace. Integration and comparison to the calibration curve established a 70% Faradaic efficiency.

To show stepwise catalysis by UV-Vis (Figure 2.6), a 200 mL capacity divided cell was used. The Pt wire was positioned in 3 mL in 0.1 M pH 7 phosphate buffer across a frit from the RVC working electrode and Ag/AgCl reference electrode. A 0.3 mM solution of 1 (40 mL 0.1 M pH 7 phosphate buffer) was added to the working electrode chamber and degassed. UV-Vis were obtained by syringing 3 mL of solution into septa-capped cuvettes under N$_2$. The samples were returned to the cell after the spectra were taken. Spectra were collected at five points: initially, after exhaustive electrolysis at -0.9 V, after exhaustive photolysis, after a second electrolysis, and after a final photolysis.

Chronoamperometry was carried out in the standard H-cell, electrode configuration, and lamp positioning described above for CV. The potential was held between −0.4 and −1.1 V, based on the location of the reduction wave observed by cyclic voltammetry. At each potential, two traces were obtained in the light and in that dark with electrode polishing between each experiment. The ratio of the current in the light ($i_{\text{cat}}$) to the current in the dark ($i_{\text{diff}}$) was fit to the following equation:
where $k_{obs}$ is the rate constant for the turnover-limiting chemical step and $t$ is time. The data was least-squares fit between 5 and 10 s using the Excel solver function. Though deviations from $k_{cat}$ are suggestive of mechanistic complexity, the CA traces at low applied potentials are still indicative of catalysis.

A control reaction to test whether adsorbed species might be the true catalyst was performed as follows: a standard CA experiment was carried out at $-0.9$ V in phosphate buffer, followed by gently rinsing the carbon electrode with water and repeating the CA experiment in a fresh phosphate buffer solution containing no catalyst. When moved to a fresh electrolyte solution containing no catalyst, no current over background was observed in the CA experiment, and no current enhancement under photolysis was observed, suggesting that catalyst adsorption is not a factor in this system.
CHAPTER 3: FACILE SYNTHESIS OF (PENTAMETHYLCYCLOPENTADIENYL) -
(2,2'-BIPYRIDINE)-IRIDIUM, ANALOGUES, AND REACTIONS WITH
ELECTROPHILES

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3.1 Introduction

We were motivated to arrive at an alternative synthesis of Cp*Ir(bpy) 1 because of our
need to produce water-soluble metal hydride species The conjugate base of [Cp*Ir(bpy)(H)]+
(1H), 1 has previously been synthesized, though yields were poor. Ladwig and Kaim reduced
[Cp*Ir(bpy)(Cl)][Cl] (1Cl) in dry THF with [nBu4N][BH4] at −20°C. Crystallization afforded
23% yield of Cp*Ir(bpy).83 In our hands, successive crystallization was required to remove
unreacted [nBu4N][BH4], resulting in much lower yields.

Typically, hydride 1H has been prepared by precipitation from water with PF6− or
OTf− leading to [Cp*Ir(bpy)(H)][PF6] and [Cp*Ir(bpy)(H)][OTf], which were insoluble
above 2 mM in water.84 From our electrochemical studies in Chapter 2, we knew that the
hydride was soluble in water when paired with an appropriate counterion and that, therefore,
counterion selection was playing a critical role in solubility. We hypothesized that
Cp*Ir(bpy) would be a useful synthetic intermediate: a water-soluble hydride could be
produced by protonation with HCl to give [Cp*Ir(bpy)(H)][Cl] and reactions with other
electrophiles could generate other Ir(III) complexes of interest.
3.2 Results and Discussion

*In situ generation of Cp*Ir(bpy).* Determination of the hydricity of the parent complex [Cp*Ir(bpy)(H)]⁺ (1H) was targeted through the “potential−pKₐ” thermodynamic cycle discussed in Chapter 1. This approach, however, was stymied by the water-insolubility of the conjugate base 1, which precluded measuring acidity using a traditional bulk scale pKₐ titration.

Electrochemical reduction allowed for the observation of base 1 generated *in situ.* Two electron reduction of [Cp*Ir(bpy)(Cl)][Cl] in 0.1 M pH 7 sodium phosphate (NaPi) initially produces 1, followed by protonation to form the hydride 1H. As the pH is increased by addition of NaOH, less protonation of 1 occurs and the oxidation wave for 1 grows in at –0.26 V. At high pH, the current of the oxidation is constant with increasing pH. By assuming that the current at high pH corresponded to complete production of 1 with no protonation of the hydride 1H, the relative concentrations of 1 and 1H at each pH were determined. These concentrations led to an estimate of pKₐ = 10.6 (Figure 3.1). This estimate, however, varied with scan rate indicating that protonation is not fast enough for the solution near the electrode to achieve equilibrium on the electrochemical time scale. Additionally, the shape of the oxidation and its linear dependence (at high pH) on scan rate are indicative of product adsorption onto the electrode, which prevents accurate determination of $E_{1/2}$, as well.
Figure 3.1. A) Cyclic voltammetry of [Cp*Ir(bpy)(Cl)]|[Cl] in 0.1 M pH 7 NaPi titrated with solutions of NaOH showing the growth of the oxidation of Cp*Ir(bpy) with increasing pH. B) Fit (dashed black) of oxidation peak area (red dots) to the Henderson-Hasselbalch equation, suggesting a pK_a of 10.6 for [Cp*Ir(bpy)(H)]^+.

**Synthesis and Structure of Cp*Ir(bpy) and Analogues.** The insolubility of 1 proved to be a major obstacle to determining the pK_a of 1H and oxidation potential of 1, but this insolubility became the inspiration for a facile synthesis of Cp*Ir(bpy), with the goal of producing 1 cleanly from precipitation from water. The chloride salt of 1Cl was reduced by excess NaBH_4 in 1 M NaOH and allowed to stir for 3 h, resulting in precipitation of purple 1 in 98% yield (Scheme 3.1, ^1^H NMR spectrum: Figure 3.3). The solids were washed with water to remove residual salts and extracted into benzene.

**Scheme 3.1. Synthesis of Cp*Ir(bpy) by precipitation from basic water.**
Though previously synthesized, 1 had not been crystallographically characterized. A large purple block crystal suitable for X-ray diffraction was produced by slow evaporation of a solution of 1 in THF (Figure 3.2). Crystallographic data and refinement details are given in Table 3.1. The report of this crystal structure completes the Group 9 Cp*M(bpy) series (M = Co, Rh, Ir).\textsuperscript{86–88} Like its lighter metal congeners, 1 adopts a near-perpendicular orientation of the Cp* and bpy planes (84.68\(^\circ\)). The C–C bond connecting the pyridine rings of bpy (C5–C6 1.403(5) Å) shows the characteristic contraction observed in these electron-rich species, attributed to electron delocalization into bpy resulting in partial double bond character in the interpyridyl bond. In free bipyridine, this distance is 1.49 Å and contracts to 1.43 Å in bpy\textsuperscript{2–} and to 1.39 Å for bpy\textsuperscript{2–}.\textsuperscript{89} In the Ir complex 1, however, this bond is shorter than in either of its lighter brethren (M = Co, 1.419 Å\textsuperscript{86}; M = Rh, 1.423 Å\textsuperscript{87,88}), suggesting more electron density resides on bpy when M = Ir.

\textbf{Figure 3.2.} Structural representation of 1 with ellipsoids drawn at the 50\% probability level. Hydrogen atoms omitted. Selected distance (Å): C5-C6 1.403(5).
Table 3.1. Crystal data and structure refinement for 1.

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</tr>
</tbody>
</table>

Precipitation of reduced half-sandwich species from water following the standard conditions of Scheme 3.1 proved to be quite general: several Ir, Ru, and Rh complexes were made this way (Table 3.2). In addition to Ir(I) complex 1, three of these species—(cymene)Ru(bpy), (C_{6}Me_{6})Ru(bpy), and Cp^*Rh(bpy)—have been previously reported with reductions performed in rigorously dry organic solvents with Na, K, or TlO_{2}CH. In some cases, the current synthesis represents a marked improvement in yield, but in all cases, the synthetic conditions in this work with NaBH₄, NaOH, and H₂O are milder than those previously reported.
Table 3.2. Complexes synthesized by precipitation from water and literature precedent.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Lit. Yield</th>
<th>This work</th>
<th>Modifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*Ir(bpy)</td>
<td>23%&lt;sup&gt;83&lt;/sup&gt;</td>
<td>quantitative</td>
<td></td>
</tr>
<tr>
<td>Cp*Ir(bpy-Me)</td>
<td>Not reported</td>
<td>quantitative</td>
<td>5 M NaOH</td>
</tr>
<tr>
<td>Cp*Ir(bpy-CO&lt;sub&gt;2&lt;/sub&gt;Me)</td>
<td>Not reported</td>
<td>47%</td>
<td>pH 7 NaP&lt;sub&gt;i&lt;/sub&gt;, NaO&lt;sub&gt;2&lt;/sub&gt;CH</td>
</tr>
<tr>
<td>(cymene)Ru(bpy)</td>
<td>60–80%&lt;sup&gt;90&lt;/sup&gt;</td>
<td>quantitative</td>
<td></td>
</tr>
<tr>
<td>(C&lt;sub&gt;6&lt;/sub&gt;Me&lt;sub&gt;6&lt;/sub&gt;)Ru(bpy)</td>
<td>60–80%&lt;sup&gt;90&lt;/sup&gt;</td>
<td>quantitative</td>
<td></td>
</tr>
<tr>
<td>Cp*Rh(bpy)</td>
<td>15%&lt;sup&gt;88&lt;/sup&gt;, 87%&lt;sup&gt;87&lt;/sup&gt;</td>
<td>88%</td>
<td></td>
</tr>
</tbody>
</table>

Two complexes, Cp*Ir(bpy-Me) and Cp*Ir(bpy-CO<sub>2</sub>Me) (bpy-X is 4,4’-X-2,2’-bipyridine), were prepared that have not been previously reported. This required slight modifications of the standard conditions. For Cp*Ir(bpy-Me), a 5 M NaOH solution was used to ensure full deprotonation. Indeed, Cp*Ir(bpy-OMe) could not be prepared this way. Donation from the –OMe substituents increases the electron density at Ir and, therefore, increases the pKa of [Cp*Ir(bpy-OMe)(H)]<sup>+</sup>. No conditions tested were sufficient to deprotonate the hydride to lead to precipitation. [Cp*Ir(bpy-COOMe)(H)]<sup>+</sup>, by contrast, is quite acidic and can easily be deprotonated (pK<sub>a</sub> ~ 5, by electrochemical titration).

Saponification of the esters to form [Cp*Ir(bpy-COO)]<sup>2</sup>-, however, occurs readily under basic conditions, so a neutral solution was used in an attempt to limit the side reaction. Preliminary results indicate that CpIr(bpy) (Cp is cyclopentadienyl) can also be formed following this method.

Scheme 3.2. Synthesis of [Cp*Ir(bpy)(H)][Cl] by precipitation from ether.
**Functionalization via Electrophilic Attack.** These Ir(I), Rh(I), and Ru(0) species are electron rich and react readily with electrophiles. Grätzel noted that Cp*Rh(bpy) formed adducts with Lewis acids and oxidatively added electrophiles. Reactions with electrophiles allowed quick access to a variety of oxidized species. Metal-hydrides, for example, were readily obtained by protonation with HCl. Dropwise addition of 40 mM HCl·Et₂O to a stirring solution of 1 in Et₂O prompted precipitation of the golden yellow chloride salt of hydride 1H (Scheme 3.2). The solvent was removed in vacuo giving [1H][Cl]. Small amounts (<10%) of overprotonation products were observed, giving 1Cl impurities. For use in water, extraction and filtration of solids into water removed any unreacted Ir(I) complex 1. For use in other solvents, 1 could be removed by filtration of the solids and washing with ether. The hydride peak (δ –11.54) can be observed in pD 7 0.1 M NaPi, but we have observed this hydride NMR signal moves with changing concentrations of 1H.

**Table 3.3.** ¹H NMR Shifts of Metal-Hydrides in pD 7 0.1 M NaPi

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp*Ir(bpy)(H)][Cl]</td>
<td>–11.54</td>
</tr>
<tr>
<td>[Cp*Ir(bpy-Me)(H)][Cl]</td>
<td>–11.63</td>
</tr>
<tr>
<td>[Cp*Ir(bpy-CO₂Me)(H)][Cl]</td>
<td>–12.28</td>
</tr>
<tr>
<td>[(cymene)Ru(bpy)(H)][Cl]</td>
<td>–6.32</td>
</tr>
<tr>
<td>[(C₆Me₆)Ru(bpy)(H)][Cl]</td>
<td>–7.48</td>
</tr>
</tbody>
</table>

HCl·Et₂O protonation in Et₂O permitted access to [Cp*Ir(bpy-Me)(H)][Cl], [Cp*Ir(bpy-CO₂Me)(H)][Cl], [(cymene)Ru(bpy)(H)][Cl], and [(C₆Me₆)Ru(bpy)(H)][Cl] (Table 3.3). [(C₆Me₆)Ru(bpy)(H)][OTf] has been previously isolated, and [(cymene)Ru(bpy)(H)][OTf] has been observed in a mixture. For all of the Ir(I) and Ru(0) species formed, this protonation procedure resulted in the formation of the metal-hydride product.
Electrophiles other than protic acids can also be used in this reaction. Scheme 3.3 depicts the reactions of Cp*Ir(bpy) with electrophiles that have been carried out. Methyl iodide readily methylates Cp*Ir(bpy) ethereal solutions to form \([\text{Cp*Ir(bpy)}(\text{CH}_3)][\text{I}]\). Stripping the solvent gives the air-stable product in 95% yield. While the reaction with acid is instantaneous, the methyl species precipitates over the course of minutes. Chloromethane was a competent electrophile for methylation of Cp*Ir(bpy): allowing a solution of \(\mathbf{1}\) to stir under an atmosphere of CH\(_3\)Cl produced \([\text{Cp*Ir(bpy)}(\text{CH}_3)][\text{Cl}]\) as a yellow solid. Due to the gaseous nature of chloromethane, the reaction proceeded considerably more slowly than the methyl iodide reaction, taking hours, rather than minutes. Moving from methyl iodide to primary alkyl halides also increases reaction times: when Cp*Ir(bpy) and \(^{3}\text{PrI}\) were allowed
to mix in Et₂O, goldenrod [Cp*Ir(bpy)(^Pr)][I] precipitated over the course of hours. Cp*Ir(bpy) will oxidatively add CH₂Cl₂, and dissolving 1 in CH₂Cl₂ will result in the solution slowly changing from purple to brown to yellow as [Cp*Ir(bpy)(CH₂Cl)][Cl] is formed in solution.

Reactions of Cp*Rh(bpy) present a contrast to its heavier congener Cp*Ir(bpy). Some of the reactions proceed analogously: stirring Cp*Rh(bpy) with CH₃I in Et₂O results in precipitation of [Cp*Rh(bpy)(CH₃)][I]. Grätzel observed oxidative addition of CH₂Cl₂ by Cp*Rh(bpy) to give [Cp*Rh(bpy)(CH₂Cl)][Cl]. Protonation, however, proceeds quite differently: addition of 40 mM HCl-Et₂O to a stirring solution of Cp*Rh(bpy) in Et₂O results in a homogenous red solution. While [Cp*Rh(bpy)(H)]⁺ is initially formed, it is not stable and rapidly reacts (Chapter 5).

3.3 Conclusions

The facile synthesis of Cp*Ir(bpy) as well as other Ir(I), Rh(I) and, Ru(0) species permitted quick access to a variety of Ir(III), Rh(III), and Ru(II) species. These synthetic routes lead to hydrides that were water-soluble, critical for our aqueous hydricity investigation in Chapter 4. The generality of the synthetic techniques permitted a large collection of hydricities to be readily measured without extensive synthesis. The predictability of the protonation permitted the unusual characteristics of the protonation of Cp*Rh(bpy) to be immediately recognized, leading to the investigation into Cp* non-innocence in Chapter 5. The ease of preparation of [Cp*Ir(bpy)(CH₃)]⁺ permitted investigations into its photochemistry in analogy to [Cp*Ir(bpy)(H)]⁺, as seen in Chapter 6.
3.4 Experimental Section

**General Considerations.** Procedures were carried out under nitrogen except where noted. All solutions containing metal hydride species were protected from ambient light during preparation to prevent excited state reactions. All reagents were commercially available and used without further purification. Organic solvents were dried and degassed with argon using a Pure Process Technology solvent system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc and degassed with three freeze-pump-thaw cycles before storing over sieves in a N₂ glovebox. UV–vis spectra were obtained using an Ocean Optics USB2000+ spectrometer with a DTMINI-2GS deuterium/tungsten halogen light source controlled by OceanView software. NMR spectra were obtained on 400, 500, or 600 MHz spectrometers. 

**Synthesis.** The complexes [Cp*Ir(bpy)(Cl)]Cl (I), [(cymene)Ru(bpy)(Cl)]Cl, [(C₆Me₆)Ru(bpy)(Cl)]Cl, [Cp*Ir(bpy-Me)(Cl)]Cl, and [Cp*Ir(bpy-OMe)(Cl)]Cl were prepared following the method of Dadci et al., with final precipitation from MeOH/ether. [Cp*Ir(Cl)₂]₂, [Cp*Ir(bpy)(H)][OTf] were prepared following literature procedures. In a nitrogen filled glovebox, [Cp*Ir(bpy)(Cl)]Cl (16 mg, 0.028 mmol) and excess NaBH₄ (8.5 mg, 0.22 mmol) were allowed to stir in 2 mL of 1 M NaOH.
Dark purple solids quickly formed. After letting the solution stir for four hours, the solid was filtered off, washed 3× with water, collected in benzene, and evaporated to dryness, yielding 13 mg of 1 (0.21mmol, 98 % yield). The $^1$H NMR spectrum of 1 prepared in this way matched previously reported data (Figure 3.3).$^{83}$

![Figure 3.3. $^1$H NMR spectrum of Cp*Ir(bpy) (1) in C$_6$D$_6$.](image)

$\text{[Cp*Ir(bpy)(H)]}[\text{Cl}]$ (1H). To a stirring solution of 1 (13.3 mg, 0.028 mmol) in ether, a dilute solution of HCl·Et$_2$O (40 mM) was added dropwise until a change from a dark purple solution to bright yellow solids was observed. Typically, 1-1.5 eq of HCl were added with the excess acid immediately pumped off after completion of the addition. Samples of hydride prepared in this way typically contained small amounts (<5%) of $\text{[Cp*Ir(bpy)(Cl)]}[\text{Cl}]$ (formed by protonation of hydride releasing H$_2$), and the $^1$H NMR spectrum (Figure 3.4) is consistent with previously reported $\text{[Cp*Ir(bpy)(H)]}^+$.$^{85}$
Figure 3.4. $^1$H NMR spectrum of $[\text{Cp}^*\text{Ir(bpy)(H)}]\text{[Cl]}$ ($1\text{H}$) in 0.1 M pD 7 NaP$_1$ (referenced to dioxane).

(cymene)Ru(bpy) (4). Deep purple 4 was prepared in quantitative yield from the chloride salt of 4Cl, according to the procedure used in the synthesis of 1. The $^1$H NMR spectrum matched the previously reported data (Figure 3.5).
Figure 3.5. $^1$H NMR spectrum of (cymene)Ru(bpy) (4) in C$_6$D$_6$.

$[(\text{cymene})\text{Ru(bpy)(H)}][\text{Cl}]$ (4H). The chloride salt of 4H was prepared from 4, according to the procedure used in the synthesis of the chloride salt of 1H. $^1$H NMR (600 MHz, D$_2$O + dioxane, Figure 3.6) $\delta$ 8.78 (d, $J = 4.1$ Hz, 2H), 8.09 (d, $J = 8.2$ Hz, 2H), 7.87 (t, $J = 7.8$ Hz, 2H), 7.32 (dd, $J = 7.3$, 5.8 Hz, 2H), 5.56 (d, $J = 6.0$ Hz, 2H), 5.36 (d, $J = 6.0$ Hz, 2H), 2.53 (sept, $J = 7.1$ Hz, 1H), 2.10 (s, 3H), 0.99 (d, $J = 6.9$ Hz, 6H), -6.32 (s, 1H).
Figure 3.6. $^1$H NMR spectrum of [(cymene)Ru(bpy)(H)][Cl] (4H) in 0.1 M pD 7 NaPi (referenced to dioxane). The hydride signal at -6.32 moderately underintegrates because of scrambling with D$_2$O.

$\text{(C}_6\text{Me}_6)\text{Ru(bpy)}$ (5). Deep purple 5 was prepared in quantitative yield from the chloride salt of 5Cl, according to the procedure used in the synthesis of 1. The $^1$H NMR spectrum matched the previously reported data (Figure 3.7).
Figure 3.7. $^1$H NMR spectrum of (C$_6$Me$_6$)Ru(bpy) (5) in C$_6$D$_6$.

$[(\text{C}_6\text{Me}_6)\text{Ru(bpy)}(\text{H})]\text{[Cl]}$ (5H). The chloride salt of 5H was prepared from 5, according to the procedure used in the synthesis of the chloride salt of 1H. The $^1$H NMR spectrum is consistent with the reported spectrum for the triflate salt of 5H in water (Figure 3.8).
Figure 3.8. $^1$H NMR spectrum of [[(C$_6$Me$_6$)Ru(bpy)(H)][Cl]] (5H) in 0.1 M pD 7 NaPi (referenced to dioxane). The hydride signal at -7.48 dramatically underintegrates because of scrambling with D$_2$O.

$Cp^*$Ir(bpy-Me) (6). In a nitrogen filled glovebox, [Cp*Ir(bpy-Me)(Cl)][Cl] (5.8 mg, 0.010 mmol) and excess NaBH$_4$ (5.1 mg, 0.135 mmol) were allowed to stir in 2 mL of 5 M NaOH, and a dark violet solid quickly forms. After letting stir for four hours, the solid was extracted into C$_6$H$_6$, dried over MgSO$_4$, and evaporated to dryness, yielding 6 in quantitative yield. $^1$H NMR (600 MHz, C$_6$D$_6$, Figure 3.9) δ 8.91 (d, $J = 6.8$ Hz, 2H), 7.44 (s, 2H), 6.06 (dd, $J = 6.8$, 2.1 Hz, 2H), 2.02 (s, 6H), 1.82 (s, 15H). $^{13}$C NMR (151 MHz, C$_6$D$_6$, Figure 3.10) δ 148.20, 141.06, 127.59, 122.82, 117.92, 83.32, 21.44, 10.24. $\lambda_{abs, max}$ (C$_6$H$_6$, Figure 3.11) = 499, 641, 687 nm.
Figure 3.9. $^1$H NMR spectrum of Cp*Ir(bpy-Me) (6) in C$_6$D$_6$.

Figure 3.10. $^{13}$C($^1$H) NMR spectrum of Cp*Ir(bpy-Me) (6) in C$_6$D$_6$. 
Figure 3.11. UV-Vis spectrum of Cp*Ir(bpy-Me) (6) in C₆H₆.

[Cp*Ir(bpy-Me)(H)][Cl] (6H). The bright yellow chloride salt of 6H was prepared from 6, according to the procedure used in the synthesis of the chloride salt of 1H. ¹H NMR (600 MHz, D₂O + dioxane, Figure 3.12) δ 8.42 (d, J = 5.9 Hz, 2H), 7.80 (s, 2H), 7.18 (d, J = 5.9 Hz, 2H), 2.38 (s, 6H), 1.61 (s, 15H), -11.63 (s, 1H). ¹³C NMR (151 MHz, D₂O + dioxane, Figure 3.13) δ 155.51, 151.61, 150.78, 128.53, 124.12, 90.75, 20.85, 8.97. λ_{abs,max} (pH 7 0.1 M NaPᵢ, Figure 3.14) = 394 nm (2900 M⁻¹·cm⁻¹).

Figure 3.12. ¹H NMR spectrum [Cp*Ir(bpy-Me)(H)][Cl] (6H) in 0.1 M pD 7 NaPᵢ (referenced to dioxane). The hydride signal at -7.48 moderately underintegrates because of scrambling with D₂O.
Cp*Ir(bpy-COOMe) (8). In a nitrogen filled glovebox, 8.1 mg (0.012 mmol) [Cp*Ir(bpy-COOMe)(Cl)][Cl] and 4.7 g (0.069 mmol) NaO2CH were stirred in 2 mL pH 7 0.1 M NaP₇. While stirring for four hours, a royal purple solid precipitated from solution. The solution was filtered, and the solids were washed 3x with water, collected by dissolving in benzene, and evaporating under vacuum to yield 8 (3.4 mg, 47 % yield). ¹H NMR (600 MHz,
$\text{C}_6\text{D}_6$, Figure 3.15) $\delta$ 8.78 (d, $J = 7.0$ Hz, 1H), 8.69 (d, $J = 2.1$ Hz, 1H), 7.20 (dd, $J = 7.0$, 2.0 Hz, 1H), 3.52 (s, 2H), 1.55 (s, 6H). $^{13}$C NMR (151 MHz, $\text{C}_6\text{D}_6$, Figure 3.16) $\delta$ 166.76, 147.22, 142.02, 125.72, 115.04, 85.57, 51.76, 9.68. $\lambda_{\text{abs, max}}$ ($\text{C}_6\text{H}_6$, Figure 3.17) = 328, 389, 552 nm.

**Figure 3.15.** $^1$H NMR spectrum of Cp*Ir(bpy-COOMe) (8) in $\text{C}_6\text{D}_6$. 
Figure 3.16. $^{13}$C ($^1$H) NMR spectrum of Cp*Ir(bpy-COOMe) (8) in C$_6$D$_6$.

Figure 3.17. UV-Vis spectrum of Cp*Ir(bpy-COOMe) (8) in C$_6$H$_6$.

$[\text{Cp}^*\text{Ir}(\text{bpy}-\text{COOMe})(\text{H})][\text{Cl}](8\text{H})$. The scarlet chloride salt of 8H was prepared from 8, according to the procedure used in the synthesis of the chloride salt of 1H. $^1$H NMR (600 MHz, D$_2$O + dioxane, Figure 3.18) δ 8.89 (d, $J = 5.9$ Hz, 2H), 8.69 (s, 2H), 7.92 (d, $J = 5.9$ Hz, 2H), 4.10 (s, 6H), 1.80 (s, 15H), -12.28 (s, 1H). $^{13}$C NMR (151 MHz, D$_2$O + dioxane, Figure 3.19) δ 165.82, 155.95, 153.00, 138.06, 126.69, 123.19, 92.70, 54.39, 8.94. $\lambda_{\text{abs, max}}$
(pH 3 0.1 M NaP, Figure 3.20) = 388 nm (4200 M⁻¹·cm⁻¹), 451 nm (4300 M⁻¹·cm⁻¹), 481 nm (4400 M⁻¹·cm⁻¹).

Figure 3.18. $^1$H NMR spectrum of [Cp*Ir(bpy-COOMe)(H)][Cl] (8H) in 20 mM pD 4.3 NaOAc (referenced to dioxane). The hydride signal at -12.28 dramatically underintegrates because of scrambling with D₂O.
Figure 3.19. $^{13}$C {$^{1}$H} NMR spectrum of [Cp*Ir(bpy-COOMe)(H)][Cl] (8H) in 20 mM pD 4.3 NaOAc (referenced to dioxane).

Figure 3.20. UV-Vis spectrum of [Cp*Ir(bpy-COOMe)(H)][Cl] (8H) in 0.1 M pH 3 NaPi.

$Cp^*$Rh(bpy). In a nitrogen filled glovebox, [Cp*Rh(bpy)(Cl)][Cl] (15.6 mg, 0.034 mmol) and excess NaBH$_4$ (10.3 mg, 0.272 mmol) were allowed to stir in 3 mL of 1 M NaOH. Dark purple solids quickly formed. After stirring for two hours, the solid was filtered off, washed 3× with water, collected in benzene, and evaporated to dryness, yielding Cp*Rh(bpy)
(11.6 mg, 88 % yield). The $^1$H NMR spectrum of 1 prepared in this way matched previously reported data (Figure 3.22).$^{88}$

Figure 3.21. $^1$H NMR spectrum of Cp*Rh(bpy) in C$_6$D$_6$.

$[\text{Cp}^\ast\text{Ir(bpy)}(CH_3)]\,[I]$. A slight excess of a 50 mM solution of CH$_3$I in Et$_2$O (1.2 mL, 0.060 mmol) was added dropwise to a stirring saturated purple solution of Cp*Ir(bpy) (28.0 mg, 0.058 mmol). The fluffy yellow solid precipitated over the course of several minutes. The solid was separate by filtration and washed with Et$_2$O resulting in 34.4 mg of air-stable $[\text{Cp}^\ast\text{Ir(bpy)}(CH_3)]\,[I]$ (0.055 mmol, 95% yield). $^1$H NMR (600 MHz, CD$_3$CN, Figure 3.22) $\delta$ 8.67 (ddd, J = 5.8, 1.5, 0.8 Hz, 2H), 8.43 (dt, J = 8.2, 1.1 Hz, 2H), 8.08 (ddd, J = 8.1, 7.5, 1.5 Hz, 2H), 7.60 (ddd, J = 7.4, 5.7, 1.4 Hz, 2H), 1.68 (s, 15H), -0.04 (s, 3H). $^{13}$C NMR (151 MHz, CD$_3$CN, Figure 3.23) $\delta$ 156.01, 152.44, 139.08, 129.00, 125.32, 90.85, 8.70, -6.35. $\lambda_{\text{abs,max}}$(CH$_3$CN) = 418 nm.
Figure 3.22. $^1$H NMR spectrum of [Cp*Ir(bpy)(CH$_3$)][I] in CD$_3$CN.

Figure 3.23. $^{13}$C{$_1^1$H} NMR spectrum of [Cp*Ir(bpy)(CH$_3$)][I] in CD$_3$CN.
$[\text{Cp}^*\text{Rh(bpy)(CH}_3)]\text{][I}$]. A slight excess of a 50 mM solution of CH$_3$I in Et$_2$O was added dropwise to a stirring saturated purple solution of Cp*Rh(bpy) (4.5 mg). The fluffy yellow solid precipitated over the course of five minutes. The solid was separate by filtration and washed with Et$_2$O resulting $[\text{Cp}^*\text{Rh(bpy)(CH}_3)]\text{][I]}$. $^1$H NMR (600 MHz, CD$_3$CN, Figure 3.24) δ 8.57 (ddt, J = 5.7, 1.6, 0.8 Hz, 2H), 8.43 (dt, J = 8.2, 1.0 Hz, 2H), 8.13 (td, J = 7.8, 1.5 Hz, 2H), 7.67 (ddd, J = 7.3, 5.5, 1.4 Hz, 2H), 1.64 (s, 15H), 0.18 (d, J = 2.4 Hz, 3H). $^{13}$C NMR (151 MHz, CD$_3$CN, Figure 3.25) δ 153.44, 151.72, 138.40, 127.21, 123.62, 96.03 (d, J = 6.26 Hz), 7.67, 6.78 (d, J = 24.24 Hz).

Figure 3.24. $^1$H NMR spectrum of $[\text{Cp}^*\text{Rh(bpy)(Me)][I]}$ in CD$_3$CN.
Figure 3.25. $^{13}$C{$^1$H} NMR spectrum of [Cp*Rh(bpy)(CH$_3$)]+[I] in CD$_3$CN.

$[Cp^*Ir(bpy)(CH_3)]^-$. A purple solution of Cp*Ir(bpy) was allowed to stir in the dark under a headspace of CH$_3$Cl. Over the course of several hours, a yellow precipitate formed. The solvent was dried *in vacuo* yielding $[Cp^*Ir(bpy)(CH_3)]^-[Cl]$ in 95% purity. $^1$H NMR (500 MHz, CD$_3$CN, Figure 3.26) δ 8.67 (d, J = 4.9 Hz, 2H), 8.48 (d, J = 8.3 Hz, 2H), 8.08 (t, J = 8.0 Hz, 2H), 7.61 (t, J = 6.3 Hz, 2H), 1.68 (s, 15H), -0.04 (s, 3H).
Figure 3.26. $^1$H NMR spectrum of [Cp*Ir(bpy)(CH$_3$)][Cl] in CD$_3$CN.

$[Cp^*Ir(bpy)(^nPr)][I]$. To a stirring purple solution of Cp*Ir(bpy) (3.5 mg) in Et$_2$O was added excess $^n$PrI (10 uL). Over the course of 4 hours, a yellow precipitate formed, which was isolated by filtration and washed with Et$_2$O. $^1$H NMR (600 MHz, CD$_3$CN, Figure 3.27) $\delta$ 8.68 (ddd, J = 5.7, 1.4, 0.8 Hz, 2H), 8.49 (dt, J = 8.0, 0.9 Hz, 2H), 8.12 (ddd, J = 8.1, 7.5, 1.4 Hz, 2H), 7.64 (ddd, J = 7.4, 5.7, 1.4 Hz, 2H), 1.68 (s, 15H), 0.87 – 0.72 (m, 4H, $CH_2CH_2CH_3$), 0.61 (t, J = 6.9 Hz, 3H, $CH_2CH_2CH_3$).
Figure 3.27. $^1$H NMR spectrum of [Cp*Ir(bpy)("Pr)][I] in CD$_3$CN.

[Cp*Ir(bpy)(CH$_2$Cl)][Cl]. Solid Cp*Ir(bpy) (5.0 mg) was dissolved in CH$_2$Cl$_2$. The solution lightened from purple to yellow over the course of minutes. The solvent was removed in vacuo yielding [Cp*Ir(bpy)(CH$_2$Cl)][Cl]. $^1$H NMR (600 MHz, CD$_3$CN, Figure 3.28) δ 8.65 (ddd, J = 5.7, 1.5, 0.8 Hz, 2H), 8.56 (dt, J = 8.0, 1.1 Hz, 2H), 8.16 (td, J = 7.9, 1.5 Hz, 2H), 7.67 (ddd, J = 7.4, 5.6, 1.4 Hz, 2H), 3.60 (s, 2H), 1.68 (s, 15H).
Figure 3.28. $^1$H NMR spectrum of [Cp*Ir(bpy)(CH$_2$Cl)][Cl] in CD$_3$CN.
CHAPTER 4: AQUEOUS HYDRICITY OF LATE METAL CATALYSTS AS A CONTINUUM TUNED BY LIGANDS AND THE MEDIUM


4.1 Introduction

While the importance of metal-hydrides in the HER and other reactions in water is recognized (and discussed in Chapter 1) and while methods for measuring the strength of the M–H bond have been pioneered by DuBois and Rakowski DuBois in acetonitrile, applying these tools to the aqueous environment has lagged behind their use in organic solvents. The discrepancy is partially due to the solubility and stability challenges that hinder the investigation of organometallic species in water. A renewal of interest in catalysts compatible with water has led to increasingly frequent reports of hydricities in water in recent years: Creutz, Wayland, Yang, and Berben have published isolated studies into the hydricities of a handful of complexes. Our interest in a family of Cp*Ir-based catalysts motivated us to develop a general and expedient method for aqueous hydricity determination in this series of complexes.
Figure 4.1. Scheme illustrating the hydricity of reference complex \([\text{Cp}^*\text{Ir}(\text{bpy-COO})(\text{H})]^- (2\text{H})\) and thermochemical cycles that establish aqueous hydricity of Ir and Ru hydrides.

Preliminary studies on the parent complex \([\text{Cp}^*\text{Ir}(\text{bpy})(\text{H})]^+ (1\text{H}; \text{Cp}^* \text{is pentamethylcyclopentadienyl and bpy is } 2,2'\text{-bipyridine})\) were stymied by the water-insolubility of the conjugate base \(\text{Cp}^*\text{Ir}(\text{bpy}) (1, \text{see Chapter 3}), \) so we charted a course utilizing carboxylate groups on the ligand to confer water solubility. We would first establish the hydricity of a reference complex using a potential-pKₐ thermochemical cycle in water (Figure 4.1A) and then map the relative hydricity of other complexes based on hydride transfer equilibria (Figure 4.1B). The potential-pKₐ thermochemical cycle has been used extensively in acetonitrile, \(^{98}\) but has not been systematically applied in water. The strategy depicted in Figure 4.1 has enabled the construction of an extensive, self-consistent aqueous hydricity scale. The broad range of Ir and Ru hydricity values reveals how the polar, protic aqueous environment impacts hydride transfer thermodynamics. Substantial shifts in the hydricity values are observed relative to acetonitrile, with electronic changes to supporting ligand correlated strongly to the Hammett parameter \(\sigma_p\). A dramatic
impact of water was also observed in the primary coordination sphere: a variety of suitable ligands present in aqueous media can bind the Ir or Ru centers after hydride transfer, shifting the effective hydricity substantially. Describing the complexities of hydride transfer in water allows interpretation of previously reported catalytic reactions and predictions that can guide improvements in the hydrogenation of carboxylic acids,\textsuperscript{99} the disproportionation of formic acid to methanol,\textsuperscript{100} and other metal hydride-mediated reactions such as H\textsubscript{2} evolution\textsuperscript{85,101–103} and CO\textsubscript{2} reduction.\textsuperscript{101,104}

4.2 Results and Discussion

Characterization of Reference Complexes. The first “reference” hydride investigated was [Cp*Ir(bpy-COO)(H)]\textsuperscript{−} (2H; bpy-X = 4,4’-X-bpy), with carboxylate groups installed on the bipyridine ligand to confer good water solubility over a wide pH range, independent of metal ligation or oxidation state.\textsuperscript{63} The potential–pK\textsubscript{a} thermochemical cycle of Figure 4.1A was used to measure the hydricity of 2H.

The reduction potential of [Cp*Ir(bpy-COOH)(Cl)][Cl] (2Cl) was initially assessed using cyclic voltammetry (CV) in 1 M NaOH. Under these conditions, the chloride is displaced by hydroxide to form [Cp*Ir(bpy-COO)(OH)]\textsuperscript{−} (2OH) based on NMR and MS data, and a 2e\textsuperscript{−} reduction forms the freely diffusing species [Cp*Ir(bpy-COO)]\textsuperscript{2−} (2). Unfortunately, a large peak-to-peak separation was observed between the reduction of 2OH and the oxidation of 2. This electrochemical irreversibility, attributed to slow electron transfer or ligand dissociation, prevented the use of CV to determine \(E_{1/2}\) (Figure 4.2).
Biochemists have developed an electrochemical technique suitable for quantifying reduction potentials that are hampered by slow kinetics: *redox potentiometry*. Solutions varying the relative concentrations of 2OH and 2 were prepared by partial electrolysis of a
pH 14 solution of 2OH. Between each stage of the electrolysis, the solution was allowed to reach equilibrium (as judged by a constant open circuit potential) and the concentrations of the Ir species were determined by UV-vis (Figure 4.3A). This method provided $E^{\circ\prime} = -0.60$ V for the reduction of 2OH to 2 at pH 14 (Figure 4.3B). As thermodynamic constants for proton reduction are determined at the standard state of pH 0,\textsuperscript{36,47} this reduction was extrapolated to pH 0 by applying a 29.5 mV per pH unit shift (2e$^{-}$ reduction with loss of hydroxide), giving $E^{\circ} = -0.19$ V. Redox potentiometry is seldom used in organometallic chemistry,\textsuperscript{106,107} but this method was essential for overcoming the slow kinetics that prevented the straightforward measurement of thermodynamic values.

With a reduction potential in hand, hydricity could be determined if paired with the metal hydride pK$_a$ value. The water-soluble Ir complexes possess several acidic protons. Spectrophotometric titrations established the pK$_a$ of the carboxylic acid groups in [Cp*Ir(bpy-COOH)(OH$_2$)]$^{2+}$ and [Cp*Ir(bpy-COOH)(H)]$^+$ as 1.9 and 2.7, respectively. The acidity of 2H was then measured spectrophotometrically by addition of base to a yellow-orange solution of 2H to produce a deep purple solution of 2 (Figure 4.3C), providing pK$_a$(2H) = 12.4. The relatively acidic carboxylic acid groups provide a doubly anionic supporting ligand at pH 7 and ensure that hydride donation will not be coupled to protonation changes at the ligand.

\[
\begin{align*}
2H & \rightleftharpoons 2 + H^+ \quad (4.1) \\
2 + OH^- & \rightleftharpoons 2OH + 2e^- \quad (4.2) \\
H^+ + 2e^- & \rightleftharpoons H^- \quad (4.3) \\
2H + OH^- & \rightleftharpoons 2OH + H^- \quad (4.4)
\end{align*}
\]
The hydricity of reference complex $2\text{H}$ was established by combining the $pK_a$ of the metal hydride (Eq. 4.1), the oxidation potential of the conjugate base (Eq. 4.2), and the free energy of proton reduction to hydride (Eq. 4.3, 34.2 kcal·mol$^{-1}$).$^{47}$ This thermochemical cycle provides $\Delta G^o_{\text{H}^-}(\text{OH}) = 42.4$ kcal·mol$^{-1}$ (Eq. 4.4), employing the conventional standard state of pH 0.

The hydricity $\Delta G^o_{\text{H}^-}(\text{OH})$ is the free energy of hydride transfer from $2\text{H}$ with formation of the hydroxo complex $2\text{OH}$. Hydroxide binding is involved in the experimentally measured reduction potential, so thermochemistry involving this ligand is obtained directly. The free energy of hydride transfer from $2\text{H}$ with formation of the aquo complex $2\text{OH}_2$ can also be determined by taking into account the $pK_a$ of $2\text{OH}_2$ (Eq. 4.5, $pK_a = 7.6$ by spectrophotometric titration): $\Delta G^o_{\text{H}^-}(\text{OH}_2) = 32.0$ kcal·mol$^{-1}$.

$$2\text{OH} + \text{H}^+ \rightleftharpoons 2\text{OH}_2 \quad (4.5)$$

An unusual situation arises when taking into account the metal aquo acidity: there two different hydricity values for $2\text{H}$, $\Delta G^o_{\text{H}^-}(\text{OH})$ and $\Delta G^o_{\text{H}^-}(\text{OH}_2)$. Formal hydride transfer initially results in a 16e$^-$ complex with a vacant coordination site, and this hydride dissociation process ($\Delta G^o_{\text{H}^-}$ in Scheme 4.1) is most commonly associated with hydricity. But in many cases the coordinatively unsaturated complex rapidly binds a ligand (e.g. solvent or a counterion) during the net hydride transfer process. In organic solvents, solvation of the metal center after hydride transfer is commonly ignored in the thermochemistry: the activity of the solvent is taken as unity.$^{108-111}$ In water, several species beyond the solvent itself can ligate the final product after hydride release — and different thermochemical values are expected for water, hydroxide, phosphate, and chloride complexes.
The obtained thermodynamic values $\Delta G^\circ_{\text{H}}$(OH) and $\Delta G^\circ_{\text{H}}$(OH$_2$) include the formal hydricity and the binding affinity for the incoming ligand (Scheme 4.1). A similar situation arises for acidities when following proton loss, aggregation through hydrogen-bonding interactions, e.g. homoconjugation, influence effective acidity. To distinguish the different effective hydricity values that couple hydride transfer and ligand association, the nomenclature $\Delta G^\circ_{\text{H}}$(Y) is used, where Y is the incoming ligand.

**Scheme 4.1. Effective hydricity including ligand association.**

To better understand the role of incoming ligands, we explored the effect of other common aqueous salts on hydricity. Effective hydricity values were determined by measuring the free energy of ligand exchange with 2OH$_2$ (Figure 4.4A) and adding that thermodynamic value to $\Delta G^\circ_{\text{H}}$(OH$_2$). The relative free energy of chloride substitution was determined by NMR titration of NaCl into a pD 7 solution of 2OH$_2$, $\Delta G_{\text{OH}_2\rightarrow \text{Cl}} = -4.4$ kcal·mol$^{-1}$ (Eq. 4.6). Because ligand exchange is slow on the NMR timescale, the concentrations of the iridium species could be determined directly. The hydricity of 2H to form the chloride product is thus $\Delta G^\circ_{\text{H}}$(Cl) = 27.6 kcal·mol$^{-1}$.

$$
2\text{OH}_2 + \text{Cl}^- \rightleftharpoons 2\text{Cl} + \text{H}_2\text{O} \quad (4.6)
$$

$$
2\text{OH}_2 + \text{H}_n\text{PO}_4^{m-} \rightleftharpoons 2\text{H}_n\text{PO}_4 + \text{H}_2\text{O} \quad (4.7)
$$

The phosphate buffer presents both H$_2$PO$_4^-$ and HPO$_4^{2-}$ ligands at pH 7, either of which can bind Ir(III). Phosphate binding is apparent by NMR spectroscopy in pH 7 phosphate buffer, but rapid proton exchange prevents precise identification of the ligand. The
relative binding affinity of the phosphate mixture ($\Delta G_{\text{OH}_2 \rightarrow P_i} = -1.9 \text{ kcal} \cdot \text{mol}^{-1}$ at pH 7, Eq. 4.7) provides $\Delta G_{\text{H}_i}(P_i) = 30.1 \text{ kcal} \cdot \text{mol}^{-1}$ ($n = 1$ or $2$; $m = 3 - n$). This hydricity is strictly accurate only at pH 7, where the measurement was made for the specific $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ mixture which $P_i^-$ represents. The concentrations of $\text{H}_2\text{PO}_4^-$ and $\text{HPO}_4^{2-}$ will change based on the solution pH, however, which could impact hydride transfer.

Figure 4.4. (A) Summary of thermochemical values of $[\text{Cp}^*\text{Ir(bpy-COO)(H)}]_2^-$ (2H). Free energies (kcal·mol$^{-1}$) and reduction potentials (V vs. NHE) are cited at the standard state of pH 0, 1 M reagents, and 1 atm gases, except for $\Delta G_{\text{OH}_2 \rightarrow P_i}$ and $\Delta G_{\text{H}_i}(P_i)$ values that refer to pH 7. (B) Summary of the pH dependence of $\Delta G^\circ_{\text{H}_i}(Y)$ with the $\text{H}_2\text{O}/\text{H}_2$ and $\text{CO}_2/\text{HCO}_3^-$ couples.
Complex 2H is substantially more hydridic in water (smaller $\Delta G^0_{H-(OH_2)}$ value) than in acetonitrile, consistent with prior studies. The large differences in hydricity as a function of the ligands present in aqueous solution, however, were previously unexplored and suggest that water plays a role in hydride transfer reactions beyond simply providing a high polarity medium. Transition metal hydride transfer can be described by a manifold of hydricity values comprised of the heterolytic M–H bond strength (to release H$^-$) and the dative metal–ligand bond strength of any aqueous buffer components or salts. The effective hydricity, $\Delta G^0_{H-(Y)}$, is expected to be experimentally relevant to catalysis. Hydride transfer reactions for $d^6$ hydrides during catalysis will involve ligand association, so understanding the overall thermodynamics of that process is vital. For example, in a typical pH 7 phosphate buffer solution used in photoelectrocatalytic H$_2$ evolution, hydride 2H reacts with water to release H$_2$ and generate an equilibrium mixture of Ir(III) chloride, aquo, and phosphate complexes—representing three different H$_2$ release pathways with three different hydricity values.

In water, pH also becomes an integral factor in hydricity (Figure 4.4B). For one, the H$_2$O/H$_2$ potential will shift to lower values as pH increases ($1.36 \text{ kcal} \cdot \text{mol}^{-1} \cdot \text{pH}^{-1}$), indicating that as protons become scarcer, stronger hydrides are required to evolve H$_2$. Yet while H$_2$ is shifting, $\Delta G^0_{\text{H-}(\text{Cl})}$ and $\Delta G^0_{\text{H-}(\text{OH})}$ remain constant across the accessible pH range, altering net H$_2$ release thermodynamics. On the other hand, $\Delta G^0_{\text{H-}(\text{OH})}$ is influenced by pH as the concentration of ligand available for binding changes with pH. At pH 0, hydroxide ligation is unfavorable, leading to $\Delta G^0_{\text{H-}(\text{OH})} > \Delta G^0_{\text{H-}(\text{OH}_2)}$; while chemical intuition might suggest

---

\(^1\)Many of the transition metal hydride studied in MeCN have been $d^8$, which can minimize the influence of solvation through a geometry change after hydride transfer. See ref. 39.
that hydride transfer to form an aquo complex would be a less favorable than hydride transfer to form a complex with the more basic hydroxide ion, the extremely low concentration of hydroxide at pH 0 leads to unfavorable energetics. As the solution pH increases, however, formation of the hydroxide complex will become more favorable, and the value \( \Delta G^o_{H^-}(OH) \) will shift smoothly. Figure 4.4B illustrates that at pH 14, \( \Delta G^o_{H^-}(OH) < \Delta G^o_{H^-}(OH_2) \) and complex 2H becomes a much stronger hydride donor.

**Establishing a Second Reference Point.** Though the differences caused by different ligands in the aqueous medium are striking, their impact is best assessed by comparison to the effect of changing the metal center and supporting ligands. Modification of the structure of the hydride is the most common route to tune hydricity, and these synthetic strategies are typically assumed to have a greater influence than solvation of the product. To make these comparisons, we sought to explore a wider range of metal complexes and began by determining the hydricity of another soluble “reference” hydride, \([\text{(cymene)Ru(bpy-COO)}(H)]^- (3H)\). Hydride 3H hails from a family of (arene)Ru(diimine) catalysts that carry out aqueous transfer hydrogenation, water splitting, and CO\(_2\) reduction.\(^{104,113,114}\)

The reduction potential of \([\text{(cymene)Ru(bpy-COO)}(OH)]^- (3OH)\) between pH 8 and 12 was measured by CV. The quasi-reversible \(3OH/3\) couple (\(\Delta E_p = 60 \text{ mV}\)) shifted 26 mV per pH unit, close to the ideal value of 29.5 mV expected for a 1OH\(^-/2e^-\) process (Figure 4.5). Extrapolating the trend in \(E_{1/2}\) to pH 0 provided the standard reduction potential \(E^o = -0.30 \text{ V}\).
Figure 4.5. (A) Cyclic voltammetry of [(cymene)Ru(bpy-COOH)(OH₂)][OTf]₂ in 1 M NaOH titrated with solutions of H₃PO₄ at 50 mV/s. (B) To determine \( E° \), \( E_{1/2} \) between pH 8 and 12 were extrapolated to zero giving \( E° = -0.30 \) V (assuming oxidized and reduced species have similar diffusion properties). Though at lower pH (purple trace), the oxidation is very poorly resolved as Ru⁰ is protonated, the extrapolation is consistent with the best estimate of \( E_{1/2}(pH 7.8) \sim -0.51 \) V, or \(-0.28 \) V accounting for the deprotonation of the aquo to form the hydroxo.

Spectrophotometric titrations provided the acidity of the hydride \( 3H \), \( pK_a(3H) = 11.8 \). From the \( pK_a \) and \( E° \), \( \Delta G_{H}^{\circ} - (OH) = 36.5 \) kcal·mol⁻¹ can be determined. Including the aquo \( pK_a = 7.7 \) gives \( \Delta G_{H}^{\circ} - (OH_2) = 26.0 \) kcal·mol⁻¹. (All the relevant \( pK_a \) and \( \Delta G°_{H} \) values for this system are collected in Table 4.1). The relative aquo–chloride association free energy, \( \Delta G_{\text{OH}_2 \rightarrow \text{Cl}} = -2.9 \) kcal·mol⁻¹, was significantly smaller than that of the Ir complex. Taken together, the hydricity to form the chloride was determined to be \( \Delta G_{H}^{\circ} - (\text{Cl}) = 23.1 \) kcal·mol⁻¹.
**Building a Scale through Equilibria.** Having established two well-defined reference hydricity values, we set out to determine the hydricity of related hydrides, including the parent bpy complexes. To probe hydride transfer equilibria between Ir and Ru hydrides, however, a reliable synthetic route to these species was required. Chloride counter ions were
sought to increase water solubility (the previously reported PF\textsubscript{6}\textsuperscript{−} and CF\textsubscript{3}SO\textsubscript{3}\textsuperscript{−} salts of 1H were insoluble above 2 mM in water)\textsuperscript{84} and to reduce speciation.

Electrochemical and chemical synthetic methods were developed to provide rapid access to a wide range of water-soluble metal hydrides. In a representative controlled potential electrolysis, the chloride salt of 1Cl was converted to >20 mM of 1H in 0.1 M pH 7 NaP\textsubscript{i}. If the pH and electrolysis potential were appropriately controlled to facilitate a reduction–protonation sequence, the electrolysis method was quite general. Chemical syntheses were also carried out, as needed, according to a newly developed procedure. For example, reduction of the chloride salt of 1Cl by NaBH\textsubscript{4} in 1 M NaOH resulted in precipitation of purple 1 in nearly quantitative yield. Dropwise addition of HCl·Et\textsubscript{2}O to a stirring solution of 1 in Et\textsubscript{2}O prompted precipitation of the golden yellow chloride salt of hydride 1H. This procedure is also generally applicable, except when the metal hydride cannot be deprotonated in water or the conjugate base does not precipitate from water.

With a collection of hydride complexes (see Figure 4.6 for numbering scheme), relative hydricity could be determined by mixing a hydride donor and a hydride acceptor and allowing the system to reach an equilibrium distribution of both hydrides and acceptors. The concentrations of each species were determined by NMR, and the equilibrium constant provided the difference in hydricity (\(\Delta\Delta^G^°_{\text{H}−}\)) between the two complexes, according to Figure 4.1B.\textsuperscript{115} Figure 4.6 depicts the relative hydricity of each hydride complex, with each reaction representing a hydride/chloride exchange.

In a representative hydride equilibration, a solution of 2Cl in pD 7 0.1 M NaP\textsubscript{i} (produced electrochemically in 84% yield, with 16% unreacted 2Cl) was mixed with 1Cl. After the reaction was allowed to reach equilibrium, the concentrations of 1H, 1Cl, 2H, and
2Cl were measured by $^1$H NMR spectroscopy. The equilibrium constant, $K_{eq} = 0.35$, provided $\Delta \Delta G^\circ_{H-} = 0.6 \text{ kcal-mol}^{-1}$ (Eq.4.8) and established the hydricity of 1H in a single experiment: $\Delta G^\circ_{H-}(\text{Cl}) = 26.3 \text{ kcal-mol}^{-1}$. It is noteworthy that equilibration was established in < 15 min, and though our present focus is on thermodynamic hydricity, this contrasts with the frequently kinetically slow hydride transfer reactions reported in acetonitrile.\textsuperscript{110,115}

$$2\text{H} + \text{1Cl} \rightleftharpoons 2\text{Cl} + \text{1H}$$ \hspace{1cm} (4.8)

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure4.6.png}
\caption{Relative hydricity values of Ir and Ru complexes (blue). The equilibria used to determine hydricity are represented by blue arrows.}
\end{figure}
Figure 4.7 Aqueous hydricity scale of the complexes we report along with those previously reported in the literature. Y represents the incoming ligand such that the top scale shows $\Delta G^\circ_{H^-(Cl)}$ and the bottom scale shows $\Delta G^\circ_{H^-(OH_2)}$. TSPP = tetra(p-sulfonatophenyl)porphyrin; TMPS = tetrakis(3,5-disulfonatomesityl)porphyrin; tpy = terpyridine; DHMPE = 1,2-bis(dihydroxymethylphosphino)ethane.$^{47,49,50,116}$

A series of hydride transfer equilibrium experiments established the relative hydricity scale of Figure 4.6. Equilibrium could be established from either direction to give $\Delta \Delta G^\circ_{H^-}$ values that were identical within experimental uncertainty ($\pm 0.1$ kcal·mol$^{-1}$, see Experimental Section). Hydricity values were determined from these relative hydricities by comparison to the $\Delta G^\circ_{H^-(Cl)}$ of reference 2H for Ir complexes and reference 3H for Ru complexes, and the scale is self-consistent within the $\pm 1$ kcal·mol$^{-1}$ estimated uncertainty of the measurements.$^{98,115,117}$ The $\Delta G^\circ_{H^-(OH_2)}$ for all complexes was determined by measuring the aquo chloride exchange energy of each of these species (Table 4.2).
### Table 4.2. Aquo-chloride exchange free energy and hydricity to form ligated products in kcal·mol⁻¹.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\Delta G^\circ_{H^-(Cl)}$</th>
<th>$\Delta G^\circ_{H^-(OH_2)}$</th>
<th>$\Delta G_{OH_2-\text{Cl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.0</td>
<td>31.5</td>
<td>-4.5</td>
</tr>
<tr>
<td>2</td>
<td>27.6</td>
<td>32.0</td>
<td>-4.4</td>
</tr>
<tr>
<td>3</td>
<td>23.1</td>
<td>26.0</td>
<td>-2.9</td>
</tr>
<tr>
<td>4</td>
<td>22.3</td>
<td>25.6</td>
<td>-3.3</td>
</tr>
<tr>
<td>5</td>
<td>19.4</td>
<td>22.9</td>
<td>-3.5</td>
</tr>
<tr>
<td>6</td>
<td>26.6</td>
<td>31.1</td>
<td>-4.5</td>
</tr>
<tr>
<td>7</td>
<td>26.2</td>
<td>30.8</td>
<td>-4.6</td>
</tr>
<tr>
<td>8</td>
<td>28.6</td>
<td>33.4</td>
<td>-4.7</td>
</tr>
</tbody>
</table>

Our values are also consistent with one of the few other well-defined hydricity values available in the literature: the hydricity of $[(C_6Me_6)Ru(bpy)(H)]^+$ (5H) with formation of $5OH_2$ was reported by Creutz, $\Delta G^\circ_{H^-(OH_2)} = 22.2$ kcal·mol⁻¹,⁴⁷,⁴⁸ which we independently determined to be $\Delta G^\circ_{H^-(OH_2)} = 22.9$ kcal·mol⁻¹.

In Figure 4.7, our continuum of hydricity values is contextualized against previously reported hydricity values ($\Delta G^\circ_{H^-(OH_2)}$) for transition metal hydrides and substrates relevant to alternative energy pursuits (H⁺ and CO₂). The two parallel scales illustrate the role of the ligand bound to the product and the influence of changes to the supporting ligands or metal center. In general, the hydricity values are much smaller in water than in acetonitrile.⁸⁴,¹¹⁰

Electron-donating groups promote hydride transfer, as evidenced by a strong correlation between $\Delta G^\circ_{H^-(Cl)}$ and the Hammett parameter $\sigma_p^-$ (Figure 4.8A).¹¹⁸ The ease with which each ligand can stabilize increased electron density is reflected in electronic spectroscopy: hydricity is correlated to the metal-to-ligand charge-transfer band around 400 nm that is present in each of the Ir hydride complexes (Figure 4.8B). Interestingly, the activity of aqueous hydrogen evolution catalysis involving Cp*Ir-based catalysts also correlates with
electron-donating ability of the bipyridine ligand, suggesting that perhaps the increase in rate is due to an increase in the hydricity of the metal hydride intermediate.

**Figure 4.8.** A) Correlation between $\sigma_p^-$ and $\Delta G_{\text{H}}^\circ$ (Cl). B) Correlation between $\lambda_{\text{max}}$ of the hydride with the hydricity of that hydride.

Electronic changes to the bipyridine ligands affect the acidity of the metal hydride more dramatically than the hydricity. The hydricity difference between methoxy-substituted 7H (pH > 14) and methylester-substituted 8H (pH ~ 5) is only 2.4 kcal·mol$^{-1}$, while the acidity difference between these complexes spans ~9 orders of magnitude (~12 kcal·mol$^{-1}$). The hydricity calculation tends to moderate electronic effects as increased electron density increases $pK_a$ and shifts $E^\circ$ more negative which raise and lower hydricity, respectively.

Ligand effects on hydricity were more pronounced when changes were made to the arene rings. Cymene complex 4H and hexamethylbenzene complex 5H displayed a ~3 kcal·mol$^{-1}$ difference in hydricity that is larger than observed for bpy ligand modifications, but of a similar magnitude to the effect of chloride ligation. These differences warrant further studies into possible steric effects in these thermodynamic hydricity values.

The emerging picture of aqueous hydricity tunable by both ligands and the medium could impact catalysis. Electrocatalytic hydrogen evolution in water is usually carried out
with pH-stabilizing buffer bases, and water splitting schemes that employ salt water must wrestle with an abundance of chloride—which would lead to a ~5 kcal·mol\(^{-1}\) difference in the hydricity of Ir catalysts. The hydricity trends in Figure 4.7 also predict the pH at which \(\text{H}_2\) evolution will occur, as a function of the ligand electronics and the presence of incoming ligands in solution. All of the complexes investigated, for example, are predicted to produce \(\text{H}_2\) at pH 0 (\(\Delta G^\circ_{\text{H}_2} < 34.2\) kcal·mol\(^{-1}\)), but at pH 10 only Ru complex 5H is thermodynamically capable of forming \(\text{H}_2\) (and only at high chloride concentration). Under basic conditions, hydroxide ligation could also start to impact hydride transfer reactivity.

At pH 7, parent Ir–H 1H is not expected to make \(\text{H}_2\), consistent with our observations in electrolysis experiments. Excitation by visible light is expected to result in a more potent hydride donor. An estimation of the hydricity of the excited state can be gleaned from the extrapolation of the high energy edge of the emission of 1H in water. This method suggests that the thermodynamic hydricity of the excited state of 1H is \(-23\) kcal·mol\(^{-1}\), making 1H more than capable of making \(\text{H}_2\) in neutral water.

The ability of a hydride to reduce \(\text{CO}_2\) to formate at pH 0 can also be predicted by inspection of Figure 4.7. Species more hydridic than formate (\(\Delta G^\circ_{\text{H}_2} < 24.1\) kcal·mol\(^{-1}\)) are thermodynamically capable of \(\text{CO}_2\) reduction. An intriguing prediction arises from Figure 4.7: \(\text{CO}_2\) reduction by hydride transfer from (cymene)Ru complexes 3H and 4H should unfavorable in unbuffered water and favorable only when chloride anion is present. The less hydritic hydrides would require increased \(\text{CO}_2\) pressure to enable hydride transfer to \(\text{CO}_2\). In a prior report of \(\text{CO}_2\) hydrogenation, the Ir hydride 1H underwent slow, rate-limiting hydride transfer to \(\text{CO}_2\), while the Ru hydride 5H transferred hydride sufficiently quickly that hydride formation from \(\text{H}_2\), instead, became rate-limiting. Our studies show that 5H is more
hydridic than the parent Ir complex 1H; the hydricity scale correctly predicts that 5H will more readily hydrogenate CO₂ (and less readily cleave H₂).

4.3 Conclusions

A general strategy for the determination of hydricity in water is presented. Comparisons across a range of well-known catalytic intermediates were enabled by both an electrochemical technique well suited to the complications of water and a new synthetic routes to water-soluble hydrides. Thermodynamic hydricity in water is not only influenced by the supporting ligands, but also by the range of ligands present in aqueous media. Rather than a single value defined in terms of the hydride donor, a continuum of hydricity values should be considered. Being cognizant of the resulting product after hydride transfer makes direct comparisons between catalysts and conditions possible.

The hydricity scales suggest new strategies in aqueous catalysis. The synthetic chemist instinctively tunes catalysts through ligand modifications, but tuning the medium itself can also effect changes in hydricity. The present findings will guide further thermodynamic studies of PCET events in water and guide aqueous catalyst development.

4.4 Experimental Section

General Considerations. Procedures were carried out under nitrogen except where noted. All solutions containing metal hydride species were protected from ambient light to prevent excited state reactions. All reagents were commercially available and used without further purification. Commercial HPLC-grade water was used as a solvent, and organic solvents were dried and degassed with argon using a Pure Process Technology solvent
system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Electrochemical experiments were performed on a Pine WaveNow potentiostat or Pine WaveDriver bipotentiostat controlled by Aftermath software. Details on specific electrochemical experiments are described below. Solution pH was recorded using an OrionStar A111 pH meter with a Beckman-Coulter, Hanna, or Hach ISFET pH probe. UV-Vis spectra were obtained using an Ocean Optics USB2000+ spectrometer with a DT-MINI-2GS deuterium/tungsten halogen light source controlled by OceanView software.

NMR spectra were obtained on 400, 500, or 600 MHz spectrometers. ¹H NMR spectra were referenced to the residual solvent signals (or dioxane or NaOTs as an internal standard in D₂O). Spectra were processed using the MestReNova software suite from Mestrelab Research S. L. The solution acidity in NMR experiments is reported as pD, obtained by addition of +0.4 to the reading of a pH electrode that was calibrated using H₂O standards.

ESI-MS were obtained on a Thermo Scientific LTQ FT-ICR MS with samples introduced either through direct infusion or by LC. Inductively coupled plasma-mass spectrometry (ICP-MS, Agilent Technologies 7500x series) was employed to determine the precise Ir and Ru concentrations in UV-Vis samples (for molar extinction coefficient determination), with the aid of a calibration curve for 10-500 ppb Ir and Ru.

Electrochemistry. Electrochemical experiments were carried out with carbon working electrodes, platinum wire counter electrodes, and Ag/AgCl (3M NaCl) reference electrode in a small glass tube fitted with a Vycor glass frit. Solutions were thoroughly degassed by sparging with nitrogen for at least 15 minutes before beginning an experiment. All potentials
are reported relative to NHE, with values obtained by adding 0.21 V to the experimentally observed potential vs. Ag/AgCl.\textsuperscript{81}

Cyclic voltammetry experiments were carried out with a glassy carbon working electrode (polished with 0.05 micron alumina powder between scans) in an undivided cell. Controlled potential electrolysis experiments were carried out with reticulated vitreous carbon (RVC) as the working electrode separated from the counter electrode and reference electrodes by a fine frit in an H-cell.

Potentiometric experiments were performed in a custom-made three-compartment cell divided by fine frits and with a 10 mm x 10 mm Pyrex glass cuvette affixed to the central working electrode chamber. The solution was stirred at the base of the cuvette and by slow bubbling of N\textsubscript{2} through the length of the cuvette to ensure sufficient mixing near the electrode. An RVC electrode was used as the working electrode for both the electrolysis and open circuit potential experiments. Reduction and oxidation of the analyte was achieved via short periods of electrolysis and after each pulse of current, sufficient time was allowed for the solution components to come into equilibrium (typically 5-10 min) as judged by an unchanging open circuit potential over 30 s. After equilibrium was established, UV-vis spectra were recorded.

**Synthesis.** [Cp*Ir(Cl)\textsubscript{2}],\textsuperscript{80} [Cp*Ir(bpy-COOH)Cl][Cl]\textsuperscript{63} and [Cp*Ir(bpy)(H)][OTf]\textsuperscript{84} were prepared following literature procedures. [Cp*Ir(bpy)(OH\textsubscript{2})][SO\textsubscript{4}]\textsuperscript{100} (1OH\textsubscript{2}), [Cp*Ir(bpy-COOH)(OH\textsubscript{2})][OTf]\textsubscript{2}\textsuperscript{120} (2OH\textsubscript{2}), and [(cymene)Ru(bpy-COOH)(OH\textsubscript{2})][OTf]\textsubscript{2}\textsuperscript{114} (3OH\textsubscript{2}) were prepared following literature procedures with the appropriate silver salt.

\[\text{[Cp*Ir(bpy-COO)(H)]}^- \text{(2H) and [Cp*Ir(bpy-COOO)]}^{2^-} \text{(2). Electrolysis of 2Cl in NaP}_{1}, \text{Na}_{2}\text{SO}_{4}, \text{or NaOH electrolytes (depending on the desired use of the product) past the}\]
first reduction feature (~ −1.0 V) resulted in conversion to reduced products, consistent with previously reported spectroscopic and electrochemical properties. The form of these products (either 2H or 2) was highly dependent on solution pH, giving 2H at neutral pH, 2 at high pH, and a mixture in between. To confirm the identities of these reduced products, 2Cl (9.3 mg, 0.014 mmol) was reduced by excess NaBH₄ (3.7 mg, 0.98 mmol) by stirring for 30 min in MeOH. Filtration and evaporation produced a dark brown film. Dissolution in neutral water provided 2H, and dissolution in basic water provided 2. 2H: ¹H NMR (600 MHz, D₂O + dioxane, Figure 4.9) δ 8.69 (d, J = 5.9 Hz, 2H), 8.55 (s, 2H), 7.72 (d, J = 5.9 Hz, 2H), 1.77 (s, 15H), -11.90 (s, 1H). λ_{abs,max} (pH 7 0.1 M NaPi, Figure 4.10) = 428 nm (3700 M⁻¹ cm⁻¹) 2: ¹H NMR (400 MHz, D₂O + dioxane, Figure 4.9) δ 8.81 (d, J = 7.0 Hz, 1H), 8.42 (s, 1H), 6.82 (dd, J = 6.9, 2.0 Hz, 1H). 1.80 (s, 15 H). λ_{abs,max} (1 M NaOH, Figure 4.10) = 292 nm (22000 M⁻¹ cm⁻¹), 364 nm (10800 M⁻¹ cm⁻¹), 535 nm (23000 M⁻¹ cm⁻¹).

![Figure 4.9. ¹H NMR spectra of the electrolytically produced [Cp*Ir(bpy-COO)(H)]⁻ (bottom) and synthetically produced [Cp*Ir(bpy-COO)(H)]⁻ (middle) in 0.1 M pD 7 NaPi.](image)
Both contain small [Cp*Ir(bpy-COO)(Cl)]⁻ impurities. Electrolytically produced [Cp*Ir(bpy-COO)]²⁻ in 1 M NaOH in D₂O is shown in the top panel.

**Figure 4.10.** Molar absorptivities of [Cp*Ir(bpy-COO)(H)]⁺ (gold) and [Cp*Ir(bpy-COO)]²⁻ (purple). Samples were prepared by electrolysis and checked for purity by ¹H NMR before use. The Ir concentration in each sample was measured by ICP-MS.

\[\text{[(cymene)Ru(bpy-COOH)(Cl)]Cl (3Cl).}\] Under nitrogen, [(cymene)RuCl₂]₂ (50.3 mg, 0.082 mmol) and bpy-COOH (40.3 mg, 0.165 mmol) were allowed to stir in 8 mL DMF at 60 °C for 3 h. After filtering the solution in air to remove unreacted ligand, the DMF was removed in vacuo. The resulting film was dissolved in MeOH, and yellow 3Cl (83.4 mg, 92% yield) precipitated from solution on addition of ether. The ¹H NMR spectrum matched the previously reported data (Figure 4.11).¹¹⁴
Figure 4.11. $^1$H NMR spectrum of [(cymene)Ru(bpy-COOH)(Cl)][Cl] in CD$_3$OD.

$[(cymene)Ru(bpy-COO)(H)]^{-}$ (3H) and $[(cymene)Ru(bpy-COO)]^{2-}$ (3). The hydride 3H and reduced complex 3 were prepared according to the procedures for 2H and 2. 3H: $^1$H NMR (600 MHz, D$_2$O + dioxane, Figure 4.12) δ 8.87 (d, $J = 5.8$ Hz, 2H), 8.53 (d, $J = 1.5$ Hz, 2H), 7.64 (dd, $J = 5.9, 1.6$ Hz, 2H), 5.70 (d, $J = 6.2$ Hz, 2H), 5.51 (d, $J = 6.1$ Hz, 2H), 2.63 (sept, $J = 6.9$ Hz, 1H), 2.24 (s, 3H), 1.07 (d, $J = 6.9$ Hz, 6H), -6.21 (s, 1H). $\lambda_{abs,max}$ (pH 7.01 M NaP$_3$, Figure 4.13) = 295 nm (20800 M$^{-1}$ cm$^{-1}$), 434 nm (5500 M$^{-1}$ cm$^{-1}$) 3: $^1$H NMR (600 MHz, D$_2$O + dioxane, Figure 4.12) δ 8.82 (d, $J = 6.8$ Hz, 2H), 8.37 (s, 2H), 7.12 (d, $J = 6.7$ Hz, 2H), 4.84 (d, $J = 5.5$ Hz, 2H), 4.81 (d, $J = 5.7$ Hz, 2H), 2.32 (sept, $J = 7.7$ Hz, 1H), 1.85 (s, 3H), 0.86 (d, $J = 6.7$ Hz, 6H). $\lambda_{abs,max}$ (1 M NaOH, Figure 4.13) = 298 nm (22600 M$^{-1}$ cm$^{-1}$), 374 nm (13500 M$^{-1}$ cm$^{-1}$), 506 nm (17600 M$^{-1}$ cm$^{-1}$), 610 nm (14400 M$^{-1}$ cm$^{-1}$).
Figure 4.12. $^1$H NMR spectra of the electrolytically produced [(cymene)Ru(bpy-COO)(H)]$^-$ in 0.1 M pD 7 NaPi (top) and synthetically produced [(cymene)Ru(bpy-COO)]$^{2-}$ in 1 M NaOH in D$_2$O (bottom). Both are referenced to dioxane.

Figure 4.13. Molar absorptivities of [(cymene)Ru(bpy-COO)(H)]$^-$ (red-orange) and [(cymene)Ru(bpy-COO)]$^{2-}$ (purple-blue). Samples were prepared by electrolysis and checked for purity by $^1$H NMR before use. The Ru concentration in each sample was measured by ICP-MS.

**Thermodynamic Measurements. Hydride Equilibrations.** In a typical equilibration experiment to determine relative hydricity according to Figure 4.1B, 19.3 mg 2Cl was
dissolved by sonication in 2 mL pH 7.0 NaPi, added to the working electrode compartment of an H-cell, and degassed for 15 min. The counter electrode compartment was charged with 2 mL pH 7.0 NaPi. The solution was electrolyzed at −1.0 V for 6 h, transferred to a N₂ purged bomb flask, and brought into a glovebox. Different volumes of the electrolyzed solution (100, 200, and 300 μL) were added to three samples containing 3.5 mmol 1Cl and dioxane, and the total volume was brought to 500 μL (Scheme 4.2). Samples were monitored by ¹H NMR, and equilibrium of the experimental samples was quickly achieved; though the samples were monitored over 25 h by ¹H NMR (Figure 4.14), equilibrium ($K_{eq} = 0.35$) was established by the first time point, giving $\Delta\Delta^\circ G_{H^-} = 0.6±0.1$ kcal·mol⁻¹.

**Scheme 4.2. Representative hydride equilibration reaction.**

![Scheme 4.2](image)
Figure 4.14. Representative $^1$H NMR spectrum of a typical hydride equilibrium experiment. (top) Equilibrium mixture of $^1$H, $^1$Cl, $^2$H, and $^2$Cl formed from the addition of $^1$Cl to the mixture of $^2$H and $^2$Cl formed from electrolysis (bottom).

Alternatively, following protonation with HCl·Et$_2$O, the solid hydride was extracted into the NMR solvent (either pD 7 0.1 M NaPi or pD 4.3 20 mM NaOAc with dioxane internal standards), filtered to remove any residual Cp*Ir(bpy-$X$) or (arene)Ru(bpy-$X$), and combined with a hydride acceptor. Equilibration was followed by $^1$H NMR. In a representative experiment (Scheme 4.3), 2.0 mg [Cp*Ir(bpy)(H)][Cl] (0.004 mmol) was dissolved in 490 μL pD 7 0.1 M NaPi with 10 μL 0.5 M dioxane as an internal standard. After confirming the purity of the hydride sample by $^1$H NMR (Figure 4.15) 2.1 mg [Cp*Ir(bpy-Me)(Cl)][Cl] (0.004 mmol) was added to the NMR tube as a solid. $\Delta G^\circ_{H^-}$ was determined to be 0.4±0.1 kcal·mol$^{-1}$.
Scheme 4.3. Representative hydride equilibration reaction.

\[
\begin{align*}
\text{Me} & \quad \text{c} \quad \text{Me} \\
\text{N} & \quad \text{N} \\
\text{Me} & \quad \text{Me} \\
\text{6Cl} & \quad \text{1H} \\
\end{align*}
\]

\[
\text{Me} \quad \text{c} \quad \text{Me} \\
\text{N} \quad \text{N} \\
\text{Me} \quad \text{Me} \\
\text{1H} \quad \text{6H} \\
\text{6Cl} \quad \text{1Cl} \\
\]

\[\Delta G = 0.4 \text{ kcal mol}^{-1}\]

Figure 4.15. Representative $^1$H NMR spectrum of a typical hydride equilibrium experiment. (top) Equilibrium mixture of 1H, 1Cl, 6H, and 6Cl formed from the addition of 6Cl to 1H formed synthetically (bottom).

_Aquo-Chloride Association Equilibria._ For each species, a series of solutions of known concentration of chloride were prepared in pD 7 NaP$_i$ and monitored by NMR to ensure that the aquo, phosphate, and chloride species were in equilibrium. For example, in air, a 5.5 mM solution of [Cp*Ir(bpy-COOH)(OH$_2$)][OTf]$_2$ in 50 mM pD 7 NaP$_i$ with a dioxane internal standard was split between 6 samples each containing dry NaCl to produce final solutions with [Cl$^-$] from 0 mM to 18 mM. The samples were monitored by $^1$H NMR over 24 hours to ensure that equilibrium had been established between [Cp*Ir(bpy-
COO)(OH$_2$)]$^0$, [Cl$^-$] and [Cp*Ir(bpy-COO)(Cl)]$^-$. The initial [Cl$^-$] left from the halide abstraction with AgOTf was fit by minimizing the variance of ΔG of the 0 mM NaCl added sample with that of the remaining 5 samples. The free energy of the ligand exchange was found to be $-4.4\pm0.2$ kcal·mol$^{-1}$. The relative aquo-phosphate association free energy was determined similarly with solutions of increasing total [P$_i$] at pD 7.
CHAPTER 5: CYCLOPENTADIENE-MEDIATED HYDRIDE TRANSFER FROM RHODIUM COMPLEXES


5.1 Introduction

Transition metal catalysts capable of selective hydride transfer to the enzyme cofactor nicotinamide adenine dinucleotide (NAD\textsuperscript{+}) to form the 1,4-reduced product (1,4-NADH) are critical links between organometallic and enzymatic catalysis in emerging strategies in sustainable, enantioselective organic synthesis.\textsuperscript{52–55} Biocompatible catalytic routes for 1,4-NADH regeneration provide access to the enzymatic hydride transfer reactivity without stoichiometric amounts of the complex molecule 1,4-NADH.\textsuperscript{121} Of the organometallic catalysts that have been shown to regenerate NADH, rhodium complexes have emerged as selective and efficient catalysts for reduction at the 4-position of nicotinamides, spurring innovation in tandem bio-organometallic catalysis (Scheme 5.1).\textsuperscript{53}

In the presence of a precatalyst like [Cp*Rh(bpy)(OH\textsubscript{2})]\textsuperscript{2+} (2; Cp* is pentamethylcyclopentadienyl and bpy is 2,2’-bipyridine), generation of 1,4-NADH can be accomplished using chemical reductants (e.g. formate) or by electrochemical methods (by \(1\text{H}^+\!/2\text{e}^-\)). The mechanism is typically proposed to proceed \(\text{via} [\text{Cp*Rh(bpy)(H)}]^+\) as rhodium hydride intermediate with selectivity directed by coordination of NAD\textsuperscript{+} to the Rh centre after an \(\eta^5\)- to \(\eta^3\)-Cp* ring slip.\textsuperscript{122} Drawing on this mechanism, \(\text{Cp*Rh(bpy)}\)-based catalysts have been applied in ketone and aldehyde reductions\textsuperscript{123,124} and hydrogen evolution.\textsuperscript{91,125}
After considering the hydricity, or hydride donor ability, of the iridium analogues [Cp*Ir(bpy)(H)]^+ (Chapter 4),\textsuperscript{126} we were interested in the comparison to [Cp*Rh(bpy)(H)]^+. Relatively few hydricity values have been determined in water, and these Rh complexes provided an opportunity to learn more about an important catalytic intermediate and add new data to the emerging area of aqueous hydricity.\textsuperscript{48–50,127}

Scheme 5.1. Tandem catalytic cycle for Rh, NAD^+, and enzyme mediated reductions

5.2 Results and Discussion

Formation of a (Cp*H)Rh complex. In order to determine the hydricity of the proposed [Cp*Rh(bpy)(H)]^+ intermediate, we first needed a preparative route for this species, which had not previously been isolated. Reduction of [Cp*Rh(bpy)(Cl)][Cl] in a pH 5 formate solution (following a procedure that cleanly generates the Ir analogue [Cp*Ir(bpy)(H)][PF_6])\textsuperscript{128} produces a dark red solution from which a green solid precipitates on addition of [NH_4][PF_6]. Dissolution of the solids in CD_3CN cleanly produced a red solution containing a new species. Surprisingly, the Cp* methyl resonances were not equivalent: two singlets (6H integration each) and a doublet (J = 6.2 Hz, 3H) presented in the
aliphatic region. A quartet (δ 2.31, J = 6.2 Hz, 1H) indicated a pentamethylcyclopentadiene (Cp*H) fragment containing a new C–H bond (Figure 5.1).

Figure 5.1. $^1$H NMR spectrum of [(Cp*H)Rh(bpy)(NCCD$_3$)][PF$_6$] in CD$_3$CN.

An alternative procedure involving protonation of a reduced Cp*Rh(bpy) (1) species was also attempted. Reduction of [Cp*Rh(bpy)(Cl)][Cl] by NaBH$_4$ in 1 M NaOH led to precipitation of dark purple 1. Dropwise addition of a dilute solution of HCl·Et$_2$O to an ethereal solution of 1 produced a Cp*H-containing product similar to the one described above.

Crystals suitable for X-ray diffraction were prepared by vapor diffusion of DCM and pentane. The resulting molecular structure revealed the product to be (Cp*H)Rh(bpy)(Cl) (2), a Rh(I) complex containing a η$^4$-pentamethylcyclopentadiene ligand with the new C–H bond endo with respect to the metal center (Figure 5.2). Crystallographic data and refinement
details are given in Table 5.1. The long C1–C2 distance (1.517(2) Å) compared to the short C2–C3 (1.440(3) Å) distance confirm that the species is a diene. In contrast, the crystal structure of complex 1 shows only a 0.034 Å difference amongst the cyclopentadienyl C–C bonds. Aromaticity has clearly been broken with a C2’–C1–C2–C3 torsional angle of 31.9(2)° compared to 3.418° in 1. Crystal data, data collection parameters, and structure refinement for 2 are listed in Table 5.1. The bromide analogue (Cp*H)Rh(bpy)(Br) was concurrently isolated by Winkler, Gray and Blakemore and was being investigated relating to H₂ evolution in acetonitrile.

![Figure 5.2](image_url)

**Figure 5.2.** Structural representation of 2 with ellipsoids drawn at the 50% probability level (containing a mirror plane that bisects the Cp*H and bpy ligands). A co-crystallized CH₂Cl₂ solvent molecule and hydrogen atoms removed for clarity. Selected distances (Å) and angles (deg): C1–C2 1.517(2), C2–C3 1.440(3), Rh1–N1 2.1157(15), Rh1–Cl1 2.5440(6), C2’–C1–C2–C3 31.9(2)

**Table 5.1. Crystal data and structure refinement for 2.**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C₂₁H₂₆Cl₃N₂Rh</td>
</tr>
<tr>
<td>Formula weight</td>
<td>515.70</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>100</td>
</tr>
<tr>
<td>Space group</td>
<td>Pnma</td>
</tr>
<tr>
<td>a/Å</td>
<td>22.5211(11)</td>
</tr>
<tr>
<td>b/Å</td>
<td>12.1599(6)</td>
</tr>
</tbody>
</table>

102
The structure of the complex yields clues about the probable mechanism of its formation. The endo orientation of the hydride is consistent with C–H bond-forming reductive elimination of Cp* and a Rh–H. Reductive elimination of Cp* with hydride ligands has been observed from Rh and Ir metal hydrides with dissociation of the free diene.\textsuperscript{130,131} As shown in Scheme 5.2, a Rh hydride intermediate is also consistent with the observation that the Cp*H product is formed both by hydride transfer from formate and by protonation of 1.
The intermediacy of a hydride was probed by low temperature NMR experiments. Indeed, protonation of 1 with HCl at 233 K allowed the observation of a Rh–H resonance in by $^1$H NMR (δ –9.60, $J_{RhH} = 19.9$ Hz, Figure 5.3), which converted to diene complex 2 upon warming.

![Figure 5.3](image_url)

**Figure 5.3.** $^1$H NMR spectra showing the low temperature protonation of Cp*Rh(bpy) (4.8 mg, 0.012 mmol) in C$_6$D$_5$Cl (red). After injection of 5.5 μL 2.0 M HCl·Et$_2$O in an acetonitrile/dry ice bath. Spectrum recorded at 238 K (blue). After warming to 293 K (purple). A hydride resonance at –9.60 ppm at low temperatures is evidence for the intermediacy of [Cp*Rh(bpy)(H)]$^+$ in the formation of (Cp*H)Rh(bpy)(Cl).

Density functional theory (DFT) calculations are consistent with a Rh hydride intermediate that is unstable towards C–H reductive elimination. As illustrated in Scheme 5.3 and tabulated in Table 5.2, reductive elimination of the Rh hydride to form the Cp*H complex is favorable by –4.1 kcal·mol$^{-1}$. In contrast, for the Ir analogue [Cp*Ir(bpy)(H)]$^+$, which has been isolated and structurally characterized$^{128}$, formation of Cp*H is predicted to be unfavorable by 8.1 kcal·mol$^{-1}$. Interestingly, the only prior report of a similar bpy-
supported Rh hydride complex is the methyl-substituted complex [Cp*Rh(6,6’-Me-bpy)(H)]

**Scheme 5.3. Relative free energies for reductive elimination of Cp*H from M–H (M = Rh, Ir) in acetonitrile solvent from DFT**

![Scheme 5.3](image)

**Table 5.2. Overview of calculated change in electronic energy (ΔE), enthalpy (ΔH), entropy (ΔS), and free energy (ΔG) for the isomerization of rhodium and iridium hydrides.**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>ΔE (kcal·mol⁻¹)</th>
<th>ΔH (kcal·mol⁻¹)</th>
<th>ΔS (cal·mol⁻¹·K⁻¹)</th>
<th>ΔG (kcal·mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cp<em>Rh(bpy)(H)]⁺ → [(Cp</em>H)Rh(bpy)]⁺</td>
<td>−6.17</td>
<td>−4.02</td>
<td>0.097</td>
<td>−4.05</td>
</tr>
<tr>
<td>[Cp<em>Ir(bpy)(H)]⁺ → [(Cp</em>H)Ir(bpy)]⁺</td>
<td>+5.91</td>
<td>+7.89</td>
<td>−0.62</td>
<td>+8.07</td>
</tr>
</tbody>
</table>

The apparent instability of the Rh hydride intermediate with respect to reductive elimination raises questions about how Cp*Rh-based catalysts mediate hydride transfer reactions. Diene 2 could undergo hydride transfer indirectly via a Rh–H intermediate, or via a C–H bond-breaking direct hydride transfer. The latter mechanism illustrates the similarity
between diene 2 and a variety of transition metal complexes ligated by organic hydride donors and acceptors that have been created.132–134

**Reactivity of diene 2.** To better understand complex 2, we sought to measure the hydricity and establish hydride transfer reactivity. We focused on the closely related complex [(Cp*H)Rh(4,4’-COO-bpy)]\(^{+}\) (2\text{coo}) due to its favorable solubility profile in water. For Ir–H complexes, carboxylate substitution has a very minor impact on hydricity,\(^{126}\) and with the additional distance to the substitution site, the impact on hydricity is expected to be similarly minor for (Cp*H)Rh complexes.

The hydricity (\(\Delta G^o_H\), eq. 5.5) was established by determining the p\(K_a\) of the diene complex (eq. 5.1), the reduction potential of [Cp*Rh(bpy-COO)(OH)]\(^{-}\) (3\text{coo}) (eq. 5.2) and the p\(K_a\) of the Rh\(^{III}\) aquo complex Cp*Rh(bpy-COO)(OH\(_2\)) (eq. 5.3). Combining these experimental values with the constant free energy of 2e\(^-\) proton reduction (eq. 5.4)\(^{47}\) provides \(\Delta G^o_H\) according to Eq. 5.6.

\[
\begin{align*}
2\text{coo} & \rightleftharpoons 1\text{coo} + H^+ \quad (5.1) \\
1\text{coo} + OH^- & \rightleftharpoons 3\text{coo} + 2e^- \quad (5.2) \\
3\text{coo} + H^+ & \rightleftharpoons \text{Cp*Rh(bpy-COO)(OH\(_2\))} \quad (5.3) \\
H^+ + 2e^- & \rightleftharpoons H^- \quad (5.4) \\
2\text{coo} & \rightleftharpoons \text{Cp*Rh(bpy-COO)(OH\(_2\))} + H^- \quad (5.5) \\
\Delta G^o_H & = (1.364)pK_{a(1)} - (-46.12)E^o - (1.364)pK_{a(3)} + 34.2 \text{ kcal} \cdot \text{mol}^{-1} \quad (5.6)
\end{align*}
\]
The reduction potential was measured by cyclic voltammetry (CV) in aqueous phosphate electrolyte. Above pH 9, the 2e\textsuperscript{−} reduction of [Cp*Rh(bpy-COO)(OH)]\textsuperscript{−} (3\textsubscript{coo}) to [Cp*Rh(bpy-COO)]\textsuperscript{2−} is quasi-reversible (\(\Delta E_p = 30-80\) mV across the pH range) and \(E_{1/2}\) shifts cathodically by 24.6 mV per pH unit, close to the ideal 29.5 mV per pH unit shift expected for a 1OH/2e\textsuperscript{−} process (Figure 5.4). Extrapolating this trend to pH 0 (the standard state of aqueous thermodynamics in eqs. 5.1-5.5) provides the formal potential, \(E^\circ = -0.25\) V, for the reduction of the hydroxide complex.

![Graph showing the shift of the 2e\textsuperscript{−} reduction of [Cp*Rh(bpy-COO)(OH)]\textsuperscript{−} at 100 mV/s as the pH increases from 9.5 to 13.0 (left). \(E_{1/2}\) of the reduction plotted against pH to extrapolate to pH 0 (right).](image)

**Figure 5.4.** The shift of the 2e\textsuperscript{−} reduction of [Cp*Rh(bpy-COO)(OH)]\textsuperscript{−} at 100 mV/s as the pH increases from 9.5 to 13.0 (left). \(E_{1/2}\) of the reduction plotted against pH to extrapolate to pH 0 (right).

To confirm that products of electrochemical reduction, controlled potential electrolysis (CPE) of hydroxide 3\textsubscript{coo} was performed under basic conditions. CPE of 3\textsubscript{coo} resulted in a midnight blue solution after passing 2e\textsuperscript{−} per Rh of charge (Figure 5.5). Upon addition of pD 7 0.1 M sodium phosphate buffer, the blue solution turned red and \(^{1}\text{H} \text{NMR}\) spectroscopy confirmed formation of 2\textsubscript{coo}, as indicated by the characteristic 6:6:3 pattern of the Cp\textsuperscript{*} methyl resonances in the aliphatic region.
The acidity of diene complex $2_{\text{COO}}$ has an estimated $pK_a < 10$ based on a spectrophotometric titration adding acid to an aqueous solution of $[\text{Cp}^*\text{Rh(bpy-COO)}]^2^-$ (Figure 5.6). Both the basic starting material and its conjugate acid were observed to react on the timescale of the experiment, which leads to lower than expected absorbance at 610 nm and produces an artificially low $[\text{Cp}^*\text{Rh}]/[(\text{Cp}^*\text{H})\text{Rh}]$ ratio — and thus an overestimate of the $pK_a$.

The relative instability of these Rh species led us to carry out a complementary electrochemical titration by monitoring the growth of the oxidation of $1_{\text{COO}}$ by CV as a function of solution pH, which provided $pK_a > 8$ (Figure 5.7). The scan rate dependence indicates that protonation is slow on the electrochemical time scale. As the scan rate decreases, the reaction has longer to approach equilibrium, leading to an increase in apparent $pK_a$ — and therefore an underestimate of the true $pK_a$. Each method provides a limiting value, and we, therefore, estimate that $2_{\text{COO}}$ has $pK_a = 9 \pm 1$. 

Figure 5.5 UV-vis spectra of $[\text{Cp}^*\text{Rh(bpy-COO)}]^2^-$ formed electrochemically at pH 11.2 (blue) and added to a pH 7 0.1 M sodium phosphate buffer to protonate (yellow).
Figure 5.6. Spectrophotometric titration of $[\text{Cp}^*\text{Rh(bpy-COO)}]^2^-$ with addition of acid to form $[(\text{Cp}^*\text{H})\text{Rh(bpy-COO)}]^-$(left) and analysis of the absorbance at 610 nm to the Henderson-Hasselbalch equation giving $pK_a = 9.9$(right).

Figure 5.7. (A) CV of $[\text{Cp}^*\text{Rh(bpy-COOH)}(\text{Cl})][\text{Cl}]$ in pH 5.8 to pH 10 phosphate electrolyte at a scan rate of 100 mV/s, expanded to highlight the return wave attributed to oxidation of $[\text{Cp}^*\text{Rh(bpy-COO)}]^2^-$. In acidic water, $[\text{Cp}^*\text{Rh(bpy-COO)}]^2^-$ is protonated to form $[(\text{Cp}^*\text{H})\text{Rh(bpy-COO)}]^-$. The increasing oxidative peak current with increasing pH indicates higher concentrations of $[\text{Cp}^*\text{Rh(bpy-COO)}]^2^-$ as pH increases. (B) Plot of oxidative peak current vs. pH. At each scan rate this sigmoid was fit to the Henderson-Hasselbalch equation to determine a $pK_a$. (C) Plot of apparent $pK_a$ vs. scan rate.
The Rh$^{III}$ species exists as the aquo Cp*Rh(bpy-COO)(OH$_2$), not the hydroxo 3coo, under the neutral, aqueous conditions of most catalysis.$^{125}$ Incorporation of the pK$_a$ of the aquo complex (8.8 by spectrophotometric titration) accounts for this protonation state.

Based on the experimentally determined $E^o$ and pK$_a$ values, Eq. 6 provides the aqueous hydricity of [(Cp*H)Rh(bpy-COO)]$^-$ to form Cp*Rh(bpy-COO)(OH$_2$): $\Delta G^o_{H-}(OH_2) = 23 \pm 2$ kcal·mol$^{-1}$.

Hydride transfer to complex Cp*Rh(bpy-COO)(OH$_2$) from species with $\Delta G^o_{H-} < 23$ kcal·mol$^{-1}$, and hydride transfer to [Cp*Rh(bpy)(OH$_2$)]$^{2+}$ is expected to proceed with similar driving forces (vide supra). As expected, [(C$_6$Me$_6$)Ru(bpy)(H)]$^+$ ($\Delta G^o_{H-}(OH_2) = 22 \pm 1$ kcal·mol$^{-1}$) reacts with [Cp*Rh(bpy)(Cl)]$^+$ (Cl$^-$ is displaced in water$^{125}$) to produce the corresponding hydride transfer product 2 (Scheme 5.4). The product slowly decomposed, preventing the system from reaching equilibrium. Transfer does not occur from weaker hydride sources: combining [Cp*Ir(bpy-COO)(H)]$^-$ ($\Delta G^o_{H-}(OH_2) = 32.0$ kcal·mol$^{-1}$) with [Cp*Rh(bpy)(Cl)]$^+$ results in no reaction. In accord with the hydricity values, in the reverse reaction (Cp*H)Rh(bpy)(Cl) reacted completely with [Cp*Ir(bpy-COO)(Cl)]$^-$ to form [Cp*Ir(bpy-COO)(H)]$^-$. 
After establishing the viability of diene complex 2 in hydride transfer reactions with transition metal complexes, we turned our attention to hydride transfer involving NAD\(^+\). The hydricity of NADH is 29 kcal·mol\(^{-1}\),\(^{135,136}\) so the Rh diene complex 2 should be sufficiently hydridic to reduce NAD\(^+\). A red solution of isolated (Cp*H)Rh(bpy)(Cl) quickly turned yellow on addition of NAD\(^+\). \(^1\)H NMR spectroscopy confirmed consumption of (Cp*H)Rh(bpy)(Cl) and selective production of 1,4-NADH within 15 minutes (Figure 5.8).

Scheme 5.4. Selected hydride transfer reactions.
Figure 5.8. $^1$H NMR spectrum of a solution of (Cp*H)Rh(bpy)(Cl) after addition of 2.7 mg NAD$^+$ (4.1 μmol) in pH 7 0.1 M NaPi. The Rh species has reacted completely (best seen by the absence of any resonance at 0.7 ppm), and NADH has appeared. The nicotinamide singlet shifts from 9.3 ppm to 6.9 ppm upon reduction and a pair of diastereotopic protons appear at 2.6 and 2.7 ppm. Assignments were made by comparison to authentic samples in the same solutions and by comparison to ref. 137.

Finally, we assessed the viability of diene species 2 as an intermediate on the NAD$^+$ reduction cycle by mimicking various chemical and electrochemical catalytic conditions typically employed. Reduction of [Cp*Rh(bpy)(Cl)]$^+$ in D$_2$O with 10 equiv formate forms the red hydride migrated complex immediately, as judged by the appearance of a 6:6:3 pattern in the Cp* region. The same species is also formed upon reduction of [Cp*Rh(bpy)(Cl)]$^+$ at -0.64 V vs NHE in pH 7 0.1 M phosphate buffer. Even treatment of [Cp*Rh(bpy)(OH$_2$)]$^{2+}$ with 1 atm H$_2$ in pH 7 0.1 M phosphate buffer produced diene 2 (Figure 5.9).
Figure 5.9. $^1$H NMR spectra showing the formation of diene products (indicated by a 6:6:3 pattern in the aliphatic region) under catalytic conditions. (top) $[\text{Cp}^*\text{Rh(bpy)(OH}_2\text{)}]^2^+$ under an atmosphere of $\text{H}_2$ in $\text{pD} $ 7 0.1 M NaP$_i$, referenced to sodium tosylate. (middle) Product of electrolysis of $[\text{Cp}^*\text{Rh(bpy)(Cl)}]^+$ at $-0.64$ V in 80:20 $\text{pD} $ 7:$ \text{pH} $ 7 0.1 M NaP$_i$, referenced to dioxane. (bottom) $[\text{Cp}^*\text{Rh(bpy)(Cl)}]^+$ in $\text{D}_2\text{O}$ with 10 equiv of sodium formate, referenced to formate.

The presence of 2 under catalytically relevant conditions indicates that it is a viable intermediate. Complex 2 is not the only Rh species in these solutions, however, and this species does not exhibit long term stability under aqueous conditions. Bubbles formed on the walls of NMR tubes containing 2 in neutral aqueous solutions, indicating $\text{H}_2$ evolution. The Cp* methyl protons also scrambled H for D. Such scrambling has been observed for Cp* ligands and typically proceeds through a base-assisted mechanism via fulvene intermediates.$^{138,139}$ We have also observed the per-deuteration of Cp* in $[\text{Cp}^*\text{Ir(bpy-COO)(H)}]^-$ by $^1$H, $^2$H NMR and MS (Figure 5.10), but deuteration in the Ir manifold occurs over the course of weeks, while deuteration in the Rh manifold occurs over the course of
hours. Broad resonances shifted slightly upfield of each proteo Cp*H signal appear quickly before the signals slowly disappear altogether.

Figure 5.10. $^1$H NMR spectra showing an equilibrium mixture of [Cp*Ir(bpy)(H)]$^+$, [Cp*Ir(bpy)(Cl)]$^+$, [Cp*Ir(bpy-COO)(H)]$^-$, and [Cp*Ir(bpy-COO)(H)]$^-$ (formed by mixing electrochemically produced [Cp*Ir(bpy-COO)(H)]$^-$ with [Cp*Ir(bpy)(Cl)][Cl]$^{126}$ shortly after equilibrium had been achieved (bottom) and 7 weeks later (top). The Cp* peaks have disappeared with no changes to the aromatics indicating per-deuteration of the Cp* protons. Deuteration was also observed by $^2$H NMR. [(Cp*-d$_{15}$)Ir(bpy)(Cl)]$^+$ (m/z = 534.21 (calc), 534.33 (obs)) and [(Cp*-d$_{15}$)Ir(bpy-COONa)(Cl)]$^+$ (m/z = 666.16 (calc), 666.20 (obs)) were also observed by mass spec.

Scheme 5.5 combines our new findings with Fish’s original mechanistic proposal$^{122}$ to construct an alternative mechanistic hypothesis. Starting from the [(Cp*)Rh(bpy)(OH$_2$)]$^{2+}$ precatalyst, a $^{1}$H$^+$/2e$^-$ reduction (either by a hydride donor, e.g. formate, or through reduced species 1) transiently produces [(Cp*)Rh(bpy)(H)]$^+$. Reductive elimination yields a (Cp*H)Rh moiety. The endo orientation of the proton seems to ideally position the C–H bond to deliver hydride to a bound substrate such as NAD$^+$ ligation the Rh center. Following
hydride transfer, displacement of NADH by water regenerates the initial state of the catalyst.

Several other mechanisms can be envisioned, such as hydride transfer via reversible access to the high energy hydride intermediate [(Cp*)Rh(bpy)(H)]+. The mechanism in Scheme 5.5 offers an alternative path for substrate binding without invoking an η⁵ to η³ Cp* ring slip.

**Scheme 5.5. Proposed mechanism for the reduction of NAD⁺ through a (Cp*H)Rh(bpy) intermediate. NUN is 2,2'-bipyridine.**

5.3 Conclusions

We have prepared a pentamethylcyclopentadiene complex of Rh that is a plausible intermediate in the selective catalytic reduction of NAD⁺ to 1,4-NADH. Hydricity
measurements confirm that diene 1 is thermodynamically capable of hydride transfer to NAD+. A series of hydride transfer reactions to NAD⁺ and other transition metals are consistent with the hydricity value. This surprising ligand-based hydride transfer reactivity, involving the typically innocent pentamethcyclopentadienyl ligand, suggests new pathways for Cp*Rh-catalyzed management of protons and electrons.

5.4 Experimental Section

General Considerations. Procedures were carried out under nitrogen except where noted. All reagents were commercially available and used without further purification. Commercial HPLC-grade water was used as a solvent, and organic solvents were dried and degassed with argon using a Pure Process Technology solvent system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc. Electrochemical experiments were performed on a Pine WaveNow potentiostat or Pine WaveDriver bipotentiostat controlled by Aftermath software. Details on specific electrochemical experiments are described below. Solution pH was recorded using an OrionStar A111 pH meter with a Beckman-Coulter or Hanna pH probe. UV-Vis spectra were obtained using an Ocean Optics USB2000+ spectrometer with a DT-MINI-2GS deuterium/tungsten halogen light source controlled by OceanView software.

NMR spectra were obtained on 400, 500, or 600 MHz spectrometers. ¹H NMR spectra were referenced to the residual solvent signals (or dioxane or NaOTs as an internal standard in D₂O). Spectra were processed using the MestReNova software suite from Mestrelab Research S. L. The solution acidity in NMR experiments is reported as pD,
obtained by addition of +0.4 to the reading of a pH electrode that was calibrated using H₂O standards.⁷⁹

**Electrochemistry.** Electrochemical experiments were carried out with carbon working electrodes (glassy carbon for cyclic voltammetry and reticulated vitreous carbon for bulk electrolysis), platinum wire counter electrodes, and Ag/AgCl (3M NaCl) reference electrode in a small glass tube fitted with a Vycor glass frit. Solutions were thoroughly degassed by sparging with nitrogen for at least 15 minutes before beginning an experiment or the experiments were carried out in a N₂ filled glovebox. All potentials are reported relative to NHE, with values obtained by adding 0.21 V to the experimentally observed potential vs. Ag/AgCl.⁸¹ The glassy carbon working electrode was polished with 0.05 micron alumina powder between scans and cyclic voltammetry was performed in an undivided cell. Controlled potential electrolysis experiments were carried out in a divided H-cell with the working electrode chamber and counter electrode chamber separated by a fine frit.

**Synthetic Methods.** The complexes [Cp*RhCl₂], [Cp*Rh(bpy)(Cl)][Cl] (4), [Cp*Rh(bpy-COOH)(Cl)][Cl], [Cp*Ir(bpy-COOH)(Cl)][Cl], [(C₆Me₆)Ru(bpy)(H)][Cl] were prepared according to literature procedures.

(Cp*H)Rh(bpy)(Cl) (1). To a stirring solution of Cp*Rh(bpy) (10.3 mg, 0.026 mmol) in ether, a dilute solution of HCl·Et₂O (50 mM) was added dropwise until a change from a dark purple solution to fine red solids was observed. Typically 1-1.5 eq of HCl were added with the excess acid immediately pumped off after completion of the addition. Alternatively, less than 1 eq of 50 mM HCl in pentane was added to a solution of Cp*Rh(bpy) (10.6 mg, 0.027 mmol) stirring at −30 °C. The red solid that precipitated was filtered off and washed 3× with pentane. Samples of hydride prepared in this way typically contained small amounts
[\text{Cp*Rh(bpy)(Cl)}][\text{Cl}] (presumably formed by protonation of the diene complex to release H}_2\). \textsuperscript{1}H NMR (600 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 8.92 (d, J = 5.2 Hz, 2H), 8.09 (dt, J = 7.9, 1.2 Hz, 2H), 7.87 (td, J = 7.8, 1.6 Hz, 2H), 7.47 (ddd, J = 7.6, 5.3, 1.3 Hz, 2H), 2.50 (q, J = 6.3 Hz, 1H), 1.85 (s, 6H), 0.91 (s, 6H), 0.53 (d, J = 6.2 Hz, 3H). \textsuperscript{13}C NMR (151 MHz, CD\textsubscript{2}Cl\textsubscript{2}) δ 154.11, 151.38, 136.47, 125.90, 121.87, 92.17 (d, J = 10.1 Hz), 56.10 (d, J = 3.7 Hz), 53.26 (br s), 19.38, 12.03, 10.56.

Alternatively, [\text{Cp*Rh(bpy)(Cl)}][\text{Cl}] (5.8 mg, 0.012 mmol) was dissolved in pH 5.3 M NaO\textsubscript{2}CH. After stirring for 30 min, the solution had turned from yellow to dark red, and addition of excess [NH\textsubscript{4}][PF\textsubscript{6}] resulted in the precipitation of a light green solid. Dissolving this solid in CD\textsubscript{3}CN produced a red solution of [(\text{Cp*H})\text{Rh(bpy)(NCCD\textsubscript{3})}][\text{PF\textsubscript{6}}]. \textsuperscript{1}H NMR (400 MHz, CD\textsubscript{3}CN) δ 8.98 (dd, J = 5.2, 1.3 Hz, 1H), 8.34 (dt, J = 8.3, 1.1 Hz, 1H), 8.10 (td, J = 7.9, 1.6 Hz, 1H), 7.67 (ddd, J = 7.6, 5.3, 1.2 Hz, 1H), 2.31 (q, J = 6.2 Hz, 1H), 1.92 (s, 3H), 0.79 (s, 3H), 0.53 (d, J = 6.2 Hz, 1H).

\text{([Cp*Rh(bpy-COO)]\textsuperscript{2–}} (5coo). Electrolysis at −0.89 V of [Cp*Rh(bpy-COOH)Cl][Cl] (4.9 mg, 0.009 mmol) in 1.8 mL 0.1 M Na\textsubscript{2}SO\textsubscript{4} electrolyte in D\textsubscript{2}O passed −1.67 C (2.0 e\textsuperscript{−}/Rh) resulting in a royal blue solution of \text{[Cp*Rh(bpy-COO)]\textsuperscript{2–}}. \textsuperscript{1}H NMR (600 MHz, D\textsubscript{2}O) δ 8.85 (br s, 1H), 8.35 (s, 1H), 7.06 (dd, J = 6.5, 1.9 Hz, 1H), 1.80 (br s, 7H).

**Computational Details.**

All calculations were performed using the Gaussian09 software package.\textsuperscript{140} The PBE1PBE functional\textsuperscript{141} was used for all calculations, with the LANL2DZ basis set\textsuperscript{142} and pseudopotential used for Ir and the 6-31G(d,p) basis set\textsuperscript{143,144} used for all other atoms. After optimizing the structure, frequency optimizations were performed for each species to compute Gibbs free energy values, ensuring the absence of imaginary frequencies. A
polarizable continuum model (IEFPCM as implemented by Gaussian09) was used to approximate the effects of acetonitrile solvent.
CHAPTER 6: PHOTOCHEMICAL PRODUCTION OF ETHANE FROM AN IRIDIUM METHYL COMPLEX

6.1 Introduction

Photocatalysts capable of mediating C–C bond formation could play an important role in the light-driven generation of energy-dense liquid fuels. Ethane formation from two methyl fragments is the simplest C–C bond forming reaction leading to an alkane, and organometallic methyl complexes have been the subject of photophysical and photochemical inquiry. Though photochemical ethane generation has been observed from metal methyl complexes,\textsuperscript{145} such reactivity is notably uncommon.\textsuperscript{146}

Many approaches to integrating light absorption with C–C bond formation have been explored. In photoredox catalysis, photosensitizers can trigger C–C bond formation following an excited state electron transfer.\textsuperscript{147,148} Photochemical ligand dissociation (which opens a coordination site and triggers migratory insertion) and M–C bond homolysis (leading to radical reactivity) can also lead to formation of C–C bonds.\textsuperscript{149} Radicals are a common component of alkyl photochemistry: in the 1980s, Crabtree investigated Hg sensitization, which produces radicals, for various alkane functionalizations.\textsuperscript{150} Platinum complexes are also known to couple two alkyl ligands on a single site through a radical mechanism.\textsuperscript{151}

In thinking of ways to develop photochemical C–C bond formation, we drew inspiration from our recently discovered, bimolecular mechanism for H–H bond formation from a monohydride.\textsuperscript{29} Quantum yields of hydrogen production nearing unity can be achieved when irradiating [Cp*Ir(bpy)(H)]\textsuperscript{+} ([I]\textsuperscript{+}, Cp* is \(\eta^5\)-pentamethylcyclopentadienyl,
bpy is 2,2’-bipyridine) in the presence of acids in CH₃CN. The bond formation is initiated by electron transfer between the excited state [1]⁺* and the ground state [1]⁺, producing the reactive species Cp*Irᴵᴵ(bpy)(H) and [Cp*Ir⁴⁺(bpy)(H)]²⁺ that together form H₂. This mechanism allows a slightly endergonic excited state electron transfer process to be coupled to an exergonic bond formation.

Given that the Cp*Ir(bpy) scaffold facilitates efficient bimetallic coupling for H₂ evolution, we questioned whether substitution of a methyl group for the hydride could lead to C–C bond formation. Herein we report the synthesis and characterization of the methyl complex, [Cp*Ir(bpy)(CH₃)]⁺ ([2]⁺) and our mechanistic investigation of its photochemical C–C bond formation reactivity.

6.2 Results and Discussion

Characterization of an Ir methyl complex. Following the procedure of Chapter 3, the methyl complex [Cp*Ir(bpy)(CH₃)][I] ([2][I]) was synthesized by electrophilic methylation of the Ir(I) precursor Cp*Ir(bpy) (3). The ¹H NMR spectrum in CD₃CN shows the expected four aromatic resonances of bpy, the 15H singlet of Cp*, and an upfield 3H singlet at δ –0.04. The ¹³C NMR spectrum features a methyl resonance (δ –6.35).
Figure 6.1. Structural representation of [2][I] with ellipsoids drawn at the 50% probability level. Hydrogen atoms and iodide counter ion omitted for clarity. Selected distances (Å): Ir–C21 2.147(5), C5–C6 1.458(6)

Table 6.1. Crystal data and structure refinement for [2][I]

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<tr>
<td>Final R indexes [all data]</td>
<td>R₁ = 0.0303, wR₂ = 0.0647</td>
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Vapor diffusion of Et₂O into a solution of [2][I] in CH₃CN produced yellow crystals suitable for X-ray diffraction (XRD). Complex [2][I] takes on a ‘piano stool’ structure with a methyl ligand and an outer sphere iodide ion (Figure 6.1). Crystallographic data and refinement details are given in Table 6.1. The Ir–CH₃ distance (2.147(5) Å) falls into the
range of other reported Cp*Ir–CH₃ distances (2.03 to 2.22 Å). The Ir atom, however, is not centered below the Cp* ring: the carbons trans to methyl ligand form longer bonds to Ir (Ir–C13 2.235(5) Å and Ir–C14 2.236(4) Å) than those cis to methyl ligand (Ir–C11 2.186(4) Å, Ir–C12 2.176(4) Å, Ir–C15 2.189(4) Å). The structure of [Cp*Ir(bpy)(Cl)][ClO₄], by contrast, features Ir–C distances that do not vary around the cyclopentadienyl ring (2.163 Å). The structure of [1][PF₆]₁²₈ displays the same asymmetry found in the structure of [2][I], suggesting that this asymmetry is indicative of methyl and hydride ligands acting as strong σ-donors in [2][I] and [1][PF₆].

The structure of the Ir(III) complex [2]⁺ can be compared to its reduced Ir(I) precursor 3. The structure of [2][I] features a substantially longer C5–C6 distance (1.458(6) Å) than found in 3 (C5–C6 1.403(5) Å). The interpyridyl distance in [2][I] is similar to that of [Cp*Ir(bpy)(Cl)][ClO₄] (1.463(11) Å), in which the bpy is not considered to be partially reduced.

In acetonitrile, the UV-vis spectrum of [2]⁺ shows an absorbance with λᵥₐₓ = 418 nm (εᵥₐₓ = 3300 M⁻¹ cm⁻¹, Figure 6.2A). The absorbance of [2]⁺ is best fit by two Gaussian curves centered at 413 nm and 476 nm and estimated to have extinction coefficients of 3300 M⁻¹ cm⁻¹ and 1100 M⁻¹ cm⁻¹, respectively. To explore the nature of the orbitals involved in these transitions, we turned to time-dependent density functional theory (TD-DFT). The singlet ground-state structure of [2]⁺ was optimized using the M06 functional (LANL2DZ ECP basis set for the Ir atom and 6-311G** for all other atoms), modeling acetonitrile solvation with a polarized continuum model. Absorption properties in acetonitrile were explored using TD-DFT from the optimized ground-state geometry. The transitions at 450 nm (f' = 0.0161) and 442 nm (f' = 0.0937) reflect the observed spectrum: both calculation and
experiment feature two transitions under the MLCT with the weaker feature at a longer wavelength. According to TD-DFT, both transitions arise out of mixed HOMO and HOMO–1 states to the LUMO. The HOMO is a bonding interaction between a $d$-orbital of Ir and the $C-p_z$ orbital. HOMO–1, however, is an anti-bonding interaction between Ir-$d_{xz}$ and $C-p_x$ orbitals (Figure 6.2C). The LUMO is primarily bpy $\pi^*$-based.

Figure 6.2. A) Absorptivity (solid blue) and normalized emission (dashed red) of $[2]^+$ in CH$_3$CN solution. Excitation at 420 nm. B) Cyclic voltammogram of 1 mM $[2]^+$ in CH$_3$CN with 0.1 M [Bu$_4$N][PF$_6$] under and an atmosphere of N$_2$. Scan rate 0.25 V·s$^{-1}$. C) Orbitals from TD-DFT involved in the lowest energy transitions at 450 and 442 nm.
The absorbance spectrum of the analogous Ir hydride [1]+ in CH$_3$CN has a Gaussian MLCT transition at 428 (3000 M$^{-1}$ cm$^{-1}$), ascribed to a charge transfer from a $\sigma$ bonding HOMO (with Ir $d$-orbital and hydride $s$-orbital character) to a bpy $\pi^*$ LUMO.$^{73}$ While the LUMOs of [1]$^+$ and [2]$^+$ are similar, the presence of accessible $p$-orbitals in the carbon of the methyl ligand account for the differences in the spectra.

Upon irradiation into the MLCT absorbance of [2][I] (excitation at 420 nm), no steady state emission was observed at room temperature in CH$_3$CN. Hypothesizing that the iodide counter anion was quenching the excited state,$^{153}$ counter ion exchange was carried out by addition of excess NH$_4$PF$_6$ to a 9:1 H$_2$O:CH$_3$OH solution of [2][I], resulting in precipitation of [Cp*Ir(bpy)(CH$_3$)][PF$_6$] ([2][PF$_6$]) as a light yellow powder.

Metathesized salt [2][PF$_6$] is weakly emissive at room temperature. In CH$_3$CN solution, excitation at 420 nm produces a broad emission feature at 702 nm with a photoluminescence quantum yield of 0.04% (Figure 6.2A). The excitation spectrum aligns with the MLCT feature of the absorbance spectrum. The energy between the singlet ground state and the triplet excited state ($\Delta G_{ST}$) can be estimated by extrapolation of the high-energy edge of the emission feature to the baseline, giving $\Delta G_{ST} = 50 \text{ kcal}\cdot\text{mol}^{-1}$ (Figure 6.3).
Figure 6.3. Instrument and background corrected emission (green) of [2][PF₆] in CH₃CN solution with excitation at 420 nm. The extrapolation of the high energy edge used to measure ΔGₜ (dashed red) intercepts the x-axis at 17300 cm⁻¹ or 50 kcal·mol⁻¹.

The electronic structure of methyl complex [2]⁺ was investigated by cyclic voltammetry. A 1 mM solution of [2][PF₆] was prepared in CH₃CN containing 0.1 M [⁴Bu₄N][PF₆]. A reversible reduction (ΔEₚ = 77 mV, iₑᵝ/iₑᵢ = 0.94) of [2]⁺ was observed at E₁/₂ = −1.82 V and a pseudo-reversible oxidation (ΔEₚ = 95 mV, iₚᵣ/iₑᵝ = 0.30, 0.25 V·s⁻¹) was observed at E₁/₂ = 0.74 V (Figure 6.2B). The reduction, formally Ir(III) to Ir(II), may also be described as a bpy-based reduction, [2]⁺/[C₆Ir(III)(bpy⁻)](CH₃). The oxidation, formally [2]⁺/[C₆Ir(IV)(bpy)(CH₃)]₂⁺, extends across the Cp*, Ir, and CH₃ fragments according to our DFT.

Excited state reduction potentials can be calculated from the ground state potentials and ΔGₜ. The excited state can be reduced at E°(III*/II) = 0.35 V, and it can be oxidized at E°(III*/IV) = −1.42 V (Scheme 6.1).
Table 6.2. Comparison of electrochemical and photophysical features of [1]+ and [2]+.

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</tbody>
</table>

Our initial hypothesis was that methyl [2]⁺ might undergo similar excited state reactivity to hydride [1]⁺, which undergoes self-quenching electron transfer from an MLCT excited state. To determine the energetics of self-quenching of [2]⁺, the driving force for electron transfer between excited state [2]⁺* and its ground state [2]⁺ (Δ$G_{ET}^\circ$) can be determined using either an excited state and ground state potential ($0.74$ V – $0.35$ V = $0.39$ V) or according to eq. 6.1. Δ$G_{ET}^\circ$ is determined to be about 9 kcal·mol⁻¹ endergonic. Though a sizable barrier, it may be surmountable when coupled to a thermodynamically favorable chemical step, as has been observed for uphill electron transfers with [Ru(bpy)₃]²⁺.¹⁵⁴ Self-
quenching of $[1]^+$ is $\sim3$ kcal·mol$^{-1}$ endergonic and occurs with high efficiency at high concentration.$^{29}$

$$\Delta G^\circ_{\text{ET}} = 23.06(E^\circ(\text{IV/III})) - 23.06(E^\circ(\text{III/II})) - \Delta G_{\text{ST}} \quad (6.1)$$

From the comparison of electrochemical and photophysical properties of hydride $[1]^+$ and methyl $[2]^+$ in Table 6.2, and from the structural features discussed above, the electronic similarities of the complexes are apparent. The similarity of the emission features of $[1]^+$ and $[2]^+$ gives rise to similar $\Delta G_{\text{ST}}$: the value of $\Delta G_{\text{ST}}$ of $50$ kcal·mol$^{-1}$ determined here for $[2]^+$ falls within the range of $47 < \Delta G_{\text{ST}} < 52$ kcal·mol$^{-1}$ previously determined for $[1]^+$. While the reduction potentials of $[1]^+$ and $[2]^+$ are similar, the oxidation of $[2]^+$ is $240$ mV more positive than that of $[1]^+$. Additionally, this oxidation is noticeably more reversible for $[2]^+$ than for $[1]^+$. Fast scan rates ($200$ V·s$^{-1}$) were required to observe the re-reduction process for hydride $[1]^+$, but for methyl $[2]^+$, a reduction feature is apparent even at a scan rate of $0.05$ V·s$^{-1}$.

**Photochemical production of ethane and methane.** Encouraged by the similarities in the electronic structures of $[1]^+$ and $[2]^+$, we sought to probe for similarities in photochemical reactivity. Inspired by the ability of $[1]^+$ to undergo light-induced $\text{H}_2$ formation in the presence of a $\text{H}^+$ source, we considered the analogous reaction for $\text{C}–\text{C}$ bond formation: light-induced ethane formation from $[2]^+$ and a $\text{CH}_3^+$ source.

A CD$_3$CN solution of $[2][\text{PF}_6]$, excess CH$_3$I, and a mesitylene internal standard was illuminated with a $443$ nm LED for $3.5$ hours. $^1$H NMR spectroscopic analysis showed the characteristic resonances of ethane, methane, and propionitrile (Figure 6.4). Product yields were determined by measuring gaseous concentrations by GC and by measuring dissolved gasses by $^1$H NMR spectroscopy. Yields are reported relative to $[2]^+$ consumed in the
reactions. Ethane, methane, and propionitrile were produced in 19%, 39%, and 9% yield, respectively. *As hypothesized, photolysis of [2]+ forms C–C bonds.*

**Figure 6.4.** Representative $^1$H NMR spectrum of a 6.7 mM [2][PF$_6$], 0.1 M CH$_3$I with a 3 mM mesitylene internal standard in CD$_3$CN after irradiation with a 443 nm light source for 3.5 hours. The iridium species has been converted to [4]$^+$ while ethane, methane, and propionitrile have appeared.

The primary Ir-containing species after photolysis was [Cp*Ir(bpy)(I)]$^+$ ([4]$^+$, 95%). Iodide [4]$^+$ was observed by HR-MS in solutions after photolysis, and [4]$^+$ was also independently prepared by addition of 3 equiv NaI to a solution of [Cp*Ir(bpy)(OH)$_2$][OTf]$_2$ in CD$_3$CN. The resulting $^1$H NMR spectrum was consistent with the product of photolysis. The UV-vis spectrum of [4]$^+$ in CH$_3$CN shows absorbance at $\lambda_{\text{max}} = 375$ nm (2500 M$^{-1}$ cm$^{-1}$).

Weaker CH$_3$$^+$ sources were also investigated. Samples of [2][I] with CH$_3$OTs (OTs is tosylate) in CD$_3$CN were irradiated with 443 nm light for 22 hours, and ethane and methane, but not propionitrile, were observed by $^1$H NMR spectroscopy. The appearance of the same
products suggests that the reaction may be proceeding through the same mechanism as with CH$_3$I.

**Scheme 6.2. Possible reaction pathways of metal methyls from the excited state.**

**Mechanistic considerations.** Scheme 6.2 shows several possible reaction pathways from the excited state of [2]$^+$. Reactions that lead to bond breaking are shown in color and electron transfers are shown in black. To probe for CH$_3^+$ formation, [2]$^+$ was irradiated at 443 nm in CD$_3$CN with 7 equiv pyridine to act as a CH$_3^+$ trap through the formation of 1-methylpyridinium. No reaction was observed over 5 h of photolysis. To ensure that the reaction was not reversed upon stopping photolysis, Ir(I) complex 3 and 5 equiv 1,4-dimethylpyridinium iodide in CD$_3$CN were allowed to mix in the dark for 24 h. No methylation of 3 was observed; thus, the red pathway of Scheme 6.2 forming methyl cation is unlikely to be operative.

**Scheme 6.3. Pathways for ethane production from [2]$^+$.**
To investigate the other mechanistic possibilities, we examined the intermediates that would lead to ethane formation for two likely reactions: a self-quenching mechanism (Scheme 6.3, top) and a radical homolysis mechanism (Scheme 6.3, bottom). In the case of self-quenching, the methyl ligands of two equivalents of [2]+ couple in order to make ethane. Further reaction of resultant 3 with CH3I would regenerate [2]+. With a radical homolysis pathway, methyl radical reacts with CH3I to produce C2H6 and the resulting iodine atom traps [Cp*Ir(bpy)]+ to form [4]+. Though the products of these simplified mechanisms are indistinguishable, reactions from intermediate species can differentiate the two pathways.

Preliminary reactions gave indications of an intermediate methyl radical. In addition to CH4, partially-deuterated CH3D was formed (eq. 6.2) along with the distinctive 1:2:3:2:1 pentet (J_{HD} = 1.1 Hz) indicative of propionitrile isotopologue CH3CD2CN (eq. 6.3). Both results indicate D’ abstraction from the solvent CD3CN, which is a thermodynamically favorable reaction for ’CH3 (vide infra). Attempts were made to examine the solvent decomposition specifically, but photolysis in the absence of added substrate produced an intractable mixture of products, as occurs for [1]+.

\[
\begin{align*}
\text{’CH}_3 + \text{CD}_3\text{CN} &\rightarrow \text{CH}_3\text{D} + \text{’CD}_2\text{CN} & (6.2) \\
\text{’CD}_2\text{CN} + \text{CH}_3\text{I} &\rightarrow \text{I’} + \text{CH}_3\text{CD}_2\text{CN} & (6.3)
\end{align*}
\]

If ethane formation follows a self-quenching mechanism, ethane, 3 and [Cp*Ir(bpy)(NCCH3)]2+ would likely be the initial products, according to the top pathway of Scheme 6.3. We have shown that acetic acid will readily protonate reduced 3 to form [1]+.\textsuperscript{29,84} In the presence of AcOH, then, a reaction following a self-quenching pathway would be expected to initially form ethane and then form H2 as the [1]+ formed in situ reacts. Irradiation of [2][PF6] in the presence of excess AcOH produced CH4 and CH3D, observed
by $^1$H NMR and GC headspace analysis (Figure 6.5). Methane was detected in 50% yield, but only trace amounts of ethane were observed by $^1$H NMR spectroscopy and headspace GC analysis, and H$_2$ was not detected. The primary Ir-containing product was [Cp*Ir(bpy)(OAc)]$^+$ (86%). The absence of propionitrile in this reaction and in the reaction with CH$_3$OTs suggests that propionitrile is formed from a reaction between activated solvent and CH$_3$I. Detecting neither H$_2$ nor hydride [1]$^+$ suggests that Ir(I) complex 3 is not produced in situ.

**Figure 6.5.** $^1$H NMR spectra of 6 mM [2][PF$_6$] and 0.15 M AcOH in CD$_3$CN (bottom) photolyzed with 443 nm light for 3.5 hours (top). Methane and [Cp*Ir(bpy)(OAc)]$^+$ are the primary products.

**Evidence for a radical based mechanism.** To investigate the mechanism of ethane formation, unlabeled [Cp*Ir(bpy)($^{12}$CH$_3$)][PF$_6$] was photolyzed in the presence of labeled $^{13}$CH$_3$I. The isotope composition was tracked by $^1$H NMR spectroscopy over the course of a 30 min photolysis of [2][PF$_6$] and $^{13}$CH$_3$I with 443 nm light in CD$_3$CN. In that period, 20%
of methyl [2]⁺ had reacted to form iodide [4]⁺. During photolysis, ¹²CH₃ scrambled into the methyl iodide at approximately the same rate as [2]⁺ was consumed, but only a small amount of ¹³CH₃ (1% enrichment) was incorporated into [2]⁺. No isotopic scrambling was observed in the dark.

**Scheme 6.4. The initial steps of isotope scrambling**

These scrambling rates are telling of the initial steps in the reaction (Scheme 6.4). If Ir(I) complex 3 were formed in the course of the reaction and methyl [2]⁺ were regenerated by methyl iodide (as in Scheme 6.3, top), ¹³CH₃ would be expected to be incorporated into [2]⁺ at half the rate with which [2]⁺ is consumed. The observed rates fit a mechanism in which initial cleavage of the Ir–¹²CH₃ bond produces a radical pair that can either separate or recombine. Once separated, the ¹²CH₃ radical reacts with ¹³CH₃I to form ¹³CH₃ radical, which because of its excess in solution, becomes the dominant radical carrier. Recombination of the radical with [Cp*Ir(bpy)]²⁺ after the pair separates must be rare to account for the minimal ¹³C enrichment of [2]⁺.
Figure 6.6. Time course of dissolved methane and ethane during photolysis of [2]+ and $^{13}$CH$_3$I in CD$_3$CN, showing that incorporation of $^{13}$C into organic products outpaces that of $^{12}$C. $^{13}$CH$_4$ and $^{13}$CH$_3$D (closed red squares), $^{12}$CH$_4$ and $^{12}$CH$_3$D (open red squares), $^{13}$C in ethane (closed blue circles), $^{12}$C in ethane (open blue circles).

The dominance of $^{13}$CH$_3$ radical as the primary radical carrier in solution is also seen in the distribution of organic products. Because of the complex $^1$H NMR splitting pattern of $^{12}$CH$_3$,$^{13}$CH$_3$ and overlapping peaks from different isotopologues, precise quantification of the ethane distribution was untenable. Integration of the satellites gives the total concentration of $^{13}$C incorporated in ethane either in $^{12}$CH$_3$,$^{13}$CH$_3$ or $^{13}$CH$_3$$^{13}$CH$_3$ (Figure 6.6, closed blue circles) while the center peak gives $^{12}$C concentration in $^{12}$CH$_3$,$^{13}$CH$_3$ or $^{12}$CH$_3$$^{12}$CH$_3$ (Figure 6.6, open blue circles). Because this treatment is counting carbons individually, the ethane concentration is half the sum of the two measurements. About five times as much $^{13}$C is incorporated into ethane than $^{12}$C. Consistent with this, $^{13}$CH$_4$ and $^{13}$CH$_3$D were generated at a faster rate than $^{12}$CH$_4$ and $^{12}$CH$_3$D (Figure 6.7). These results suggest that the methyl radical that forms on irradiation undergoes non-productive radical reactions with the excess of $^{13}$CH$_3$I before forming methane or ethane.
Figure 6.7. Growth of $^{13}$CH$_4$, $^{13}$CH$_3$D, $^{12}$CH$_4$, and $^{12}$CH$_3$D over 443 nm 30 min of photolysis of 12.5 mM [2][PF$_6$] and 80 mM $^{13}$CH$_3$I in CD$_3$CN with a 3 mM mesitylene internal standard. The downfield satellite was used for $^{13}$C-containing methane integration.

Scheme 6.5. Reaction with radical trap TEMPO.

Figure 6.8. Concentrations from $^1$H NMR spectroscopy following the irradiation at 443 nm of a solution of 5.6 mM [2][PF$_6$] (black squares), 12 mM CH$_3$I, and 24 mM TEMPO in CD$_3$CN. TEMPO-CH$_3$ (red circles) grows in at twice the rate as iodide [4]$^+$ (blue triangles).
The decrease in \([\text{CH}_3\text{I}]\) (not shown) accounts for half of the methyl of TEMPO-\(\text{CH}_3\). Methyl \([2]^+\) is consumed at a slightly faster rate than \([4]^+\) appears: a minor iridium (open triangles, 10\%) containing species grows in as evidence of a side reaction.

Radical probes were employed to provide further evidence for the presence of free radicals during photolysis. Photolysis of 5.6 mM \([2]^+\) and 12 mM \text{CH}_3\text{I} in CD\(_3\)CN was carried out with 443 nm light for 90 min in the presence of 24 mM radical trap TEMPO. Irradiation exclusively produced TEMPO-\(\text{CH}_3\) to the exclusion of methane and ethane. The iridium product was \([4]^+\), which was formed at half the rate with which TEMPO-\(\text{CH}_3\) appeared (Scheme 6.5). Ir–\(\text{CH}_3\) homolysis will produce 1 equiv of TEMPO-\(\text{CH}_3\), and to account for rates and electrons, the formed [\text{Cp}^*\text{Ir(bpy)}]^+ must cleave \text{CH}_3\text{I} forming an additional equivalent of TEMPO-\(\text{CH}_3\) and the final species \([4]^+\).

**Scheme 6.6. Reaction of the radical clock complex, [5][Br].**
An intramolecular alkyl radical clock was also synthesized to probe radical intermediates. 5-hexenyl radical is known to quickly cyclize to form cyclopentylmethyl radical.\(^{156}\) To access this radical, an excess of 6-bromo-1-hexene was added to a purple solution of Ir(I) complex 3 in Et\(_2\)O and allowed to stir in the dark for 2 days. Over that time, a yellow solid precipitated from solution and was isolated by filtration and washed with ether giving \([\text{Cp}^*\text{Ir(bpy)}((\text{CH}_2)_4\text{CHCH}_2)]\)\([\text{Br}] ([5][\text{Br}])\).

Irradiation of a solution of [5][Br] in CD\(_3\)CN gave methylcyclopentane (confirmed by spiking with an authentic sample) and 1,5-hexadiene (Scheme 6.6). The Ir products were 3, [Cp*Ir(bpy)(Br)]\(^+\) and a new minor species. ESI-MS of the product mixture showed a peak at m/z = 567.23452. This is the same as the starting material [5]\(^+\) (calc m/z = 567.2351), but NMR data showed that the starting material was fully consumed (Figure 6.9); the same mass
would also be consistent with a ring-closed product \([\text{Cp}^*\text{Ir}(\text{bpy})(\text{CH}_2\text{C}_5\text{H}_9)]^+\). The presence of methylcylopentane in the product mixture is evidence for the homolysis of the Ir–C bond. Following homolysis, 1,5-hexadiene is formed by H• abstraction by \([\text{Cp}^*\text{Ir}^{\text{III}}(\text{bpy})]^+\) from the formed 5-hexenyl radical. This produces \([\text{Cp}^*\text{Ir}^{\text{III}}(\text{bpy})(\text{H})]^+ ([1]^+)\) which can supply the additional H atom equivalent need to form methylcyclopentane. The final Ir(I) and Ir(III) products could be formed by disproportionation of \([\text{Cp}^*\text{Ir}(\text{bpy})]^+\). Similar mechanisms for light-induced β-hydride elimination have been previously proposed for Ir\(^{157}\) and this is a common mechanism in cobalt alkyl photochemistry\(^{158,159}\).

**Differentiating mechanisms with excited state lifetime and kinetic order.** Ir–C bond homolysis could occur through either monometallic homolysis from the excited state (Scheme 6.2, blue) or following an electron transfer which weakens the Ir–CH\(_3\) bonds (Scheme 6.2, black). Excited state lifetimes and kinetic order were investigated to determine which of these pathways was operative.

Excited state lifetimes and luminescence quantum yields were investigated to look for self-quenching directly. No change in photoluminescent quantum yield was observed in the range of 0.02 mM to 0.6 mM of \([2]^+\) (Figure 6.10). The lifetime of \([2]^+\) was found to be 50 ns by time-correlated single photon counting, with no dependence on \([2]^+\) from 0.02 mM to 0.9 mM (Figure 6.11A). Both results indicate that \([2]^+\) is not efficiently quenched by \([2]^+\). Quenching by methyl iodide (\(E_{1/2} = -2.18\) V\(^{160}\)) was also investigated: no change in lifetime was observed to 1 M CH\(_3\)I (Figure 6.11B).
Figure 6.10. Self-quenching Stern-Volmer analysis for [2][PF$_6$] in CH$_3$CN at room temperature. $I_0$ is the emission extrapolated to infinite dilution. $I$ is the corrected and normalized emission at a given concentration of [2]$^+$. The absence of upward trend indicates the absence of self-quenching.

Figure 6.11. A) Photoluminescent lifetime of varying concentrations of [2][PF$_6$] in CH$_3$CN measured by time-correlated single photon counting. B) Photoluminescent lifetime of [2][PF$_6$] in CH$_3$CN with varying concentration of CH$_3$I. Laser excitation at 444.2 nm source with 73.3 ps pulse width at 2 MHz pulse rate. Emission detected at 680 nm with a 5 nm bandwidth. The independence of lifetime with concentration indicates the absence of quenching.

The reaction of [2]$^+$ and CH$_3$I in CH$_3$CN during irradiation with 443 nm light was also monitored by UV-vis spectroscopy in quartz cuvettes. The disappearance of the MLCT feature of [2]$^+$ was monitored at 443 nm, and quantum yields for the disappearance of [2]$^+$
were calculated over the course of 10% consumption. Samples which were photolyzed until no further change occurred were consistent with the spectrum of $[4]^+$ (Figure 6.12).

**Figure 6.12.** Representative experiment following the reaction of $[2][PF_6]$ with CH$_3$I in CH$_3$CN. The sample was irradiated at 443 nm ($1.58 \times 10^{-6}$ moles of photons min$^{-1}$) in 30 s intervals for the first 5 min (from the red trace to the blue trace) to calculate quantum yield. Photolysis for longer periods produces the green spectrum. The expected spectrum of $[4]^+$ is shown in the dashed black spectrum.

**Figure 6.13.** Dependence of quantum yield on [CH$_3$I] (blue squares) and $[[2]^+]$ (red circles) in CH$_3$CN photolyzed with 443 nm light. The dashed-line marks the constant concentration of CH$_3$I and $[2]^+$ (0.1 M and 0.14 mM respectively) held while the other reagent varied. The lack of dependence in CH$_3$I indicates the reaction is zero order in substrate, while the lack of dependence on $[2]^+$ indicates an overall first order as $[2]^+$ is the chromophore.

Order in Ir was determined using by monitoring the disappearance of $[2][PF_6]$ in an irradiated quartz cuvette in the presence of 0.1 M CH$_3$I in CH$_3$CN. The quantum yield for consumption of starting material remained constant at 1.0(5)% from 0.08 mM to 0.28 mM
[2]+ (Figure 6.13). Because calculating quantum yield includes normalizing for sample absorbance, a lack of dependence on the chromophore concentration indicates an overall first order dependence on chromophore [2]+. Order in CH₃I was determined by varying the concentration of substrate from 0.02 M to 0.3 M at constant [[2]+]. No dependence of quantum yield on substrate concentration was observed, indicating that the reaction is zero-order in CH₃I.

**Figure 6.14.** Dependence of quantum yield on [AcOH] (blue squares) and [[2]+] (red circles) in CH₃CN photolyzed with 443 nm light. The dashed-line marks the constant concentration of AcOH and [2]+ (0.1 M and 0.12 mM respectively) held while the other reagent varied. The lack of dependence in AcOH indicates the reaction is zero order in substrate, while the lack of dependence on [2]+ indicates an overall first order as [2]+ is the chromophore.

Order in Ir and substrate was similarly investigated for the reaction of [2]+ in the presence of AcOH to probe the reaction with a different substrate. Variation of [2]+ concentration from 0.8 mM to 0.21 mM in the presence of a constant 0.1 M AcOH in CH₃CN resulted in no change in quantum yield (1.7(5)%, Figure 6.14). To probe higher iridium concentrations, solutions of 1 mM to 8 mM [2]+ in CD₃CN and 0.1 M AcOH were irradiated in standard NMR tubes with 443 nm light and monitored by ¹H NMR spectroscopy. No
change in quantum yield was observed. Varying [AcOH] caused no change in quantum yield, indicating a zero-order dependence on substrate.

Figure 6.15. Growth of Ir-containing products on 443 nm photolysis of 1 mM (red), 2 mM (purple), 4 mM (blue), and 8 mM (green) [2][PF$_6$] in CD$_3$CN with 10 mM AcOH. The consistent increases indicate quantum yield is not changing across this concentration range.

Additionally, if a bimolecular reaction of two cationic iridium species were occurring, one might expect an increase in quantum yield on addition of electrolyte. Quantum yields for the disappearance of [2]$^+$ with and without 0.1 M [$^+$Bu$_4$N][PF$_6$] were identical in four trials with concentrations of [2]$^+$ at 0.07 and 0.18 mM with 0.05 M AcOH acid, indicating that the reaction does not involve the close approach of two charged species.

From a kinetic analysis indicating that the reaction is first-order in [2]$^+$ and zero-order in substrate, several characteristics of the reaction become apparent. The first is that bimolecular self-quenching cannot play a significant role in the reaction. The second is that reactions involving the added organic methyl source must occur after the rate-determining step. Additionally, the radical chain is not significantly propagated through radical attack on [2]$^+$ to produce either Ir(II) or methyl radical. Such a process would result in an additional pathway consuming [2]$^+$ and typically results in 3/2 order in [2]$^+$.\textsuperscript{161}
Many of the species that would be formed to continue propagation of methyl radical in solution—ICH$_2$CN and I$_2$—have particularly weak bonds (44.7 and 36.4 kcal·mol$^{-1}$, respectively$^{162}$) and are unlikely to be generated in high concentrations. Indeed, attempts to detect ICH$_2$CN by photolyzing a solution of [2][PF$_6$] with excess CH$_3$I in 9:1 CH$_3$CN:CD$_3$CN produced no iodoacetonitrile by $^1$H NMR spectroscopy (Figure 6.16).

Instead, evidence for another C–C bond forming event was observed: half an equivalent of succinonitrile ((CH$_2$CN)$_2$) was detected per [2]$^+$, presumably produced by the termination of two acetonitrile radicals. Given that iodide [4]$^+$ was formed in this reaction as well, CH$_3$I must be involved in other radical reactions, and therefore, short chain reactions must occur.

![Figure 6.16](image)

**Figure 6.16.** $^1$H NMR spectrum of [2][PF$_6$] and 0.1 M CH$_3$I in 9:1 CH$_3$CN:CD$_3$CN photolyzed with 443 nm light for 3.5 hours. Methane, succinonitrile, and [4]$^+$ are formed.

Succinonitrile could not be detected in experiments in CD$_3$CN because it would be fully deuterated and $^1$H NMR silent, and it is not volatile for GC detection. Curiously, ethane was not detected in this experiment, which suggests that the slightly more inert C–D bond of
CD$_3$CN encourages ethane formation. Given the difference in product distribution in protio and deutero solvent, we investigated the quantum yield for the reaction of [2]$^+$ in CD$_3$CN with CD$_3$I and found no decrease. Therefore, the isotope effect is product-determining, but not rate-determining. Either initial homolysis or solvent separation of the radical pair is likely the rate-determining step.

Table 6.3. Relevant bond dissociation energies.

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<tr>
<td>H$_3$C–Ir(Cp*)(PMe$_3$)(CH$_3$)</td>
<td>56</td>
<td>164</td>
</tr>
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**Understanding the preference for homolysis.** The collected data indicate that ethane and methane are produced following monometallic Ir–CH$_3$ bond homolysis from the excited state. Bond dissociation enthalpies relevant to this discussion are collected in Table 6.3. Deuterium atom abstraction by •CH$_3$ from CD$_3$CN forms CH$_3$D. Methyl radical is thermodynamically capable of abstracting a hydrogen atom from acetonitrile.$^{162}$ The absence of propionitrile in reactions with AcOH and CH$_3$OTs suggests that propionitrile-d$_2$ results from the reaction of •CD$_2$CN with CH$_3$I. Ethane could be formed either in a reaction of •CH$_3$
with CH₃I or in a termination step upon recombination of two methyl radicals. Addition of I• to the primary Ir photoproduct [Cp*IrH(bpy)]⁺ offers an organometallic termination pathway that affords the observed iodide complex.

To better understand the mechanism change from electron transfer with [1]⁺ to homolysis with [2]⁺, relevant thermodynamic parameters were considered. One possibility is that homolysis of an Ir–CH₃ bond is thermodynamically favorable relative to homolysis of an Ir–H bond. While the hydrogen atom and methyl radical are almost equally stable (ΔH(H–H) = 104 kcal·mol⁻¹ while the ΔH(H₂C–H) = 105 kcal·mol⁻¹), related systems suggest that the bond dissociation enthalpies of Ir–H in [1]⁺ and Ir–CH₃ in [2]⁺ may differ dramatically. The most similar system for which M–CH₃ and M–H bond strengths have been measured is Cp*Ir(PMe₃)X₂ (where X = H, CH₃). In this system, ΔH(Ir–H) = 74 kcal·mol⁻¹ while ΔH(Ir–CH₃) = 56 kcal·mol⁻¹. This ~20 kcal·mol⁻¹ decrease in bond dissociation enthalpy from ΔH(Ir–H) to ΔH(Ir–CH₃) is consistent with other Ir systems in which both have been measured. This is a striking difference, especially when considered in light of the overall similarity of [1]⁺ and [2]⁺.

Homolysis is also consistent with the nature of the orbitals involved in the MLCT transition. The largest contribution to the excitation depopulates a σ bond between Ir and CH₃ (HOMO, Figure 6.2C). Irradiation of this transition would, therefore, be expected to weaken the Ir–C bond.

While a more accessible homolysis pathway explains much of the observed chemistry, the differences in quantum yields for [1]⁺ and [2]⁺ suggest that there may be other factors. The quantum yields for conversion of [2]⁺ are low, especially when compared with quantum yields for H₂ evolution for [1]⁺ that approach unity. Homolysis may be out-
competing electron transfer, and low quantum yields could be a result of efficient recombination from the radical pair. Alternatively, the discrepancy may be explained by self-quenching being thermodynamically inaccessible. As discussed above, self-quenching for \( [2]^* \) and \( [2]^+ \) lies 9 kcal·mol\(^{-1}\) uphill. This is a larger barrier than for \( [1]^* \) and \( [1]^+ \) (3 kcal·mol\(^{-1}\)) and may, indeed, be insurmountable even with a following reaction. Such self-quenching reactions are often kinetically limited as well. Self-quenching of \([\text{Ru(bpy)}_3]^{2+}\) with its excited state is thermodynamically favorable, but only occurs when suitable electron donors and acceptors are included in solution.\(^{165,166}\) In the absence of a viable electron transfer pathway for \( [2]^+ \), homolysis provides a feasible pathway to dissipate the energy of the excited state.

### 6.3 Conclusions

A new iridium methyl complex, \([\text{Cp*Ir(bpy)(CH}_3\text{)}]^+\), was prepared and characterized. Photolysis of this complex forms C–C bonds: ethane, propionitrile, and succinonitrile are all formed. The mechanism of C–C bond formation was shown to proceed through monometallic radical homolysis, rather than the bimetallic electron transfer mechanism that led to H–H bond formation from \( [1]^+ \). The minor structural change of substituting a methyl ligand for a hydride ligand, despite modifying the electrochemical and photophysical properties of the molecule only slightly, was sufficient to give rise to drastically different reactivity. Comparison of the bond dissociation enthalpies of similar complexes suggests that the change in mechanism can be explained by the weaker Ir–CH\(_3\) bond in comparison to the Ir–H bond. The dramatic differences underscore the changes in reactivity that can be observed on minor synthetic variation.
6.4 Experimental Section

General Considerations. Procedures were carried out under nitrogen except where noted. All solutions containing metal methyl species were protected from ambient light during preparation to prevent excited state reactions. All reagents were commercially available and used without further purification. Organic solvents were dried and degassed with argon using a Pure Process Technology solvent system. Deuterated solvents were purchased from Cambridge Isotope Laboratories, Inc and degassed with three freeze-pump-thaw cycles before storing over sieves in a N₂ glovebox. UV–vis spectra were obtained using an Ocean Optics USB2000+ spectrometer with a DTMINI-2GS deuterium/tungsten halogen light source controlled by OceanView software. NMR spectra were obtained on 400, 500, or 600 MHz spectrometers. ¹H and ¹³C NMR spectra were referenced to the residual solvent signals. Spectra were processed using the MestReNova software suite from Mestrelab Research S. L. Mass spectrometry was carried out with an LTQ FT (ICR 7T) (ThermoFisher, Bremen, Germany) mass spectrometer. Samples (in acetonitrile solution) were introduced via a microelectrospray source at a flow rate of 3 μL/min. Xcalibur (ThermoFisher, Breman, Germany) was used to analyze the data. Molecular formula assignments were determined with Molecular Formula Calculator (v 1.2.3). For ICP-MS, samples were prepared in 2% nitric acid solution diluted with 18.2 MΩ/cm water and were analyzed with an Element XR inductively coupled plasma (ThermoFisher, Bremen, Germany) mass spectrometer (ICP-MS). Samples were introduced via a peristaltic pump connected to an Elemental Scientific SC autosampler (Omaha, Nebraska). Iridium 193 was monitored in low resolution mode for 30 sec for each sample (~300 scans). All UV-vis and photoluminescence samples were prepared in an N₂ glovebox in 1 cm path length 4-sided quartz cuvettes, sealed with
screwcaps, and reinforced with parafilm on removing from the glovebox, unless otherwise noted. Single-crystal X-ray diffraction data were collected on a Bruker APEX-II CCD diffractometer at 100 K with Cu Kα radiation (\(\lambda = 1.54175\) Å). Using Olex2,\textsuperscript{95} the structures were solved with the olex2.solve\textsuperscript{96} structure solution program using Charge Flipping and refined with the XL\textsuperscript{97} refinement program using least squares minimization. The complex Cp*Ir(bpy) was prepared following literature procedures.\textsuperscript{126}

**Electrochemistry.** Cyclic voltammograms were measured with glassy carbon working electrodes (polished with 0.3 and 0.05 μm alumina powder before use), platinum wire counter electrodes, and a Ag pseudo-reference electrode. An undivided cup cell was used. Experiments were carried out in an N\textsubscript{2} filled glovebox using a Pine WaveNow potentiostat controlled by Aftermath software connected to a computer outside of the glovebox by a custom USB feed through. Ferrocene was added at the end of data collection, and all potentials are reported relative to the Fc\textsuperscript{0+/+} couple.

**Photoluminescence Studies.** Steady-state emission and excitation spectra were recorded at room temperature on a Photon Technology, Inc. Quantamaster 4SE-NIR5 spectrometer PC-controlled by FelixX32 software. Excitation light was provided by a 75 W Xenon light source coupled to a single monochromator outfitted with a 1200 L/mm grating blazed at 400 nm. A 300 nm long pass filter was placed before the sample to prevent deep UV excitation from a second order grating effect. Emission was collected at a right angle relative to excitation, focused into a single monochromator (grating blazed at 500nm with 1200 L/mm) and detected by a Hamamatsu R928P photomultiplier tube used in single photon counting mode. Slit widths for both emission and excitation monochromators were fixed at 0.5 mm. All spectra were corrected for system response.
Absolute photoluminescence quantum yield was measured on an Edinburgh FLS-920 emission spectrophotometer with detection by a Hamamatsu R2658P photomultiplier tube to count photons to 950 nm by which wavelength the phosphorescence had decayed to zero. Photoluminescent lifetimes were measured by time-correlated single photon counting on the Edinburgh instrument with excitation by a 443 nm, 73.3 ps width laser.

**Synthesis.** \([\text{Cp}^*\text{Ir(bpy)(CH}_3\text{)}][\text{PF}_6]\) ([2][PF6]). In air, complex [2][I] (54.1 mg, 0.086 mmol) was dissolved in 75 mL 9:1 H2O:MeOH. Excess [NH4][PF6] (160 mg) was added as a solid resulting in the immediate precipitation of a fine yellow solid. The solid was separated by filtration through a fine frit and flushed with water resulting in 49.8 mg [2][PF6] (0.077 mmol, 89% yield). 1H NMR (600 MHz, CD3CN, Figure 6.17) δ 8.67 (d, \(J = 5.7\) Hz, 2H), 8.43 (d, \(J = 8.1\) Hz, 2H), 8.08 (t, \(J = 7.8\) Hz, 2H), 7.60 (t, \(J = 6.6\) Hz, 2H), 1.68 (s, 15H), -0.04 (s, 3H). 13C NMR (151 MHz, CD3CN, Figure 6.18) δ 156.01, 152.45, 139.07, 129.00, 125.33, 90.85, 8.70, -6.36. Anal. Calcd for C21H26F6IrN2P: C, 39.19; H, 4.07; N, 4.35. Found: C, 38.94; H, 3.89; N, 4.15.
Figure 6.17. $^1$H NMR spectrum of [Cp*Ir(bpy)(Me)][PF$_6$] ([2][PF$_6$]) in CD$_3$CN.

Figure 6.18. $^{13}$C-$^1$H NMR spectrum of [Cp*Ir(bpy)(Me)][PF$_6$] ([2][PF$_6$]) in CD$_3$CN.
$[\text{Cp}^*\text{Ir(bpy)}(\text{I})]^+$ ([4]$^+$). $[\text{Cp}^*\text{Ir(bpy)}(\text{I})]^+$ was prepared by addition of 3 eq NaI to 3.9 mg $[\text{Cp}^*\text{Ir(bpy)}(\text{OH}_2)][\text{OTf}_2]$. $^1\text{H NMR}$ (500 MHz, CD$_3$CN, Figure 6.19) δ 8.88 (d, $J = 5.7$ Hz, 2H), 8.46 (d, $J = 8.1$ Hz, 2H), 8.18 (t, $J = 8.1$ Hz, 2H), 7.75 – 7.71 (m, 2H), 1.74 (s, 15H).

$\lambda_{\text{abs, max}}$ (CH$_3$CN, Figure 6.20) = 375 nm (2500 M$^{-1}$ cm$^{-1}$).

**Figure 6.19.** $^1\text{H NMR}$ spectrum of $[\text{Cp}^*\text{Ir(bpy)}(\text{I})]^+$ ([4]$^+$) in CD$_3$CN.

**Figure 6.20.** Absorptivity of $[\text{Cp}^*\text{Ir(bpy)}(\text{I})]^+$ in CH$_3$CN. Sample prepared by addition of 3 equiv NaI to a solution of $[\text{Cp}^*\text{Ir(bpy)}(\text{OH}_2)][\text{OTf}_2]$. Ir concentration determined by ICP-MS.
To a purple stirring solution of **Cp*Ir(bpy)((CH$_2$)$_4$CHCH$_2$)][Br]** ([5][Br]). To a purple stirring solution of Cp*Ir(bpy) (5.1 mg, 0.01 mmol) in Et$_2$O was added excess 6-bromo-1-hexene (20 µL). The solution was allowed to stir for 3 days over which a yellow solid precipitated, which was filtered to separate and washed 3x with ether giving 5.2 mg [5][Br]. (0.008 mmol, 77%). The solid was assessed to be 93% pure by $^1$H NMR. **$^1$H NMR** (600 MHz, CD$_3$CN, Figure 6.21) δ 8.68 (dt, J = 5.8, 1.1 Hz, 2H), 8.53 – 8.49 (m, 2H), 8.12 (td, J = 7.9, 1.4 Hz, 2H), 7.64 (ddd, J = 7.3, 5.7, 1.4 Hz, 2H), 5.65 – 5.53 (m, 1H, Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 4.83 – 4.73 (m, 2H, Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 1.74 (q, J = 7.3 Hz, 2H, Ir-CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 1.68 (s, 15H), 1.00 (p, J = 6.9 Hz, 2H, Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 0.85 – 0.77 (m, 4H, Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$). **$^{13}$C NMR** (151 MHz, CD$_3$CN, Figure 6.22) δ 154.98, 151.18, 139.03 (Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 137.64, 127.58, 124.06, 113.51 (Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 89.97, 32.96 (Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 32.78 (Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 29.58 (Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 12.48 (Ir-CH$_2$CH$_2$CH$_2$CH$_2$CHCH$_2$), 7.24.
Figure 6.21. $^1$H NMR spectrum of [Cp*Ir(bpy)((CH$_2$)$_4$CHCH$_2$)][Br] ([5][Br]) in CD$_3$CN.

Figure 6.22. $^{13}$C($^1$H) NMR spectrum of [Cp*Ir(bpy)((CH$_2$)$_4$CHCH$_2$)][Br] ([5][Br]) in CD$_3$CN.
Representative photolysis monitored by $^1$H NMR spectroscopy. In a nitrogen filled glovebox, 4.8 mg [2][PF$_6$] was dissolved in 1 mL CD$_3$CN. 0.98 mL of this solution were transferred to a vial containing 6 µL MeI and 20 µL of a 150 mM mesitylene solution in filtered CD$_3$CN was added as an internal standard. The solution was split between two screw cap NMR tubes. $^1$H NMR spectra were recorded after removing the tubes from the glovebox and reinforcing the seal with parafilm. One tube remained wrapped in aluminum foil, while the other was irradiated with 443 nm light (Thor Multi-channel) until [2]$^+$ had fully reacted. Using a gas-tight, locking syringe, 0.3 mL of the headspace was removed and analyzed by GC to determine yields of methane and ethane.

Representative photolysis monitored by UV-vis spectroscopy. Samples for analysis by UV-vis spectroscopy were typically prepared in sets of four. In a nitrogen filled glovebox, excess CH$_3$CN was filtered through a pipet filter to remove sieve dust from storage. Stock solutions of [2][PF$_6$] and CH$_3$I were prepared, and delivered to the cuvettes with volumetric syringes. The total volume of solution was brought to 2 mL by addition of CH$_3$CN. After capping with screwcap, the samples were removed from the glovebox, parafilmed around the cap, and stored in the dark. Samples were photolyzed sequentially. Each was irradiated in 30 s segments (Thor Multi-channel, 2.37 x 10$^{-6}$ moles of photons min$^{-1}$, determined by chemical actinometry$^{29}$) followed by collection of a UV-vis spectrum. Samples were photolyzed for a total of 3 min.

Computational Methods. Geometry optimizations, frequency, and time-dependent calculations were done using the hybrid functional M06 as implemented in Gaussian 09$^{140}$ with the LANL2DZ ECP basis set$^{167,168}$ for the iridium atom and 6-311G** for all other atoms. The PCM implicit solvation models (CH$_3$CN solvent) was employed for all
calculations. This strategy has been effective for Ir TD-DFT in the literature.\textsuperscript{169,170} Calculations were analyzed using the Chemcraft suite.
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