Catalysts for Molecular Photoelectrochemical Hydrogen Evolution

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Abstract

Production of hydrogen from light-driven water splitting, photoelectrochemical hydrogen evolution for example, is an attractive method to store solar energy. Typically, photoelectrocatalytic systems require an expensive high purity semiconductor light absorber (e.g. silicon) and a precious metal heterogeneous catalyst (e.g. platinum). The Miller group recently reported a semiconductor-free approach to photoelectrochemical hydrogen evolution with a single homogeneous photoelectrocatalyst, $[Cp*Ir(2,2'-bipyridine)(H)]^+$ (Cp* = pentamethylcyclopendienyl). To better understand this approach to hydrogen production, a series of structural analogues have been prepared and analyzed. Ligand alteration changes the characteristics of the catalyst and understanding the influence of different ligands will guide future catalyst design. Complexes containing pyridine, di(2-pyridyl)ketone, and various alpha-diimine ligands have been synthesized and studied using electrochemical techniques such as cyclic voltammetry and chronoamperometry under irradiation. A new catalyst, $[Cp*Ir(pyridine)_2(Cl)][OTf]$, has been discovered for molecular photoelectrochemical hydrogen evolution.

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1. Introduction

This research investigates how to store energy from visible light in chemical bonds by using hydrogen evolving molecular photoelectrocatalysts. The modern energy economy is based on burning fossil fuels, which produce carbon dioxide, a greenhouse gas accumulating in Earth's atmosphere.¹ With the growing demand for energy and diminishing fossil fuel sources, clean pathways for producing energy are being explored. The sun, which irradiates the Earth with more energy in one hour (4.3•10²⁰ J) than the whole world consumes in a year (4.25•10²⁰ J), has inspired research into capturing and storing sunlight to meet energy demands.²

Unlike commercial photovoltaics which produce electricity directly, production of hydrogen has been proposed as a way to store solar energy. Light energy can be stored by splitting water into hydrogen and oxygen. The idea is simple: break the bonds in water and form a new, higher energy bond between two hydrogens. Subsequent combustion of hydrogen produces water: it does not form any carbon dioxide.

One method for hydrogen evolution is photoelectrochemical water-splitting. Typically, photoelectrocatalytic systems require a light absorber like a semiconductor (e.g. silicon) and a hydrogen producing catalyst (e.g. platinum). When a photon is absorbed by the semiconductor, an electron is promoted to the conduction band. The electron is then transferred to the platinum which catalyzes the formation of the H-H bond.³

Recent research from the Miller Group has developed a single homogeneous complex that both absorbs light to form hydrogen and is regenerated by electrons.⁴ The molecular photoelectrocatalyst studied is $[Cp*Ir(bpy)(H)]^+$ (Cp* = pentamethylcyclopendienyl, bpy = 2,2'-



bipyridine), as shown in the catalytic cycle in Figure 1. [Cp*Ir(bpy)(Cl)]Cl undergoes a two electron reduction and, in neutral water, is protonated to become [Cp*Ir(bpy)(H)]⁺. When the complex is irradiated at 460 nm, H₂ is released, regenerating the

Figure 1. The prototype complex, $[Cp*Ir(bpy)(H)]^+$ showing the desired molecular photoelectrocatalyst activity. The catalytic cycle involves forming the hydride from the chloride.

catalyst. Because the photoelectrochemical production of H_2 by a single homogeneous complex is a novel approach, interest has turned to exploring the limits of this system by changing the structure of the complex. Analyzing different ligands changes the chemical structure and electronics of the complex. Through comparison to $[Cp*Ir(bpy)(Cl)]^+$, the ligand features that are important for molecular photoelectrochemical hydrogen evolution can be determined.

New molecular photoelectrocatalysts were synthesized and analyzed by using different ligands in place of bpy. [Cp*Ir(bpy)(H)]⁺ and closely related complexes combine photochemical and electrochemical process into a single catalytic cycle, but greater activity at lower applied potentials is sought. Modifications to bpy can move the reduction to lower potentials, but the complex can simultaneously become more acidic and less stable.



 Figure 2. The ligands that were used for analysis of the molecular photoelectrochemical hydrogen
 ligands of Figure 2

 evolution are shown above.
 each possess desired features to help for the determination of the structural requirements for

 molecular photoelectrochemical hydrogen evolution

The alpha-diimine ligands were chosen because the conjugation is different between the nitrogen rings from the bpy. Alpha-diimine ligands have been known to catalyze hydrogen transfer to ketones in ruthenium complexes⁵ and to help form stereospecific polymerizations in palladium complexes.⁶ Half-sandwich iridium complexes with these ligands formed novel compelxes. The two alpha-diimine ligands chosen were 1,4-diphenyl-2,3-dimethyl-1,4-dizabutadiene (pm-DAB) and bis[N-(p-tolyl)imino]acenaphthene (p-tolyl BIAN) to determine if the hydrogen evolving catalytic cycle can occur without the nitrogen being part of an aromatic ring.

The pyridine ring was used to make a bis-pyridine product. $[Cp*Ir(pyridine)_2(Cl)]^+$ determined if the two rings require a connection between them to produce the desired results and to form a stable complex. To study the effects of electron withdrawing groups on the reduction potential, were added to the para position of the pyridine.

Di(2-pyridyl)ketone (dpk), has similar features to pyridine, but with some conjugation between the pyridine rings. Dpk has been used on palladium catalyst to help in alkene activation.⁷ The dpk ligand helped with the determination of if the connection between the rings is important for the observed reactivity. The connection between the rings might help defer ligand loss during photochemical processes. The goal was to study each of these ligands on the iridium catalyst to find a stable alternative for molecular photoelectrochemical hydrogen evolution.

For catalytic turnover in molecular photoelectrochemical hydrogen evolving systems, the hydride must be electrochemically generated and then, with the assistance of a photon, protonated by water to release H₂. The analyses for the electrochemical reduction were conducted using electrochemical techniques, cyclic voltammetry. Photochemical hydrogen formation was analyzed using Chronoamperometry, comparing experiments in the light and the dark.

2. Results

2.1 Synthesis and Characterization of [Cp*Ir(Cl)(dpk)]Cl

[Cp*Ir(Cl)(di-pyridyl ketone)]Cl (1) was prepared from $[Cp*Ir(Cl)_2]_2$ and di(pyridyl) ketone following a modification of the synthesis of $[Cp*Ir(Cl)(bpy)]Cl.^8$ The complex was determined to be pure by ¹H NMR.

The dpk ligand has been observed to attach to the iridium catalyst at the oxygen as well as the nitrogen (Figure 3),⁹ which could affect the formation of the hydride. The NMR [¹H



Figure 3.In the DPK ligand, the oxygen is known to coordinate to the metal center.

NMR(CD₃CN): δ 8.94 (d, 2H), 8.23 (m, 4H), 7.88 (ddd, 2H), 1.32 (s, 15H)] shows that complex with the nitrogen bonding if formed with comparison to literature values on rhodium.⁹

In order to determine the potentials that electron transfer occurs, cyclic voltammetry was used. In a Cyclic Voltammogram (CV), the potential is changed at variable rates and the current



passing through the electrodes is measured. [Cp*Ir(bpy)(Cl)]Cl has two reduction potentials, one for the two electron

Figure 4.. The steps for the reduction of $[Cp*Ir(bpy)(Cl)]^+$ as identified through CV.

transfer to form the hydride $[Cp*Ir(bpy)(H)]^+$ and a more negative one electron transfer for the Ir-H^{III}/Ir-H^{II} reduction. This suggests the two electron process forms Cp*Ir(bpy) and is followed by rapid pronotation. The reaction is shown in Figure 4 for $[Cp*Ir(bpy)(Cl)]^+$.

CVs in 0.1 M pH 7 phosphate buffer of [Cp*Ir(Cl)(dpk)]Cl showed three irreversible reduction features at – 0.62 V,–

0.72 V and at – 1.2 V referenced to an Ag/AgCl electrode as shown in Figure 5. During the course of the experiment, the first peak decreased in current while the second peak grew as the solution changed from yellow to clear.



Figure 5. The CVs for [Cp*Ir(Cl)(dpk)]Cl in 0.1 M pH 7 phosphate buffer.

[Cp*Ir(dpk)(Cl)]⁺ decomposed in water over time accounting for the color change in the solution which is due to loss of the ligand.

To analyze photochemical H₂ formation, chronoamperometry (CA) was used with the added variable of light produced either by a 460 nm LED lamp or a broad spectrum white tungsten halogen lamp. Chronoamperometry tracks the change in current over time at a fixed potential; we changed the variable of light to see if photochemistry was involved. The CA measurement taken at -0.8 V showed that the complex was not active under these conditions. A ¹H NMR spectrum showed that [Cp*Ir(dpk)(Cl)]⁺ was not stable in methanol, with six peaks compared to the three expected in the aromatic region indicating that two different complexes were being present. Mass spectrometry analysis was completed to determine that in one of the products a methoxy group was replacing the chloride to form [Cp*Ir(OCH₃)(dpk)]Cl. Electrochemical studies of [Cp*Ir(dpk)(Cl)]⁺ completed in a acetonitrile solution did not pass a higher current when exposed to light, but irreversible reduction peaks were observed at -1.01 V and -1.85 V referenced to Ag/AgCl.

2.2 Synthesis and Characterization of [Cp*Ir(Cl)(p-tolyl BIAN)]Cl





Using an analogous method used for (1), [Cp*Ir(Cl)(p-tolyl BIAN)]Cl (3) was formed. The complex was deteremined to be pure by ¹H NMR.

Electrochemical analysis was completed in 0.1 M pH 7 phosphate buffer which revealed a

peak at -0.32 V was believed to be the hydride oxidation peak. As 1 M H_3PO_4 was added, the oxidation decreased to the extent seen in Figure 6, but did not disappear even under very acidic conditions (pH 1.15). This oxidation peak could be due to some silver being in present in the solution. The disappearance of the more negative potential at -0.61 V could be the $Ir^{I/III}$ transition. There was no light dependence observed with 460 nm LED lamp in these conditions.

2.3 Synthesis and Characterization of [Cp*Ir(Cl)(pm-DAB)]Cl

Using an analogous method for (1), [Cp*Ir(Cl)(pm-DAB)]Cl (2) was formed.



Figure 7. The CVs for [Cp*Ir(Cl)(pm-DAB)]Cl in 0.1 M pH 7 phosphate buffer with the addition of $1M H_3PO_4$.

Electrochemical analysis was started in 0.1 M pH 7 phosphate buffer. A reversible reduction peak was observed at -0.44 V. 1 M H₃PO₄ was added to the solution and the oxidation peak decreased in current. The current increased when exposed to white light as CVs were taken at slow scan rates suggesting a slow electron transfer reaction was occurring. This increase in current is shown in Figure 7.

Bulk electrolysis, which holds the electrode at one potential for an extended time, was used to isolate the product of the reduction in hopes of forming a hydride. Bulk electrolysis at -0.6 V in 1 M HCl was completed in the dark to form the hydride. During this experiment, the complex decomposed into an opaque white solid and a yellow solution suggesting that the complex was not stable under these conditions.

Synthesis and Characterization of [Cp*Ir(Cl)(py)₂]OTf

The synthesis of $[Cp*Ir(Cl)(py)_2]OTf(4)$ was carried out using a procedure that was by analogous to that used for the preparation of (1). The ¹H NMR

exhibited a 8:30 ratio of aromatic pyridine protons to Cp* protons. From literature, the ratio suggested the



Figure 8. The synthesis of the bis-pyridine complexes required the addition of silver triflate.

[Cp*Ir(Cl)₂(pyridine)]⁺ was formed. The addition of silver triflate to the synthesis formed the



desired

 $[Cp*Ir(Cl)(py)_2]OTf.$ ¹⁰

CVs taken in 0.1 M

pH 7 phosphate buffer

show a reduction wave at -

1.32 V and an oxidation

wave at -0.03 V. The CAs

Figure 9. Rate of catalysis for $[Cp*Ir(Cl)(py)]_2OTf$ with blue light

showed increase in current under irradiation at -1.65 V with the blue lamp and white lamp. The rate of catalysis with blue light was calculated to be 0.014 s^{-1} , which is half the rate for $[\text{Cp*Ir(bpy)(Cl)}]^+$ hydrogen evolution. The rate was calculated by taking CAs of 0.1 M pH 7 phosphate buffer solution with $[\text{Cp*Ir(Cl)}(\text{py})_2]$ OTf in both the dark and with blue light exposure at different potentials. The rates were background corrected by subtracting out the CAs taken at the same potentials in 0.1 pH 7 phosphate buffer solutions without any complex present in the solution.

Electrolysis at -1.55 V protected from light for 90 min produces a red-orange solution from a light yellow starting material. Three peaks were observed in the hydride region of the ¹H NMR, -9.94 ppm, -12.87 ppm, and -15.54 ppm meaning that three different hydride complexes were formed. It is likely that one or both of the ligands could have been removed from the complex which would give the other hydrides. When the NMR tube was photolysized, the peak at -9.94 ppm decreased while the two other hydride peaks remained a constant intensity. In [Cp*Ir(bipyridine)(Cl)]⁺, the hydride forms the chloride complex and hydrogen gas when exposed to blue light.

To better understand the product of bulk electrolysis, chemical synthesis of $[Cp*Ir(py)_2(H)]^+$ was attempted. $[Cp*Ir(Cl)(py)_2]OTf$ (10 mg, 0.013 mmol) was stirred in 3 mL



3 M pH 5 NaO₂CH under inert atmosphere. After one hour, the vial was vented to release the pressure formed by carbon



dichloromethane. The dichloromethane fraction was pumped down and ¹H NMR was taken. One peak was observed in the hydride region at -12.76 ppm. A second attempt at forming the hydride used sodium borohydride in methanol. The solution immediately turned red then to green over time. The solution was pumped down. ¹H NMR was taken to reveal three different hydride peaks at -9.90, -13.36 and -13.56 ppm.

Since the $[Cp*Ir(Cl) (py)_2]OTf$ had a much more negative potential than was desired, more complexes with this general structure were analyzed. Electron withdrawing groups (-CN, -CF₃, and –COOH) were placed in the para-position of the pyridine in hopes of shifting the reduction to a more positive potential.

2.5 Synthesis and Characterization of [Cp*Ir(Cl)(nicotinic acid)₂]OTf

[Cp*Ir(Cl)(nicotinic acid)2]OTf (6) was formed with the same synthesis of (4). Despite the presence of 24% free ligand, preliminary photoelectrocatalytic screening was performed to test the viability of the catalyst. Though two irreversible reduction features were observed at -1.32 V and -1.49 V, no light dependence was observed. An oxidation peak was observed at 0.10 V. The CAs were inconclusive about light dependence due to the negative reduction potential being on the edge of the potential window in water. The catalytic rate without background correction was calculated to be 0.010 s^{-1} , which is lower than it would be with background correction.

2.6 Synthesis and Characterization of [Cp*Ir(Cl)(trifluoromethyl pyridine)₂]OTf

 $[Cp*Ir(Cl)(trifluoromethyl pyridine)_2]OTf (5)$ was formed with the same synthesis of (4). The ¹H NMR revealed that free ligand was containment in a 10:1 ratio. Electrochemical analysis was completed in pH 7 phosphate buffer. A poorly resolved reduction peak was observed at -1.45 V and an oxidation peak at 0.22 V. The CAs displayed 460 nm LED light dependence at -1.40 V. Further studies need to be completed to determine the photochemical reaction.

2.7 Synthesis of [Cp*Ir(Cl)(cyanopyridine)₂]OTf

Synthesis of [Cp*Ir(Cl)(cyanopyridine)2]OTf (7) was synthesized using an analogous processes to (4). The ¹H NMR revealed that more than one complex was being formed and there was a 50% free ligand containment. Therefore, the synthesis was completed in dichloromethane from an adapted literature synthesis.¹⁰ The ¹H NMR revealed one complex with free ligand as a contaminant in a 3:1 ratio. Electrochemical analyses are under way.

3. Discussion

3.1 Synthesis of Iridium Complexes

The iridium complexes shown in Figure 11were synthesized and purified using methods in analogy to the literature. For all of the complexes, the main impurities were the starting materials, both free ligands and the unreacted [Cp*Ir(Cl)₂]₂. Through a process of recrystallization complexes, it was possible to obtain high purity samples of (1), (2), and (4) became clean. Attempts to purify (3), (5), (6), and (7) are still underway.





Figure 11. Iridium complexes studied for molecular photoelectrochemical hydrogen evolution.



The complexes were colorful as can be seen in Figure 12. The color observed is the complimentary to the wavelength of light that is absorbed. The UV/Vis for these

Figure 132. The colors of complexes 1-4 complexes are shown in Figures 13-14.





Figure 113. The UV/Vis for complexes 1-3.

Figure 124. The UV/Vis for complexes 4-6, the bis-pyridine derivatives.

A table comparing the wavelength of maximum absorbance is in Table 1. The reduction and

oxidation potentials are also recorded.

Table 1. The wavelength of maximum absorbance, reduction potential, and oxidation potential for the chloride complexes 1-6.

	λ _{max} (nm)	Reduction Potential (V)	Oxidative Potential (V)
[Cp*lr(DPK)Cl] (1)	327	-0.62, -0.72, and -1.2	
[Cp*lr(pm-DAB)Cl] (2)	390	-0.44	
[Cp*Ir(p-tolyl BIAN)Cl] (3)	362	-0.32	
[Cp*lr(py) ₂ Cl] (4)	297	-1.32	-0.03
[Cp*Ir(trifluoromethyl pyridine) ₂ Cl] (5)	302	-1.45	0.22
[Cp*Ir(nicotinic acid)₂Cl] (6)	307	-1.32 and -1.49	0.1

Complexes 2 and 3 have reduction potentials that are more positive than [Cp*Ir(bpy)(Cl)]⁺ which means the hydride take less energy to form. Complexes 2 and 3 absorb light over longer wavelengths. Comparing the bis-pyridine compelexes (4-6), reduction potentials do not change between 4 and 6 and get more negative with complex 5.

Hydride formation

The ability to form hydrides from collection of $[Cp*Ir(Cl)(NN)]^+$ complexes was analyzed through a combination of a search for appropriate the reduction peaks in their respective CVs, bulk electrolysis, and chemical synthesis. [Cp*Ir(Cl)(bpy)]Cl has two reduction potentials, an irreversible two electron reduction is at $E_{p,c} = -0.61$ V for [Cp*Ir(Cl)(bpy)]Cl and the one electron transfer to reduce Ir(III) to Ir(I) at -1.25 V in aqueous solutions.¹¹ Complexes (1), (2), and (3) each have reduction features at more positive potentials than [Cp*Ir(Cl)(bpy)]Cl. However, for (2) and (3), there was an oxidation peak at pH 7, which was not observed at lower pHs. The reversibility of the reduction under neutral conditions indicated that the catalyst does not form a hydride. A hypothesis of the process is shown in Scheme 1.



Scheme 1. The addition of acid allowed for the hydride to be formed.

The reduction potentials for (4), (5), and (6) are at a more negative potentials than $[Cp*Ir(bipyridine)(Cl)]^+$. The reduction potential for (6) was the same as (4), but (5) was more negative. These complexes require more energy to form the hydride than the analogous bipyridine complex.

Bulk electrolysis was completed on complexes (3) and (4) to isolate the hydride electrochemically. Complex (3) decomposed most likely through ligand loss during the reaction. The solution of (4) went from yellow to orange-red during the reaction. Three peaks were observed in the hydride region in the ¹H NMR. The chemical syntheses of $[Cp*Ir((py)_2(H)]^+$ with sodium formate and borohydride revealed different hydride peaks correlating to different complexes than the hydride produced through electrolysis.

3.2 Photochemical Activity

Light dependence was measured by comparing the current passed at a potential in the dark to the current passed when white or blue light was directed at the electrode.

Complexes (4) and (5) passed higher currents when the 460 nm LED lamp was directed at the electrode compared to when the electrochemical measurement was carried out in the dark. Complex (3) passed the same amount of current with the 460 LED lamp as in the dark, but passed more current under the broad spectrum tungsten halogen white light source indicating that the complex was not activated by 460 nm light, but is activated by white light.

 $[Cp*Ir(py)_2(H)]^+$ formed by bulk electrolysis was light sensitive. The hydride peak at -9.96 ppm decreased in intensity after thirty minutes of irradiation by the white LED lamp. The ¹H NMR was taken again after thirty minutes in the dark and the peak at -9.96 increased in intensity. It is possible that the ligand was coming off and then reassembling with time.



Figure 1414. A summary of light dependence for Complexes 1-7.

4. Conclusion

The requirements for molecular photoelectrochemical hydrogen evolution were analyzed using different ligands. Each ligand was picked to test how structural differences affects electron reduction and light activation.

The complex $[Cp*Ir(pyridine)_2(Cl)]OTf$ displayed similar reduction features as the known catalyst, [Cp*Ir(bpy)(Cl)]Cl. However, the energy required to activate this system was much higher. Without the connection between the two pyridine rings, the process to form the hydride analog from the chloride complex was more difficult. The addition of electron withdrawing groups to the para position of the pyridine rings did not change the potential in the desired manner. [Cp*Ir(trifluoromethyl pyridine)₂(Cl)]OTf had a more negative reduction potential and [Cp*Ir(nicotinic acid)₂(Cl)]OTf had the same reduction potential as $[Cp*Ir(py)_2(Cl)]OTf$. The α -diimine ligand complexes (2) and (3) have lower reduction potentials, but are less stable than the bpy. Both complexes require a very acidic environment in order to be protonated. The [Cp*Ir(dpk)(Cl)]Cl complex had a more positive reduction potential but showed no increase in current under irradiation. When $[Cp*Ir(bpy)Cl]^+$ is reduced from Ir(III) to Ir(I), the electrons move towards the ligand. Ir(I) state is an Ir(II) with a ligand centered radial, making the energetics the ligand important for the system. The ligand radical stability should correlate with a complex that is reduced at lower potentials. More electron withdrawing ligands should be more stable as radicals. From (4), (5) and (6), this trend is not observed. However, (2) and (3) have large electron withdrawing groups which correlate with a more positive reduction potential.

5. Future Work

The goal of this research was to determine the limits of molecular photoelectrochemical hydrogen evolution. To continue with this project, bulk electrolysis under different conditions for $[Cp*Ir(Cl)(pm-DAB)]^+$ should be explored due to the promising positive reduction potential and the light activation. CAs with irradiation from the white lamp should be studied for $[Cp*Ir(Cl)(p-tolyl BIAN]^+$. Chemical synthesis of both $[Cp*Ir(H)(pm-DAB)]^+$ and $[Cp*Ir(H)(py)_2]^+$ can be continually studied to determine the stability of this species. Even though $[Cp*Ir(Cl)(py)_2]^+$ has a more negative reduction potential than $[Cp*Ir(Cl)(bpy)]^+$ continual study by analogy can help elucidate how the catalytic cycle to form hydrogen gas works.

Analysis of the gas formed during the reaction to determine the identity and rate of formation would be important next steps.

A very interesting pathway of study is to use self-assembly ligands to form an iridium complex and analyze the stability.

A. Experimental

A.1 Cyclic Voltammetry

In an undivided electrochemical cell, 0.1 M pH 7 phosphate buffer was sparged with nitrogen gas for 15 minutes. A glassy carbon electrode working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode was used. For 0.1 M TBA PF_6 acetonitrile solution, a Ag/Ag⁺ counter electrode was used. The glassy carbon was polished before each run. A background CV was taken after preparation of a solution.

1 mM of complex and the solution was again sparged with nitrogen gas for 15 minutes. CVs were taken at different scan rates.

A.2 Chronoamperometry

In a fritted H-cell, 0.1 M pH 7 phosphate buffer was sparged with nitrogen gas for 15 minutes. A glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode was used. For 0.1 M TBA PF₆ acetonitrile solution, a Ag/Ag⁺ counter electrode was used. Care was taken to make the cell as oxygen free as possible. A LED lamp (white or 460 nm) was held under the glassy carbon electrode. The white LED lamp produced heat, so the electrode was raised 1 cm from the middle LED. In the 460 nm LED lamp, the cell sat directly on the lamp surface. The glassy carbon was polished with 0.3 silica for 20 seconds then with 0.05 silica for 20 seconds. A background CV was taken after preparation of a solution.

1 mM of complex and the solution was again sparged with nitrogen gas for 15 minutes. CAs were taken at different potentials with varying the light. The glassy carbon working electrode was polished between each run.

A.3 Bulk Electrolysis

In the H-cell with a pressure bridge, 0.1 M pH 7 phosphate buffer was sparged with nitrogen gas for 15 minutes. A glassy carbon working electrode, an Ag/AgCl reference electrode, and a platinum counter electrode was used. Care was taken to make the cell as oxygen free as possible. A background CV was taken. A stir bar was added. Enough complex was added to make the electrolyte solution to make 1 mM solution of complex and the solution was again sparged with nitrogen gas for 15 minutes. The cell was covered with aluminum to allow the reaction to be carried out in the dark. Bulk electrolysis was set to go at a potential more negative than the reduction potential for two hours.

B. Synthesis

B.1 Synthesis of Iridium Complexes

- (1) [Cp*Ir(di(2-pyridyl)ketone)(Cl)]Cl: In a nitrogen glove box, 24.4 mg (0.0306 mmol) [Cp*IrCl₂]₂ was added to 5 mL of methanol. Then, 11.3 mg (0.0613 mmol) of di(2-pyridyl)ketone was added. A yellow solution resulted. The solution was allowed to stir for 24 hours and precipitated out with hexanes. The solids were filtered and washed with hexanes. ¹H NMR(CD₃CN): δ 8.94 (d, 2H), 8.23 (m, 4H), 7.88 (ddd, 2H), 1.32 (s, 15H)
- (2) [Cp*Ir(Cl)(pm-DAB)]Cl: In a nitrogen glove box, 31.4 mg (0.0394 mmol)
 [Cp*IrCl₂]₂ was to 5 mL of methanol. Then, 18.6 mg (0.0788 mmol, 2 eq) of 1,4-diphenyl-2,3-dimethyl-1,4-dizabutadiene was added. A red solution resulted. The solution was allowed to stir for 24 hours and then filtered and dried in vacuo. ¹H NMR(CDCl₃): δ 7.82 (d, 2H), 7.60 (d, 2H), 7.52 (q, 4 H), 7.35 (t, 2H), 2.56 (s, 6H), 1.18 (s, 15H)

- (3) [Cp*Ir(Cl)(p-tolyl BIAN)]Cl: In a nitrogen glove box, 10 mg (0.0126 mmol)
 [Cp*IrCl₂]₂ was to 5 mL of methanol. Then, 9.04 mg (0.251 mmol, 2 eq) of bis[N-(p-tolyl)imino]acenphthene was added. A red solution resulted. The solution was allowed to stir for 24 hours and then filtered and dried in vacuo. ¹H NMR(MeOD): δ
 8.25 (d, 2H), 8.70 (d, 2H), 7.63-7.57 (m, 8H), 7.19 (d, 2H), 2.58 (s, 6H), 1.31 (s, 15H)
- (4) [Cp*Ir(py)₂(Cl)]OTf: In a nitrogen glove box, 25 mg (0.326 mmol) [Cp*IrCl₂]₂ was added to16.1 (0.0328 mmol, 2 eq) AgOTf with 5 mL of methanol. The solution was stirred until a homogenous yellow solution occurred. Then, 0.014 mL (0.126 mmol, 4 eq) of pyridine was added. A yellow solution resulted and a white precipitate was observed. The solution was allowed to stir for 24 hours and then filtered and pumped down. The powder was washed with ether to remove any unreacted ligand. ¹H NMR(CDCl₃): δ 9.17 (d, 4H), 7.85 (tt, 2H), 7.60 (d, 4H), 1.51 (s, 15H)
- (5) [Cp*Ir((4-(trifluoromethyl)-pyridine)₂(Cl)]OTf: Under a nitrogen atmosphere, 25 mg (0.0326 mmol) [Cp*IrCl₂]₂ and 16.1 (0.0628 mmol, 2 eq) AgOTf were mixed in 5 mL of methanol. To the solution, 0.013 mL (0.126 mmol, 4 eq) of 4-trifluoromethyl pyridine was added and allowed to stir under a nitrogen atmosphere for four hour. The solution was filtered and a white solid separated out. ¹H NMR(MeOD): δ 9.19 (d, 4H), 7.91 (d, 4H), 1.56 (s, 15H)

- (6) [Cp*Ir(nicotinic acid)₂(Cl)]OTf: In a nitrogen glove box, 25 mg (0.0314 mmol)
 [Cp*IrCl₂]₂ was added to 16.1 mg (0.062 mmol, 2 eq) AgOTf with 5 mL of dichloromethane. The solution was stirred until a homogenous yellow solution occurred. Then, 15.5 mg (0.126 mg, 4 eq) of nicotinic acid was added. A yellow solution resulted and a white precipitate was observed. The solution was allowed to stir for 24 hours and then filtered and pumped down. The powder was washed with ether to remove any unreacted ligand. ¹H NMR(MeOD): δ 9.07 (d, 4H), 8.03 (d, 4H), 1.55 (s, 15H)
- (7) [Cp*Ir(cyanopyridine)₂(Cl)]OTf: In a nitrogen glove box, 25 mg (0.031 mmol)
 [Cp*IrCl₂]₂ was added to 16.1 mg (0.0628, 2 eq) AgOTf with 5 mL of
 dichloromethane. The solution was stirred until a homogenous yellow solution
 occurred. Then, 13.1 mg (0.13 mmol, 4 eq) of cyanopyridine was added. A yellow
 solution resulted and a white precipitate was observed. The solution was allowed to
 stir for 24 hours and then filtered and pumped down. The powder was washed with
 ether to remove any unreacted ligand. ¹H NMR(CD₂Cl₂): δ 9.41 (d, 4H), 7. 86 (d,
 4H), 1.49 (s, 15H)

¹ Srivastava, S. C. Journal of Scientific and Industrial Reserch **1993**, 52(1), 8-12.

² Lewis, Nathan S.; Nocera, Daniel G. PNASI **2006**, 103(**43**), 15729-15735.

³Lewerenz, H.J; Heine, C.; Skoruska, K.; Szabo, N.; Vo-Dinh, T.; Campbell, S. A.; Klemm, H. W.; Munoz, A. G. *Energy and Environmental Science* **2010**, *5*, 748-760.

⁴ Pitman, C.L.; Miller, A.J.M. ACS Catalysis 2014, 4, 2727.

⁵ Guibin, Ma, McDonal, Robert, Ferguson, Micheal, et all. *Organometallics* **2007**, *26*(4), 846-854.

⁶ Van Belzen, Rudd; Elsevier, Cornelis J.; Dedieu, Alain; Veldman, Nora; Spek, Anthony L. *Oragnometallics* **2003**, 22(4), 722-736.

⁷ Haitao, Zhu; Chen, Pinhog; Liu, Guosheng. Organic Letters 2015, 17(6), 1485-1488.

⁸ Pitman, C.L.; Miller, A.J.M. ACS Catalysis **2014**, *4*, 2727.

⁹ Morias, T.S.; Silva, T.J.L.; Marques, F.; Robalo, P.; Avecilla, F.; Madera, P.J.A.; Mednes, P.J.G.; Santos, I.; Garcia, M.H. *Journal of Inorganic Biochemistry* **2012**, *114*, 65-74.
¹⁰ Hintermair, Ulrich; Campos, Jesus; Brewster, Timothy P.; et all. *ACS Catalysis* **2013**, *4*, 99-108.
¹¹ Pitman, C.L.; Miller, A.J.M. *ACS Catalysis* **2014**, *4*, 2727.