RHENIUM-PYRIDYL-NHCS FOR PHOTOCATALYTIC CO\textsubscript{2} REDUCTION

by
Emily Anne Sharpe

A thesis submitted to the faculty of the University of Mississippi in partial fulfillment of the requirements of the Sally McDonnell Barksdale Honors College.

Oxford
May 2016

Approved by

___________________________
Advisor: Professor Jared Delcamp

___________________________
Reader: Professor Jonah Jurss

___________________________
Reader: Professor Gregory Tschumper
ACKNOWLEDGEMENTS

We would like to thank the National Science Foundation (NSF OIA-1539035), the University of Mississippi, and the UM Sally McDonnell Barksdale Honors College for funding this research project. E.A.S. would also like to thank Dr. Jared Delcamp, Dr. Aron J. Huckaba and the rest of the graduate and undergraduate researchers in the Delcamp group for their support and guidance in the completion of this project.
ABSTRACT

The ability to transform CO$_2$ into a useable fuel source would have a remarkably positive impact on the environment by taking the vast amounts of previous unusable CO$_2$ from the atmosphere and reducing it to CO, which can then be turned into fuel. This project involves the synthesis and testing of air and water stable Re (I) pyridyl N-heterocyclic carbene (NHC) compounds for photocatalytic reduction of CO$_2$ into CO using a simulated solar spectrum. Previous research in this area focused on the use of Re(bpy)CO$_3$X, which quickly became the benchmark of homogeneous CO$_2$ reduction photocatalysts. The Re (I) pyridyl NHC catalysts were stabilized because of a stronger bonded NHC ligand substitution in place of a pyridine on the bipyridal ligand and could be quickly synthesized and purified. The presence and absence of two components, a photosensitizer $fac$-Ir(ppy)$_3$ and a strong electron donor BIH, were tested along with the catalyst to determine the greatest turnover numbers (TONs) of CO$_2$ to CO. It was found that each of the five catalysts worked to reduce CO$_2$ to CO under conditions with the photosensitizer and BIH, with the RePyNHC(PhCF$_3$) catalyst achieving 51 TON, ~20 TON higher than the Re(bpy)CO$_3$X benchmark. Additionally, the Re-Py-NHC-(PhCF$_3$) catalyst achieved good TONs without the use of the photosensitizer, paralleling the performance of the Re(bpy)CO$_3$X catalyst in the presence of the photosensitizer.
# TABLE OF CONTENTS

INTRODUCTION .......................................................................................................................... 01

RESULTS ...................................................................................................................................... 08

SYNTHESIS ................................................................................................................................. 08

OPTICAL PROPERTIES ............................................................................................................... 10

ELECTROCHEMICAL PROPERTIES .......................................................................................... 11

PHOTOCATALYTIC PERFORMANCE .......................................................................................... 14

CONCLUSION .............................................................................................................................. 17

REFERENCES .............................................................................................................................. 18

SUPPLEMENTAL INFORMATION ................................................................................................. 22

EXPERIMENTAL: SYNTHESIS ..................................................................................................... 22

UV-VIS ........................................................................................................................................ 28

CYCLIC VOLTAMMETRY ............................................................................................................ 29

\(^1\)H NMR DATA ..................................................................................................................... 32
Introduction.

Some believe that as modern society has become more dependent on the use of electricity, technology, and fossil fuels for transportation, the atmospheric carbon dioxide levels have been on the rise.\textsuperscript{1} Fluctuations in the environmental levels of carbon dioxide have been traced back as far as 400,000 years ago. However, since the dawn of the Industrial Revolution, environmental concentrations of this greenhouse gas have been rising, which could be due to a number of factors.\textsuperscript{1,2} While the exact cause of the rapid increase in concentration cannot be pinpointed to an exact source, many argue that the spike coincides with society’s move towards more energy consuming lifestyles. To quantify the scope of this increase, climate change specialists have concluded that in the 1950s, the concentration of CO\textsubscript{2} in the environment was just about 300 parts per million (ppm) in the atmosphere, a level which historically was where the concentration levels would turn around towards lower ppm in the following few centuries. In the last 50-60 years however, the level has skyrocketed, increasing an additional 100 ppm to a massive 400 ppm or 0.04\% of the atmosphere.\textsuperscript{1,2}

As carbon dioxide emissions continue to increase, scientists are working to mediate these hazardous emissions that account for roughly 82\% of the greenhouse gas emissions in the United States.\textsuperscript{3} Greenhouse gases are a problem for the United States and the earth as a whole because of the environmental consequences that can and are already beginning to show themselves as a result of the increased CO\textsubscript{2} release into the atmosphere. The biggest, and most widely reported of those is global climate change. While these changes towards an overall warmer climate may not seem extreme, loss of sea ice, rising sea levels and stronger heat waves are all being reported by the Global
Climate Change division of NASA.\textsuperscript{2} If the carbon dioxide levels in the atmosphere are not controlled, the intensity of these issues will continue to rise, causing complete loss of Arctic ice, more potent hurricane seasons or prolonged periods of drought.

Another argument towards alternative fuel sources is the potential for energy independence for the United States.\textsuperscript{4} Along with the possibility of job opportunities that could come from further developing the renewable energy industry, working towards renewable energy and the reduction of atmospheric CO\textsubscript{2} could have significant effects on the geopolitical environment surrounding crude oil reserves and the somewhat tenuous relationships that exist between the United States and countries like Saudi Arabia, Iran and Iraq.\textsuperscript{5} A relationship between the United States and Saudi Arabia began as early as the 1930s regarding the exchange of the valuable oil commodity, which became even more of a necessity as World War II began.\textsuperscript{6} National and international oil companies all have vested interest in the success and security of Middle Eastern countries that have become more and more war-torn leading to fluctuated pricing and causing the need for oil reserves and war to become increasingly interconnected.\textsuperscript{5} Moving away from oil and fossil fuels as a primary source of energy for the United States could drastically reduce the need for military presence in these countries and stabilize transport fuel pricing.\textsuperscript{4,6}

In an effort to combat the challenges facing our climate and the geopolitical environment, some scientists have turned to CO\textsubscript{2} reduction research, with the aim of taking atmospheric CO\textsubscript{2} and reducing it through a number of chemical processes to other useable by-products such as methane, methanol, formate, formic acid or carbon monoxide. These possible reduction products present various benefits and challenges
when analyzing their application on a commercial level. Table 1 shows the energies required to transform carbon dioxide into each reduction product.\(^7\)

<table>
<thead>
<tr>
<th>CO(_2) Reduction Reaction</th>
<th>Reduction Potential vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2)+ 2 H(^+)+ 2 e(^-) → CO+ H(_2)O</td>
<td>(E^0 = -0.53) V</td>
</tr>
<tr>
<td>CO(_2)+ 2 H(^+)+ 2 e(^-) → HCO(_2)H</td>
<td>(E^0 = -0.61) V</td>
</tr>
<tr>
<td>CO(_2)+ 6 H(^+)+ 6 e(^-) → CH(_3)OH + H(_2)O</td>
<td>(E^0 = -0.38) V</td>
</tr>
<tr>
<td>CO(_2)+ 8 H(^+)+ 8 e(^-) → CH(_4)+ 2 H(_2)O</td>
<td>(E^0 = -0.24) V</td>
</tr>
</tbody>
</table>

**Table 1:** Reduction potentials of the major CO\(_2\) reduction products.

The reduction of CO\(_2\) to methane or methanol would have the most direct applications as an alternative fuel source. Methanol is a liquid fuel that could be burned like gasoline and processes are known for using methane as a renewable natural gas.\(^8,9\) However, to reduce CO\(_2\) to methanol or methanol, 6 and 8 electrons respectively are required to achieve the reduction. Currently, compounds are not known that could simultaneously hold the added electron equivalents. In terms of electrons needed to achieve the reduction, formate or formic acid is the next best option because it only requires 2 electrons to achieve the reduction, and the majority of the carbon-oxygen bonds remain intact. Formate is a common photocatalytic reduction product but it is not as directly useful as methane or methanol.\(^8\) Additionally, processes using formate for further transformations to a usable liquid fuel such as hydrogenation to methanol are limited.

The other common photocatalytic reduction product is carbon monoxide, which has been most closely pursued because of its use in commercial processes. The reduction only involves two electrons, which is much more practical than processes forming methanol or methane. By reducing carbon dioxide to carbon monoxide, the gas can be used as a component of syngas (CO and H\(_2\)) in the Fischer-Tropsch process, which was a
catalytic procedure developed in the 1920s by Franz Fischer and Hans Tropsch as a way to make liquid fuels from natural gas during World War II.\textsuperscript{10} This process has become of increasing interest lately as environmental and governmental agencies warn of the consequences of excess atmospheric CO\textsubscript{2} levels.\textsuperscript{11} The general reaction taking place at the production plants is:

\[(2n+1) \text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O}\]

This transformation can be done by a variety of catalysts, the most common being iron and cobalt for industrial applications. Nickel and ruthenium can also be FT catalysts, with the ability to create higher molecular weight hydrocarbon fuels.\textsuperscript{12} Temperature, starting gas composition, pressure and catalyst type are all variables that play a role in the selectivity of the process, however, no processes have been found that create a perfect mixtures of a desired length hydrocarbon and water. Most reactions will produce a variety of olefins, paraffins as well as oxygenated products like alcohols, ketones, aldehydes and acids, which presents a synthetic challenge.\textsuperscript{11} CO\textsubscript{2} can be used directly in the Fischer-Tropsch process but there is little return on the energy investment.\textsuperscript{13} Scientists continue to work to better improve the chemistry behind the Fischer-Tropsch as CO\textsubscript{2} reduction research works towards the development of procedures that will find ways to transform this greenhouse gas to CO.

One major area of CO\textsubscript{2} reduction research involves the use of solar energy to achieve catalysis. This has the added environmental benefit of harvesting an abundant, renewable energy resource for the power to perform the reduction instead of electricity or extreme temperatures and pressures, as in the Fischer-Tropsch processes which use CO\textsubscript{2}. Photocatalysts have shown the ability to function under one of the following catalytic
cycles. The first of those shown in Figure 1 is the non-sensitized catalytic cycle. In this sequence, light excites the catalyst when then takes an electron from the sacrificial electron donor. The reduced catalyst then bonds with carbon dioxide and upon the addition of a second electron, carbon monoxide is released and the catalyst is regenerated. Figure 1 also illustrates the photosensitized catalytic cycle where the catalyst first interacts with a reduced photosensitizer molecule to become reduced. In this sequence, the photosensitizer has been excited by a light source and reduced by the sacrificial electron donor. From there, the reduced catalyst bonds to the carbon dioxide present in the system, then releases CO after further reduction by an additional electron.

**Figure 1:** Non-sensitized (left) and photosensitized (right) catalytic cycles.

Rhenium carbonyl catalysts are one of three catalysts reported in the literature that are capable of both absorbing light from the solar spectrum and performing catalytic CO₂ reduction. The other catalyst series include Ir(ppy)(ppy)Cl catalysts and Ir[(thiazole)₂bipyridine] catalyst systems. In the rhenium photocatalysis field, Re(bpy)CO₃X has come to be considered the benchmark catalyst. This catalyst was introduced in 1983 and has since shown selectivity for CO₂ reduction to CO with good turnover numbers.
(TONs). The literature reports TONs around 27 for catalysts in the Re(bpy)CO\textsubscript{3}X series.\textsuperscript{18,19} In this research, the goal was to substantially modify the parent Re(bpy)CO\textsubscript{3}X catalyst in such a way that would increase TONs for this photocatalyst to reduce CO\textsubscript{2} to CO.

The catalysts in this research vary from this benchmark catalyst in the replacement of one of the pyridyl rings with substituted NHC ligands of different electron donating and withdrawing strengths, as shown in Figure 2. Research has recently expanded in this area due to results showing great advances in catalytic activity using NHC ligands.\textsuperscript{20} As compared to the electron deficient pyridine ring systems in the Re(bpy)CO\textsubscript{3}X catalysts, NHC ligands are considered strongly electron donating, which presents a challenge. Re(bpy)CO\textsubscript{3}X catalysts worked effectively because the initial proposed step of the catalytic mechanism involves metal-to-ligand charge transfer (MCLT) following photoexcitation of the molecule. The molecule then gains an electron from the sacrificial electron donor. Because the pyridine system is electron deficient, it more readily accepts electron density, due to the fact that the lone pairs of the bipyridyl nitrogens are involved in the pi system. In the Re-Py-NHC(CO)\textsubscript{3}X catalysts, the lone pairs of the nitrogens are in conjugation with the pi system, increasing the electron density, potentially inhibiting the complexes willingness to accept the electron from the sacrificial electron donor.
Figure 2: Re(bpy) photocatalyst benchmark (1) and proposed Re-Py-NHC catalysts with varying electron donating and withdrawing natures (2-5), as well as the photosensitizer Ir(ppy)₃ and the sacrificial electron donor BIH.

In following with the hypothesized catalytic mechanism, the NHC ligand with the most strongly electron withdrawing substituent would function the best as a CO₂ reduction catalyst because it would be able to best support the electron density added to the complex during the reduction by the electron donor. Testing of this hypothesis was completed through the synthesis of NHC ligands substituted with an aryl electron donating group –OC₆H₁₃, an electronically neutral unsubstituted aryl and an electron withdrawing aryl –CF₃ substituent. Additionally, a methylated NHC catalyst was also synthesized to complete the series and evaluate the effects of arylation versus alkylation.
Results and Discussion.

Synthesis of Catalysts 2-5:

Figure 3: Synthetic scheme for the preparation of catalysts 2-5.

Preparation of all the catalysts was done using a three step synthetic series shown above in Figure 3. More detailed syntheses and sources of previously known synthetic pathways are outlined in the supplemental information. The synthetic goal was to create catalysts with a range of electron withdrawing and electron donating groups on the NHC to test the substituent effects on catalytic performance. Synthesis of catalyst 2 began with copper-catalyzed imidazole coupling to the 2-bromopyridine followed by methylation of the newly formed imidazole system and salt metathesis with NaPF$_6$. This gave compound 7 which was refluxed with toluene, TEA and Re(CO)$_5$X, where X=Br or Cl, to give the bromide or chloride of complex 2 depending on the salt used. Compounds 3-5 began as an aryl bromide substituted with the desired electron donating or withdrawing group. These compounds underwent a copper-catalyzed coupling reaction with imidazole to form the ligand precursors. After the coupling reaction, the imidazole
precursor was headed with 2-bromopyridine to synthesize the complete ligand. The desired ligand was refluxed with toluene, TEA and Re(CO)$_5$X, where X=Br or Cl, to form the bromide or chloride, which could be purified by column chromatography and were both stable to ambient conditions.

![Chemical reaction](image)

**Figure 4:** Synthesis of BIH, a sacrificial electron donor.

Additional synthesis was required for the formation of BIH, 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole, shown in Figure 4. The synthesis was completed in two steps, beginning with double alkylation of the commercially available 2-phenylbenzimidazole followed by reduction of the imidizolium salt to give the final product, BIH. This compound is important to the catalytic studies because it acts as a high-energy sacrificial electron donor in the reduction.
Optical Properties:

In order to determine the viability of the Re-Py-NHC catalysts complexes as photocatalysts, the catalysts must exhibit light absorption in the ultraviolet and visible region. Figure 5 shows the absorption of top-performing catalyst 5 in comparison to the benchmark Re(bpy) catalyst 1, measured in acetonitrile. Catalyst 5 shows a shift of about 25 nm and a molar extinction coefficient ($\epsilon$) of 4800 M$^{-1}$cm$^{-1}$, as compared to the molar absorption coefficient for Re(bpy) of 2890 M$^{-1}$cm$^{-1}$, showing a stronger ability to absorb light at the $\lambda_{max}$. The absorption spectra of catalysts 2-4 are plotted along with catalysts 1 and 5 in the supporting information. Amongst the catalysts, very little difference was observed between the absorption maxima.

![Molar absorptivity spectra of catalysts 1 and 5. Data collected by Dr. Aron Huckaba.](image)

Figure 5: Molar absorptivity spectra of catalysts 1 and 5. Data collected by Dr. Aron Huckaba.\textsuperscript{28}
Electrochemical Properties:

Following the confirmation of the light absorption by the complexes, the next requirement was ensuring the catalyst has appropriately placed energy levels to achieve reduction of carbon dioxide. This determination was done using cyclic voltammetry measurements in acetonitrile under nitrogen and carbon dioxide environments, shown in Figure 6. By comparing the reduction potentials of the catalysts under nitrogen to the same potentials under carbon dioxide, it is possible to ensure the energy levels are viable for the catalysts to perform CO$_2$ reduction. Each catalyst was run in 1 mM concentration in acetonitrile using 0.1 M NBu$_4$PF$_6$ as the electrolyte, also in acetonitrile. A Pt quasi-reference electrode, Pt counter, and glassy carbon disk working electrodes were used at a scan rate of 100 mV/s. Spectra were referenced to an internal standard, ferrocence (Fc) using a value of Fc/Fc$^+$ = 0.4 V versus saturated calomel electrode (SCE). Under these conditions, two irreversible reductions and an irreversible oxidation were observed. The red curves illustrate the CV curve of the catalysts in a nitrogen atmosphere. Across all four catalysts, there was a strong increase in the first and second reduction peaks upon vigorous bubbling of CO$_2$ through the acetonitrile solutions for 15 minutes.
Figure 6: Cyclic Voltammetry measurements of catalysts 2-5.

Using the graphs from Figure 6, the reduction potentials were determined. The results for $E_{(S/S^-)}$ are reported below in Table 2, along with the reduction potentials for carbon dioxide and the iridium photosensitizer. The energy levels of catalysts 1-5 were found to be positioned appropriately for electron transfer from the photosensitizer to the catalysts followed by a subsequent transfer of the electron to carbon dioxide to complete the reduction. The benchmark Re(bpy) catalyst exhibited the lowest reduction potential vs. SCE (saturated calomel electrode). Catalysts 2-5 varied slightly in their reduction potentials, with the most stable catalyst being catalyst 5, whose energy was about 60-80 mV more stable than the catalysts containing electron donating or electronically neutral substituents. Additional CV curves showing the full oxidation and reduction potentials of the catalysts are available in the supplemental information.
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reduction Potential vs. SCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.55 V&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>2</td>
<td>-1.58 V</td>
</tr>
<tr>
<td>3</td>
<td>-1.56 V</td>
</tr>
<tr>
<td>4</td>
<td>-1.56 V</td>
</tr>
<tr>
<td>5</td>
<td>-1.50 V</td>
</tr>
<tr>
<td>Carbon Dioxide at pKa ~17</td>
<td>-0.9 V</td>
</tr>
<tr>
<td>Carbon Dioxide at pKa 0</td>
<td>-0.53 V&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>Ir(ppy)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-2.19 V</td>
</tr>
</tbody>
</table>

**Table 2:** Experimentally determined catalyst reduction potentials. <sup>a</sup>This is the second reduction potential because no catalytic activity achieved at the first reduction potential of -1.20 V. <sup>b</sup>The CO₂ reduction potential is pH dependent. In these experiments, the pH of the environment is based on carbonic acid in acetonitrile with a pKa ~17.
Photocatalytic Performance:

The final and most important information that was acquired about the catalysts was the ability to effectively convert carbon dioxide to carbon monoxide. Without this critical characteristic, the light absorption or well-placed reduction potential levels would be insignificant. To test the photocatalytic performance of each catalysts, 0.2 μmol of the catalyst, 2 mL of 5% TEA (as an additional electron donor source) and acetonitrile were combined with 0.2 μmol fac-Ir(ppy)_3 and 0.02 mmol of BIH. Prior to irradiation, each solution was bubbled vigorously with CO_2 gas then irradiated with an AM 1.5 G filtered solar simulating 150 W Xe lamp. The headspace of the screw-cap test tube was tested at 1, 2 and 4-hour increments using gas chromatography with a FID to detect CO, as well as CH_4. This method allows for smaller scale reactions than would be possible using a TCD system and the addition of a Ni-catalyst methanizer allows for the detection of CO even though there are no hydrogen atoms to combust. Figure 7 shows the turnover number (TON) for each catalyst, including the benchmark, after 4 hours of irradiation and is an average of two runs. After the 2-hour mark, the catalyst performance began to plateau at its maximum turnover number and by 4 hours, no further TONs were observed.
As predicted, catalyst 5 performed the best of the catalysts with a TON of 50.8, likely because of the electron withdrawing nature of the –PhCF₃ substituent on the NHC heterocyclic that allowed for broader dispersion of electron density across the complex. The –CH₃, –Ph, and –PhOHx catalysts were found to show slightly lower turnovers at 16.4, 26.9 and 22.2 TON respectively. This data compares to the TON of 33.2 for the benchmark Re(bpy) catalyst. In keeping with our original hypothesis, the electron donating and electronically neutral catalysts did not perform as strongly because they were unable to disperse the electron density as well as catalyst 5. Table 2 shows data that catalyst 5 outperformed the benchmark catalyst under the conditions.

![Graph showing catalytic turnover numbers (TONs) for Catalysts 1-5 after 4 hours of radiation by the AM 1.5 solar simulator. Data collected by Dr. Aron Huckaba.](image)

**Figure 7:** Catalytic turnover numbers (TONs) for Catalysts 1-5 after 4 hours of radiation by the AM 1.5 solar simulator. Data collected by Dr. Aron Huckaba.²⁸

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Bromide TON</th>
<th>Chloride TON</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.2</td>
<td>32.2</td>
</tr>
<tr>
<td>2</td>
<td>16.4</td>
<td>17.1</td>
</tr>
<tr>
<td>3</td>
<td>26.9</td>
<td>22.0</td>
</tr>
<tr>
<td>4</td>
<td>22.2</td>
<td>22.4</td>
</tr>
<tr>
<td>5</td>
<td>50.8</td>
<td>13.0</td>
</tr>
</tbody>
</table>

**Table 2:** Halide TON comparison.
Table 2 also illustrates the effect of the halogen on the catalyst performance. In general, the bromide catalyst performed comparably to the chloride counterpart. However, this is not seen in comparison of the different halides of catalyst 5. The bromide complex performed nearly 17 TON more than the benchmark Re(bpy), while the chloride complex was tested to be the lowest performing CO₂ reduction catalyst of all with only 13 TON. It is suggested that halide dissociation is one of the primary steps in the reduction process of the catalyst. Because the bromide ligand can dissociate much more rapidly from catalyst 5 than a chloride ligand, the reduction of CO₂ to CO occurs at a faster rate than that of the chloride catalyst. The bromide is predicted to dissociate more rapidly because it is a strong leaving group than chloride. In the complex, the –CF₃ electron-withdrawing group tends to strengthen the halide-Re bond because it does not want to lose more electron density. Further testing on catalyst 5 showed significant contribution of BIH to the catalytic cycle. When the catalyst was run without the sacrificial electron donor in solution, the TON dropped to 0.5. The catalyst was also tested without the presence of the fac-Ir(ppy)₃ photosensitizer and was found to have a turnover number of 32, which is comparable to the benchmark catalyst with photosensitizer. Testing of the catalyst was also done outdoors during peak daylight hours, giving similar results to those values obtained from tests run using the solar simulator. Overall, the results showed near recording setting performance by catalyst 5, with TONs nearly two times the capability of the prior best rhenium catalyst, securing the title of second highest TON catalyst and, to the best of our knowledge, the highest turnover frequency (TOF) catalyst due to high CO₂ reduction during the first hour of catalytic activity.
Conclusion.

To the aim of photocatalytic CO\textsubscript{2} reduction, air and water stable Re (I) pyridyl N-heterocyclic carbene (NHC) compounds were synthesized and tested based on modifications to Re(bpy)CO\textsubscript{3}X, the widely-recognized benchmark of rhenium-based CO\textsubscript{2} reduction photocatalysts. Substitution of the pyridine ring with alkylated or arylated NHC-ligands of various electron donating and withdrawing substituents were examined. In conclusion, all catalysts were shown to exhibit some level of CO\textsubscript{2} reduction capability in solution with a sacrificial electron donor, BIH, and a photosensitizer, fac-Ir(ppy)\textsubscript{3}. Catalyst 5, with its –PhCF\textsubscript{3} substituent, was shown to outperform the benchmark Re(bpy) catalyst by almost 20 turnover numbers under these conditions. In the absence of a photosensitizer, catalyst 5 was also able to perform strongly as a CO\textsubscript{2} reduction catalyst, exhibiting comparable TONs to the Re(bpy) catalyst with a photosensitizer. To the best of our knowledge, the NHC-ligated catalysts are some of the world’s top performing Re-based CO\textsubscript{2} reduction catalysts by performing almost two times more turnovers than the benchmark and only about 20 TON below the world record holder. Also, catalyst 5 can claim the record for highest turnover frequency (TOF), based on strong catalytic performance during the first hour of catalysis.
References.


Supplemental Information

Experimental: Synthesis

General Information

Reagents obtained commercially were used as received. Reactions were performed under a nitrogen atmosphere unless otherwise specified. HPLC grade acetonitrile was used for photocatalysis experiments. Thin-layer chromatography (TLC) was done on Sigma T-6145 precoated TLC Silica gel 60 F254 polyester sheets. Potassium permanganate staining and UV light were used to visualize TLC spots. Flash column chromatography was performed with Sorbent Tech P60, 40–63 µm (230–400 mesh). 1H NMR spectra were recorded on a Bruker Avance-300 (300 MHz) and a Bruker Avance DRX-500 (500 MHz spectrometer and are reported in parts per million using solvent as an internal standard (CDCl3 at 7.26 ppm). Data reported as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration. High resolution time of flight mass spectrometry (HRMS) was used to confirm the presence of bromide and chloride Re-Py-NHC complexes after the metallation step.

Known Syntheses:

Syntheses of fac-{2,2′bipyridyl}tricarbonylrhenium(I)X (1 or 1-Cl),21 2-(imidazol-1-yl)pyridine (6),22 2-(3-methylimidazol-1-yl)-pyridine hexafluorophosphate (7),23 fac-{3-methyl-1-(2′-pyridyl)-imidazolin-2-ylidene}tricarbonylrhenium(I) (2-Cl),24 1-phenylimidazole (8),25 2-(3-phenylimidazol-1-yl)pyridine bromide (10),26 fac-{3-phenyl-1-(2′-pyridyl)imidazolin-2-ylidene}tricarbonylrhenium(I) (3 and 3-Cl),26 and 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]-imidazole (BIH)27 are known, however the...
use and study of these compounds as photocatalysts is new research, to the best of our knowledge. 1-bromo-4-hexyloxybenzene and 1- (4-trifluorophenyl)imidazole are commercially available.

Novel Syntheses:

**Synthesis of 1-(4-Hexyloxybenzene)imidazole (9).** Imidazole (1.02 g, 14.96 mmol), 1-bromo-4-hexyloxybenzene (2.38 g, 10.68 mmol) and dry, degassed DMF (11 mL) were added to a flame-dried flask with a stir bar, followed by solid CuI (0.41 g, 2.14 mmol) and K$_3$PO$_4$ (4.54 g, 21.4 mmol). The solution was heated to 130 °C with stirring for 20h and monitored by $^1$H NMR. After the reaction was determined to have reached completion, the reaction mixed was cooled to room temperature. The cooled solution was diluted with Et$_2$O (100 mL), then washed three times with H$_2$O (200 mL) and dried using MgSO$_4$. The Et$_2$O layer was concentrated and the crude product was further purified through a silica plug, first flushed with 50% hexanes: 50% Et$_2$O, followed by EtOAc to collect the product, which was concentrated to give a pale yellow oil (1.44 g, 64%). $^1$H NMR (500 MHz, CDCl$_3$): δ 7.75 (s, 1H), 7.28 (d, J = 8.5 Hz, 2H), 7.20 (s, 1H), 7.19 (s, 1H), 6.97 (d, J = 8.6 Hz, 2H), 3.90 (t, J = 7 Hz, 2H), 1.79 (m, 2H), 1.48 (m, 2H), 1.36 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H).

**Synthesis of 2-(3-(4-Hexyloxyphenyl)imidazol-1-yl)pyridine Bromide (11).** Compound 9 (0.5 g, 2.38 mmol) and 2-bromopyridine (0.45 mL, 0.75 g, 4.76 mmol) were combined in a sealed tube under N$_2$, and heated to 175 °C for 6 hours. After the reaction was completed as determined via $^1$H NMR, the mixture was cooled to room temperature.
As the product cooled, a precipitate formed that was soluble in dichloromethane. To the dichloromethane solution, Et₂O was added to precipitate out a pale brown microcrystalline solid (0.293 g, 33%). IR (neat, cm⁻¹): 3134.4, 2930.9, 2857.3, 1598.2, 1542.3, 1255.1, 1186.9, 825.3, 778.4. 1H NMR (500 MHz, CDCl₃): δ 11.8 (s, 1H), 9.2 (d, J = 8 Hz, 1H), 8.51 (s, 2H), 8.09 (t, J = 7.7 Hz, 1H), 8.0 (d, J = 8.5 Hz, 2 H), 7.79 (s, 1H), 7.47 (t, J = 10 Hz, 1H), 7.05 (d, J = 8 Hz, 2H), 3.96 (t, J = 6 Hz, 2H), 1.77 (m, 2H), 1.44 (m, 2H), 1.34 (m, 4H), 0.91 (t, J = 6.4 Hz, 3H). HRMS: Calcd for [M–Br]+ C₂₀H₂₄N₃O = 322.1919; Found for [M–Br]+ C₂₀H₂₄N₃O = 322.1914.

**Synthesis of fac-{3-(4-Hexyloxyphenyl)-1-(2’-pyridyl)imidazolin-2-Ylidene}Tricarbonylbromorhenium(I) (4) and fac-{3-(4-Hexyloxyphenyl)-1-(2’-pyridyl)imidazolin-2-Ylidene}tricarbonylchlororhenium(I) (4-Cl).**

A flame-dried flask with stirbar was connected to a reflux condenser. To the apparatus compound 12 (0.05 g, 0.17 mmol), Re(CO)₅Cl (0.049 g, 0.17 mmol), dry, degassed toluene (3 mL) and TEA (0.14 mL, 0.16 g, 1.6 mmol) were added. The reaction solution was heated to reflux under N₂ and ran for 21 hours. The solution was concentrated using a rotatory evaporated and purified with column chromatography. 10% EtOAC/CH₂Cl₂ was the solvent solution with sufficient polarity to elute the product. Two spots were collected off the column. The first was determined to be the bromide complex after concentration to a pale yellow solid (0.016 g, 21% yield) and the second spot was the chloride complex (0.017 g, 22% yield). IR (neat, cm⁻¹): 3133.4, 29321, 2015.7, 1918.0, 1888.2, 1543.8, 1488.1,
1248.2, 772.9. 1H NMR (500 MHz, CDCl3): δ 8.81 (s, 1H), 8.95 (d, J = 4.5 Hz, 1H), 8.06 (ap q, J = 6.5 Hz, 1H), 7.69 (s, 1H), 7.62 (d, J = 8 Hz, 1H), 7.58–7.56 (m, 2H), 7.33 (ap q, J = 8 Hz, 1H), 7.05 (d, J = 8.4 Hz, 2H), 4.02 (t, J = 7.6 Hz, 2H), 1.81 (m, 2H), 1.45 (m, 2H), 1.35 (m, 4H), 0.92 (t, J = 6.8 Hz, 3H). 13C NMR (300 MHz, CDCl3): δ 197.3, 195.2, 194.6, 188.6, 160.4, 154.4, 153.4, 140.1, 132.1, 127.9, 125.0, 124.9, 123.8, 123.7, 116.1, 115.8, 111.9, 68.8, 31.9, 29.3, 25.9, 22.9, 14.3. HRMS: Bromide Calcd for [M+Cs]+ C_{23}H_{23}BrN_{3}O_{4}ReCs = 803.9467, Found for [M+Cs]+ C_{23}H_{23}BrN_{3}O_{4}ReCs = 804.02; Chloride Calcd for [M+Cs]+ C_{23}H_{23}ClN_{3}O_{4}ReCs = 759.9980, Found for [M+Cs]+ C_{23}H_{23}ClN_{3}O_{4}ReCs = 759.9850.

**Synthesis of 2-(3-(4-Trifluoromethylphenyl)imidazol-1-yl)pyridine Bromide (12).** 1-(4-trifluorophenyl)-imidazole (0.5 g, 2.35 mmol) and 2-bromopyridine (0.41 mL, 0.72 g) were heated under N\textsubscript{2} at 175 °C for 3 days in a sealed tube. The reaction mixture was monitored for completion by \textsuperscript{1}H NMR. When the solution was cooled to room temperature, solids formed, which were dissolved in dichloromethane then precipitated from solution using Et\textsubscript{2}O to yield a light brown, microcrystalline solid (0.270 g, 53%). IR (neat, cm\textsuperscript{−1}): 3058.9, 3022.7, 1547.1, 1134.2, 8371, 779.7. 1H NMR (500 MHz, DMSO): δ 10.75 (s, 1H), 8.79 (s, 1H), 8.72 (d, J = 4.1 Hz, 1H), 8.68 (s, 1H), 8.3 (t, J = 8.2 Hz, 1H), 8.23–8.20 (m, 3H), 8.14 (d, J = 8.2 Hz, 2H), 7.71 (t, J = 7.6 Hz, 1H). 13C NMR (500 MHz, DMSO): δ 149.3, 146.2, 140.7, 137.7, 134.9, 130.1, 127.4, 125.6, 124.7, 123.3, 122.5, 122.3, 120.1, 114.8. HRMS: Calcd for [M−Br]\textsuperscript{+} C_{15}H_{11}N_{3}F_{3} = 290.0827; Found for [M−Br]\textsuperscript{+} C_{15}H_{11}N_{3}F_{3} = 290.0778.
Synthesis of fac-{3-(4-Trifluoromethylphenyl)-1-(2’-pyridyl)imidazolin-2-ylidene}tricarbonylbromorhenium(I) (5). A flame-dried flask with a stir bar was filled with compound 12 (0.10 g, 0.27 mmol), Re(CO)\(_5\)Br (0.11 g, 0.27 mmol), dry, degassed toluene (4.55 mL) and TEA (0.38 mL, 0.27 g, 2.7 mmol), which was then fitted with a reflux condenser. The solution was heated to reflux for 4 days, until completion determined by \(^1\)H NMR. The crude reaction mixture was concentrated using a rotary evaporator, followed by purification by column chromatography. 10% EtOAc/CH\(_2\)Cl\(_2\) was used to elute fractions that were concentrated to give a pale yellow solid (0.098 g, 54% yield). IR (neat, cm\(^{-1}\)): 2089.1, 2924.1, 1917.8, 1890.2, 1487.4, 1323.1, 774.1. \(^1\)H NMR (500 MHz, d\(_6\)-DMSO) \(\delta\) 8.89 (d, \(J = 5.4\) Hz, 1H), 8.73 (d, \(J = 2.3\) Hz, 1H), 8.39 (d, \(J = 3.5\) Hz, 2H), 8.06 (m, 3H), 7.94 (d, \(J = 8.3\) Hz, 2H), 7.58 (ap q, \(J = 5.3\) Hz, 1H). \(^{13}\)C NMR (300 MHz, CDCl\(_3\)): \(\delta\) 196.8, 195.4, 194.9, 187.9, 154.4, 153.1, 142.1, 141.1, 132.7, 129.4, 127.5, 127.4, 125.6, 124.3, 124.1, 116.9, 112.1. HRMS: Calcd for [M + Na]\(^+\) \(C_{18}H_{16}BrF_3N_3O_3\text{ReNa} = 727.9312;\) Found for [M–Br]\(^+\) \(C_{18}H_{16}BrF_3N_3O_3\text{ReNa} = 661.9422.\)

Synthesis of fac-{3-(4-Trifluoromethylphenyl)-1-(2’-pyridyl)imidazolin-2-ylidene}tricarbonylchlororhenium(I) (5-Cl). Both the chloride and bromide complexes were synthesized at once using mis-matched halogens. The reagent stoichiometries were the same as compound 5, however two products formed that could be
separated by column chromatography. The first product spot to elute off the column was concentrated by rotary evaporation to give a pale yellow solid identified as the bromide complex, while the second spot was concentrated to yield the chloride complex. HRMS: Bromide Calcd for [M+Cs]$^+$ $C_{18}H_{10}BrF_3N_3O_3ReCs = 771.8452$, Found for [M+Cs]$^+$ $C_{18}H_{10}BrF_3N_3O_3ReCs = 772.1396$; Chloride Calcd for [M+Cs]$^+$ $C_{23}H_{23}ClN_3O_4ReCs = 727.8974$, Found for [M+Cs]$^+$ $C_{23}H_{23}ClN_3O_4ReCs = 727.9111$. 
UV-Vis Absorption Spectra: All catalysts
Cyclic Voltammetry:

The figures below show the expanded cyclic voltammetry measurements in order to show the first and second reduction potentials (on the right) and the single oxidation (on the left). These experiments were run in acetonitrile and are referenced to ferrocene (Fc+/Fc).

Catalyst 1
Catalyst 2

Catalyst 3