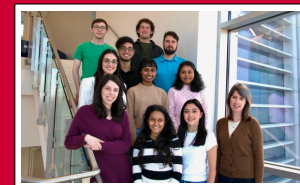


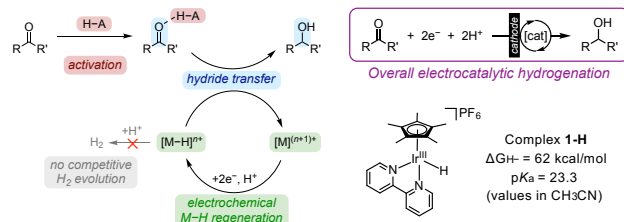
# Exploring the Role of Hydricity for Iridium-Catalyzed Electrocatalytic Hydrogenation

Amy A. Ekka, Navar M. White, Prof. Kate M. Waldie  
Rutgers – The State University of New Jersey



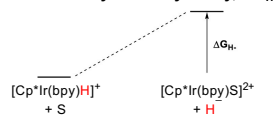
## Introduction

Electrocatalytic hydrogenation is an emerging sustainable alternative to traditional thermal hydrogenation, with potential application in biofuel upgrading, renewable energy storage with liquid organic hydrogen carriers, and fine chemical synthesis. In this context, our group is targeting electrochemical ionic hydrogenation with iridium-hydride complexes for the reduction of carbonyl compounds, utilizing a Brønsted to activate the substrate and regenerate the catalyst, thus eliminating the need for H<sub>2</sub> gas.

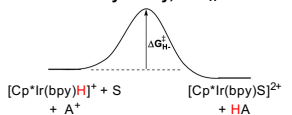


Metal-hydride complexes provide a valuable platform for mechanistic investigations into the key electron and hydrogen transfer processes involved in electrocatalytic hydrogenation. A central focus lies in understanding how catalyst properties influence thermodynamic and kinetic hydricity, from which structure-activity relationships can be elucidated to guide further optimization.

### Thermodynamic Hydricity, $\Delta G^{\ddagger}_{H-}$

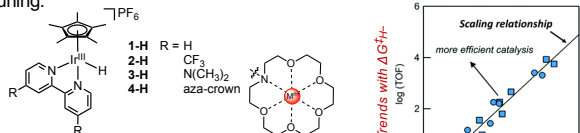


### Kinetic Hydricity, $\Delta G^{\ddagger}_{H-}$

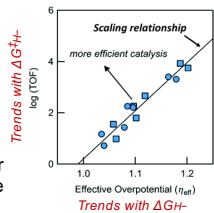
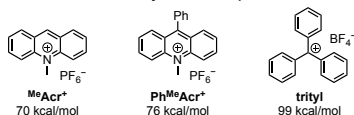


## Target Systems for Hydricity Studies

Previously, Mercer White showed that 1-H reduces acetophenone to 1-phenylethanol with TFA (60% yield, 10% Faradaic efficiency) due to H<sub>2</sub> evolution. Ligand modification may improve efficiency. Hydricity is correlated with reduction potential—better hydride donors have more negative potentials, but substrate-dependent data remain limited. Complexes 2-H and 3-H follow expected electronic trends, while 4-H varies with Lewis acid-dependent redox tuning.

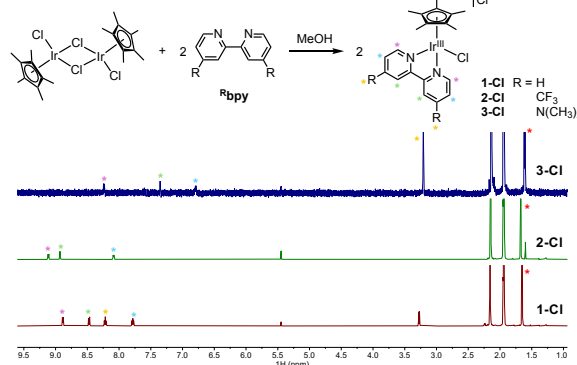


Selected hydride acceptors were chosen for their strong thermodynamic ability to promote hydride transfer from Ir-hydride complexes.

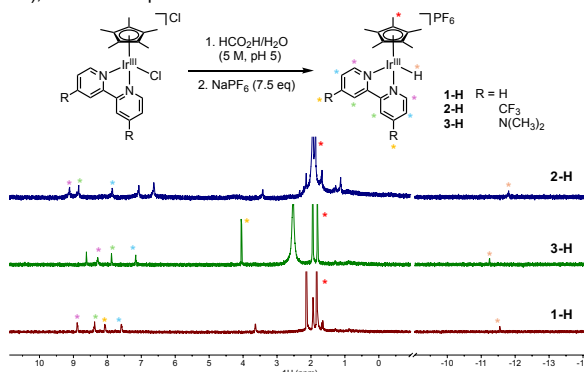


## Synthesis of Iridium Complexes

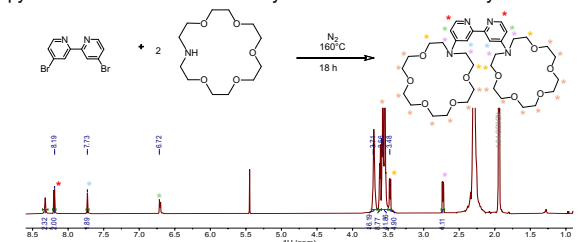
To access the iridium-hydride complexes, the iridium-chloride complexes are prepared first. Treatment of an iridium precursor with two equiv. of the desired bipyridine ligand in methanol provides 1-Cl – 3-Cl in good yield (>80 %).



To prepare the iridium-hydride complexes, 1-Cl – 3-Cl are treated with an aqueous formic acid (pH 5), followed by NaPF<sub>6</sub> anion exchange. Complexes 1-H and 3-H have been obtained by recrystallization from THF/hexanes (>89% yield), while further purification of 2-H is needed.

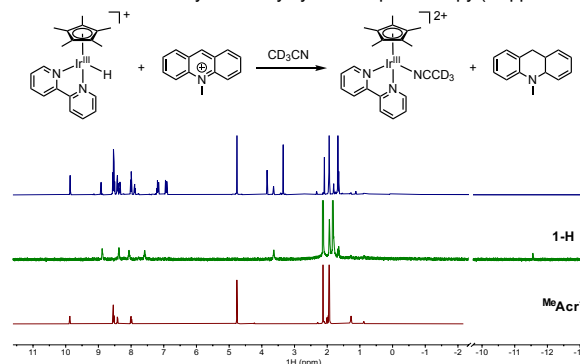


The crown-bpy ligand is obtained from the reaction of 4,4'-dibromo-2,2'-bipyridine with 1-aza-18-crown-6. Synthesis of 4-Cl is underway.



## Initial Hydride Transfer Reactivity

In preliminary work, the accessibility of hydride transfer from 1-H to four hydride acceptors was examined by <sup>1</sup>H NMR under equimolar conditions. In each case, hydride transfer is complete within 15 min. Measurements of the reaction rates are currently underway by UV-vis spectroscopy (stopped-flow).



## Conclusions and Future Work

A series of bpy-substituted Iridium hydrides is being studied to examine the electronic and steric effects on the hydride transfer rates, which will help in the design of efficient, selective, and low overpotential electrocatalysts for the hydrogenations.

In the future, UV-Vis and stopped-flow studies will quantify kinetic parameters. New complexes bearing crown ether and cationic groups will probe electrostatic effects, potentially disrupting traditional hydricity–redox correlations and offering new insights into metal-hydride reactivity and electrocatalytic performance.

## Acknowledgements

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