Center for Hybrid Approaches in Solar Energy to Liquid Fuels

Catalysts for Conversion of Ethanol to *n*-Butanol in Water

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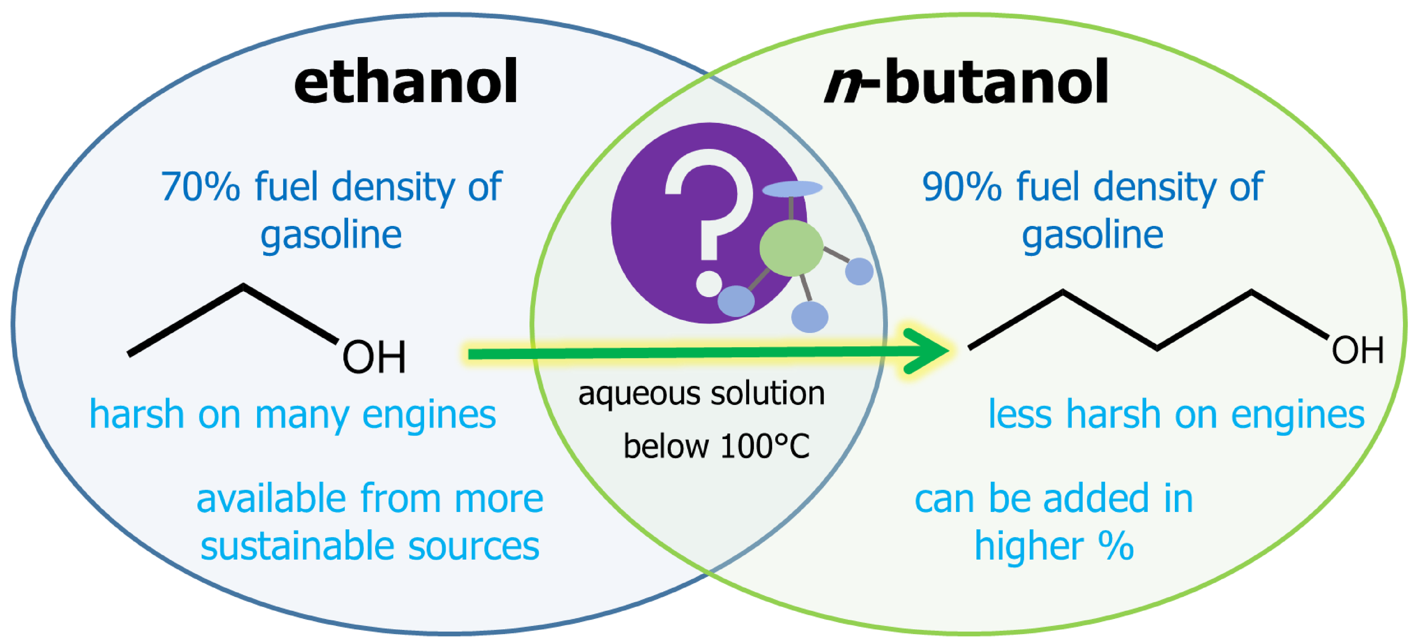
Introduction

The Need for Different Fuels

Fuels are used around us and by us every day: in heating and lighting our homes and work, making us goods, and transporting us to where we need to go. Many efforts have been made to find more sustainable alternatives to one of the most common types of fuel, gasoline.

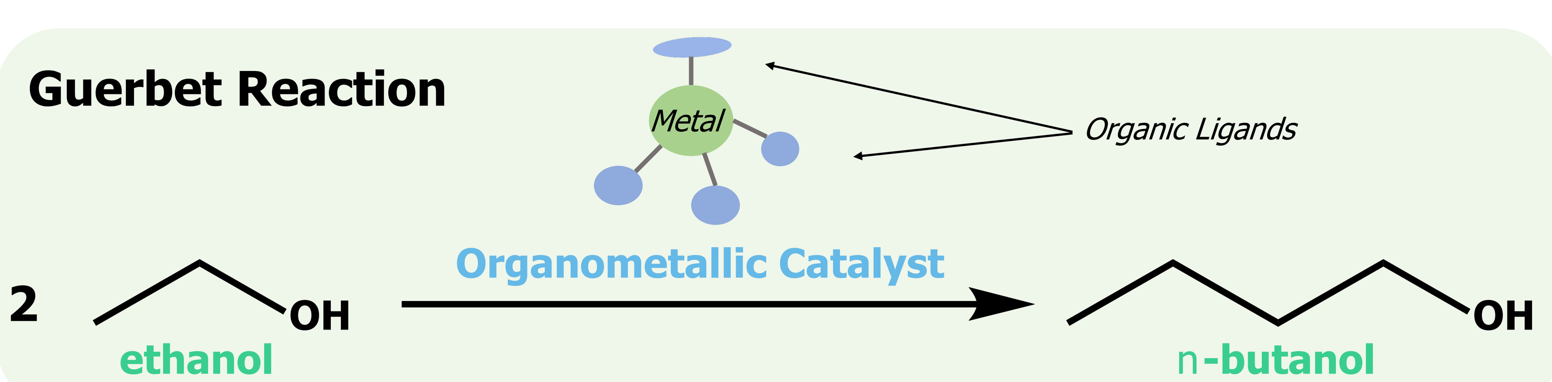
Strengths of *n*-butanol



- Most gasoline available at the pump has ethanol in it- a less dense fuel substitute that can be damaging to certain engines.
- This work aimed to take ethanol and convert it into the 20% more fuel dense *n*-butanol from CHASE ethanol feeds.

The Guerbet Reaction

The **Guerbet reaction** converts an alcohol (like ethanol) to a longer chain alcohol (like *n*-butanol).



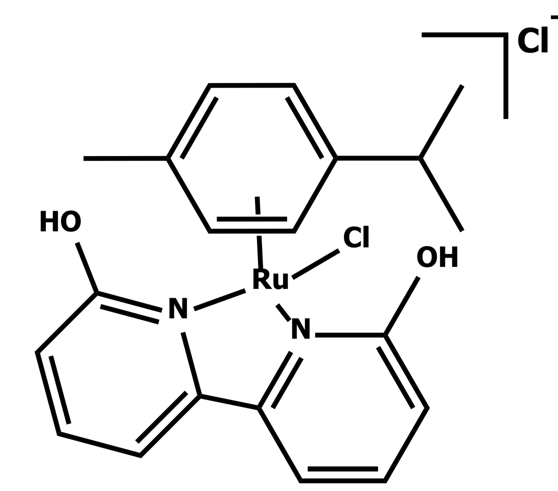
Coupling to Ethanol Production

- Traditionally the organometallic catalysts chosen for the **Guerbet reaction** require a temperature of over 100° C and to be in neat alcohol conditions to achieve high yields.
- Coupling this process to ethanol production, both traditionally and through CHASE initiatives requires a catalyst that works in temperatures under 100 °C and in aqueous conditions.

Catalyst Selection

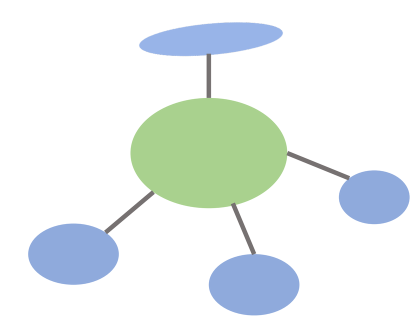
Strength of the Jones Catalyst

- Prior to the discovery of the Jones Catalyst no catalyst achieved a yield above 20% *n*-butanol and not in more than 5% H_2O.
- The Jones catalyst was able to achieve a 29% yield of *n*-butanol from ethanol at 85 °C and at a 84:16 H_2O to ethanol ratio.



Jones Catalyst

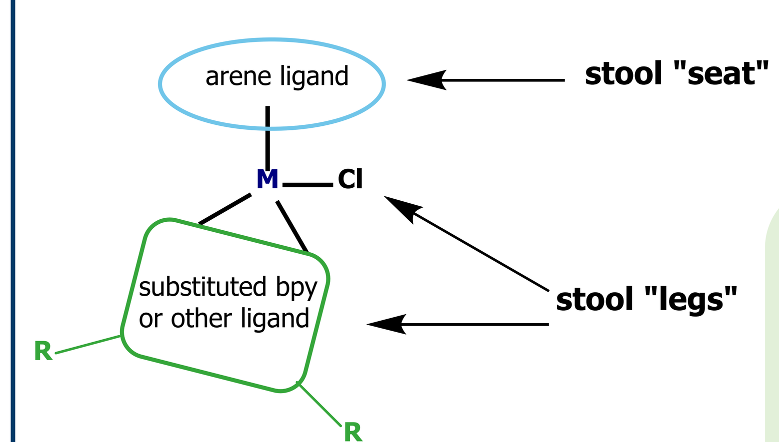
Project Goals

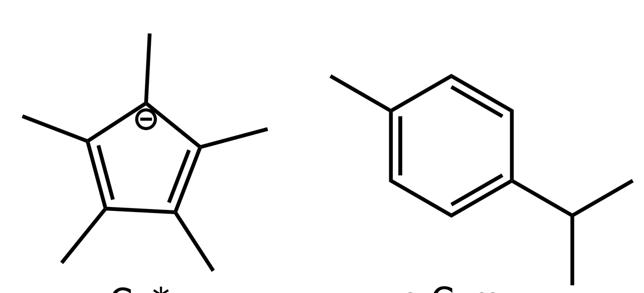


- To build upon the success of the Jones Catalyst and identify other Guerbet reaction catalysts that could be optimized to perform at even higher *n*-butanol yields
- To identify key design features of the Jones and similar catalysts that contribute to their success in converting ethanol to *n*-butanol

Design Elements

Piano-Stool Structure





Cp*　p-Cym

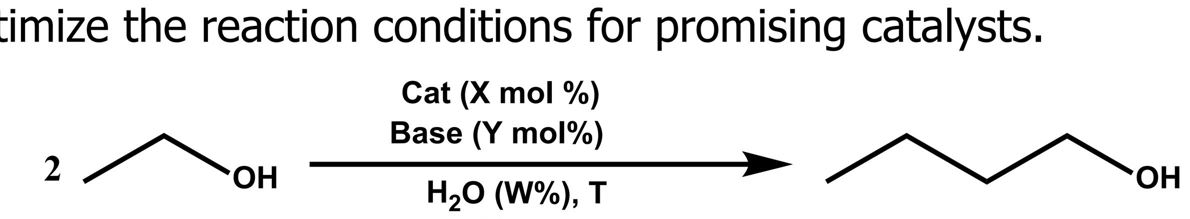
- The Jones catalyst has a "piano-stool" shape
- Variations on the Jones catalyst can change the "legs", "seat", or metal center.

- **Metal Center**: Ruthenium or Iridium
- **"Seat":** pentamethyl-cyclopentadiene (Cp*) or para-cymene (p-Cym)
- **"Legs":** L2 hydroxy or methoxy bipyridine derivatives OR an organic LX ligand

11 distinct catalysts were synthesized and tested.

Future Research Plans

- Optimize the reaction conditions for promising catalysts.

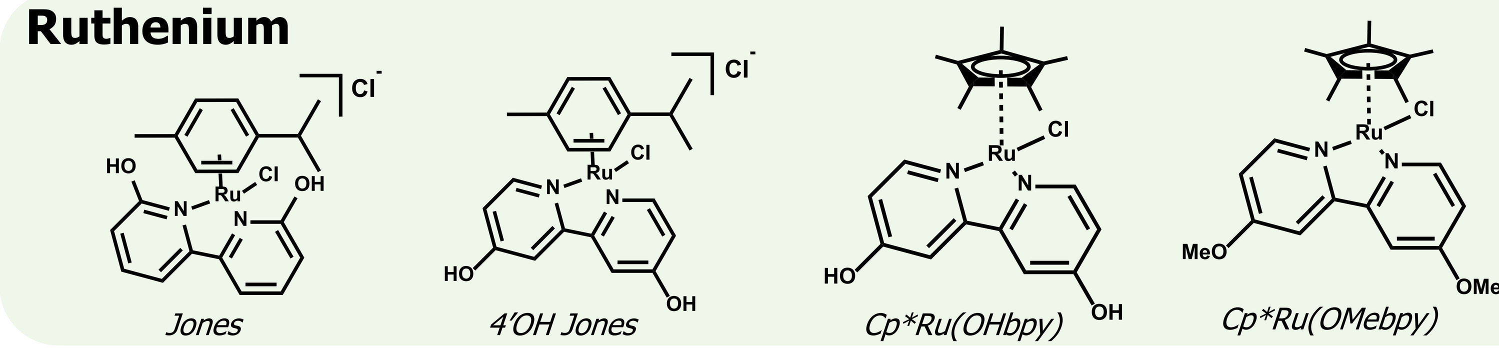


- Perform mechanism and kinetics studies to better inform catalyst design.

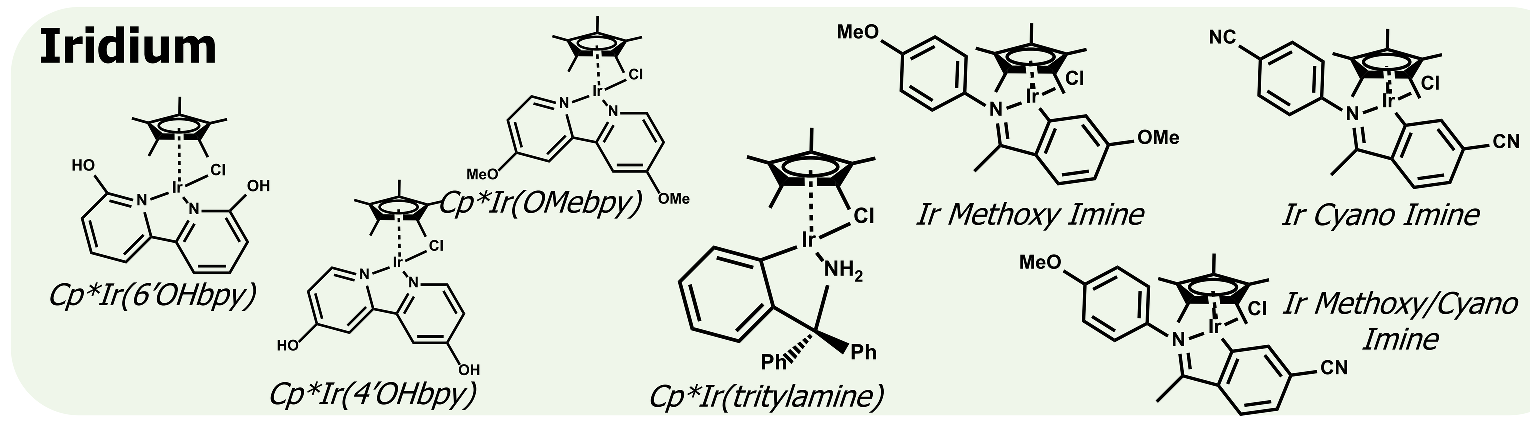
Catalyst Screening

Catalysts

Ruthenium

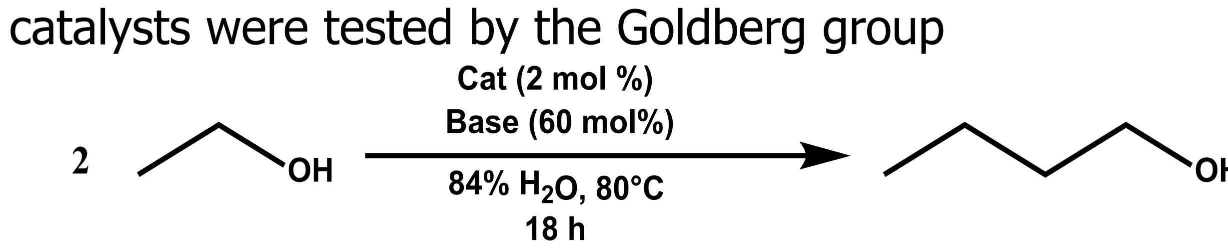


Iridium

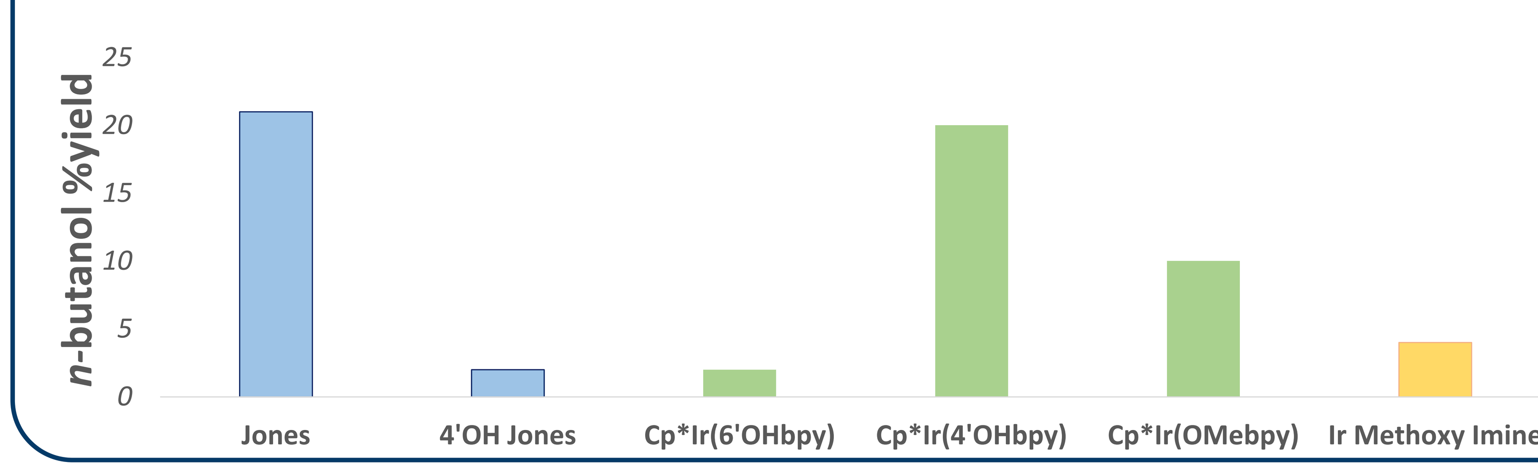


Key Results

- All catalysts were tested by the Goldberg group



- Most catalysts did not come close to the Jones in yield
- The Cp*Ir(4'OHbpy) catalyst was comparable to the Jones
- The catalysts will need their reaction conditions to be individually optimized
- **The difference in trends between the 4' and 6' substituted iridium and ruthenium complexes may indicate different mechanistic pathways**



References

Jones, W. D. *J. Am. Chem. Soc.* **2015.** Jones and Dibenedetto, *Organometallics*, **2021.** Balavoine. *Organometallics*, **1992.** Hest and Rutjes. *Beilstein J. Org. Chem.* **2013.** Zhao *Ang. Chem.* **2020.** Ziao. *Ang. Chem.* **2010.** Jones and Martin. *Org. Biomol. Chem.*, **2009**. Xiao and Wang, *Chem. Commun.,* **2013.**

Acknowledgements

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