

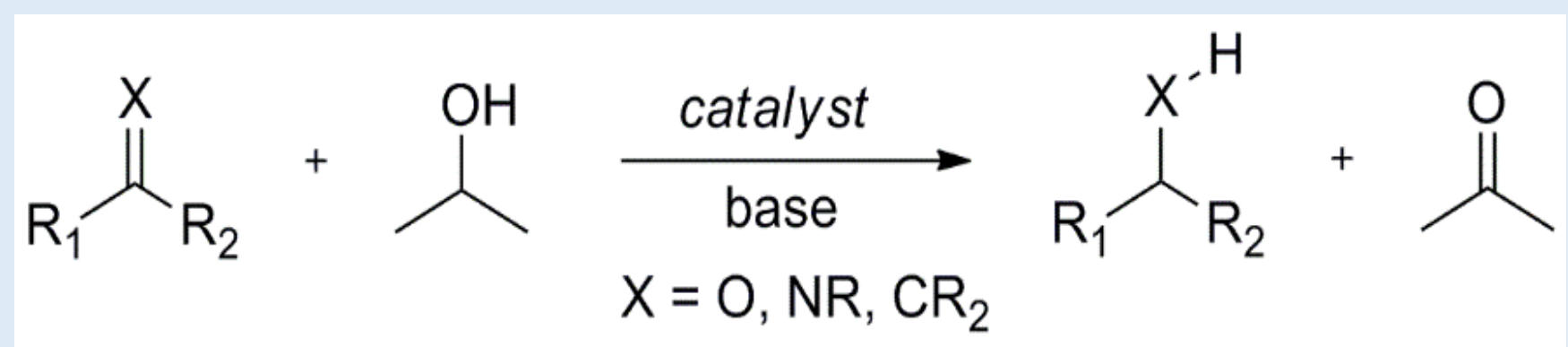


# Ruthenium Complexes of Primary Amido-Functionalized N-Heterocyclic Carbenes

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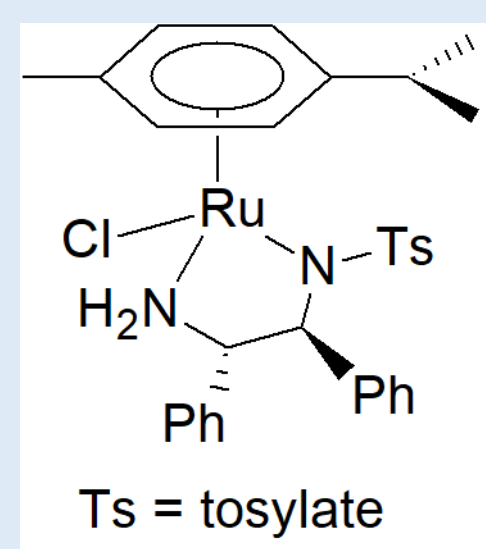
## Introduction Transfer Hydrogenation

Transfer hydrogenation involves the addition of H<sub>2</sub> through hydrogen surrogates, such as secondary alcohols, to double and triple bonds.

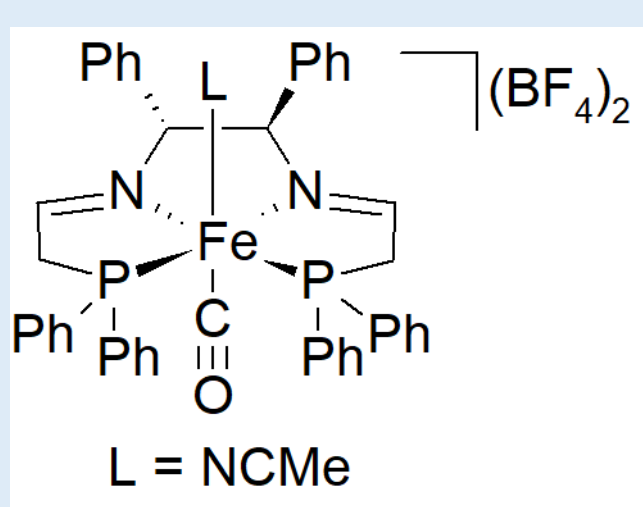


Dong Wang and Didier Astruc  
*Chemical Reviews* **2015** 115 (13), 6621-6686  
DOI: 10.1021/acs.chemrev.5b00203

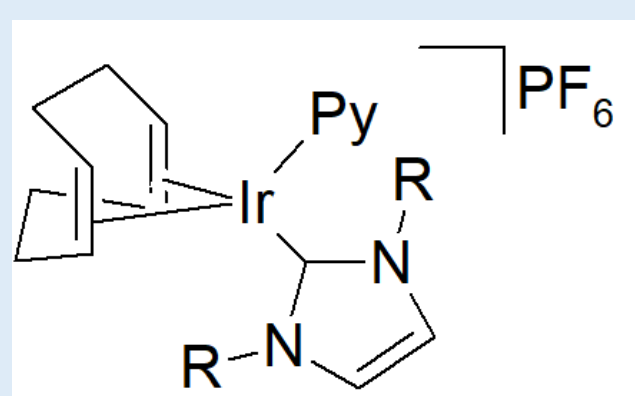
Benefits of transfer hydrogenation include that it avoids the use of high pressures of flammable hydrogen gas or the use of more expensive metal hydride salts (e.g., LiAlH<sub>4</sub>).  
Examples of previous transfer hydrogenation catalysts



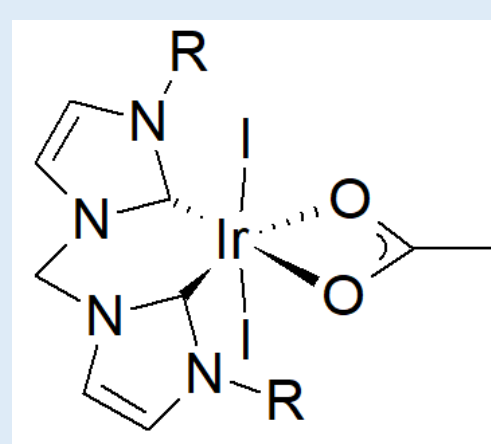
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Catalysts with metal-ligand cooperation

Catalysts with NHC ligands

Metal-ligand cooperation refers to when the metal and the ligand work together to react with the substrate. Normally, the ligand is there as a spectator to simply change the properties of the metal center.

### Project Goals

**Objective:** Develop ruthenium catalysts for base-free transfer hydrogenation reactions under aerobic conditions.

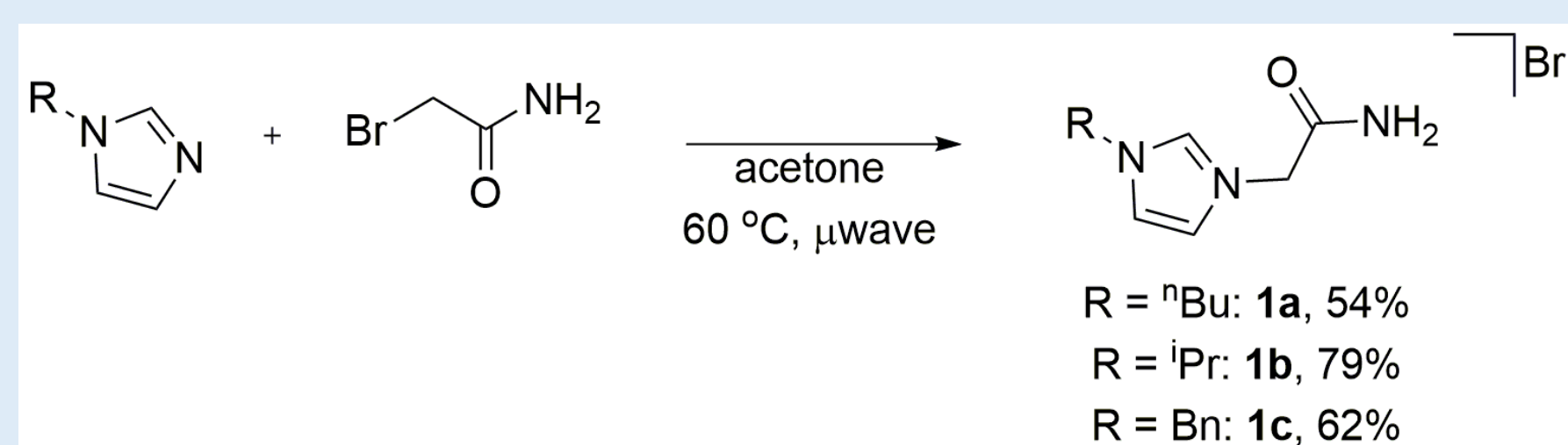
Our goal is to combine the use of metal-ligand cooperation, which produces highly active catalysts, and NHC ligands, which form stable catalysts.

Why base-free and in air?

Most transfer hydrogenation catalysts require inert atmosphere and added base. It would simplify the reaction setup and allow for the reaction of base-sensitive substrates.

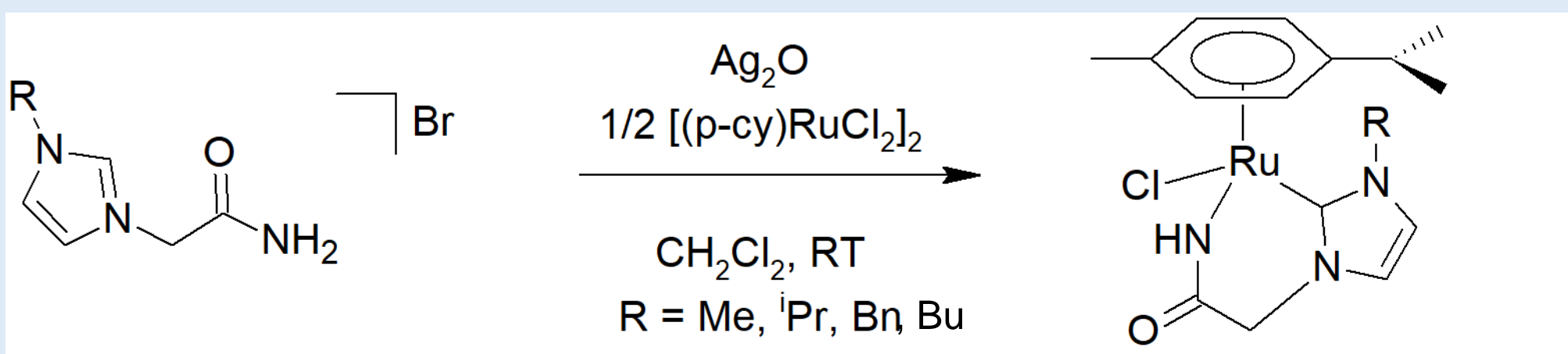
## Results and Discussion

### Synthesis of NHC Ligand Precursor



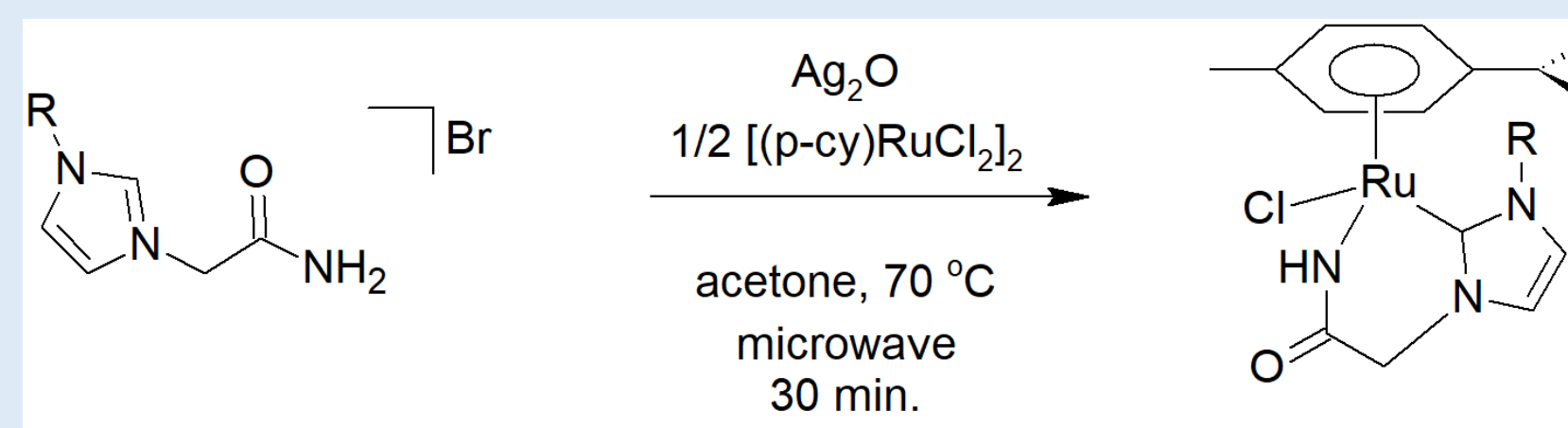
R = <sup>n</sup>Bu: **1a**, 54%  
R = <sup>i</sup>Pr: **1b**, 79%  
R = Bn: **1c**, 62%

### Synthesis of Ruthenium Chloride Complexes of the NHC Ligand



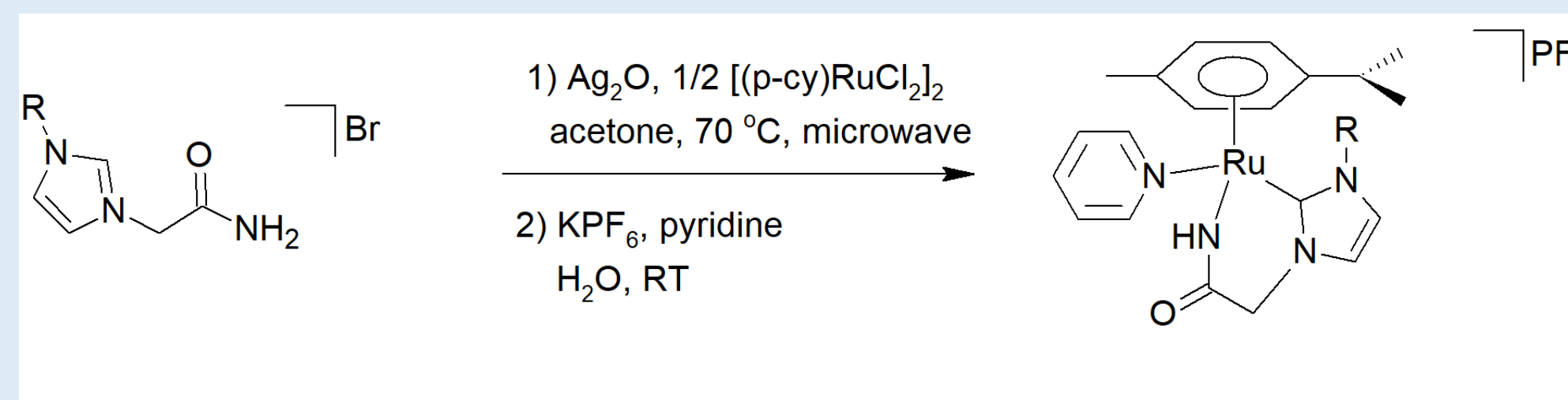
## Results and Discussion cont.

- Initial synthesis of chloride complexes were used with Ag<sub>2</sub>O in DCM. These were long reactions using DCM and had low recoveries.
- Synthesis of chloride complexes using Ag<sub>2</sub>O in acetone with microwave to avoid a long reaction time (30 minutes) and using a greener solvent. The chloride complexes were difficult to get spectroscopically clean.

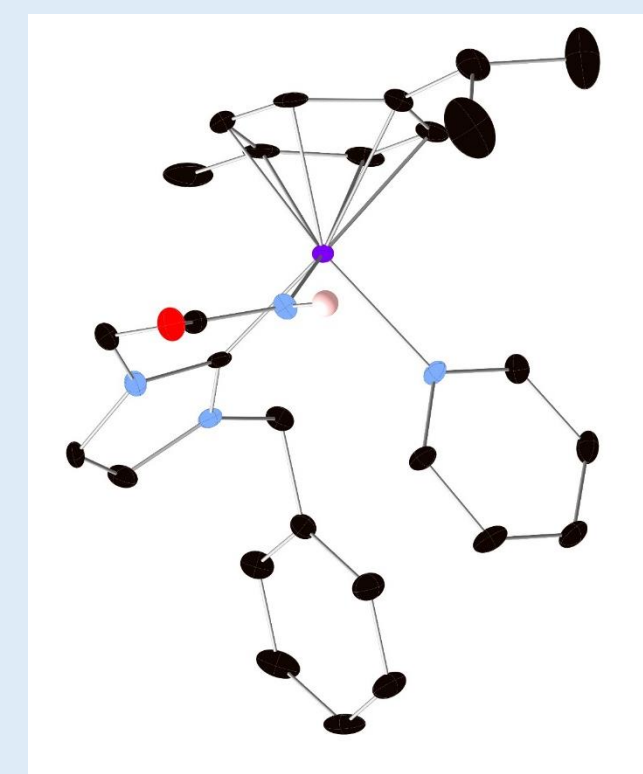


### Synthesis of Ruthenium-Pyridine Complexes of the NHC Ligand

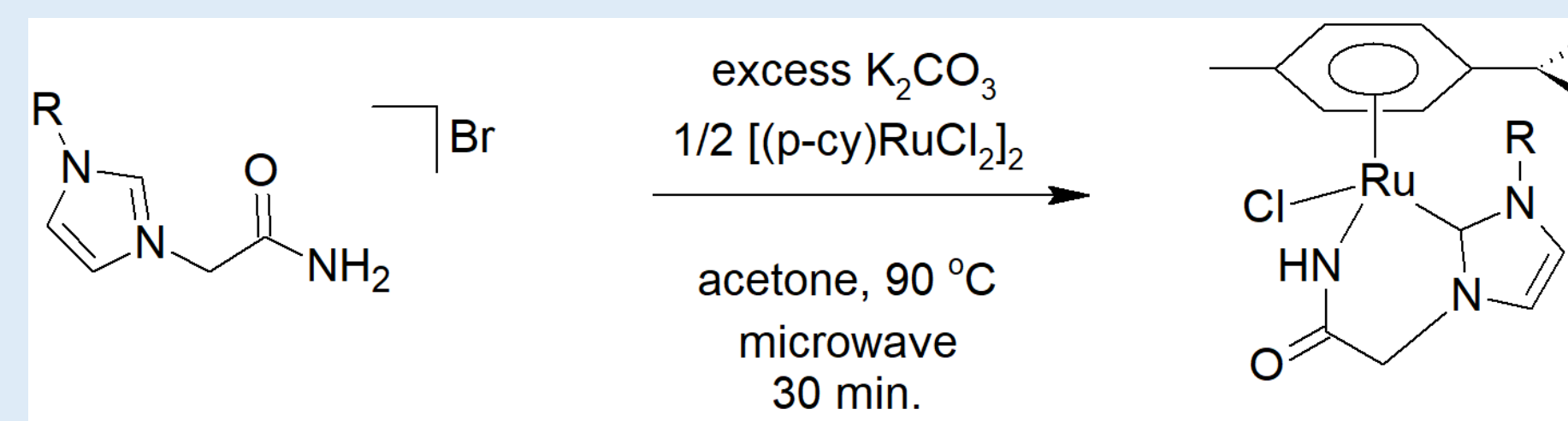
- Synthesize pyridine complexes to isolate cleaner complexes that could be crystallized.
- The hypothesis was that cationic complexes would change the solubility of the complexes such that crystallization would be easier.



- These complexes were spectroscopically clean, but elemental analyses indicated impurities.
- Difficulty getting bulk crystallization, we were able to obtain crystals suitable for a single-crystal X-ray diffraction study.



- We hypothesized that there could be deviation in the elemental analysis data due to poor combustion from the PF<sub>6</sub><sup>-</sup> ion. Using NaBPh<sub>4</sub> in place of KPF<sub>6</sub> did not give any improvements in purity.
- Attempted to make the chloride complexes and pyridine complexes using K<sub>2</sub>CO<sub>3</sub> in place of Ag<sub>2</sub>O due to the possibility of silver impurities.
- Potassium carbonate is more economical and environmentally friendly. The reactions works, but purity is still an issue.



## Conclusion and Ongoing Work

- While a variety of ruthenium complexes could be made, isolating analytically pure complexes has been challenging.
- Able to synthesize and characterize ruthenium complexes with NHC ligand.
- Ruthenium complexes were able to go through base free transfer hydrogenation.
- Preliminary data with impure samples suggest that these complexes will be active catalysts.

## Acknowledgments

We thank Dr. Benny Chan from the College of New Jersey for solving the crystal structure. The X-ray diffractometer at TCNJ was purchased with funds from the National Science Foundation. Research at Stockton University was supported by Stockton University and Donors of the American Chemical Society Petroleum Research Fund.