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Synthesis of Bipyridine-Derived Iron Catalysts for Hydrogenation

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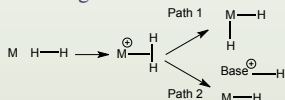
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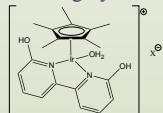
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Introduction

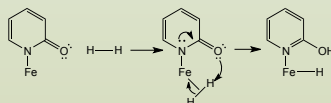
- Industrially, alkene and carbonyl hydrogenations are common reactions catalyzed by the highly expensive and toxic metals iridium, rhodium, and ruthenium.¹
- Path 1 below shows the traditional homolytic cleavage of hydrogen. Path 2 shows the alternative heterolytic cleavage. Both form a catalyst for hydrogenation, with differing results.²



- Pyridone based iridium catalysts utilizing ligand-assisted heterolytic cleavage have been shown to be highly effective (below).³

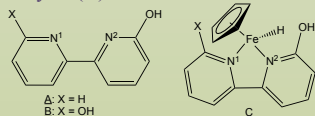


- Using instead an iron catalyst of similar design would reduce cost and environmental impact (example below).



Objectives

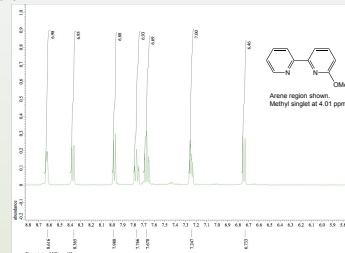
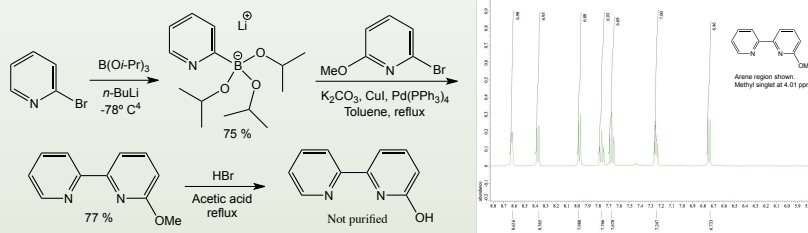
- Synthesize bipyridine ligands with one (A) and two (B) hydroxyl groups.
- Attach ligands to iron center to produce catalysts (C).



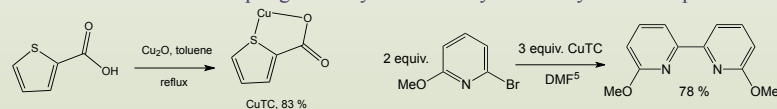
- Test catalytic properties in alkene and carbonyl hydrogenations.

Results

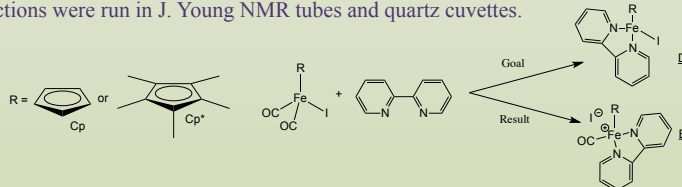
- Monohydroxyl ligand A was synthesized by palladium catalyzed Suzuki-Miyaura cross-coupling and hydrolysis. Six different conditions were tested in optimizing the cross-coupling step, altering reflux time, solvent and presence of CuI.



- 6,6'-dimethoxy-2,2'-bipyridine (precursor to ligand B) was synthesized by CuTC promoted room temperature Ullman coupling. Purification difficulties prevented hydrolysis during the time allotted. The Ullman coupling can only be used to synthesize symmetrical products.



- Replacement of iron complex CO groups by amines was attempted using 2,2'-bipyridine to model future ligand attachment. All tested conditions produced complex E instead of target D. Iron reactions were run in J. Young NMR tubes and quartz cuvettes.



Bipyridine-Iron Complex Reaction Conditions Yielding Complex E

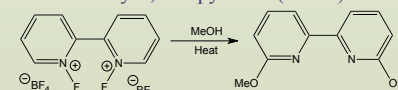
Entry	Reactant Fe Complex R =	Temperature (°C)	Photolysis & Bubbling N ₂	Solvent
1	Cp*	80	No	Benzene-d ₆
2	Cp*	80	No	Benzene-d ₆
3	Cp	80	No	Benzene-d ₆
4	Cp	80	No	Benzene-d ₆
5	Cp	25	Yes	THF
6	Cp	65	Yes	THF

Conclusions

- Both ligand syntheses are possible and intermediate reactions were optimized.
- While Suzuki cross-coupling could be used to synthesize both ligands, Ullman coupling synthesis of ligand B significantly reduces reaction time and difficulty.
- Intermediate reaction coproducts make purification challenging.
- Removal of both iron complex CO groups proved more difficult than expected.

Future Work

- Purify and hydrolyze 6,6'-dimethoxy-2,2'-bipyridine to yield dihydroxyl ligand B.
- Purify monohydroxyl ligand A.
- Develop method to remove both iron complex CO groups.
- Test catalytic properties.
- Attempt alternate synthesis of 6,6'-dimethoxy-2,2'-bipyridine (below).



Acknowledgements/Literature Cited

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²Hartwig, J. *Organotransition Metal Chemistry: From Bonding to Catalysis*, 1st ed.; University Science Books; 2010.

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⁴Billingsley, K. L.; Buchwald S. L. *Angew. Chem. Int. Ed.* **2008**, *47*, 4695-4698.

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