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The Synthesis, Characterization, and Reactivity of a Heterobimetallic Organometallic Complex with a *trans* Bidentate Ligand for Catalytic Carbon-Hydrogen Bond Activation

Sophia E. Neglia, Dr. John P. Lee, and Dr. Jared A. Pienkos

Introduction

Fossil fuel resources represent the major source of both fuels and the starting point for more complex industrial and pharmaceutical molecules. The production of styrene in manufacturing also produces ethylbenzene along with its di-substituted forms (Scheme 1). A process called C-H activation can produce styrene alone by selectively breaking and functionalizing a carbon-hydrogen bond (C-H activation) in the presence of an oxidant. This can be accomplished by a transition metal catalyst such as palladium (Pd) by performing an atom economical reaction (Scheme 2)¹. Pd with acetate (OAc) can facilitate C-H activation of inert hydrocarbons where the acetate can serve as an intra- or intermolecular base (Figure 1). Some ligands can bite into a metal, and are fittingly called bidentate ligands, and the L-Pd-L angle can range from 90° (*cis*-isomer) to 180° (*trans*-isomer) with the former being more common². Pd can already be coordinated with ethynyl pyridine ligands on a titanium (Ti) complex in *trans* geometry (Figure 2)³. I propose to work with a *trans* bidentate ligand on ruthenium (Ru) for C-H activation, which has not been used before in C-H activation.

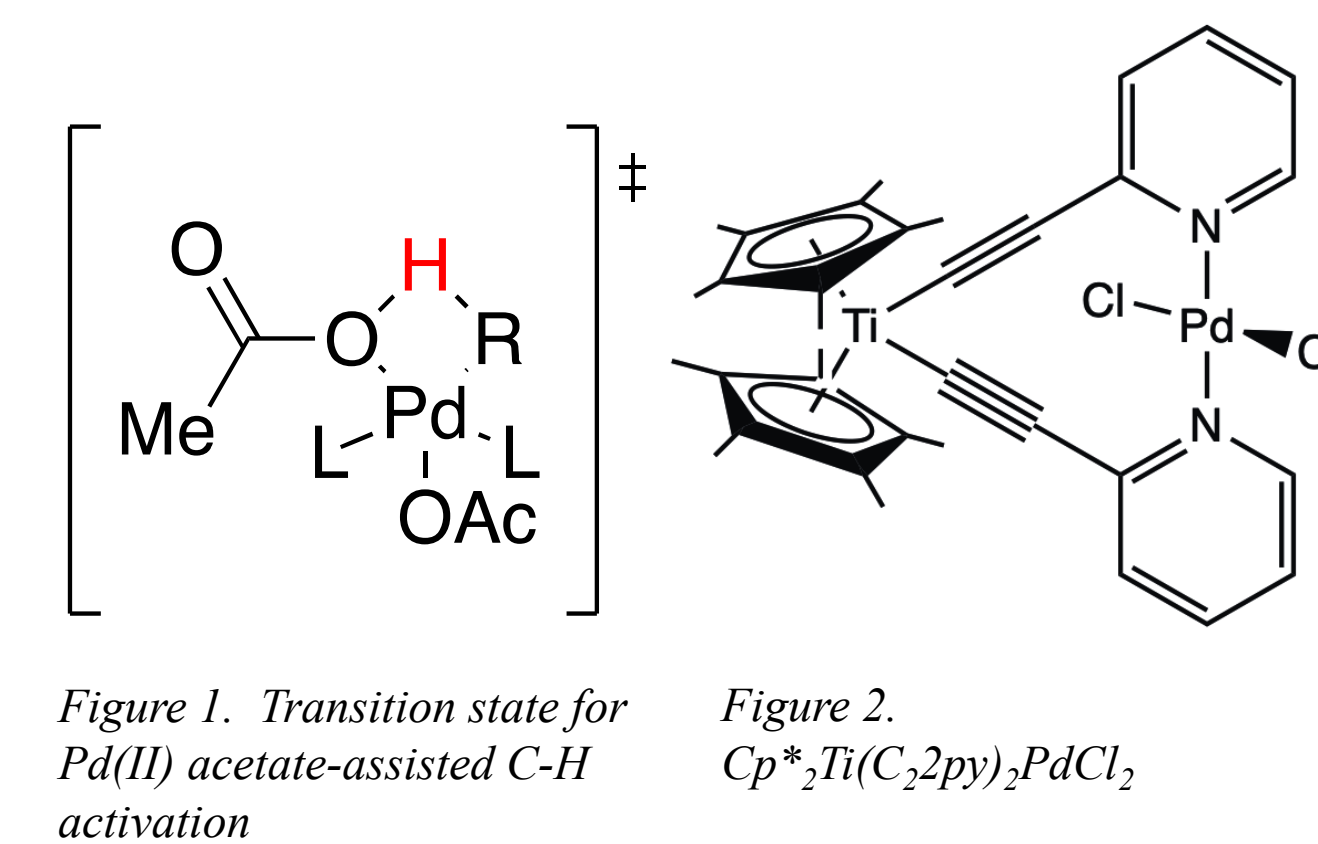
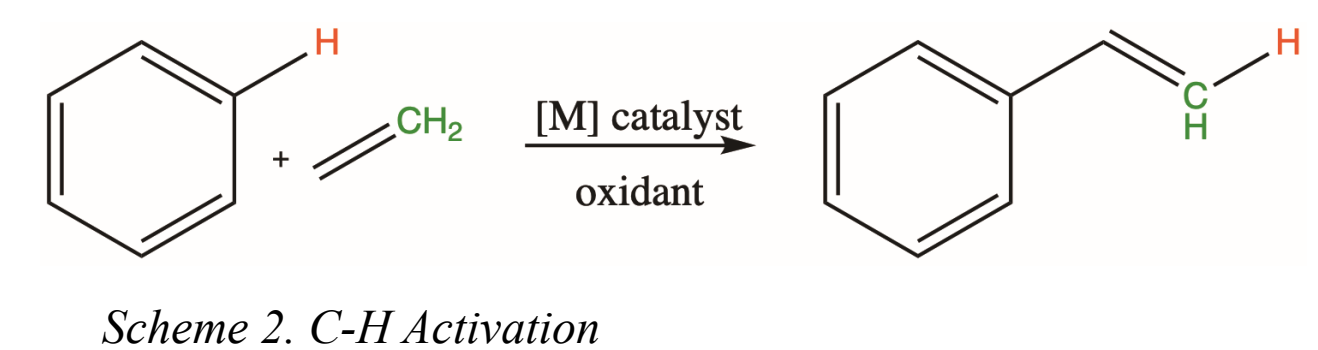
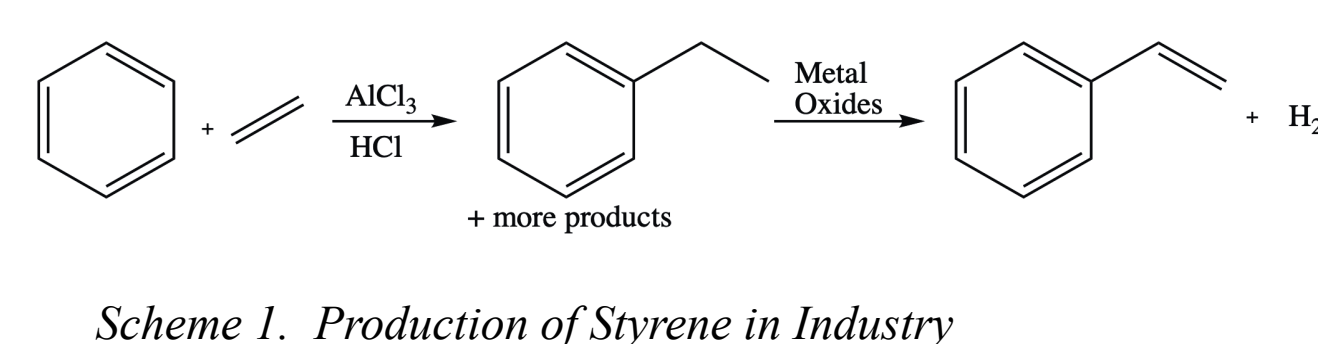


Figure 1. Transition state for Pd(II) acetate-assisted C-H activation

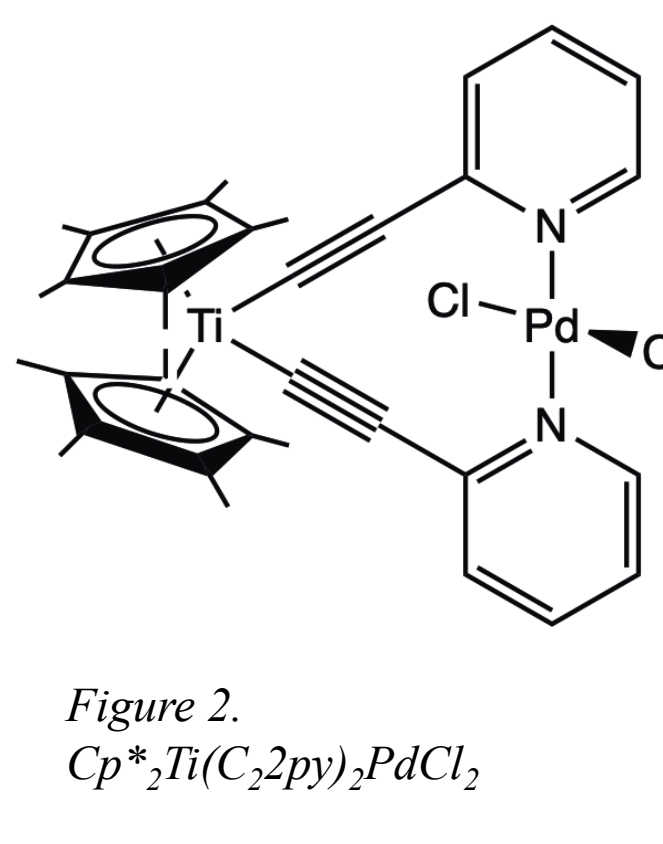
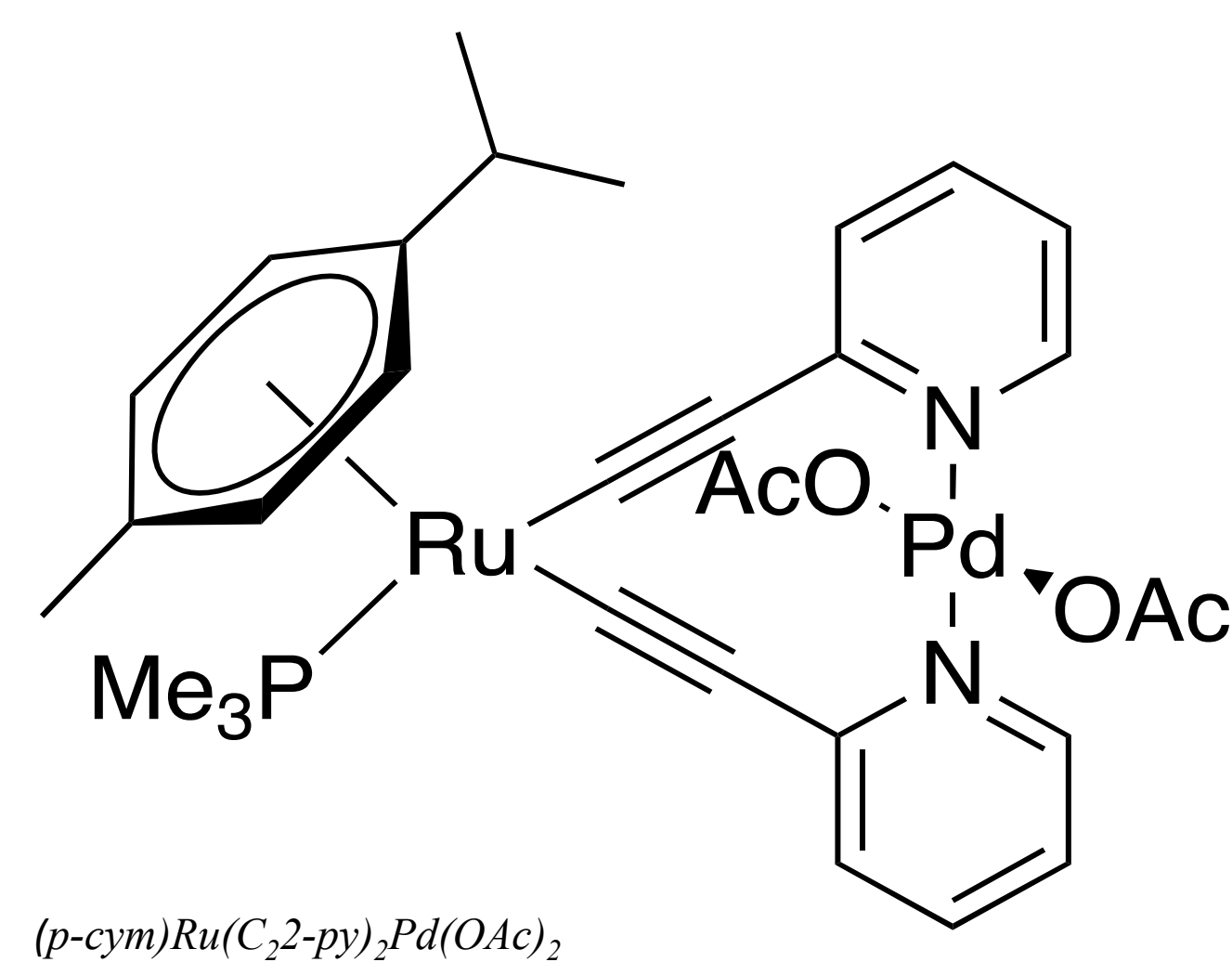


Figure 2. Cp*,Ti(C₂-2py)₂PdCl₂

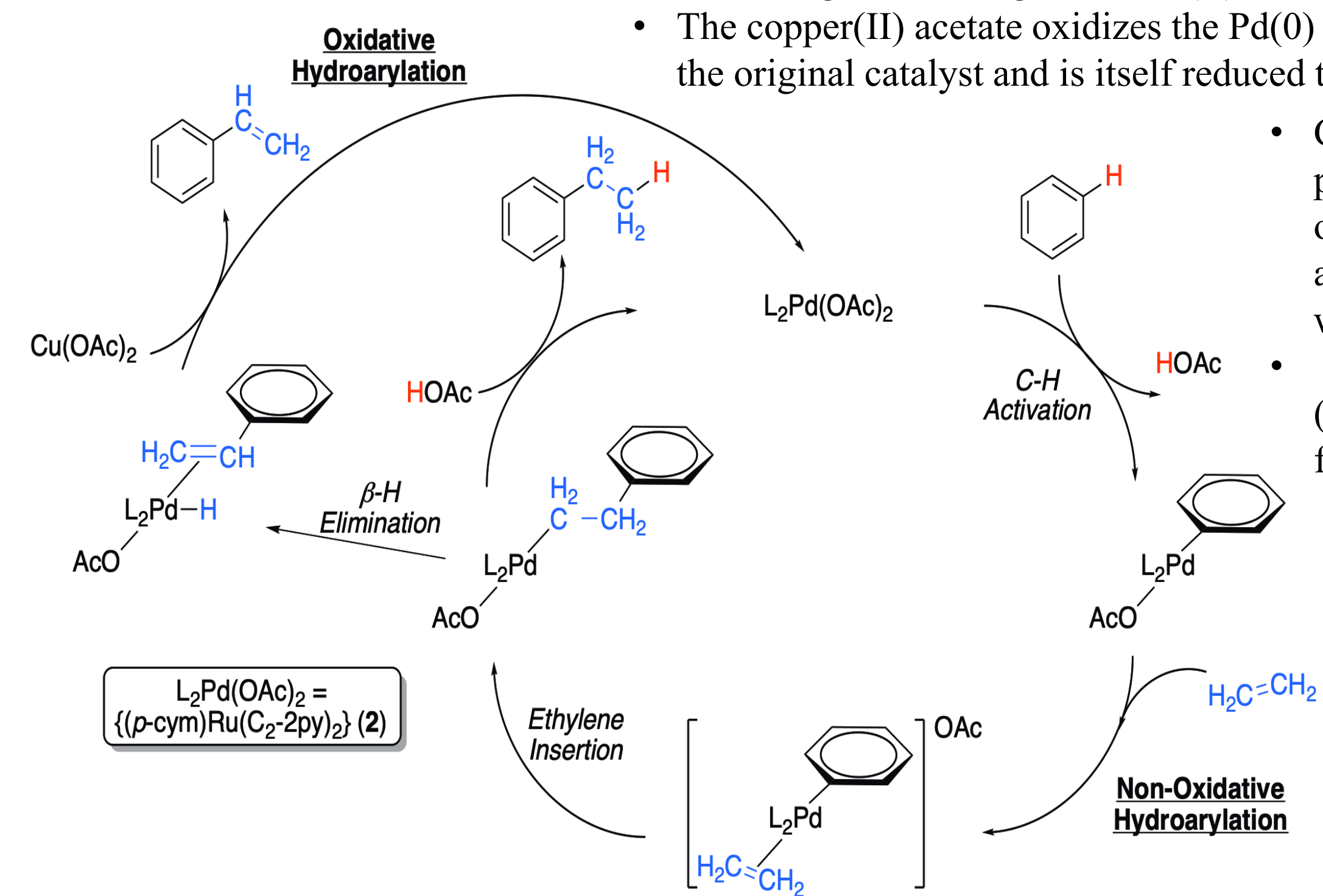
Proposed Catalyst



- (*p*-cym) helps direct activity to the other face of the octahedral complex
- PMe₃ is electron rich which is proposed to help support the alkynyl ligands
- *Cis* alkynyl ligands attached to Ru gives space for Pd(OAc)₂ to attach
- Using the Ru(II) has a "hinge"
- Will allow for the pendant pyridines to coordinate in a *trans* fashion

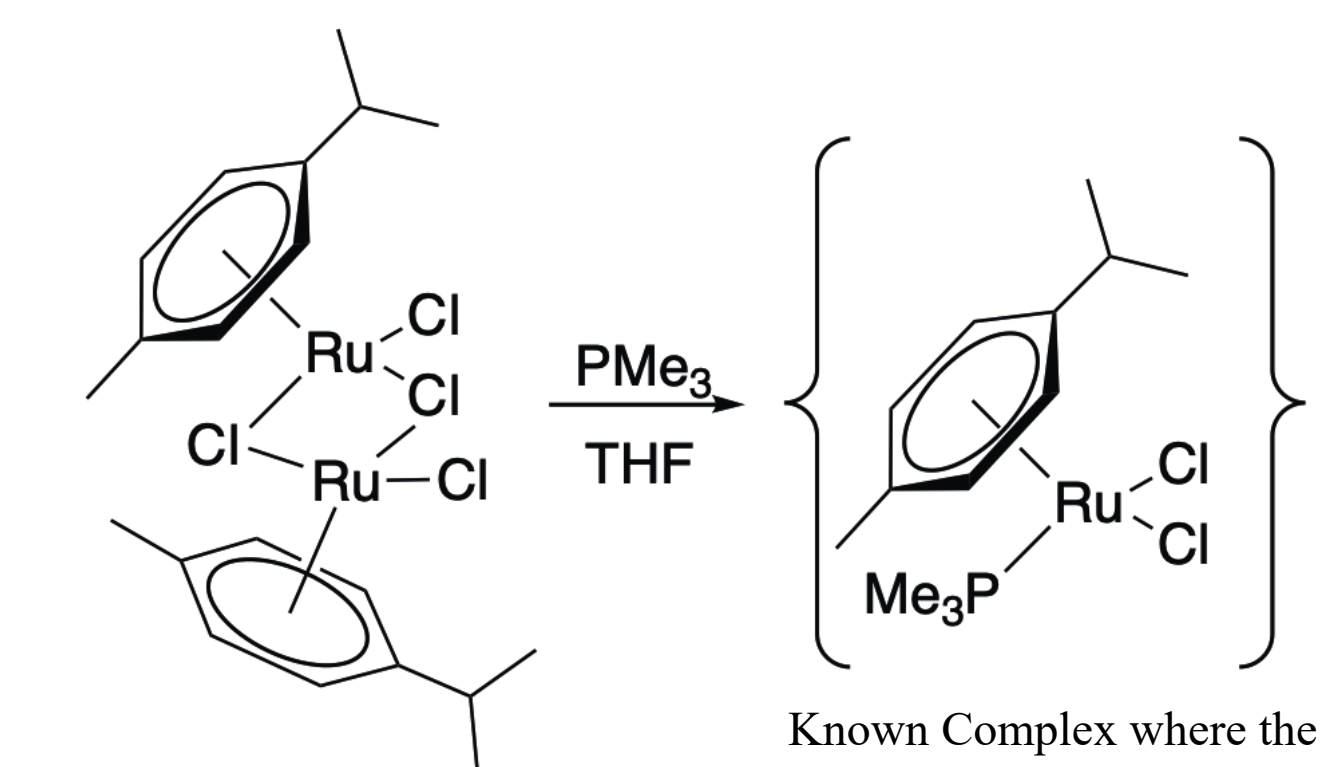
Proposed Catalytic Cycle

- Oxidative hydroarylation has been observed with *cis* bidentate ligands on square planar Rh(I) and Pd(II)^{4,6}
- Our interest lies in whether such a cycle will work using a *trans* bidentate ligand on square planar Pd(II)
- Removing Pd-H will go from Pd(II) to Pd(0)
- The copper(II) acetate oxidizes the Pd(0) back to Pd(II) to regenerate the original catalyst and is itself reduced to copper(I) acetate
- Copper(I) acetate in the presence of oxygen can be re-oxidized to copper(II) acetate and oxygen is reduced to water
- Thus, those 2 hydrogens (blue and red) wind up forming a water molecule

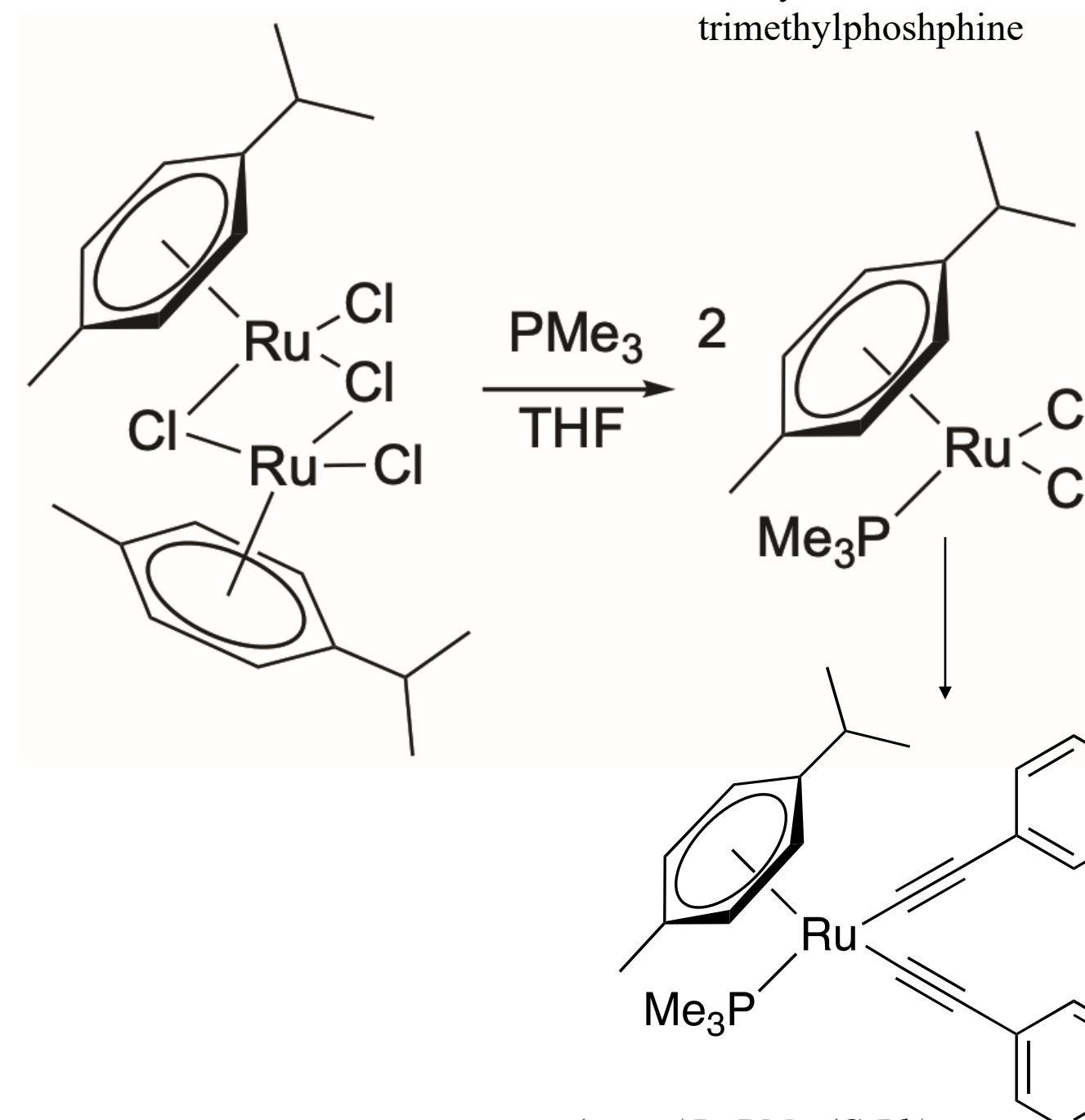


Proposed catalytic non-oxidative (inner loop) or oxidative (outer loop) hydroarylation catalyzed by Complex 2 to produce either ethylbenzene or styrene, respectively, from benzene (red) and ethylene (blue)

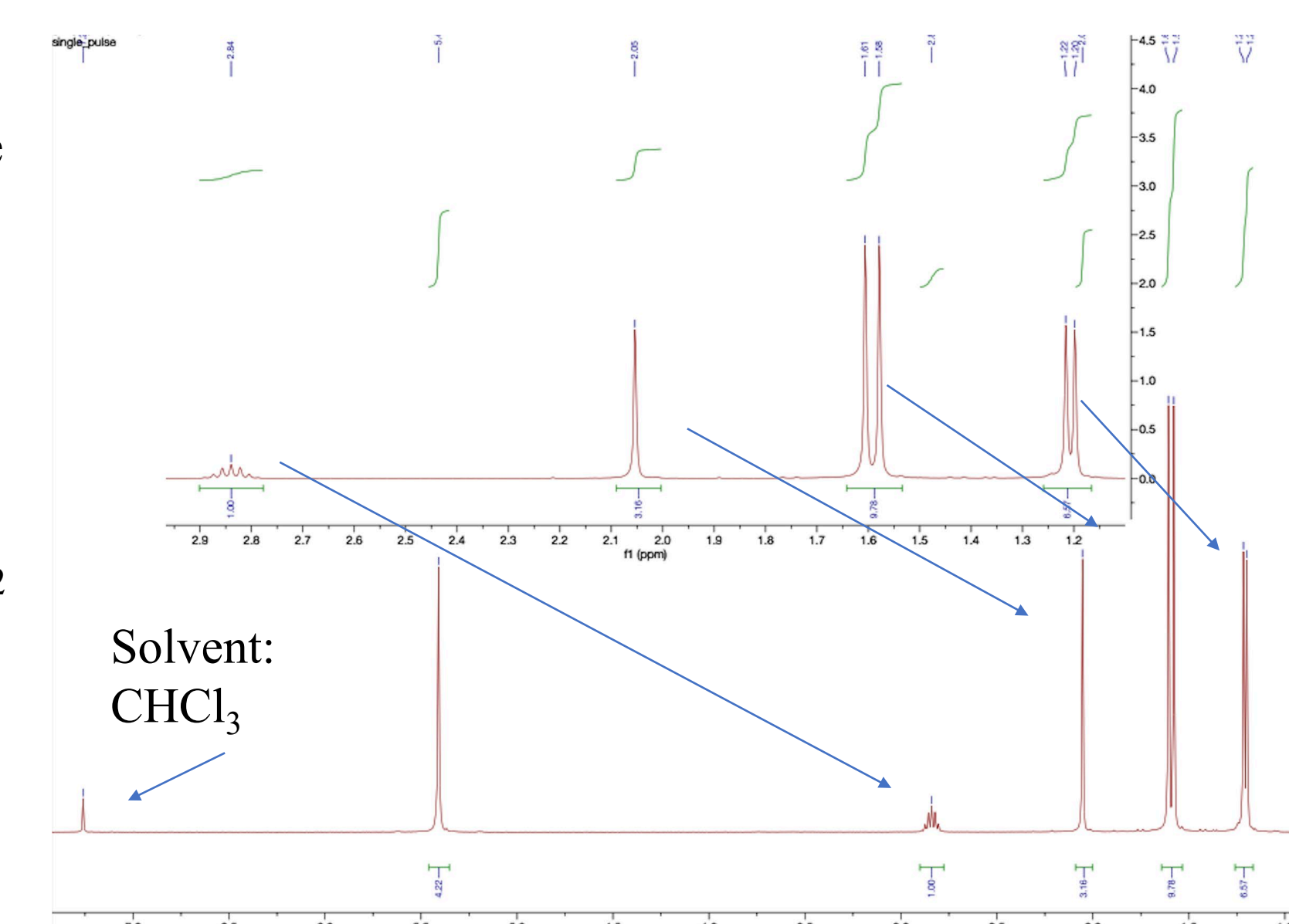
Design and Methods



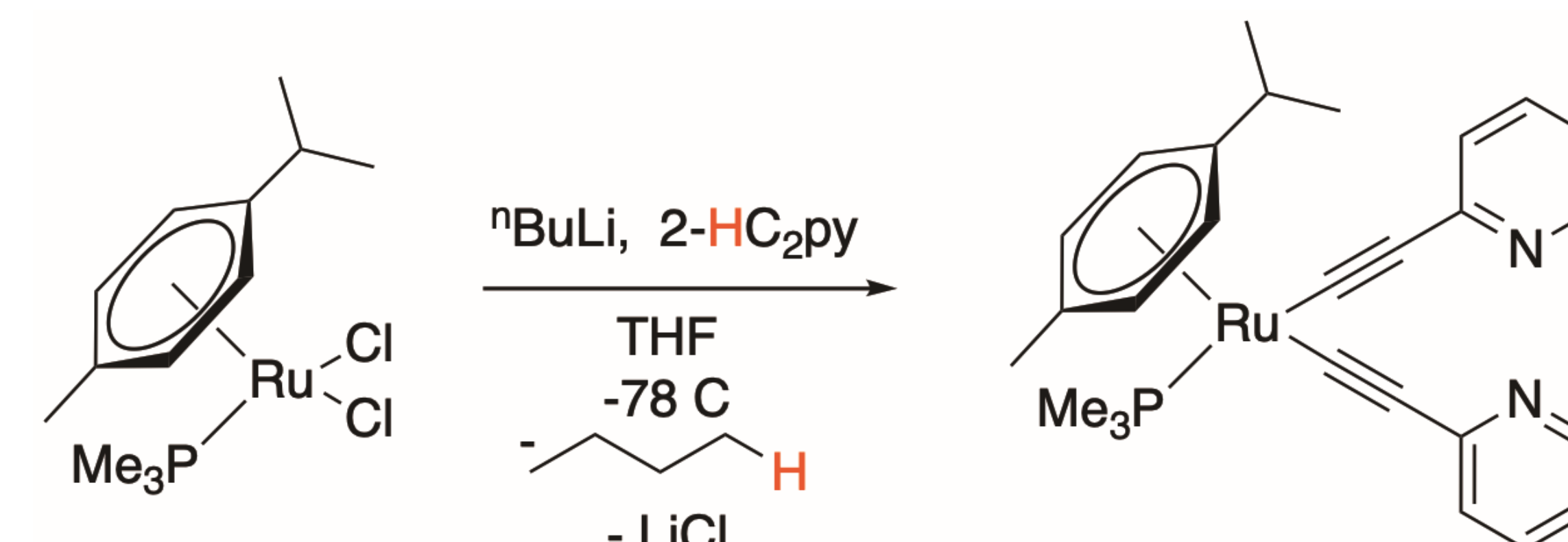
Known Complex where the electronic and sterics can be readily modulated at the trimethylphosphine



- Technique done on the Schlenk line
- Final product is an orange solid used for starting material in making (*p*-cym)Ru(PMe₃)(C₂py)₂
- Yield > 80%
- ³¹P NMR peak at 5ppm

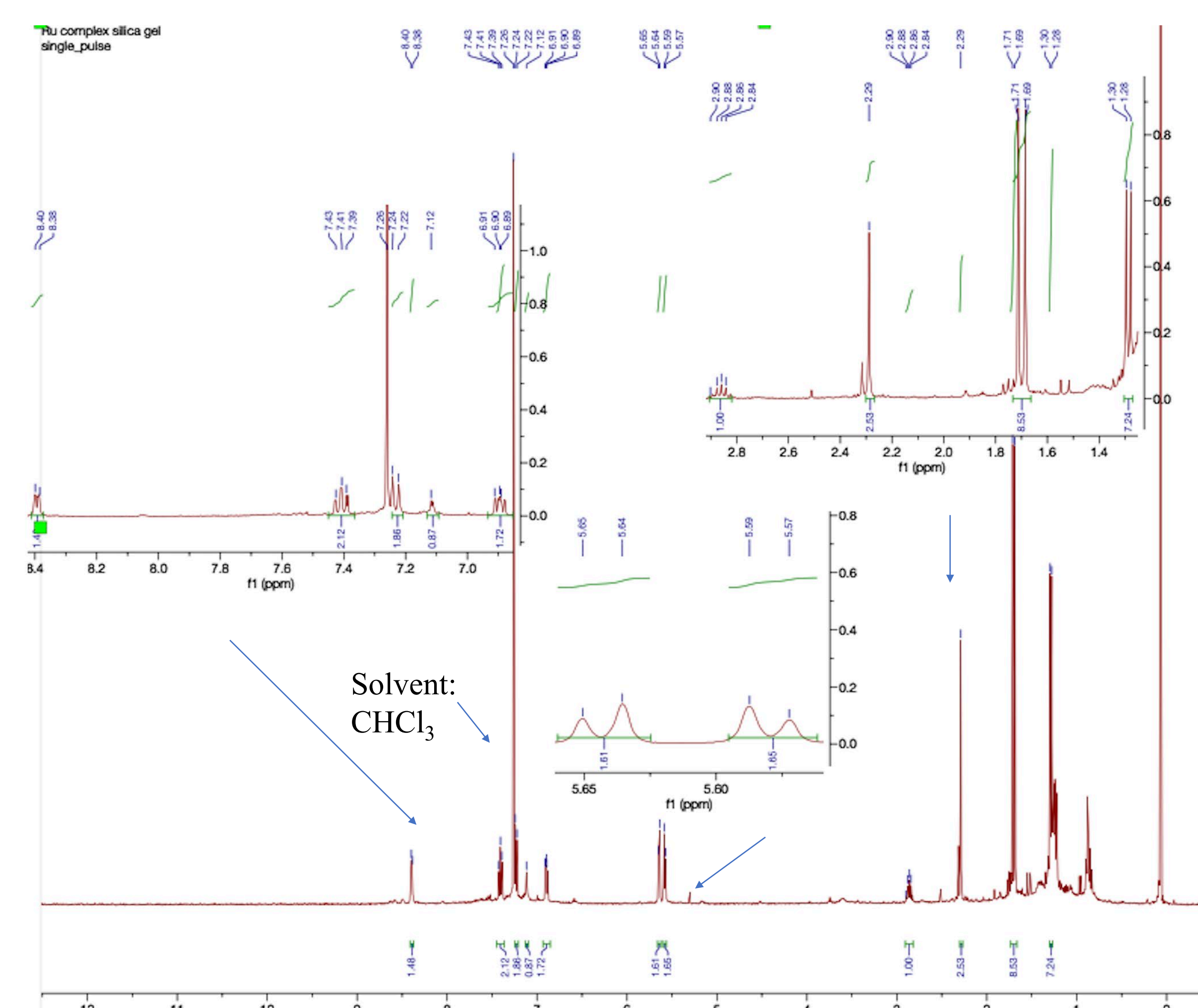


Step 2:

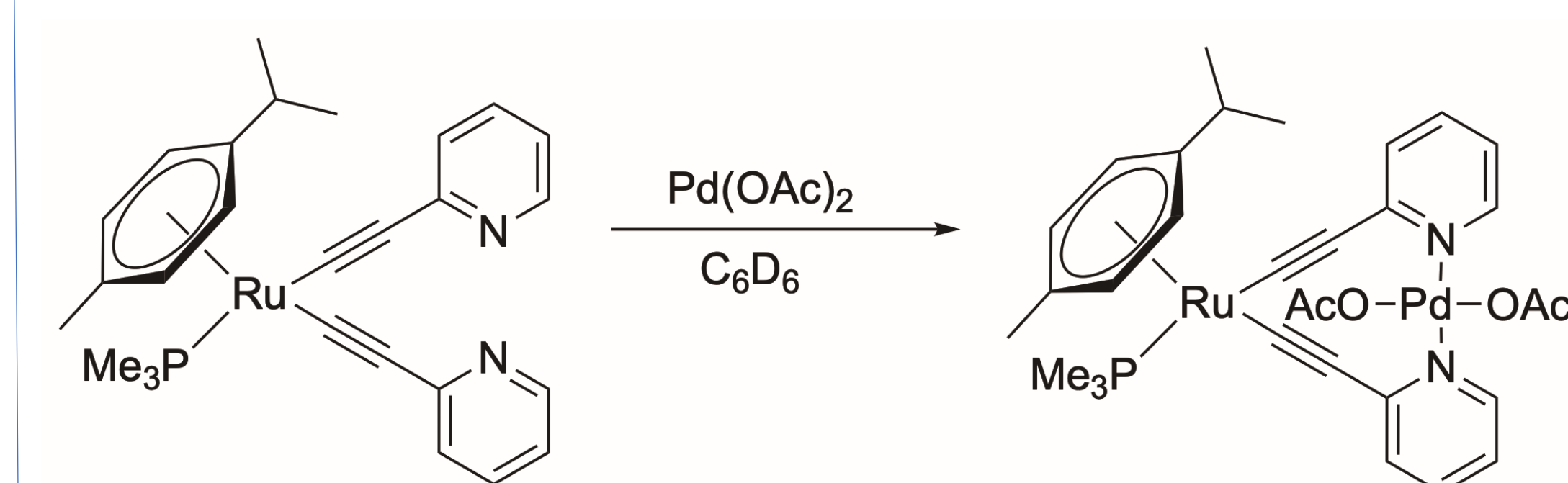


- Made 2-HC₂py standard solution in THF to avoid using microliter syringe
- Did not let reaction stir overnight
- Crude ¹H and ³¹P NMR are consistent with desired product and starting material
- ³¹P NMR showed peak at 15ppm
- Crude solid isolated had 40% yield

¹H NMR of (*p*-cym)Ru(PMe₃)(C₂-2py)₂



Conclusions and Future Work



- Does not make significant difference to start with the Ru Dimer or (*p*-cym)Ru(PMe₃)Cl₂
- Reaction with ⁿBuLi and 2-HC₂py standard in THF works to prepare (*p*-cym)Ru(PMe₃)(C₂-2py)₂
- ¹H NMR is consistent with two ethynylpyridine ligands displacing both chloride ligands
- Will work towards using new reagents for the deprotonation step
- Still need to work on purification technique
- Need cleaner product and higher yield
- Once purified attempt reaction with Pd(OAc)₂ coordination on larger scale

Acknowledgements

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References

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