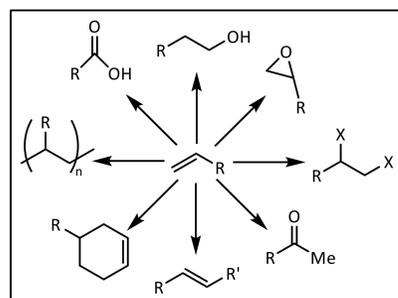
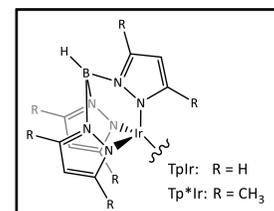


## Introduction



As shown in the left diagram, alkenes are important precursors for fuel and chemical production. The current commercial-scale conversion of alkanes to alkenes involves expensive and toxic oxidizers and high reaction temperatures. Homogeneous catalysts can affect dehydrogenation with better selectivity and lower energy input. For this project, we are focused on synthesizing a transition metal catalyst that is compatible with molecular oxygen (O<sub>2</sub>) as an oxidant. Molecular oxygen is the ideal “green” oxidant as it is inexpensive, abundant, and environmentally harmless.

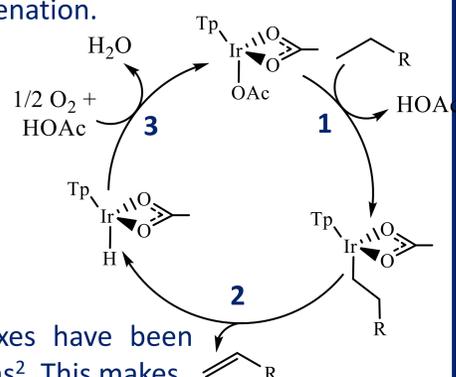
## Ligand-Metal System Selection



Iridium(III) bis-acetate complexes have been shown by the Goldberg Group to successfully activate C-H bonds in benzene and octane. Additionally, the systems studied proceed through bond activations via concerted metalation-deprotonation (CMD) and can maintain Ir(III) oxidation state.<sup>1</sup> This avoids low valent Ir(I) species that are very reactive with nitrogen, water, oxygen, or alkene, and will inhibit dehydrogenation.

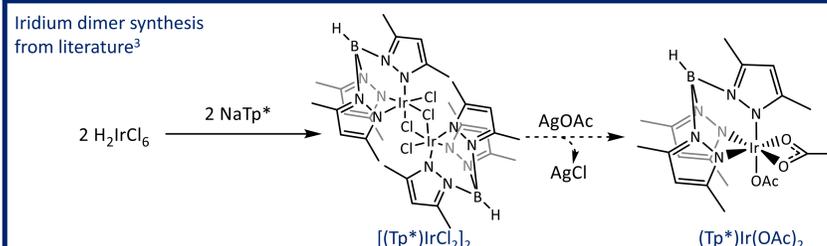
The diagram to the right shows the ideal three-step catalytic cycle:

1. C-H activation
2. β-H elimination
3. Regeneration

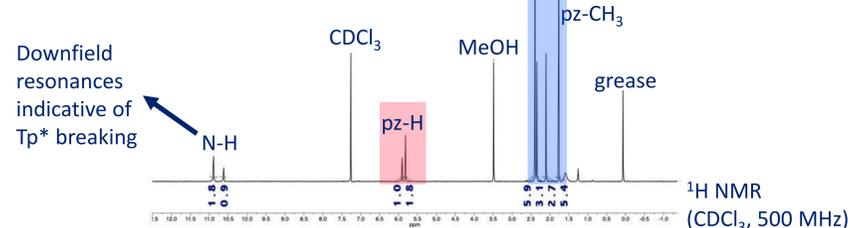
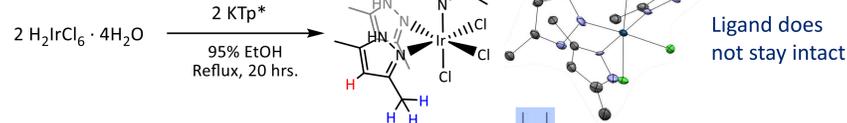


Additionally, (Tp\*)Ir(III) complexes have been known to undergo C-H activations<sup>2</sup>. This makes a (Tp\*)- or (Tp)-iridium(III) bis-acetate the target complex for this project's goal of aerobic alkane dehydrogenation [Tp = hydrotris-pyrazolylborate, Tp\* = hydrotris(3,5-dimethylpyrazolyl)borate]. For characterization, we used X-ray crystallography, proton (<sup>1</sup>H) NMR, and ESI mass spectrometry.

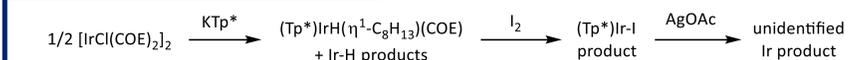
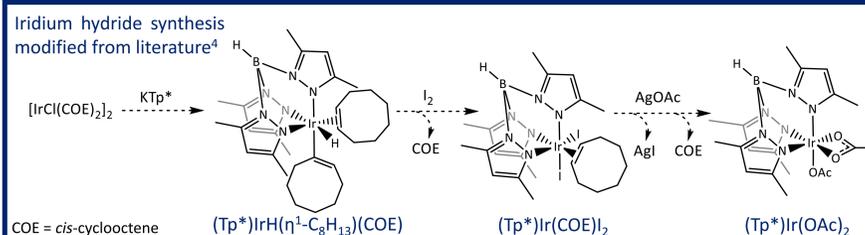
## Attempted Synthesis of [(Tp\*)IrCl<sub>2</sub>]<sub>2</sub>



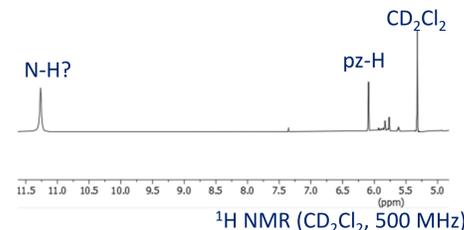
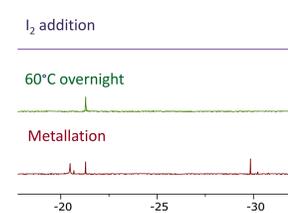
All syntheses were performed under an inert (N<sub>2</sub>) atmosphere with use of a glovebox or Schlenk line manipulations.



## Proposed (Tp\*)Ir(OAc)<sub>2</sub> Synthesis

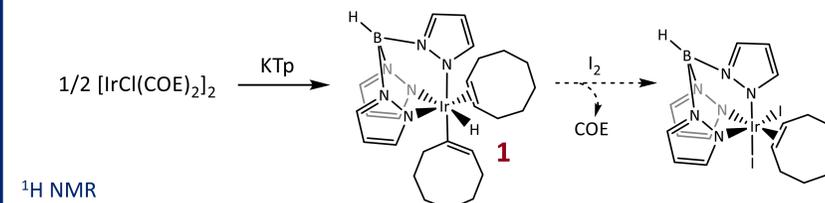


NMR below shows the multiple Ir-H species resolve to a single resonance after heating.

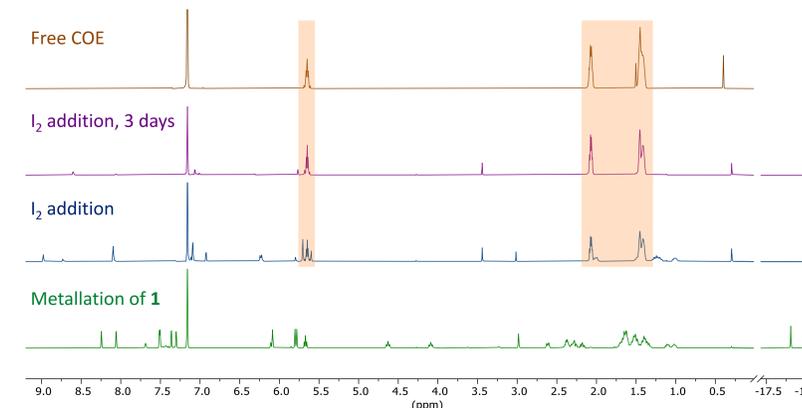


The NMR spectrum above shows probable decomposition after AgOAc addition, seen in the large downfield signal and missing ligand pyrazole peaks.

## Proposed (Tp)Ir(OAc)<sub>2</sub> Synthesis



<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500 MHz)



Metallation with Tp gives 1, which we characterized with the green NMR spectrum. After treatment with I<sub>2</sub> the hydride disappears, and free COE can be seen in the spectra. Both changes indicate possible formation of our target Ir-I<sub>2</sub> complex (top right).

## Future Research

- Synthesize target (Tp)Ir(OAc)<sub>2</sub> complex and test for C-H activation of alkanes.
- Explore different methods of I<sub>2</sub> addition and acetate installation.
- Obtain X-ray crystallographic data.

## References

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