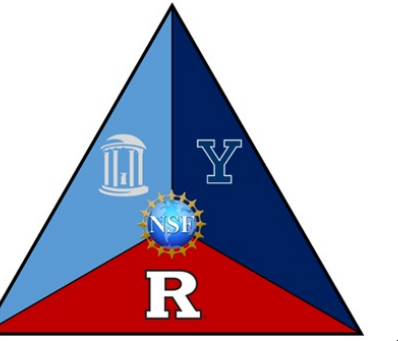




# Pursuing Electrochemical Dinitrogen Fixation with a Re(V) Dioxo

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## Introduction: Nitrogen Fixation

### The Haber-Bosch Process – Successes and Failures



- 50% of the N atoms in the average human have been through the Haber-Bosch Process
- H<sub>2</sub> comes from steam-reforming methane

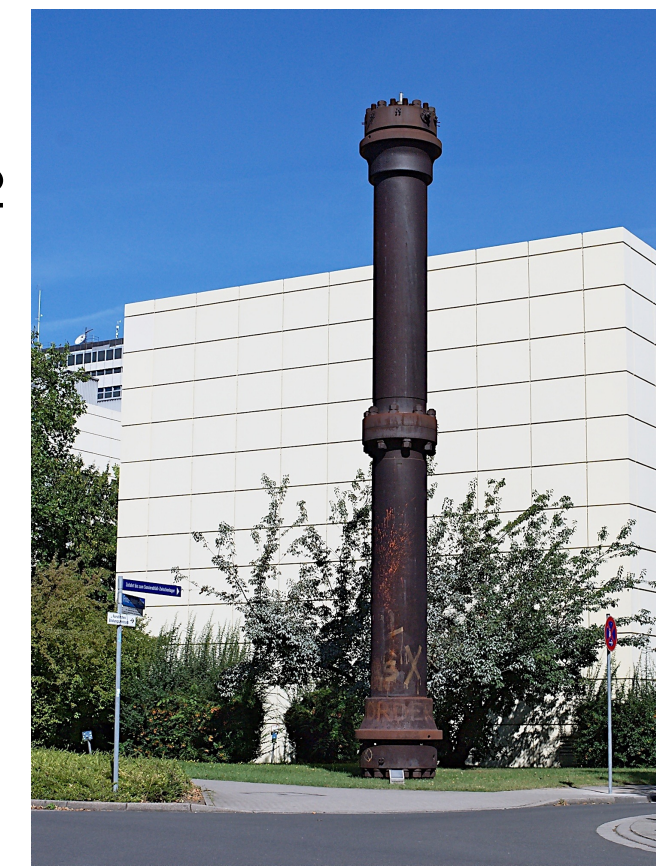


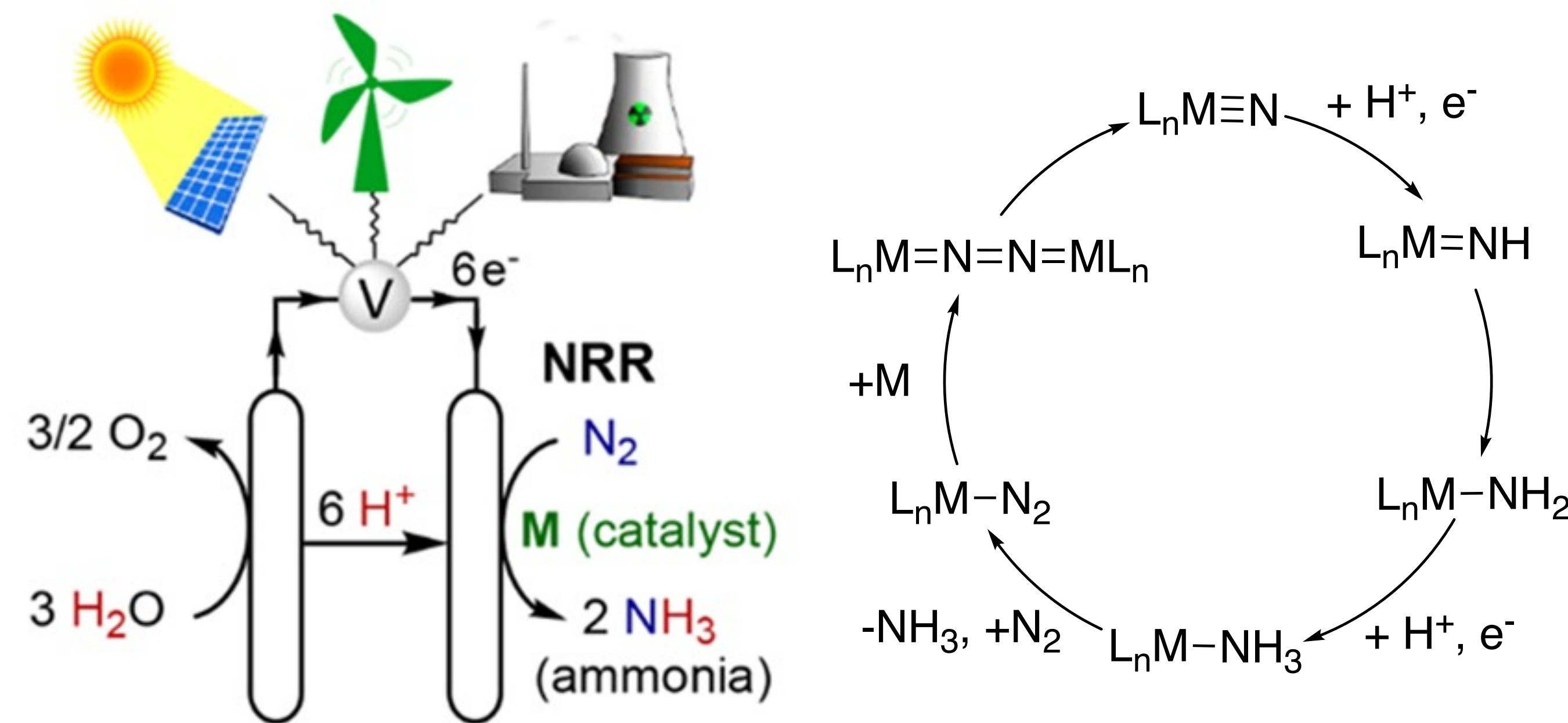
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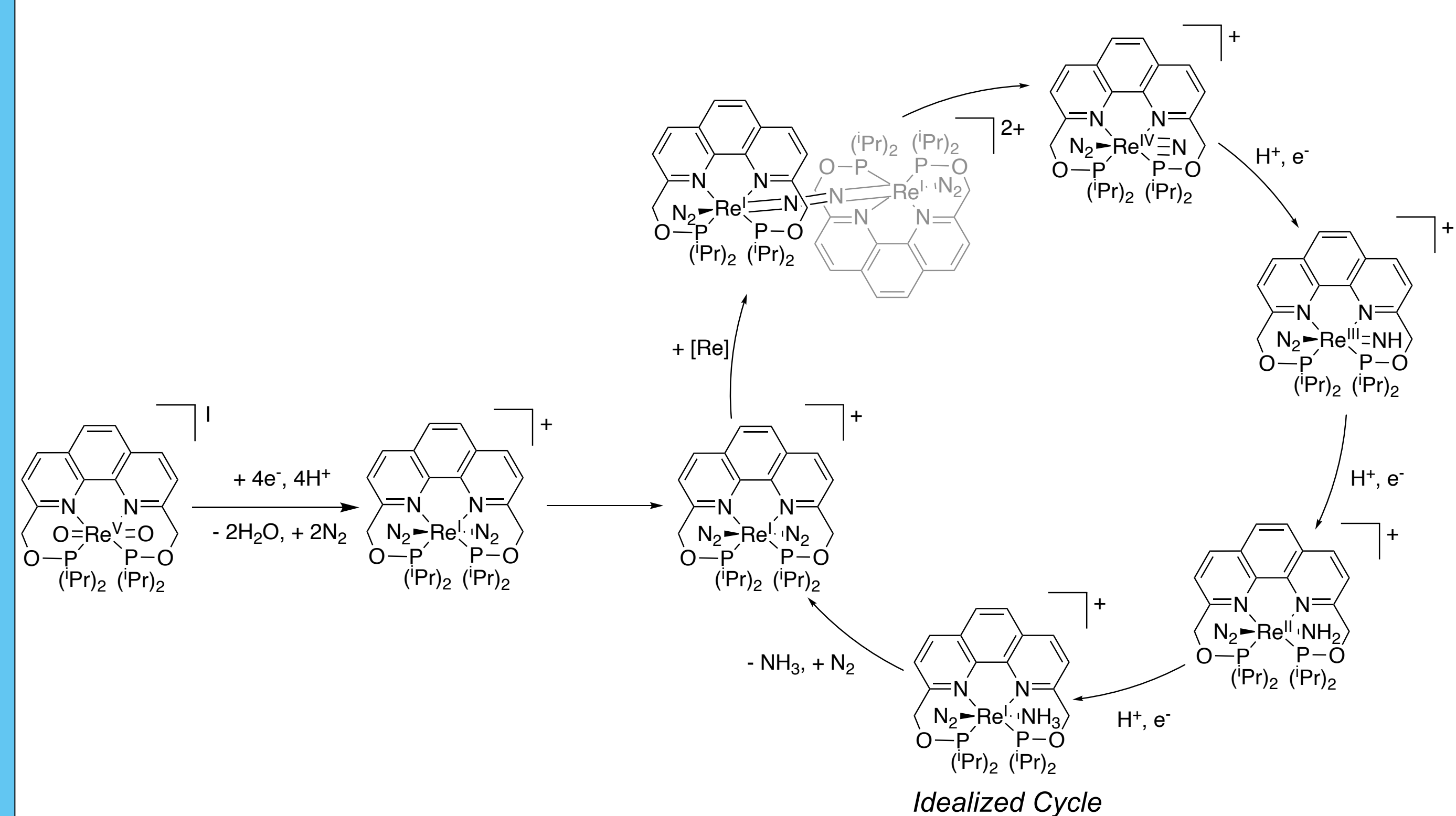
Chen, et al. *Science* 2018.

### Electrocatalysis as a Sustainable Source of NH<sub>3</sub>



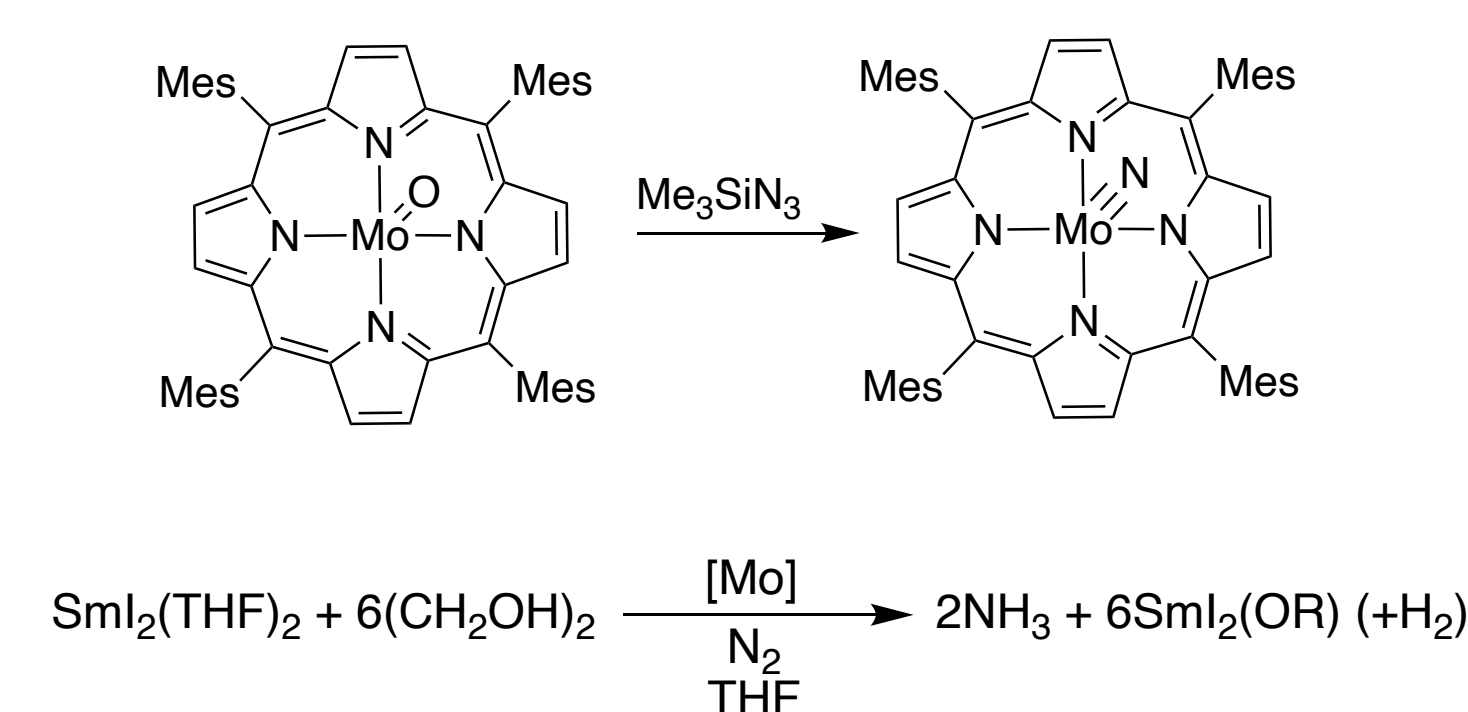
McMillion, et al. *ACS Catalysis*. 2020.

### Entering the Cycle



Idealized Cycle

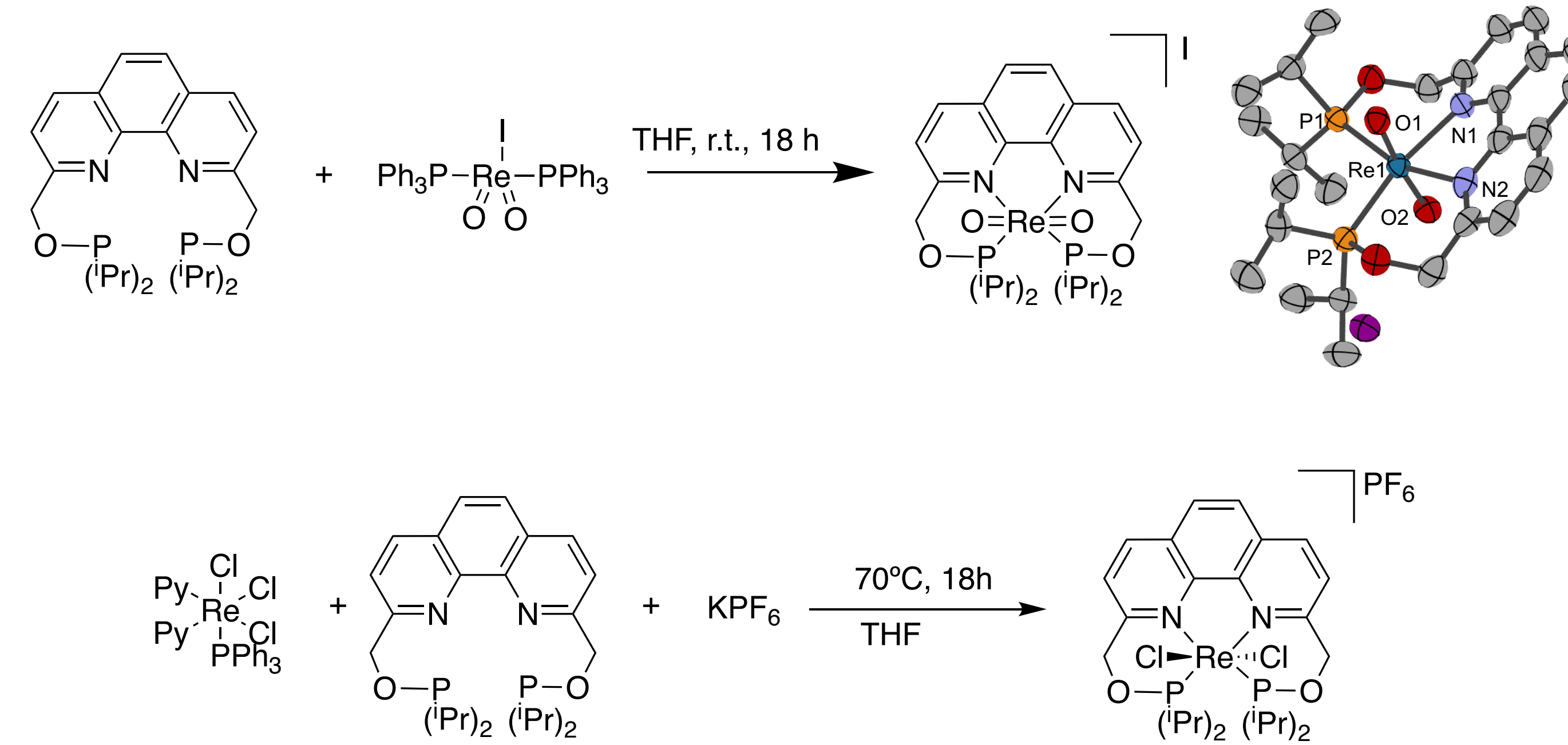
### N<sub>2</sub> Fixation: Precedent for Metal-Oxo Complexes



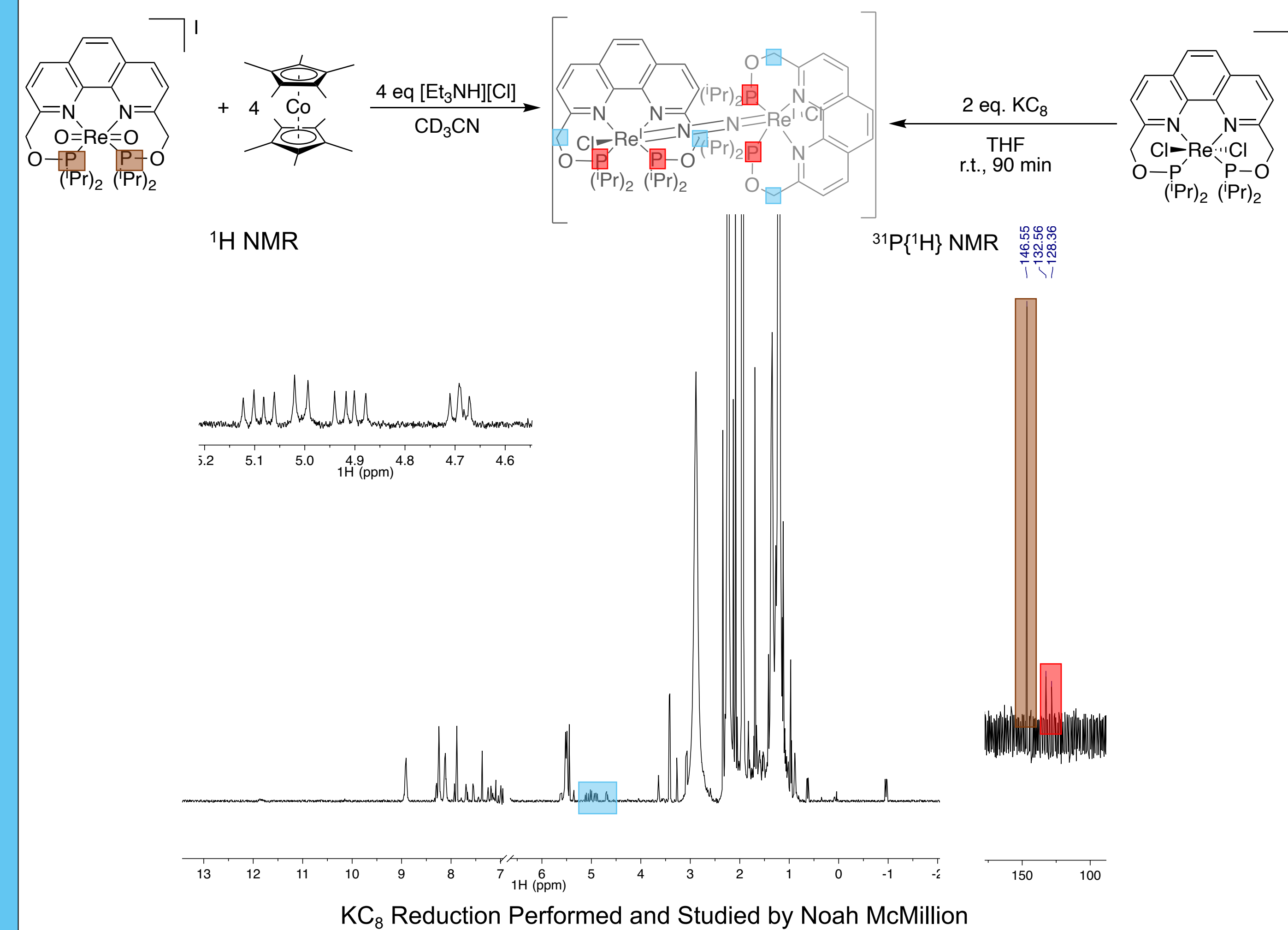
Hegg, et al. *Faraday Discuss.* 2022.

## Chemical Reductions of (POphenOP)-Re

### Synthesis of Target Complexes

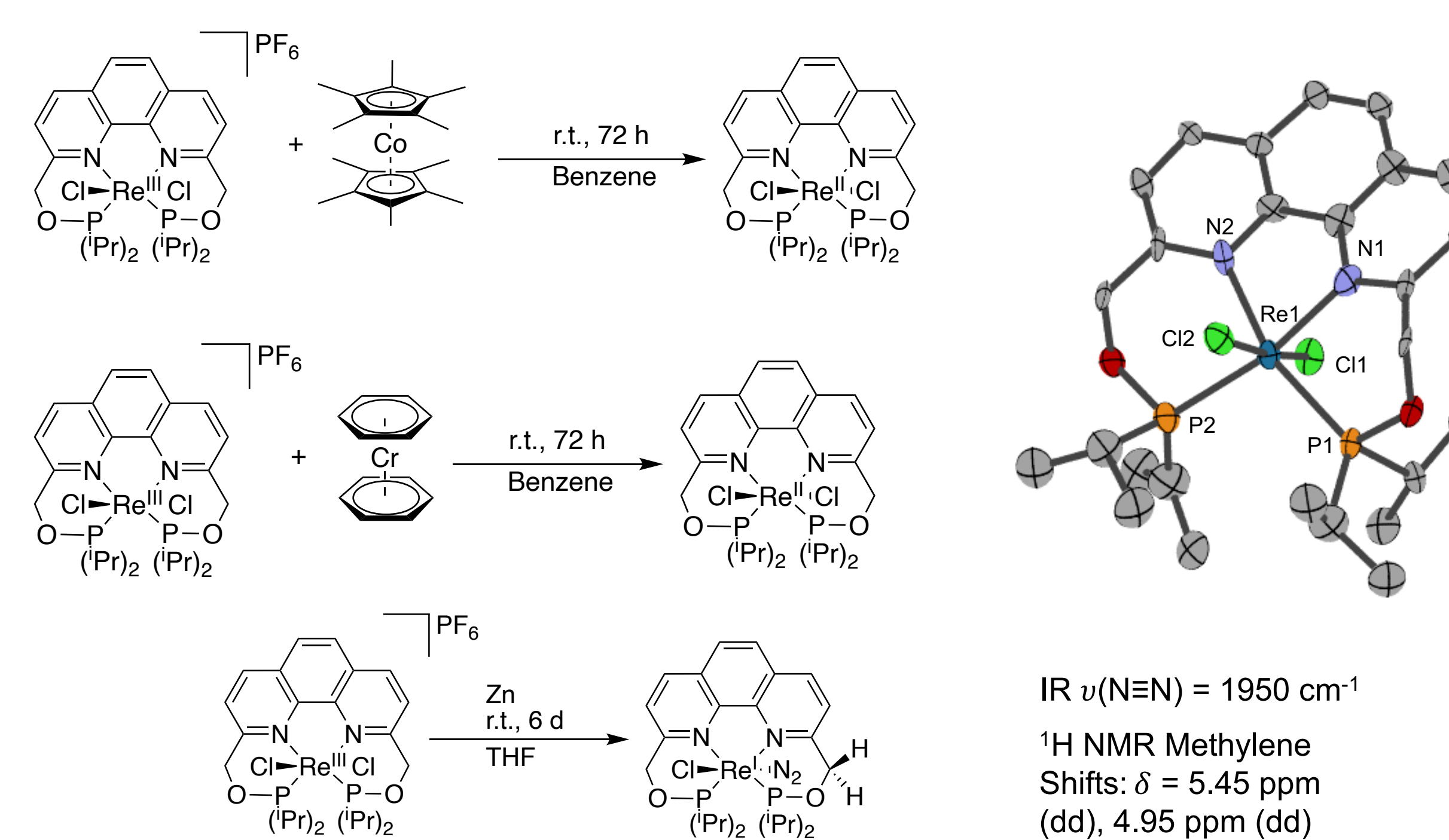


### Chemical Reduction of a Re(V) Dioxo



KC<sub>8</sub> Reduction Performed and Studied by Noah McMillion

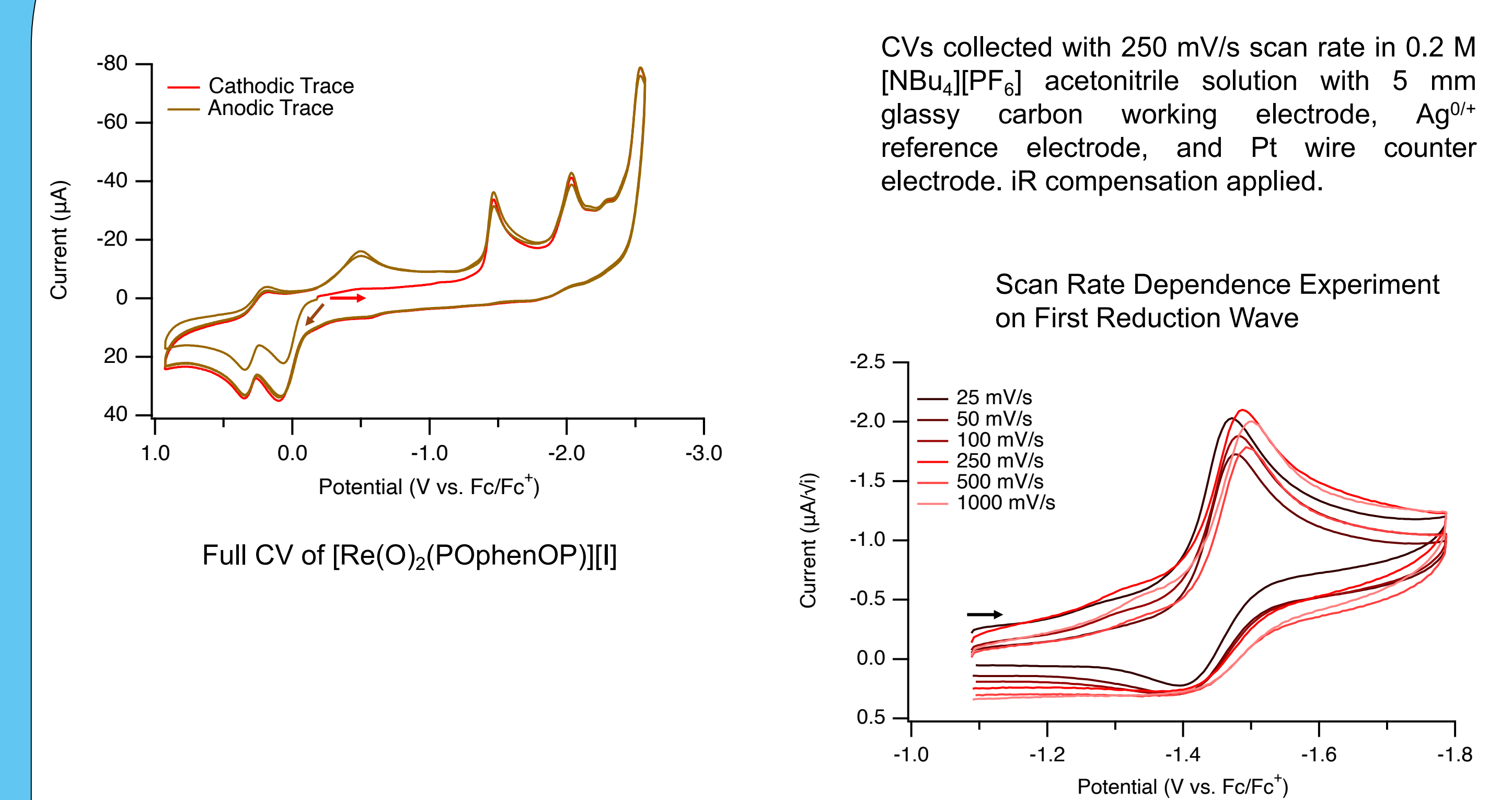
### Chemical Reduction of a Re(III) Dichloride



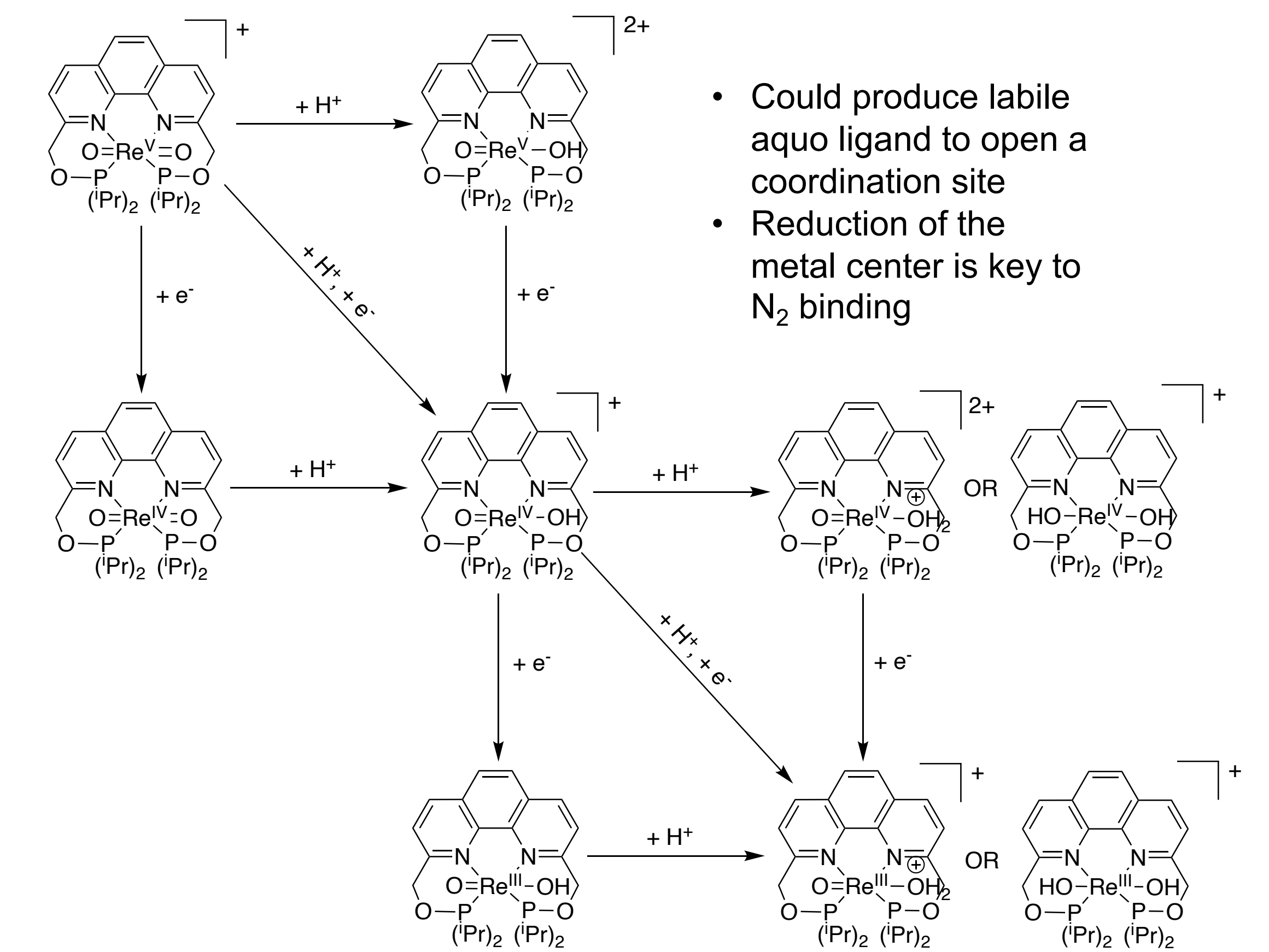
XRD and IR Characterization by Noah McMillion

## Electrochemical Studies of [Re(O)<sub>2</sub>(POphenOP)]<sup>+</sup>

### Cyclic Voltammetry of a Re(V) Dioxo

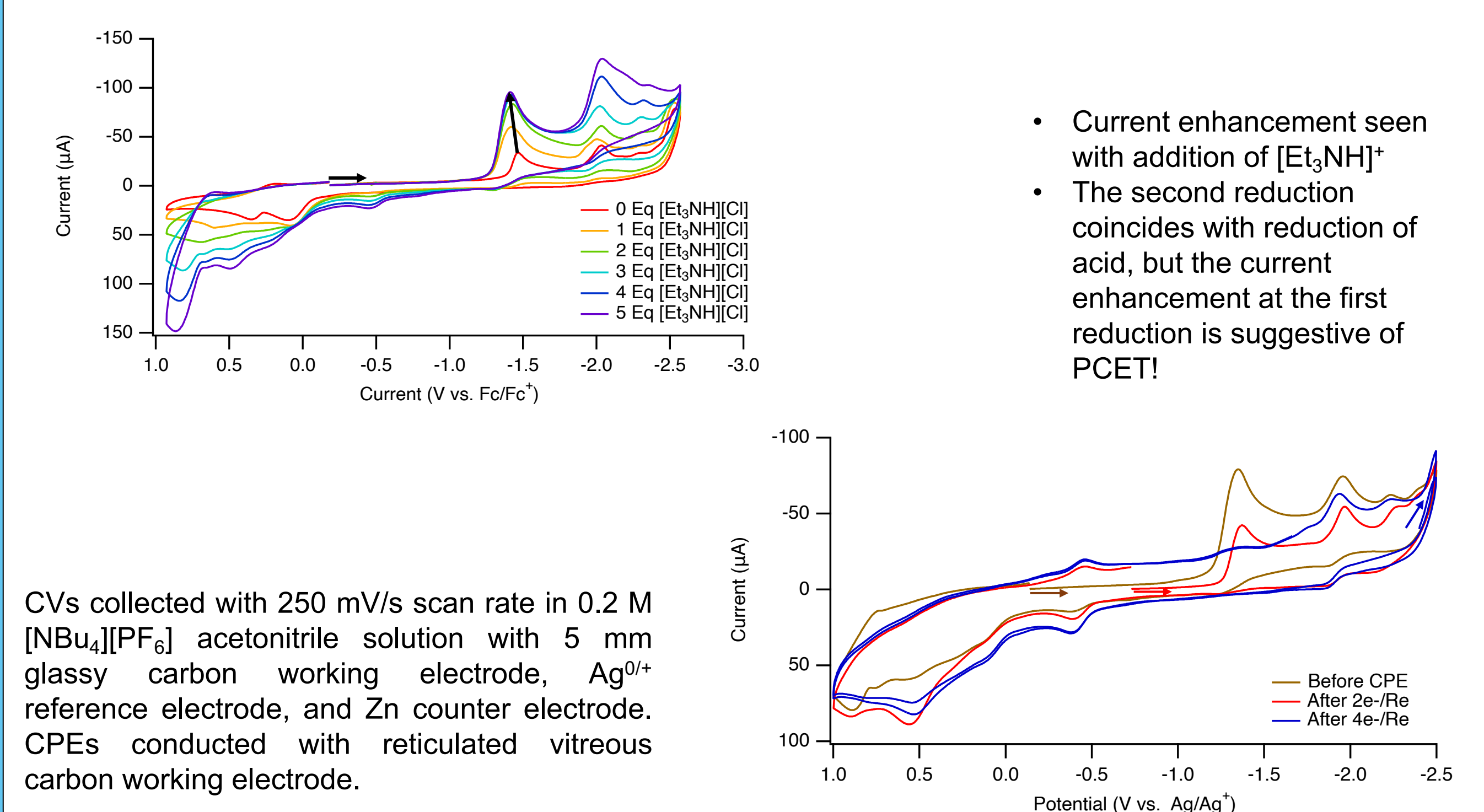


### Targeted PCET/PCET-Like Reactions



- Could produce labile aquo ligand to open a coordination site
- Reduction of the metal center is key to N<sub>2</sub> binding

### Electrochemical Reactivity with [Et<sub>3</sub>NH]<sup>+</sup> Salts



CVs collected with 250 mV/s scan rate in 0.2 M [NBu<sub>4</sub>][PF<sub>6</sub>] acetonitrile solution with 5 mm glassy carbon working electrode, Ag<sup>0</sup>/Ag<sup>+</sup> reference electrode, and Zn counter electrode. CPEs conducted with reticulated vitreous carbon working electrode.

### Acknowledgements

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