



Towards Exploration of Indium's Redox Chemistry

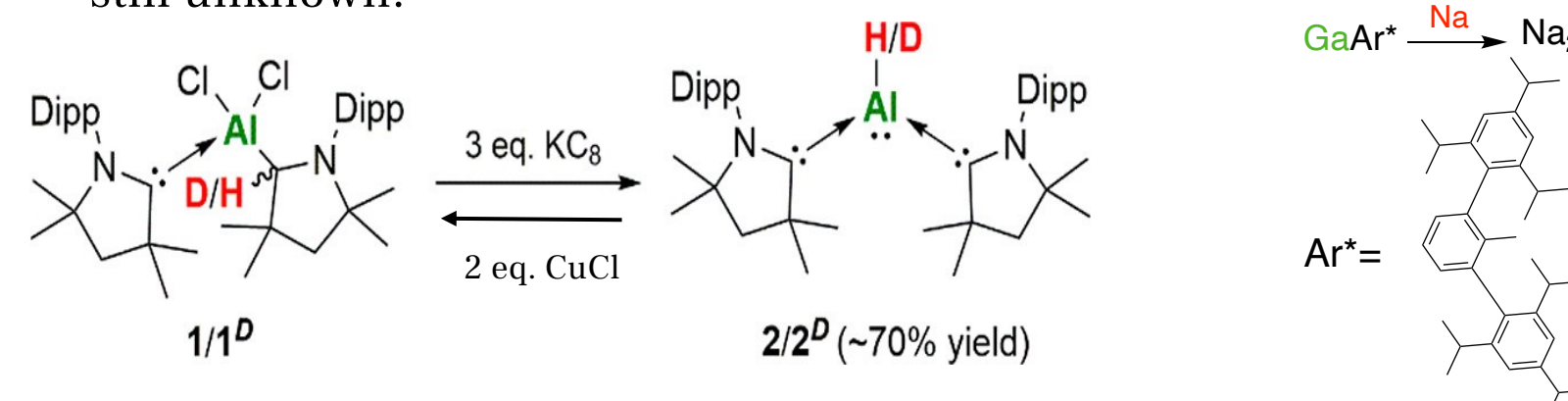
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Introduction

Why Indium (I)?

- It was long believed that stable complexes of group 13 could only exist in the +3 oxidation state, owing to the thermodynamic instability of the +1 and +2 states. However, the late '80s' and early '90s' saw rapid developments towards the isolation of stable, molecular low oxidation state aluminum compounds, with general stabilization strategies usually involving the use of sterically demanding and/or highly σ and π -donating ligand systems.

- Reduction and lower oxidation state chemistry of other group 13 elements such as aluminum and gallium have been of interest recently, yet the redox study of indium is still unknown.



Braunschweig et al.
2019

Robinson et al.
1997

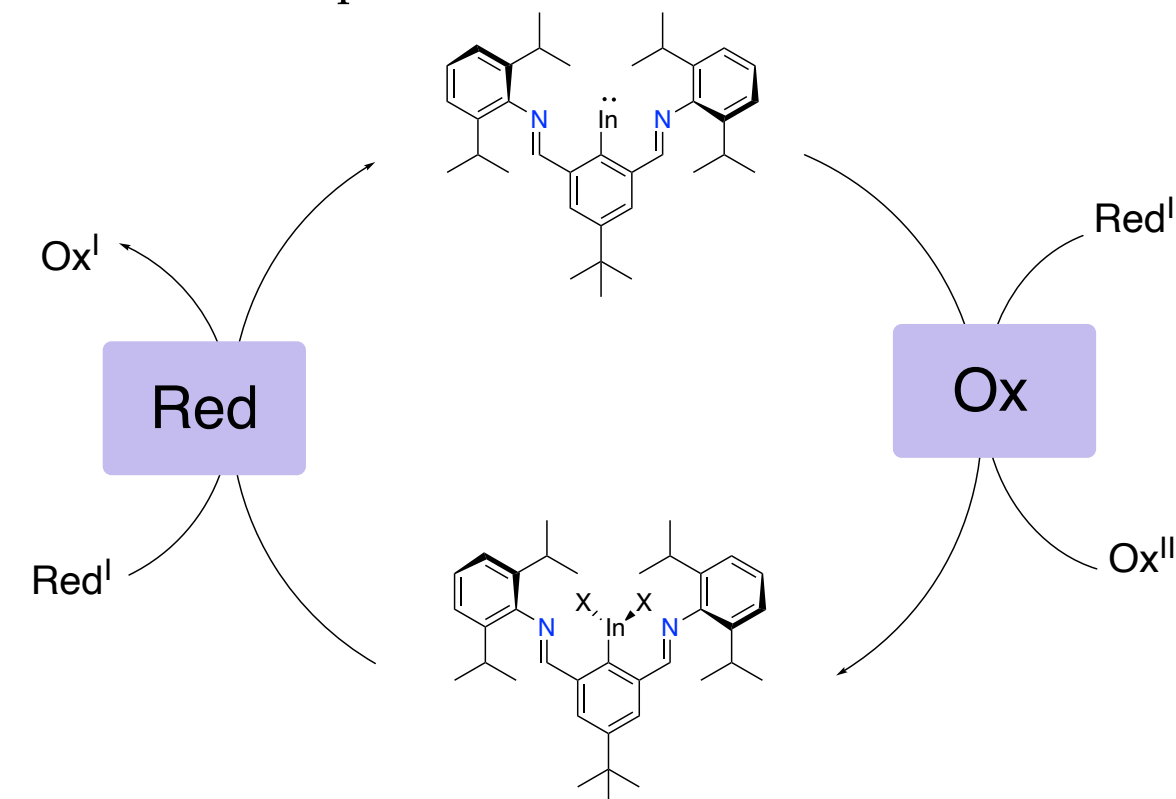
- Oxidation state of I is possible for indium. Due to inert pair effect, closed shell of d orbitals shield the valence s orbital and make the oxidation state of I more possible.



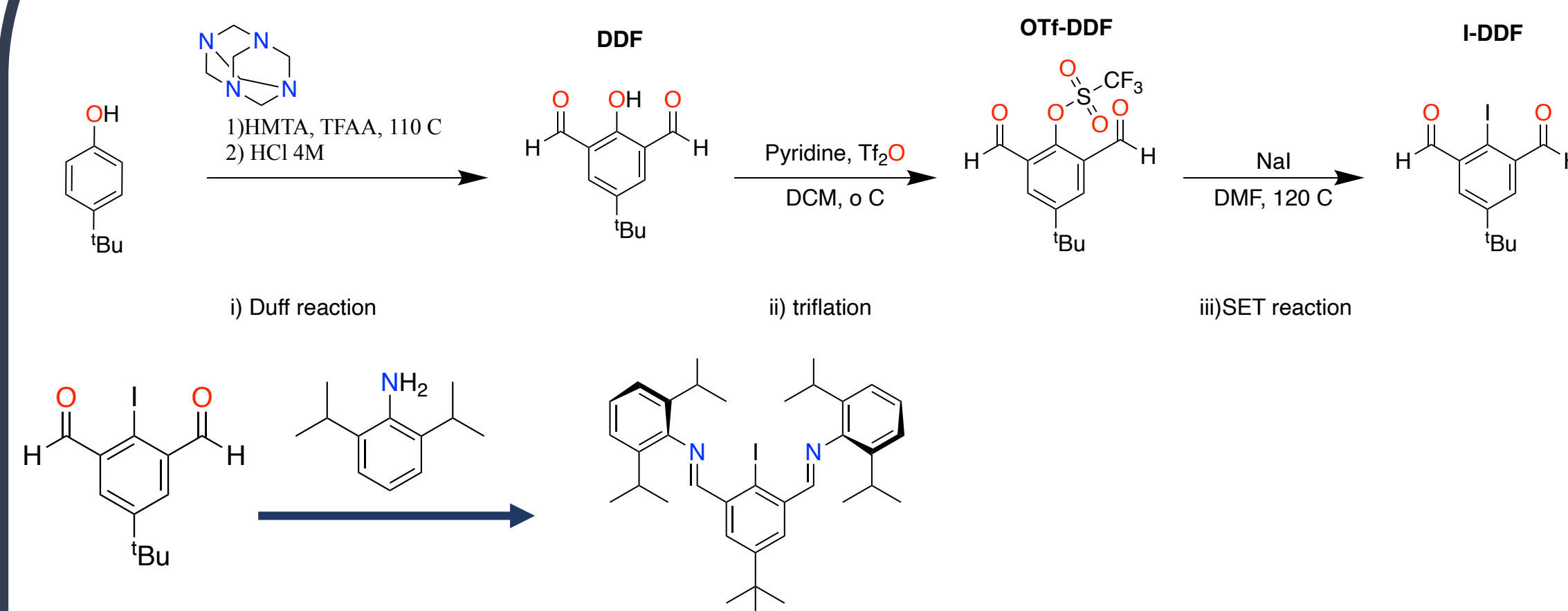
- Indium(I), as it is, is unstable and tends to disproportionate or aggregation.
- However, they are of interest since they can act as both Lewis acids and Lewis bases.
- This geometry of the ligand is able to pull the metal ion closer to the ligand, thus introducing steric hindrance and stabilizing the whole monomeric complex.

Goals

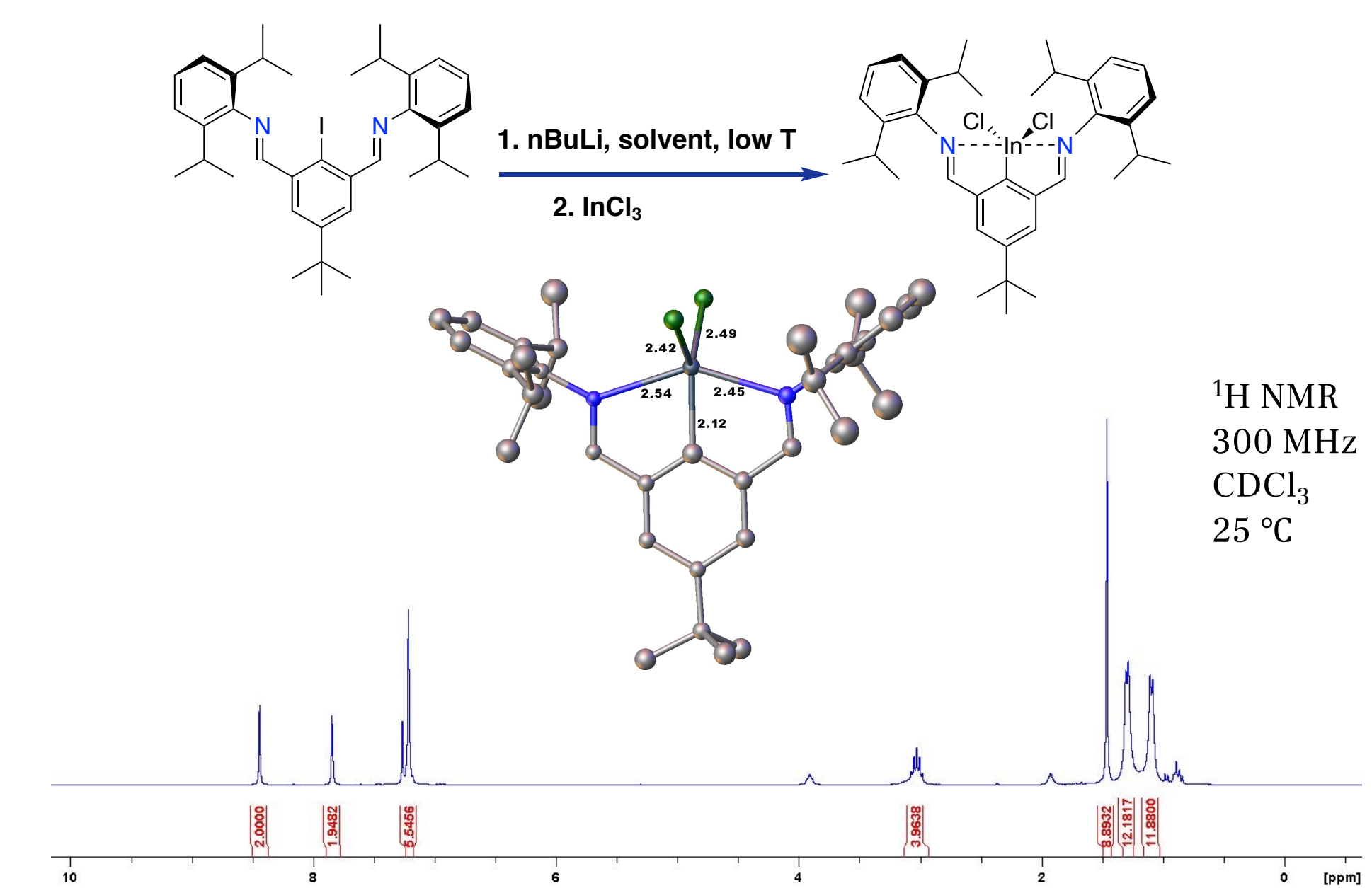
- We try to achieve a monomeric stable indium (III) and its indium (I) counterpart complex and study their **redox activity** using an NCN pincer ligand.
- The aim is to achieve a reversible reduction and oxidation in order to unlock catalytic or reactivity abilities these complexes



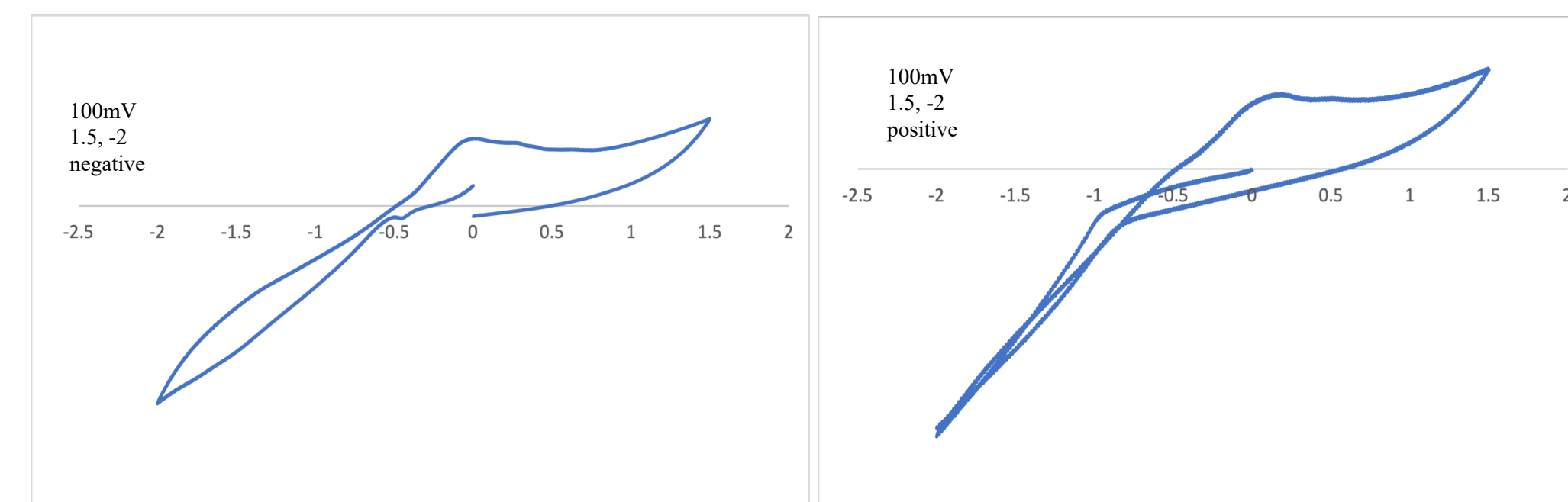
Synthesis of the Target ligand



Synthesis and Characterization of the Metal Complex



Choice of a Proper Reducing Agent: Cyclic Voltammetry



- Internal standard: Fc+/Fc redox couple
- Supporting electrolyte: (nBu₄N)PF₆
- 0.01M of analyte in THF
- No redox activity within the window activity of the solvent

Reduction: Moderate to Strong Reducing Agents

Reducing Agent	Temperature/°C	Time	Equivalence	Result
11. KC ₈	r.t.	30 min	2	Mixture/ over reduction
10. LAH	r.t.	30 min	0.5	Resulted in diiodo
9. Cp ₂ Co	r.t.	2 hr	1.9	No rxn.
8. Cp ₂ Co	r.t.	overnight	2.1	No rxn
7. Cp ₂ Co	r.t.	overnight	3.1	No rxn
6. KC ₈ Flash Reduction Column	-30	Instantly	Excess	No rxn
5. Rieke Mg	r.t.	4 days	2.4	No rxn
4. Na naphthalene	r.t.	4 days	2.4	No rxn
3. K	r.t.	4 days	2.4	No rxn
2. Li(Et,BH)	r.t.	1h	2	Ethylated In(III)
1. K(secBu,BH)	r.t.	1h	2	Salt Metathesis Product

- ❖ According to the condition of reactions, no reduction is observed.

Conclusion / Future Work

- We successfully were able to synthesize the target pincer ligands to stabilize the indium (III) complex.
- The geometry of the ligand allows pulling the metal ion closer to the complex.
- Optimization of the reactions might be key to access indium (I).
- Different oxidizing agents to oxidize the indium (I) complex should be tested.
- Study the reversible redox activity of In(III) to indium (I) and their reactivity towards different applications.

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Reference

- Schneider, U.; Kobayashi ShU. Low-Oxidation State Indium-Catalyzed C–C Bond Formation. *Accounts of Chemical Research* **2012**, *45* (8), 1331–1344.
- Gray, T. W.; Mann, N. *The elements: A visual exploration of every known atom in the universe*; Black Dog & Leventhal Publishers: New York, 2012.
- Møllerup, S. K.; Cui, Y.; Fantuzzi, F.; Schmid, P.; Goettel, J. T.; Bélanger-Chabot, G.; Arrowsmith, M.; Krummenacher, I.; Ye, Q.; Engel, V.; Engels, B.; Braunschweig, H. Lewis-Base Stabilization of the Parent Al(i) Hydride under Ambient Conditions. *Journal of the American Chemical Society* **2019**, *141* (42), 16954–16960.
- Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. How Short Is a -Ga:Ga- Triple Bond? Synthesis and Molecular Structure of na₂[Mes*₂c₆h₃-Ga:Ga-c₆h₃mes*₂] (Mes* = 2,4,6-i-pr₃c₆h₂): The First Gallyne. *Journal of the American Chemical Society* **1997**, *119* (23), 5471–5472.