

Adduct-Mediated CO₂ Conversion

A Novel Approach to CO₂ Chemistry

7/15/2011

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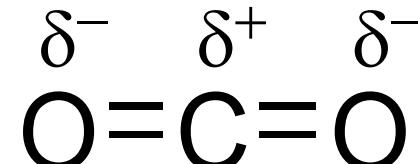
Outline

- **Introduction**
 - Properties of CO₂
- **Background Knowledge**
 - The Kemp Group Approach
 - Producing CO₂ Adducts
- **Personal Contributions**
- **Acknowledgements**



Introduction to CO₂

- Why CO₂?
 - CO₂ is somewhat useless and abundant, its constituents are useful; form fuels including methanol and ethanol
 - We produce more CO₂ now than ever before
- CO₂ is a highly stable, very low energy compound
- CO₂ has a 180° bond structure
 - Because of its linear structure, forming CO₂ adducts presents many challenges
- CO₂'s Carbon center is electrophilic, while its Oxygen atoms are nucleophilic
 - This plays a key role in the formation of CO₂ adducts



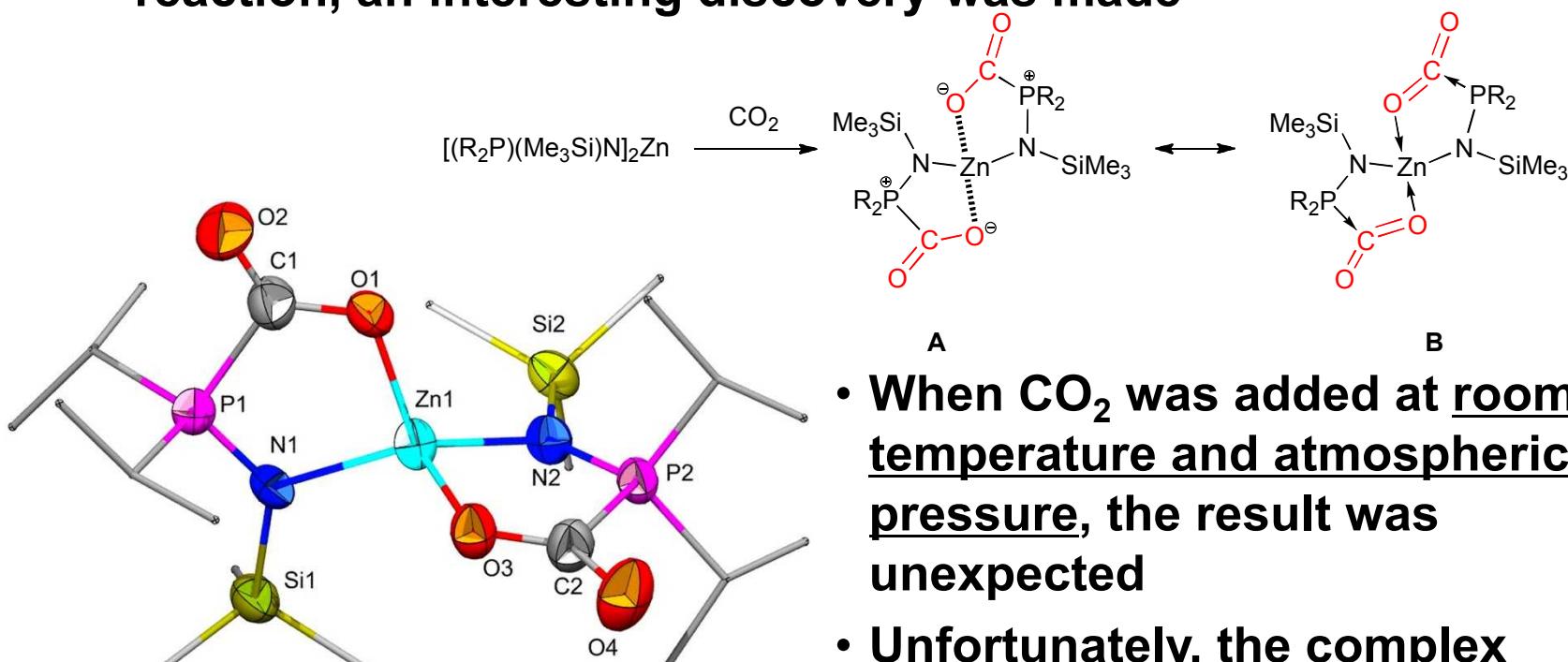


Traditional vs. Kemp Group Approaches

- Current Methods of Research on CO₂ chemistry
 - Use high-heat
 - High-energy electrochemical (required to bend CO₂ to where it can be reduced)
- We use metal complexes as catalysts for CO₂ conversion
- Our ultimate goal: Cheaply convert CO₂ into something useful using a catalytic process at room temperature and atmospheric pressure
 - Corresponds with the low energy requirements of CO₂ adduct formation

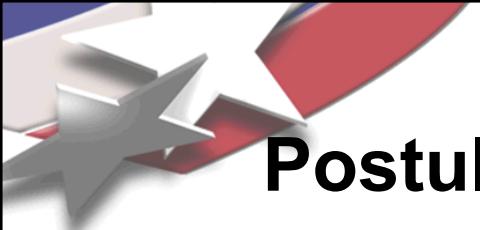
The Group's First CO₂ Adduct

- While performing a Zn-CO₂ carbamate (elimination product) reaction, an interesting discovery was made



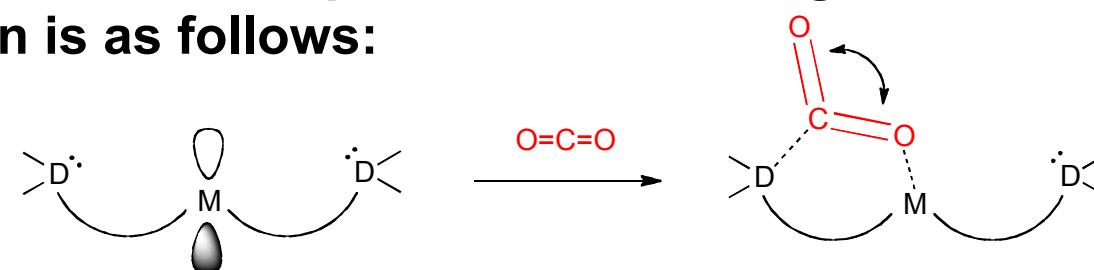
Bis-amido zinc complex
by Diane Dickie

- When CO₂ was added at room temperature and atmospheric pressure, the result was unexpected
- Unfortunately, the complex didn't survive electrochemical experiments



Postulating Necessities for CO₂ Adduct Formation

- The goal is now to synthesize metal complexes from which to form different CO₂ adducts with properties including:
 - Higher stability under electrochemical conditions
 - Varying bond strength to CO₂
 - Metals with varying reduction potential
 - Different bond angles with CO₂
- The general concept that drives our ligand/metal complex design is as follows:



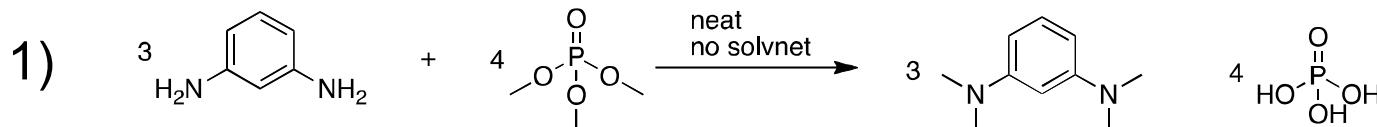
Basic Lone Pair on Donor (D)

Acidic Empty p Orbital on Metal (M)

Lewis Acid-Base Adduct

Precursor to My Work

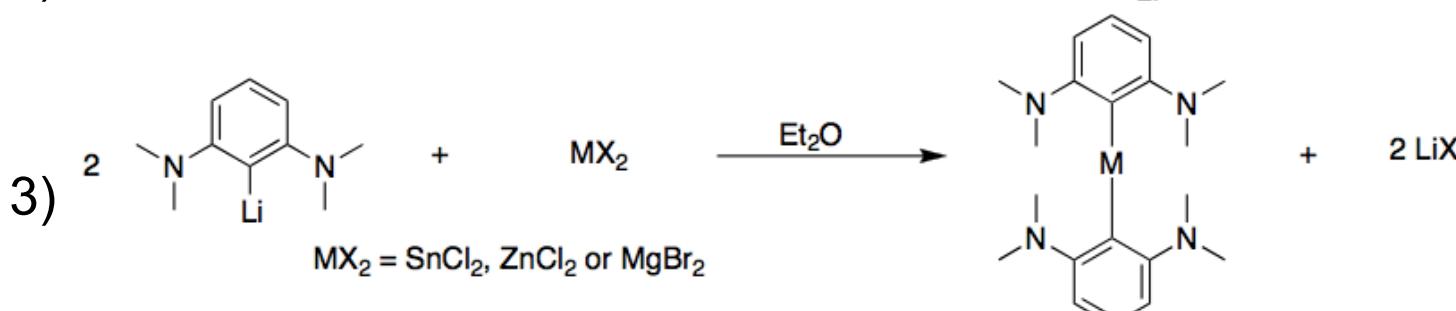
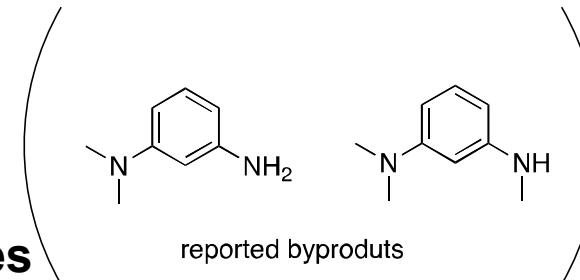
N,N,N',N'-tetramethyl-*m*-phenylenediamine



- **Purification required**

Column chromatography

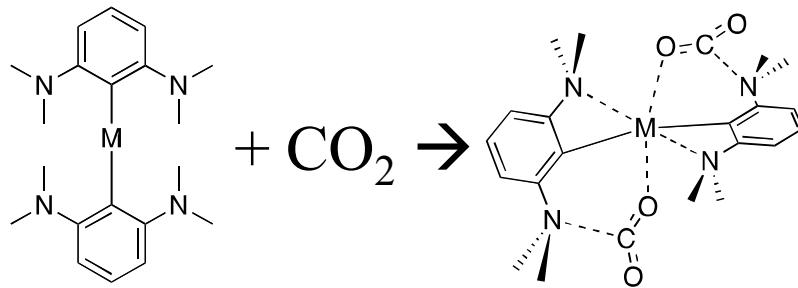
- Due to many similar
boiling points and polarities



Reaction by Brian Barry

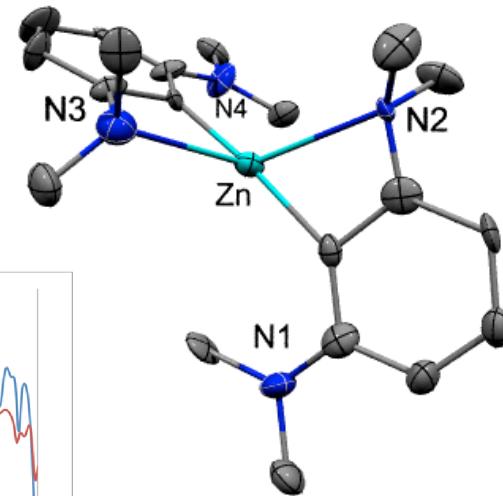
Precursor to My Work (Results)

Proposed synthesis



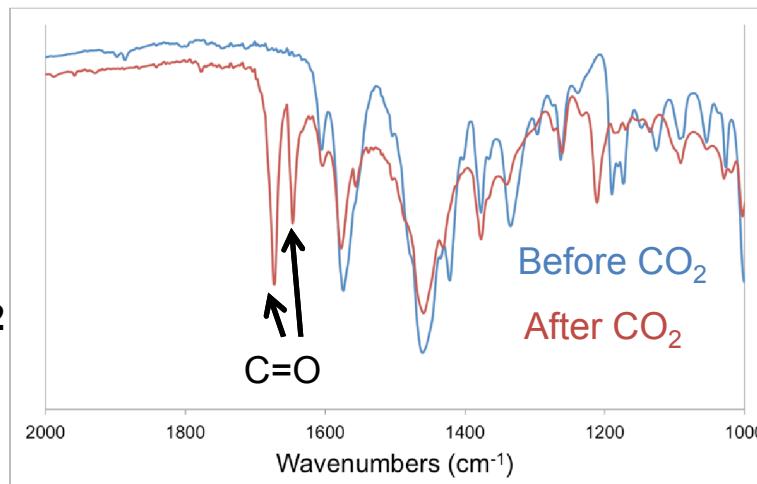
Zn^{2+} Complex

- New crystal structure
- CO_2 reactivity unclear



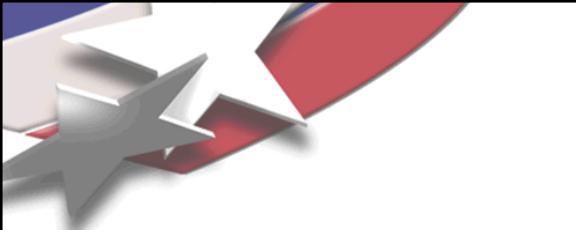
Sn^{2+} Complex

- Known compound
- Reacts w/ CO_2
- Unable to crystalize



- Relative success led to my first ligand attempt

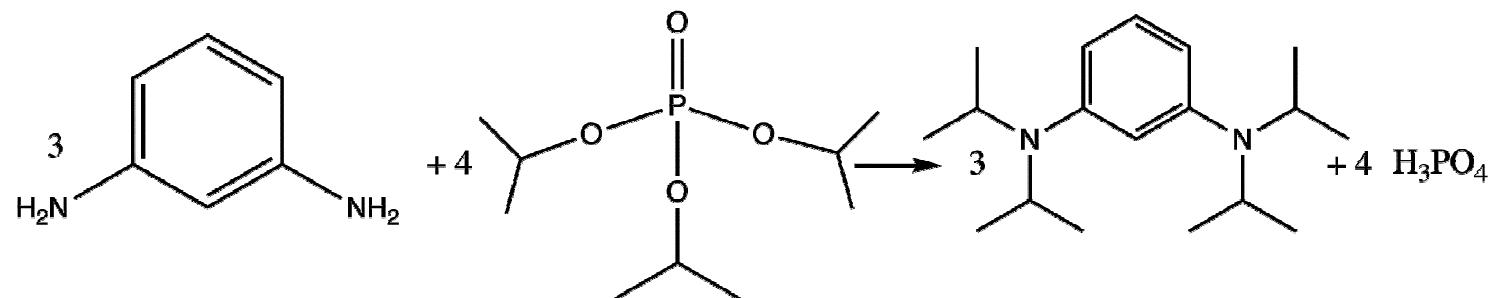
Reaction by Brian Barry



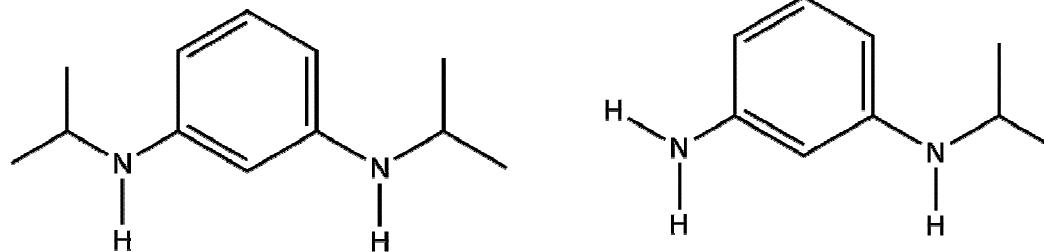
My First Synthesis

N,N,N',N'-tetraisopropyl-m-phenylenediamine

Proposed
Synthesis:



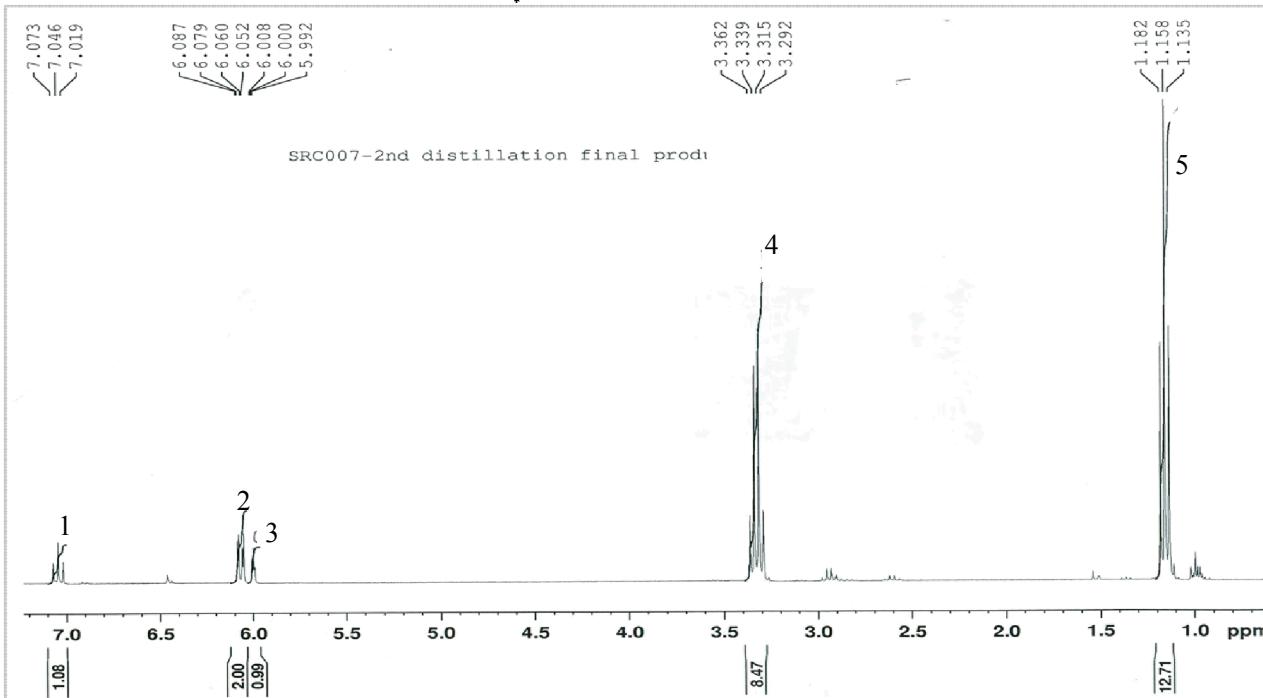
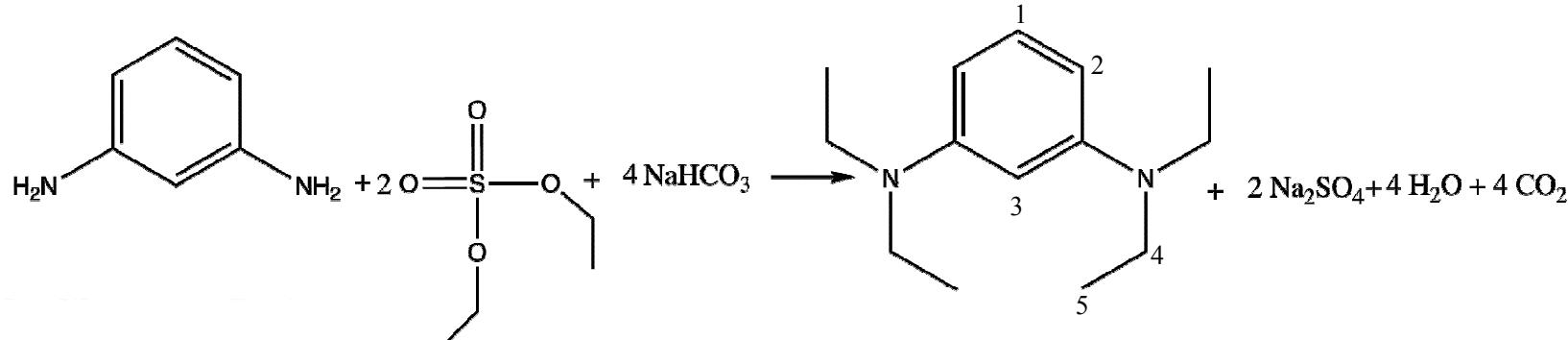
Products
Formed:



- Possible Explanation
 - Took a week to work up reaction
 - The similar boiling points of products requires column chromatography to separate
 - May have better outcome if reaction times and temps increase

My Second Synthesis

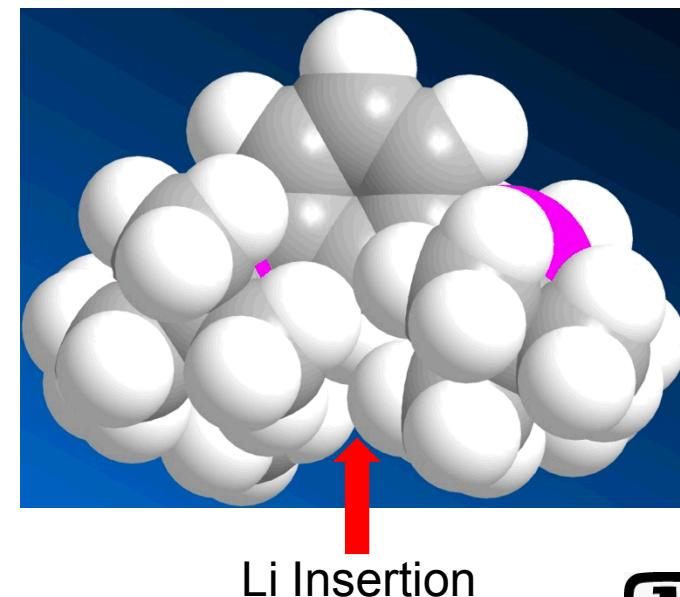
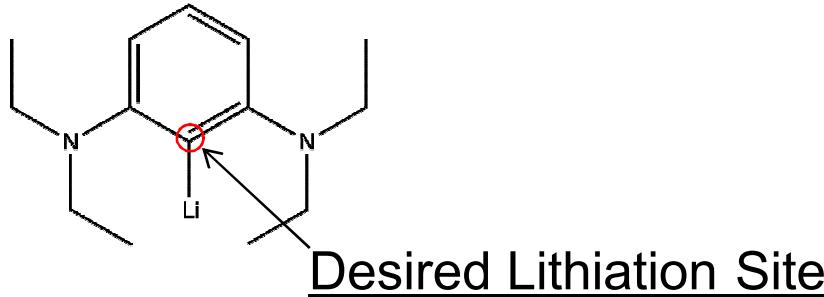
- N,N,N',N'-tetraethyl-*m*-phenylenediamine
 - Ligand synthesis was successful with high yield



- Product Confirmed by NMR
 - Evidenced by shifts and integration

My Second Synthesis

- Several attempts made at lithiating ligand were unsuccessful
 - Included using n-butyllithium for several hours to using tert-butyl lithium, refluxing overnight
 - Possible explanation: electron clouds physically blocked lithiation of the ligand



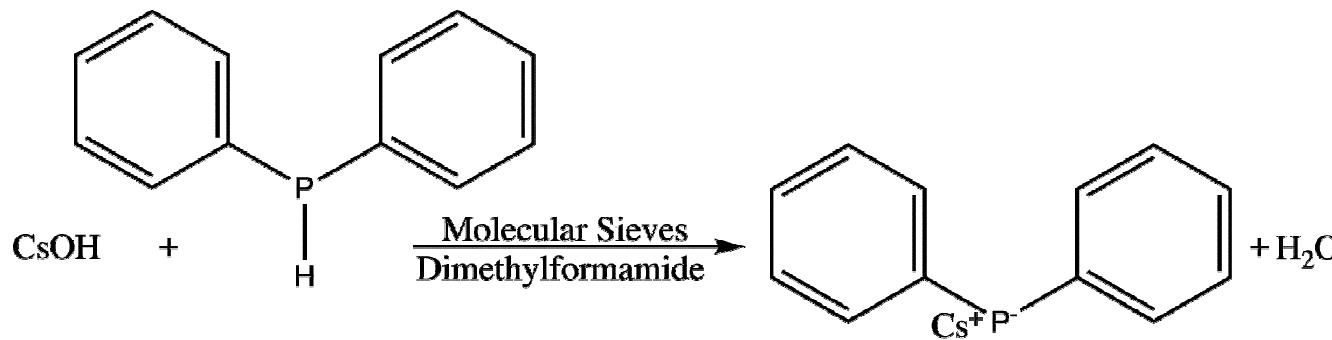
- Set ligand aside and moved on



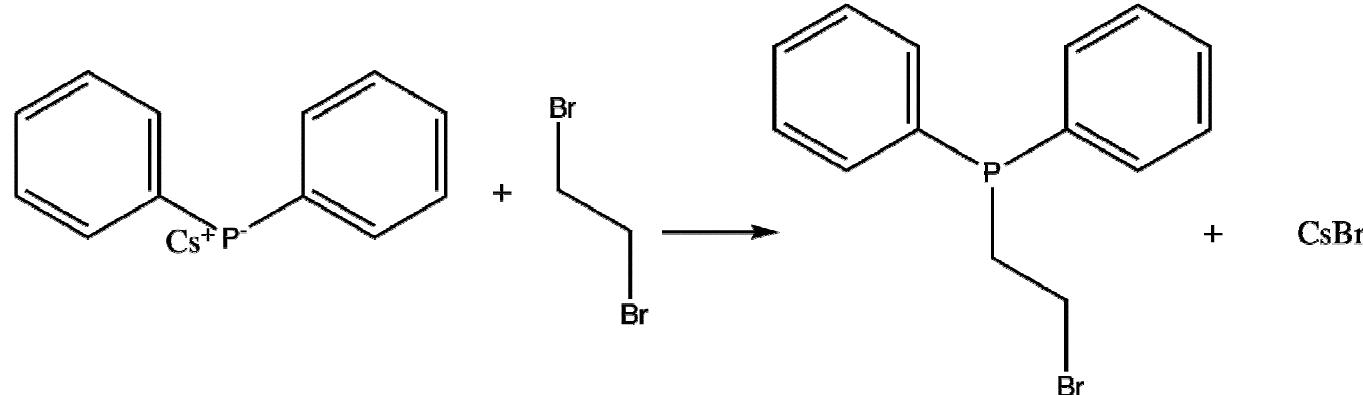
My Third Synthesis (Currently Ongoing)

Ethylbromide-Diphenylphosphine

1)

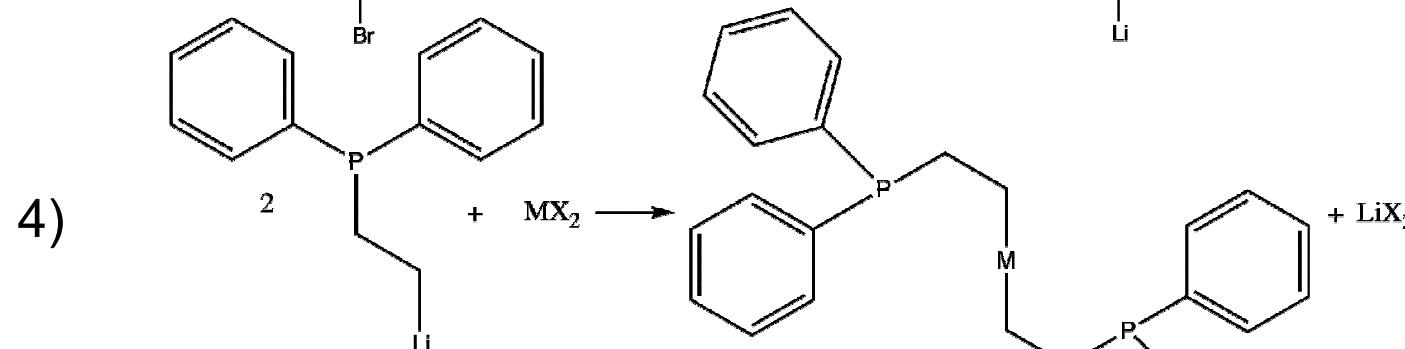


2)

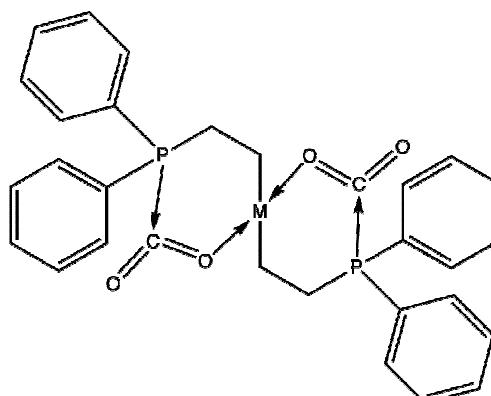




My Third Synthesis (Currently Ongoing)



- **Ultimate goal:**
 - Adduct with CO_2





Acknowledgements

- Doctor Brian M. Barry
- Professor Richard A. Kemp
- All others in the *Kemp Group*