

# Adduct-Mediated CO<sub>2</sub> Conversion

## A Novel Approach to CO<sub>2</sub> Chemistry

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# Outline

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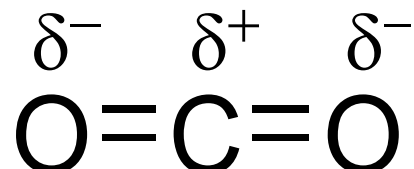
- **Introduction**
  - Properties of CO<sub>2</sub>
- **Background Knowledge**
  - The Kemp Group Approach
  - Producing CO<sub>2</sub> Adducts
- **Personal Contributions**
- **Acknowledgements**



# Introduction to CO<sub>2</sub>

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- **Why CO<sub>2</sub>?**
  - CO<sub>2</sub> is somewhat useless and abundant, its constituents are useful; form fuels including methanol and ethanol
  - We produce more CO<sub>2</sub> now than ever before
- **CO<sub>2</sub> is a highly stable, very low energy compound**
- **CO<sub>2</sub> has a 180° bond structure**
  - Because of its linear structure, forming CO<sub>2</sub> adducts presents many challenges
- **CO<sub>2</sub>'s Carbon center is electrophilic, while its Oxygen atoms are nucleophilic**
  - This plays a key role in the formation of CO<sub>2</sub> adducts





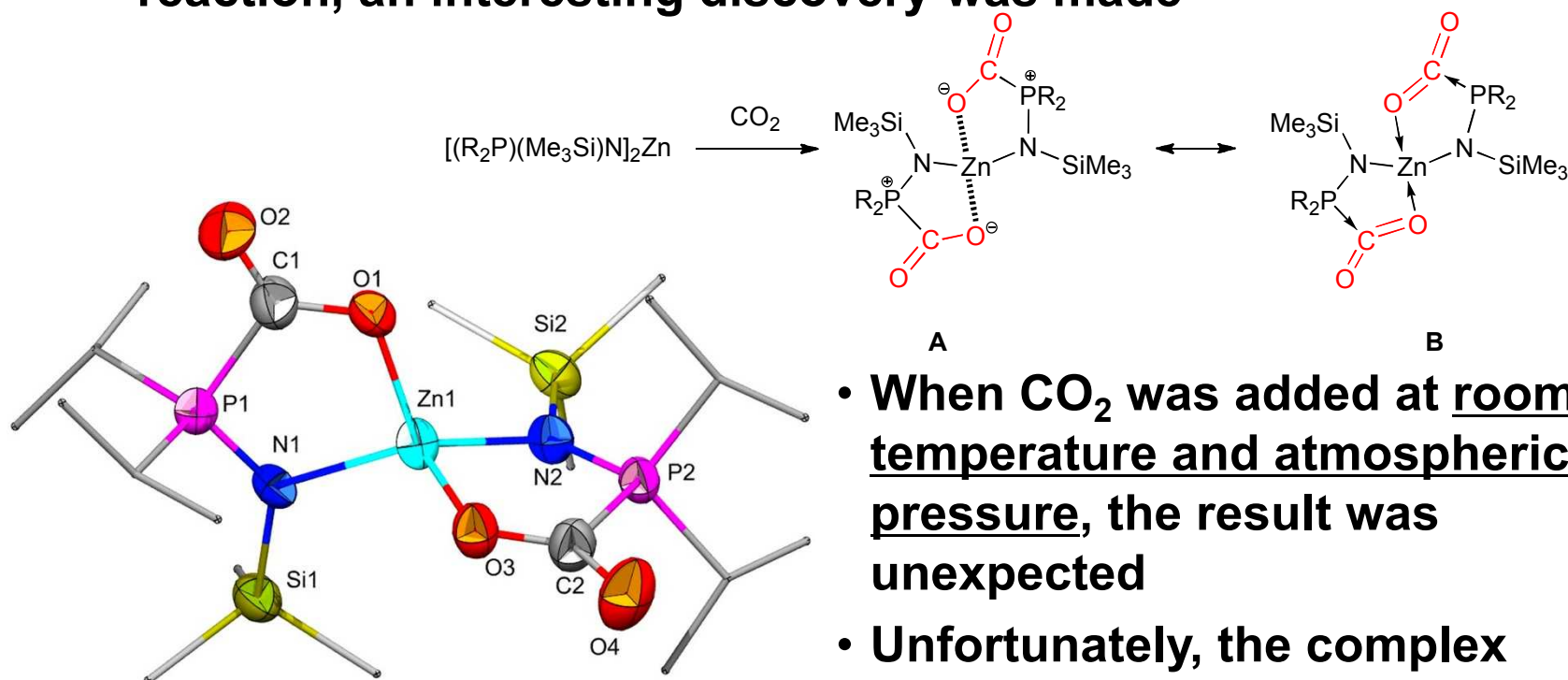
# Traditional vs. Kemp Group Approaches

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- **Current Methods of Research on CO<sub>2</sub> chemistry**
  - Use high-heat
  - High-energy electrochemical (required to bend CO<sub>2</sub> to where it can be reduced)
- **We use metal complexes as catalysts for CO<sub>2</sub> conversion**
- **Our ultimate goal: Cheaply convert CO<sub>2</sub> into something useful using a catalytic process at room temperature and atmospheric pressure**
  - Corresponds with the low energy requirements of CO<sub>2</sub> adduct formation

# The Group's First CO<sub>2</sub> Adduct

- While performing a Zn-CO<sub>2</sub> carbamate (elimination product) reaction, an interesting discovery was made

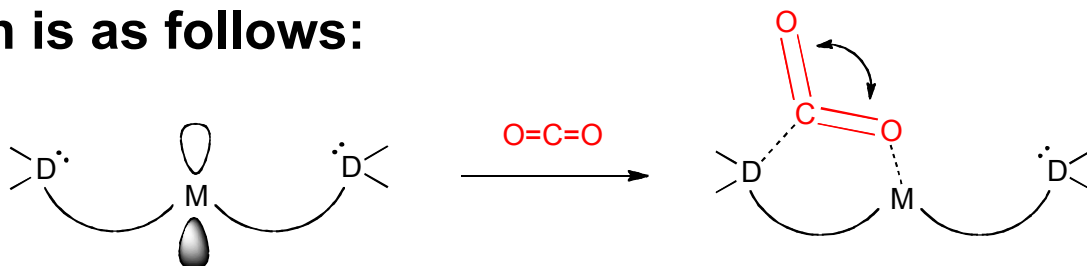


*Bis-amido zinc complex  
by Diane Dickie*

- When CO<sub>2</sub> was added at room temperature and atmospheric pressure, the result was unexpected
- Unfortunately, the complex didn't survive electrochemical experiments

# Postulating Necessities for CO<sub>2</sub> Adduct Formation

- The goal is now to synthesize metal complexes from which to form different CO<sub>2</sub> adducts with properties including:
  - Higher stability under electrochemical conditions
  - Varying bond strength to CO<sub>2</sub>
  - Metals with varying reduction potential
  - Different bond angles with CO<sub>2</sub>
- The general concept that drives our ligand/metal complex design is as follows:



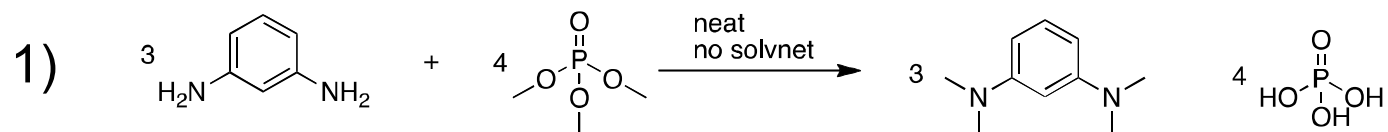
*Basic Lone Pair on Donor (D)*

*Acidic Empty p Orbital on Metal (M)*

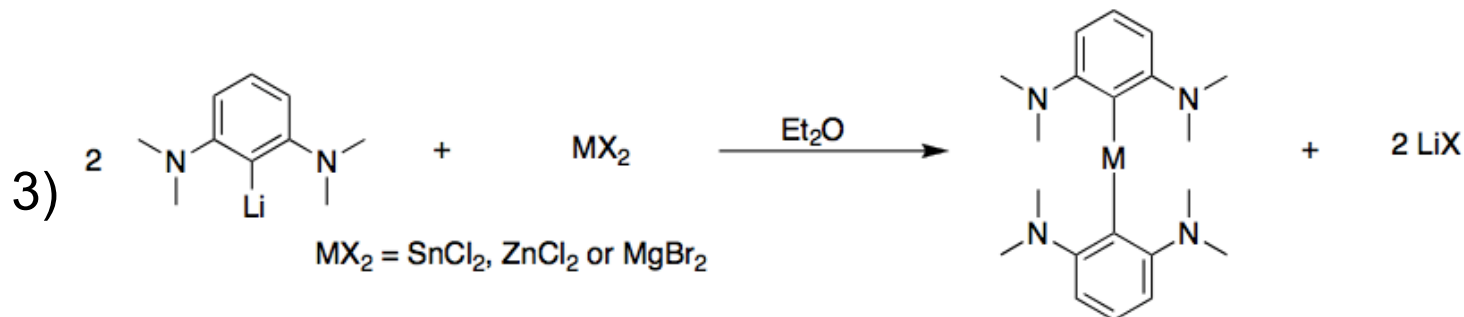
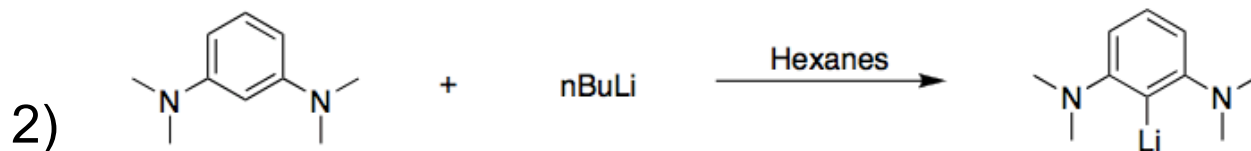
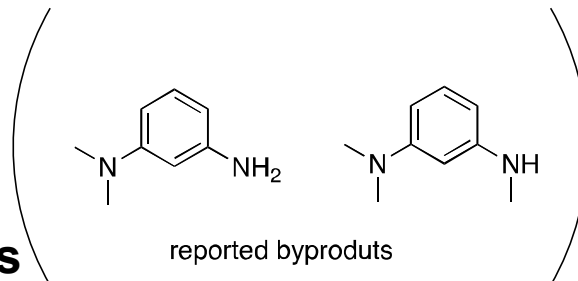
*Lewis Acid-Base Adduct*

# Precursor to My Work

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

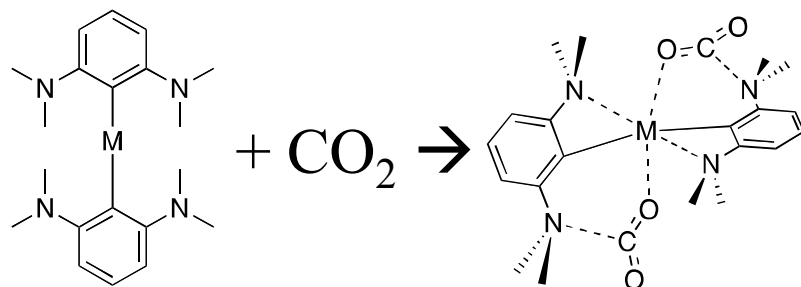


- Purification required
- Column chromatography
  - Due to many similar boiling points and polarities



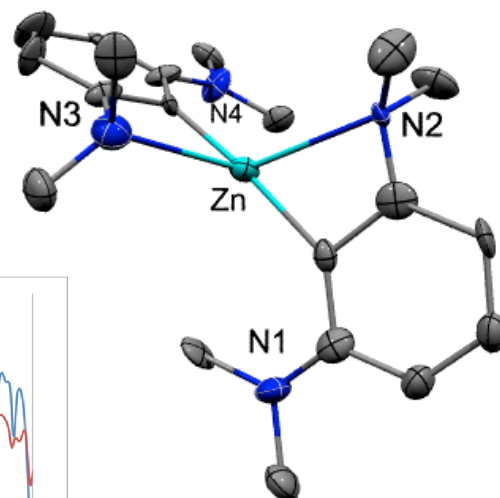
# Precursor to My Work (Results)

## Proposed synthesis



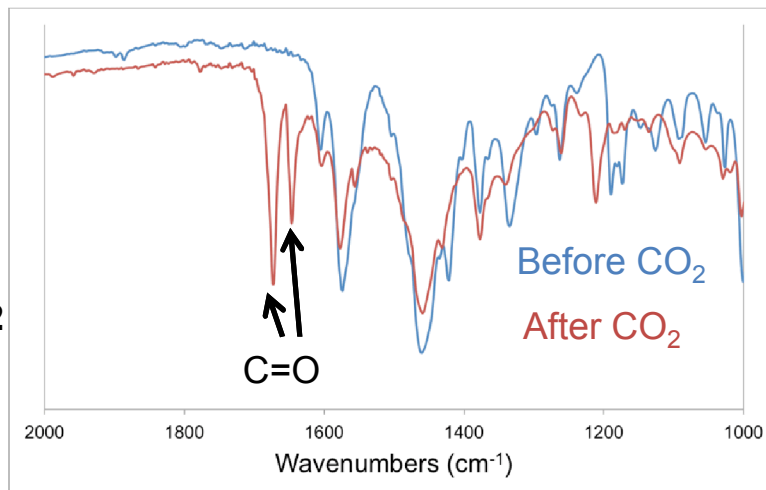
## $\text{Zn}^{2+}$ Complex

- **New crystal structure**
- **$\text{CO}_2$  reactivity unclear**



## $\text{Sn}^{2+}$ Complex

- **Known compound**
- **Reacts w/  $\text{CO}_2$**
- **Unable to crystalize**



- **Relative success led to my first ligand attempt**

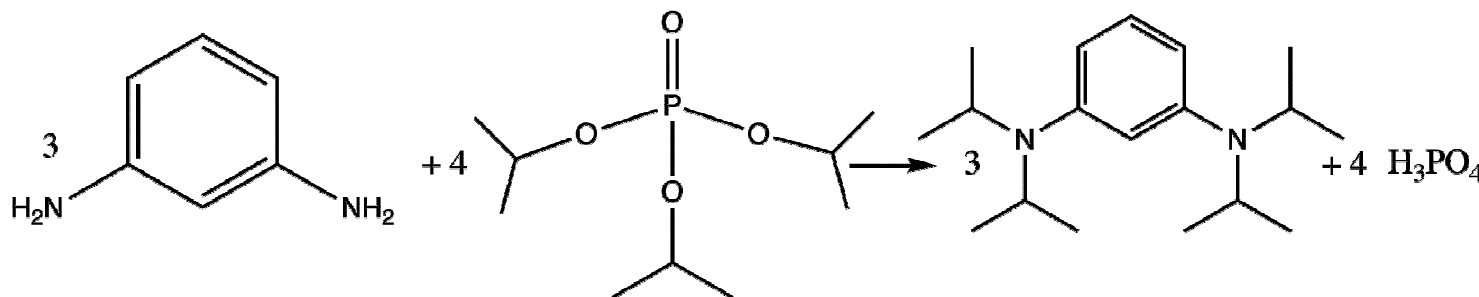
Reaction by Brian Barry



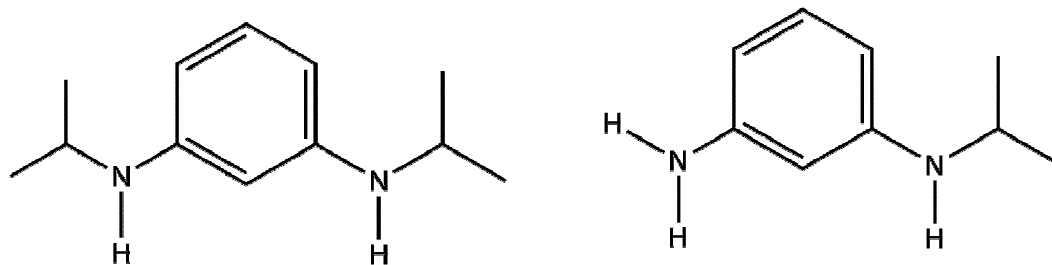
# My First Synthesis

## N,N,N',N'-tetraisopropyl-*m*-phenylenediamine

Proposed  
Synthesis:



Products  
Formed:

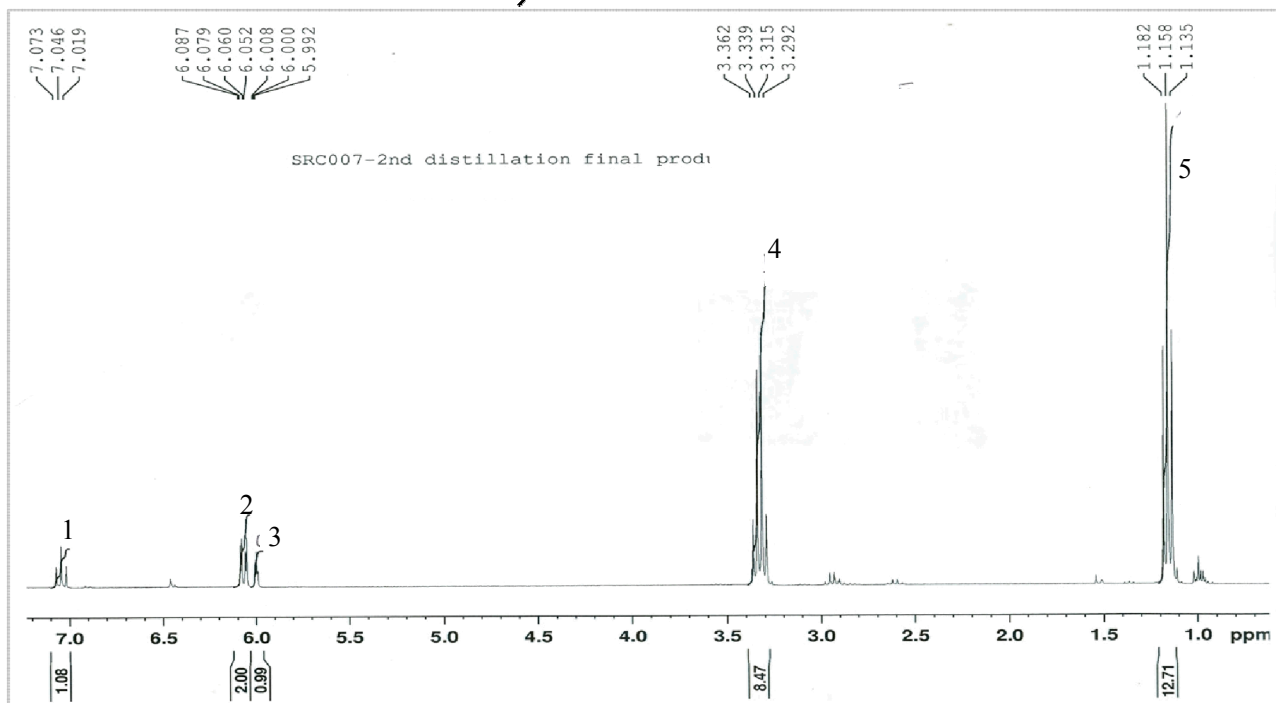
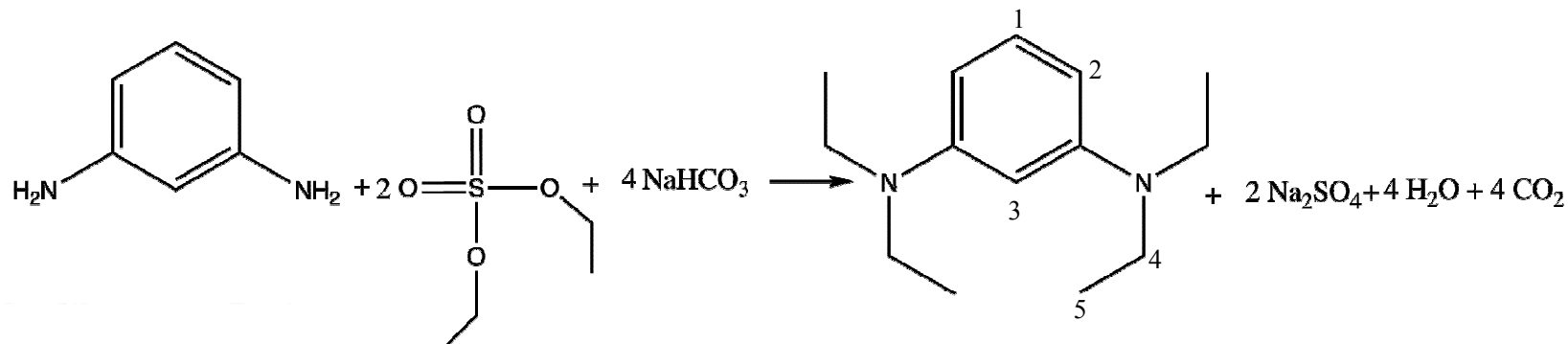


### • Possible Explanation

- 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

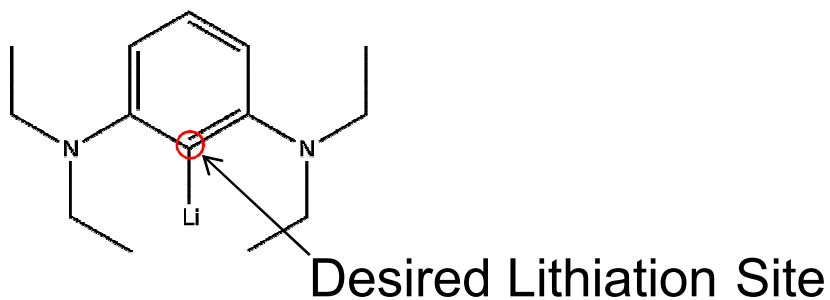
- N,N,N',N'-tetraethyl-*m*-phenylenediamine
  - Ligand synthesis was successful with high yield



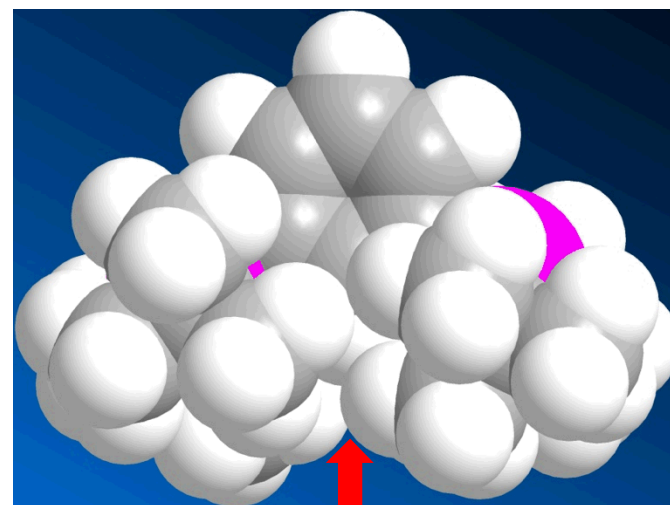
- **Product Confirmed by NMR**
  - Evidenced by shifts and integration

# 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

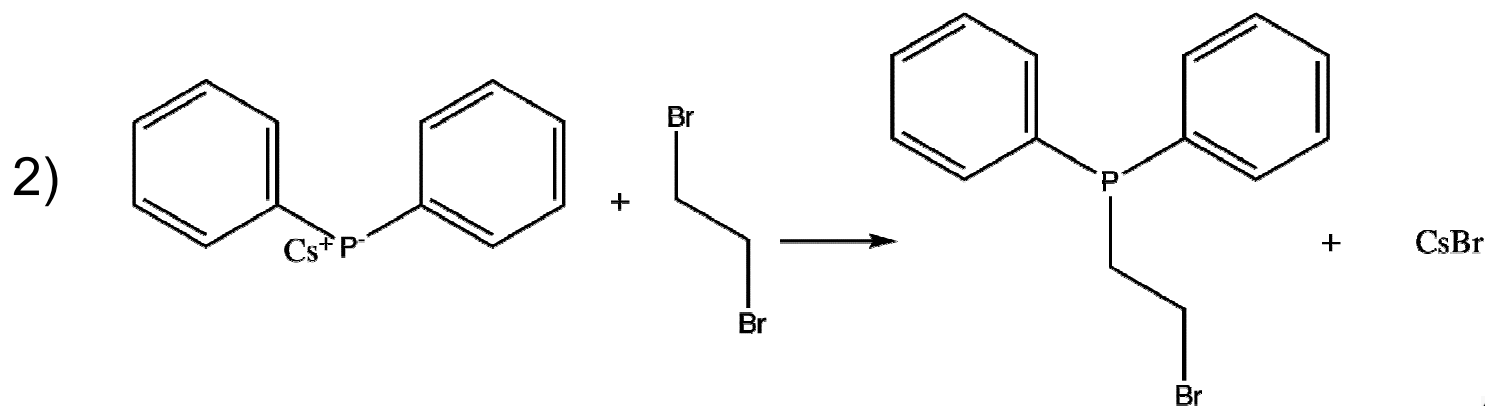
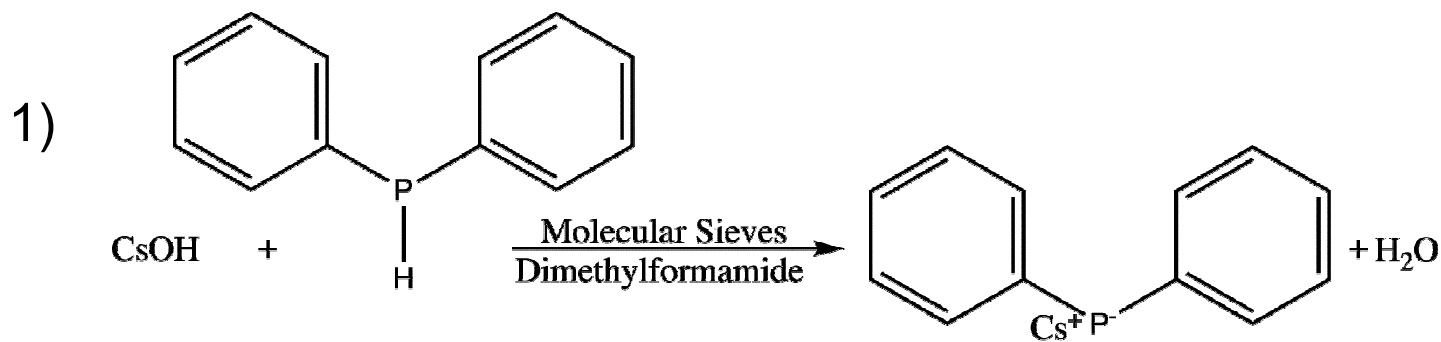


- Set ligand aside and moved on

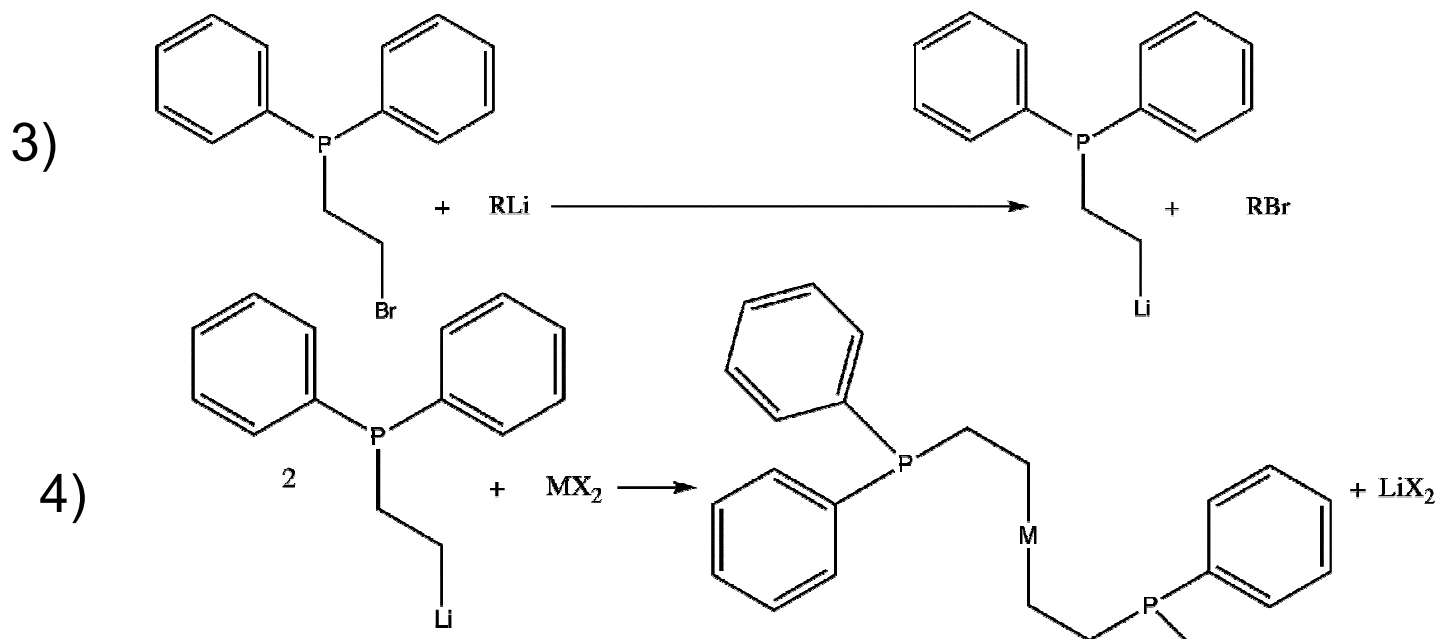


# My Third Synthesis (Currently Ongoing)

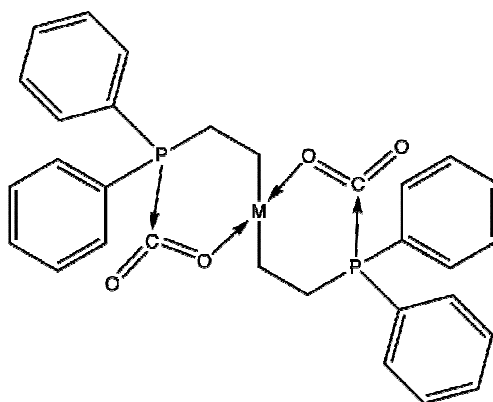
## Ethylbromide-Diphenylphosphine



# My Third Synthesis (Currently Ongoing)



- **Ultimate goal:**
  - Adduct with  $\text{CO}_2$





# Acknowledgements

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