Development of novel organometallic catalysts for the copolymerization of carbon dioxide and epoxides

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ND Energy
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Abstract

In keeping with the RET theme of Engineering a More Sustainable Energy Future, Dr. Henderson's group is working on a project to create catalysts that promote co-polymerization of carbon dioxide (CO_2) with epoxides to produce polycarbonates. These polycarbonates are higher-value polymers with applications in many areas (i.e. lightweight, shatterproof lenses) and could potentially provide a cost offset to carbon capture and sequestration efforts.

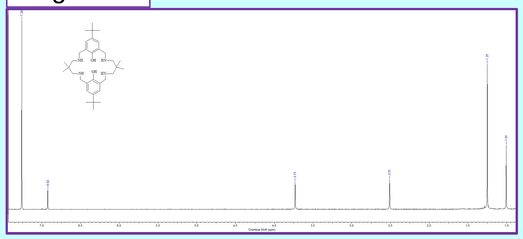
Introduction

Most polycarbonates are synthesized using phosgene, which is highly toxic, and *bis*-phenol-A, which is derived from petroleum. Current metal based catalyst systems utilize expensive, toxic and highly colored metals (e.g. Cr or Co). These catalysts have shown high activity for the copolymerization of epoxides with carbon dioxide. The Henderson group is working on designing catalysts using elements such as Mg, Ca, Al, Zn as these metals are more abundant, biocompatible and environmentally benign.

Results

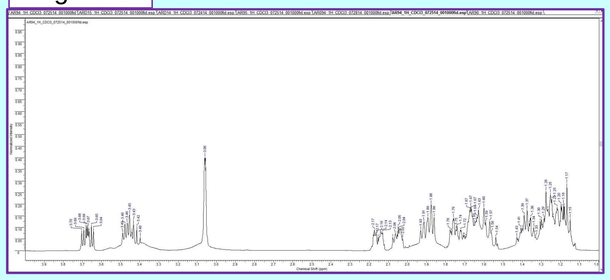
I confirmed the synthesis of H_2L^5 by NMR spectroscopy (Figure 5).

Figure 5



NMR of the product(s) of one attempt at epoxide ring opening. (Figure 8).

Figure 8



The organometallic complexes were also characterized by NMR spectroscopy ($[Zn_2OAc_2L^5]$ Figure 6) ($[Ca_2OAc_2L^5]$ Figure 7).

Figure 6

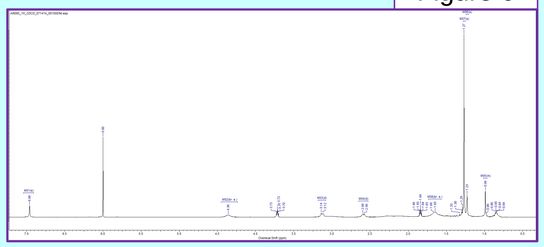
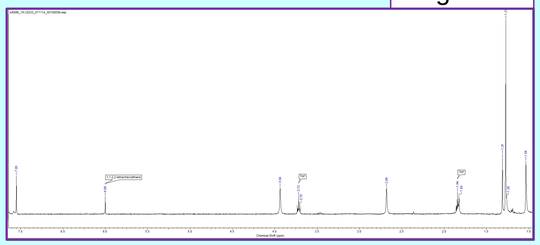
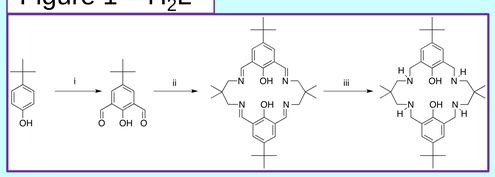


Figure 7



Synthesis

Figure 1 – H_2L^5



Reaction Conditions
i) hexamethylenetetramine, trifluoroacetic acid, reflux 24 h.
ii) 2,2-dimethyl-1,3-propanediamine, methanol.
iii) NaBH4, methanol, 0 °C.

Figure 2 – H_2TPP

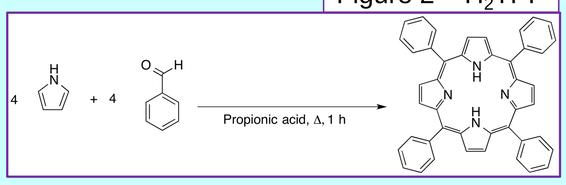
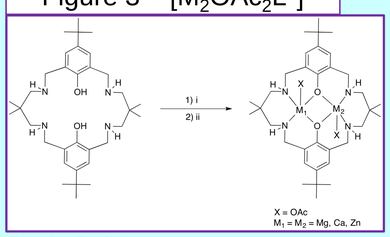
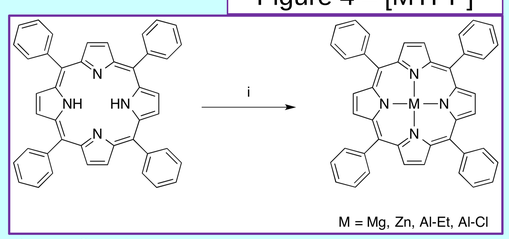


Figure 3 – $[M_2OAc_2L^5]$



Reaction Conditions
i) diethylzinc, stir for 2 h. ii) acetic acid, stir overnight

Figure 4 – [MTPP]



Reaction Conditions
i) diethylzinc, stir for 2 h

Conclusions

The two ligand syntheses are straightforward and produce moderate to good yields. H_2TPP readily complexes with magnesium and zinc. Difficulties were encountered when attempting to isolate the target aluminum complex. H_2L^5 readily reacted with magnesium, calcium and zinc to form organometallic complexes. I only had time to test the efficiency of one organometallic complex, $[Zn_2OAc_2L^5]$, at epoxide ring opening. The products of this reaction were difficult to characterize, but did not seem to be either acetate esters or polyethers , which is what we were expecting.

Bibliography

1. Kember, M. R., & Williams, C. K. (2012), *J. Am. Chem. Soc.*, *134*, 15676–9.

Curriculum Project

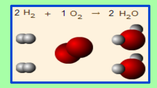
One aspect of the unit on Stoichiometry is Percent Yield. After students learn about mole ratios and how to calculate the amount of product expected, we move into the real world, where most chemical reactions do not yield 100% product. So chemists use "percent yield" to measure the efficiency of a particular reaction. During my summer research, not only was I attempting to synthesize the organometallic complexes, but it was also important to produce a significant amount of each complex to demonstrate that they would be worthwhile to make on an industrial scale.

DAY 1
Introduction to Percent Yield

- We will begin this section with an activity during which the students will move from station to station where they will work with different situations that model percent and percent yield.
- This will be followed by a presentation to formally introduce the concept of percent yield.

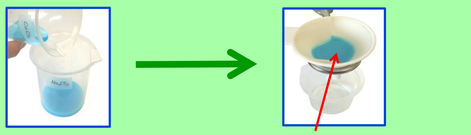
DAY 2
Practice with Percent Yield

- First, I will demonstrate solving a percent yield problem for the whole class.
- Then the students will work in pairs to solve other problems.
- The second half of the period will be devoted to preparing for the next day's lab, which is also their performance assessment.
  - I will preview important details of the procedure.
  - The students will construct data tables in their lab notebooks.
  - We will review the meaning and significance of the term "error".



DAY 3
Performance Assessment
Stoichiometry: Quantitative Precipitation

- This lab activity will provide the students with an opportunity to demonstrate their lab skills.
- The calculations and analysis they will write as part of their lab report will demonstrate their understanding of the concept of percent yield.



$CuCl_{2(aq)} + K_2CO_{3(aq)} \longrightarrow CuCO_{3(s)} + 2KCl_{(aq)}$