

# Synthesis and Characterization of Organometallic Catalyst Complexes and Their Ligand Subcomponents

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With the use of laboratory techniques, such as reflux synthesis, wash/extraction purification, nitrogen purged systems and rotational evaporation, fifteen separate synthesis experiments were performed out of which a library of four related ligands and a cobalt centered metal catalytic complex was produced. Although clear data was not able to be collected for four other solid products because of solubility issues, these uncharacterized products match corresponding article descriptions of similar reaction events and produced species. Instrumental characterization included  $^1\text{H}$  and  $^{13}\text{C}$  NMR, X-ray crystallography, and FT-IR spectroscopy, I can conclude that I was successful in synthesizing several of the target compounds and providing procedural improvements and spectral data as insight into the preparation and structural qualities of the target ligands and metal complexes.

## INTRODUCTION

The study of catalyst materials has become a major focus in chemical research and development because catalyst compounds increase the rate of specific reactions and the yield of products formed by lowering the energy needed for the reaction to take place. Petrochemical manufacturing, pharmaceutical engineering, and the majority of industrial processes depend on catalysts to create the most efficient reactions possible. The vast emission of carbon dioxide as a waste product of the combustion of fossil fuels in automobile operation and electricity generation and of iron and steel production causes a major threat to the health of the environment. Since carbon dioxide is recognized as the leading greenhouse gas released through human activities, the prevention of  $\text{CO}_2$  pollution is vital in protecting the environment. Fortunately, emerging research has shown that the application of specific organometallic catalyst provides a reaction in which  $\text{CO}_2$  is sequestered and combined to form polymer compounds that could possibly be reused for the mass production of plastics, synthetic fibers, and rubber (Darensbourg 2010). Therefore, with the use of this family of organometallic catalysts that will be synthesized and analyzed, harmful  $\text{CO}_2$  pollutant can not only be prevented but also recycled into valuable byproducts through the resulting filtration reaction. Also further research has shown that similar catalyst complexes offer biological benefit due to their ability to act as artificial enzymes (Breslow 1996).

Figure 1 demonstrates the general structure of the organometallic catalysts that were pursued during experimentation. Each R group represents functional groups that include a mixture of alkyl (carbon chains) and halogen substitutions. Although the demonstration above shows cobalt (Co) as the central metal atom, synthesis attempts were also performed with chromium (Cr) and Zinc (Zn). The incorporations of the central metal atom to the ligand complexes are crucial because they are responsible

for generating the electrochemical properties based on the central metal ion's oxidation state which is determined by the number of electrons an ion could possess. The central metal also provides the necessary bonding points for additional end groups during the copolymerization reaction of  $\text{CO}_2$  and epoxides (Gray, Meade, and Takeuchi 1992). For example, the chlorine groups (Cl) bonded to the central metal atom represent various halide and other ligand substituents that are essential to the catalytic reactivity of these complexes. However, before the metal complexes were created, various subcomponent ligands were synthesized by following a procedure adapted from (Zhuang, Chen, Nishide *et al.*, 2010) and were used as reactants in the metal addition reaction. Then the organic complexes were characterized to insure the purity of the product.

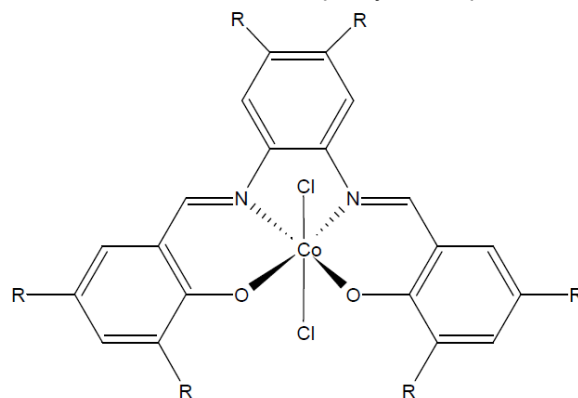
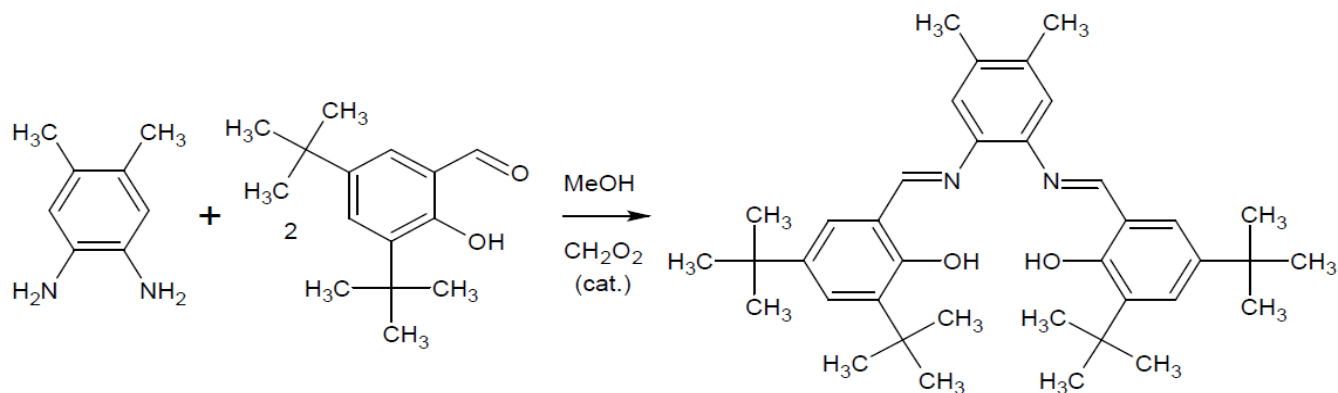


Figure 1. Sample Metal Complex

In the ligand synthesis reaction below the diamine backbone, 4,5-Dimethyl-1,2-phenylene Diamine (labeled A), is combined with two molar equivalents of a salicylaldehyde variant, 3,5-Di-tert-butyl-2-hydrobenzaldehyde (labeled B), to form the organic ligand structure (labeled C). By using salicylaldehydes with various substitutes, including

alkyl and halogen, the exterior structure of the ligands and resulting organometallic catalysts can be manipulated. This ligand variability is significant because published research has shown that the degree of polarization and the strength of the central cobalt-oxygen bonds for the axial coordination strongly influence the catalytic rate during polymerization (Zhuang, Chen, Nishide *et al.*, 2010). Therefore, the structure of the ligand complexes attached to the central metal ion affects the catalytic properties of the organometallic complexes.

Once the desired ligands were created, several attempts were made to synthesize and characterize metal centered catalyst complexes. However, three distinct reaction procedures, adapted from three separate journal articles, were used for each metal addition type. Both the chromium and cobalt metal addition required initial stirring in a nitrogen charged atmosphere free from oxygen in order to prevent oxidation of the metal atoms (Darensbourg 2004; Zhuang, Chen, Nishide *et al.*, 2010).



**Figure 2.** Ligand Synthesis Reaction For 3,5-Di-tert-butyl-2-hydrobenzaldehyde 4,5-Dimethyl-1,2-phenylene Diamine

## MATERIALS AND METHODS

**Synthesis of Prototype Ligand *N,N*-bis(salicylidene)-4,5-dimethyl-1,2-phenylenediimine (LS1):** Adapting the synthesis procedure from Darensbourg's 2004 Supplementary information (cited in references), the first prototype synthesis was performed as follows. 0.3 grams of salicylaldehyde was added to a 100mL beaker followed by 75mg of the backbone, 4,5-Dimethyl-1,2-phenylenediamine, and 30mL of methanol. This mixture created a yellow solution which was swirled for a short period of time and then set to rest for 2 hours. Yellow spine-like crystals began to form within 10 minutes of swirling and continued growing until a large quantity of solid was formed. The beaker containing the solid was then placed under the hood and allowed for slow evaporation of solvent. Yellow and bright orange spine crystals were recovered and separated. At first the difference in color hinted to a secondary product or a half reaction product; however, after further

observation the bright orange crystals began to turn yellow as they dried in air. Therefore, the variety in color was most likely due to a hydrated version of the solid product. Both orange and yellow solids were characterized through  $^{13}\text{C}$  NMR and matched predicted and confirmed spectra of prior researcher, Geoff Fontenot. Although the formic acid was never added and a reflux was never performed this fourth trial experiment provided high quality crystals that received clear and definitive data.

***N,N*-bis(3,5 Di-tert-butyl-2-hydrobenzidene)-4,5-dimethyl-1,2-phenylenediimine (LS2):** 0.25 grams of the diamine backbone was added to a addition funnel instead of the RBF. 1.3g of 3,5-Di-tert-butyl-2-hydrobenzaldehyde was used as the salicylaldehyde component, which was added to the RBF. After the solutions were combining and refluxing for thirty minutes, the clear reaction solution became cloudy with orange precipitate. Once reflux was completed, the mixture was filtered, and a fluffy bright orange

solid was obtained at a dry mass of 0.8196 grams and a percent yield above 79%. A small amount of product was left behind during transfer. A 15mg NMR sample was prepared with  $\text{CDCl}_3$  as the solvent, producing a golden yellow solution. High quality  $^1\text{H}$  and  $^{13}\text{C}$  NMR with minimal impurities were obtained and matched predicted spectra. A 30mg slow evaporation sample was also made with roughly 5mL of Chloroform, but yielded no crystals by the end of the research period.

***N,N-bis(5-Chlorosalicylidene)-4,5-Dimethyl-1,2-phenylenediimine (LS3)***: 0.25 grams of the diamine backbone was added to a addition funnel instead of the RBF 0.8g of 5-Salicylaldehyde was used as the salicylaldehyde component, which was added to the RBF. While the solutions were combining and refluxing, the clear yellow reaction solution became cloudy with creamy pale orange precipitate. Once reflux was completed, the mixture was place in a freezer overnight. Then the product mixture was filtered, and a mustard yellow-orange solid was obtained at a dry mass of 0.657 grams and a percent yield above 89%. A small amount of product was left behind during transfer. A 15mg NMR sample was prepared with  $\text{CDCl}_3$  as the solvent, producing a golden yellow solution. High quality  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra with minimal impurities were obtained and matched predicted spectra.

***Cobalt Organometallic Complex of N,N-bis(salicylaldehyde-1,2-phenylenediimine (MCS1)***  
***Reaction seen in Introduction (Figure 3)***: 0.15 grams (0.6mmol) of cobalt acetate tetrahydrate was weighed and place under the nitrogen environment in the RBF. A magnetic stir bar and 40 mL of methanol were added and allowed to stir, producing a pinkish red solution. 0.19 grams (0.6 mmol) of the ligand complex was dissolved in 4 mL of methylene chloride to produce a clear yellow solution. This solution was added to the RBF via syringe through a septum and allowed to stir for 15 minutes at room temperature. This addition caused a significant color change from pink and yellow to a dark blackish red. Residue was rinsed from walls of the flask with 5 mL of the reaction solution. Then then the flask was placed in an ice bath and stirred for 30 minutes at  $0^\circ\text{C}$ . The flask was

removed and its contents were filtered and rinsed with  $0^\circ\text{C}$  methanol ( $3 \times 50$  mL). A reddish brown solid was collected and placed in a vacuum oven for a 24 hour pressure dry. Roughly six hours into drying the pump hose failed; however, the solid product appeared dry. The experimental yield of the fine powder solid was 0.16 grams at a 73% yield, but some product was lost during transfer.

## RESULTS AND DISCUSSION

The following results of successfully characterized ligands and catalyst are arranged, correlated, and analyzed chronologically. All collected spectra were compared to predicted spectra created with ACD Lab NMR Predictor software. All data analysis of inconclusive, uncharacterized, and/or unsuccessful syntheses is available in supplementary information.

	LS1a	LS2	LS3
<b>Physical Description</b>	Bright yellow (and orange initially) spine-like crystals	Bright orange fluffy fiber-like crystals	Mustard yellow smooth crust solid
<b>Theoretical yield (g)</b>	0.0197	1.0442	0.759
<b>Experimental yield (g)</b>	0.0171	0.8196	0.679
<b>Percent Yield (%)</b>	86.8+	78.5+	89.5+

**Table 1.** Collective Synthetic Data for Ligand Complexes

With percent yields 78% and above for these three products, these syntheses were successful in obtaining relatively high yields which demonstrates that the procedure and reaction ran well and that the products most likely have minimal impurities.

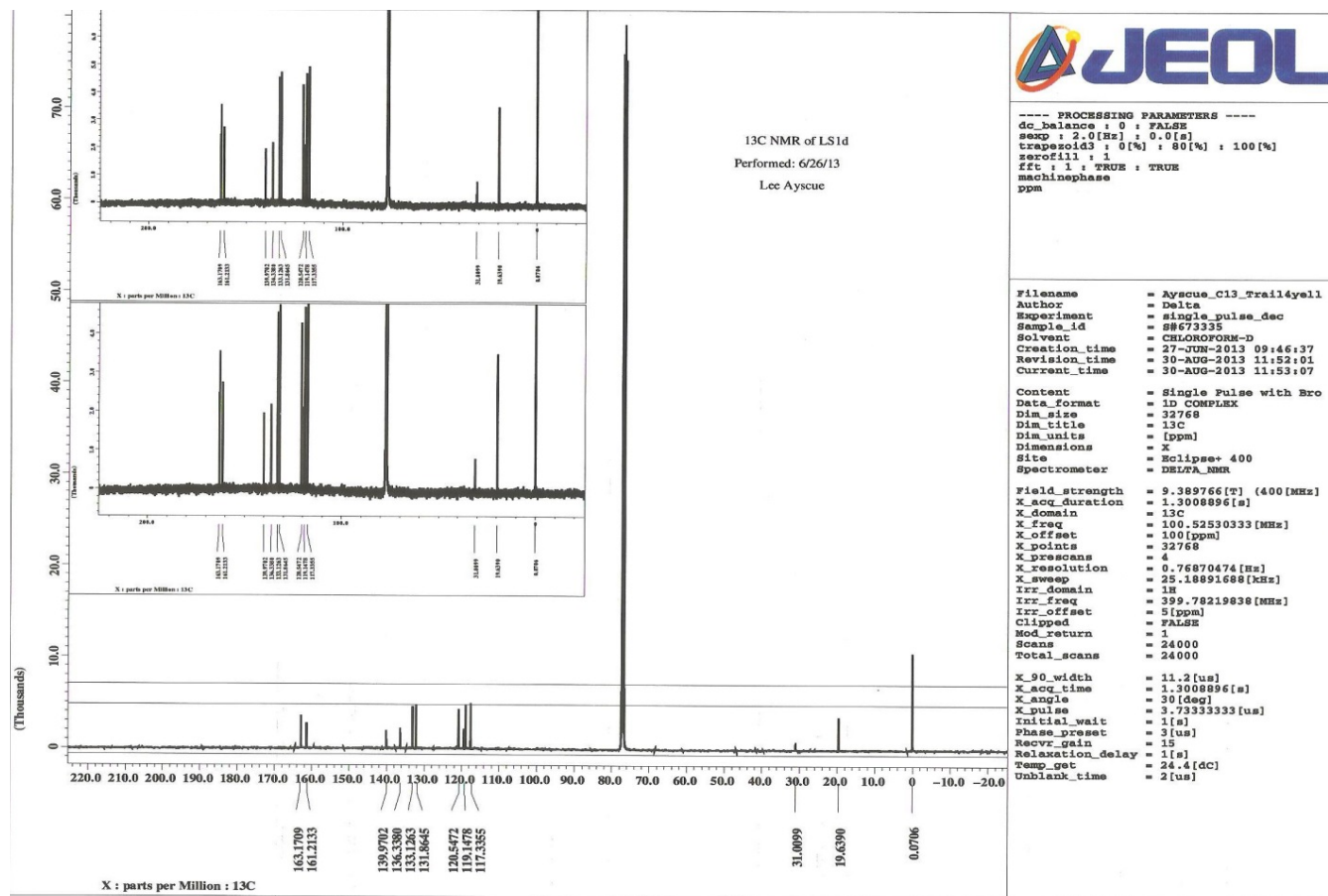


Figure 3.  $^{13}\text{C}$  Carbon NMR of N,N-bis(salicylidene)-4,5-dimethyl-1,2-phenylenediimine (LS1): (24000scans)

Predicted Chemical Shifts (ppm)	Observed Chemical Shifts (ppm)	Carbon Group Type	Predicted # of Carbons in Group (# of Peaks)	# of Peaks in Group
0-30	19.6	Alkane (CH <sub>3</sub> )	2, but symmetric (1)	1
110-150	117.3, 119.1, 120.5, 131.9, 133.1, 136.3, 139.9	Aromatic	16, but symmetric (8)	8
150-170	161.2	C-OH	2, but symmetric (1)	1
160-170	163.17	C=N	2, but symmetric (1)	1

Table 2.  $^{13}\text{C}$  Carbon NMR Data N,N-bis(salicylidene)-4,5-dimethyl-1,2-phenylenediimine (LS1)

Since the LS1d is symmetrical, this ligand has 11 different carbons with its own chemical shift value. Therefore, the  $^{13}\text{C}$  NMR should have 11 total

peaks without the TMS peak at 0 ppm. The collected spectrum has 14 prominent peaks with some insignificant peaks due to trace impurities, but the triplet between 70-80ppm is a characteristic peak of the solvent,  $\text{CDCl}_3$ . Therefore, the collected spectrum

is, in fact, a clear match to the predicted spectrum from ACD Lab Spectra Predictor. This spectral data

acts as supporting confirmation that the target ligand was constructed.

**Table 3.**  $^{13}\text{C}$  Carbon NMR Data for LS2

**Table 4.**  $^{13}\text{C}$  Carbon NMR Data for LS3

Predicted Chemical Shifts (ppm)	Observed Chemical Shifts (ppm)	Carbon Group Type	Predicted # of Carbons in Group (# of Peaks)	# of Peaks in Group
0-30	19.6	Alkane (CH <sub>3</sub> )	2, but symmetric (1)	1
20-40	29.5, 31.6	Alkane (t-butyl)	12, but shift overlap (2)	2
20-40	34.2, 35.1	Alkane (CR <sub>4</sub> )	4, but symmetric (2)	2
110-150	118.5, 120.9, 126.7, 127.9, 135.9, 137.2, 140.3	Aromatic	16, but symmetric (8)	8
150-170	158.6	C-OH	2, but symmetric (1)	1
160-170	163.9	C=N	2, but symmetric (1)	1
Predicted Chemical Shifts (ppm)	Observed Chemical Shifts (ppm)	Carbon Group Type	Predicted # of Carbons in Group (# of Peaks)	# of Peaks in Group
0-30	19.7	Alkane (CH <sub>3</sub> )	2, but symmetric (1)	1
110-150	119.1, 120.1, 120.5, 123.6, 131.2, 133.0, 137.1, 139.7	Aromatic	16, but symmetric (8)	8
150-170	159.9	C-OH	2, but symmetric (1)	1
160-170	161.5	C=N	2, but symmetric (1)	1

Since the LS2 is symmetrical, this ligand has 19 different carbons with its own chemical shift value. Therefore, the  $^{13}\text{C}$  NMR should have 19 total peaks without the TMS peak at 0 ppm. The collected spectrum has 22 prominent peaks with some insignificant peaks due to trace impurities and signal

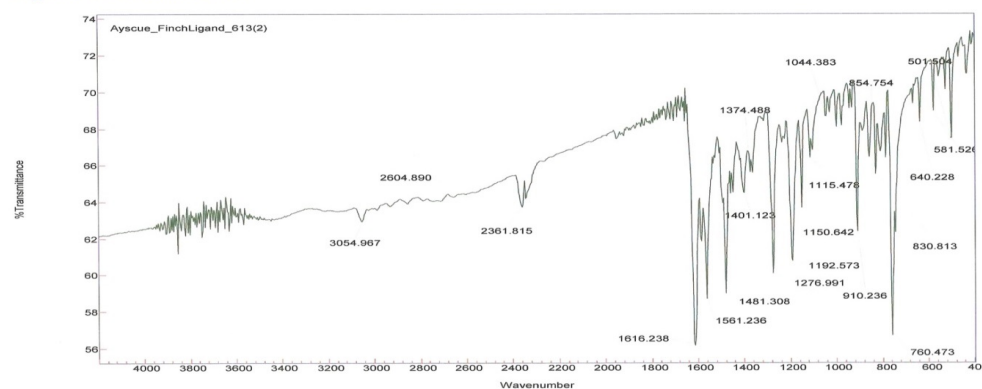
noise, but the triplet between 70-80ppm is a characteristic peak of the solvent,  $\text{CDCl}_3$ . Therefore, the collected spectrum is, in fact, a clear match to the predicted spectrum from ACD Lab Spectra Predictor. This spectral data presents convincing evidence that the target ligand was constructed.

LS3 is also symmetrical, this ligand has 11 different carbons with its own chemical shift value. Therefore, the  $^{13}\text{C}$  NMR should have 11 total peaks not including the peak TMS at 0 ppm. The collected spectrum has 15 prominent peaks with one peak at 1.1 ppm which may be caused by an impurity or by misinterpreted TMS. Also there are some insignificant

peaks due to trace impurities and signal noise, but the triplet between 70-80ppm is a characteristic peak of the solvent,  $\text{CDCl}_3$ . Therefore, the collected spectrum is, in fact, a match with minimal impurities to the predicted spectrum from ACD Lab Spectra Predictor. This spectral data provides conclusive evidence that the target ligand was constructed.

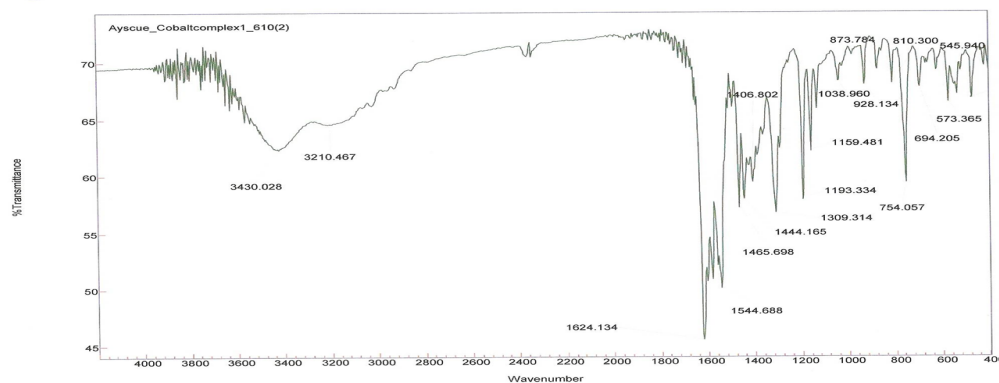
**Figure 4.** Infrared Spectrometry of N,N bis(salicylaldehyde-1,2-phenylenediimine Ligand and Corresponding Cobalt Catalyst Complex

Digilab Resolutions Pro



Name  
Ayscue\_FinchLigand\_613(2)

Digilab Resolutions Pro



Name  
Ayscue\_Cobaltcomplex1\_610(2)

In the above spectra, there is very noticeable change that occurred once the cobalt was added to the N,N bis(salicylaldehyde-1,2-phenylenediimine Ligand, which was assumed to be the correct compound, in order to produce the organometallic catalyst complex. In the ligand or first IR spectrum, characteristic aromatic ring peaks are seen in the 1500-1600 range, but more importantly there is no significant peak in the 550-600 range. This range has been determined through published research as the specific wavenumber at which a wide peak of a cobalt oxygen bond exists (Zhuang, Chen, Nishide, et al.).

By comparing the two IR spectra, the observation can be made that a small yet wide peak did, in fact, appear at  $572\text{cm}^{-1}$  where only smaller sharp peaks were present in the ligand spectra. Also the IR of the catalyst sample shows similar values ( $1610\text{cm}^{-1}$  (s, C=N);  $1595$  (s, Ar);  $1527$  (s, Ar);  $1254$  (s, C-O); and  $572$  (w, Co-O)) to that of other cobalt complexes and similar aromatic peaks to that of its own ligand component. Based on the observation that the catalyst sample spectra retained similar peaks to the ligand subcomponent, while gaining documented peaks of cobalt addition to oxygen, these spectra acts

as evidence that the target organometallic complex was made

. Although there were multiple inconclusive results due to issues like solubility or non-solid products, three Schiff-base ligands and one cobalt centered catalyst complex were successfully synthesized at high yields and purity using procedure adapted from research journal articles and verified through characterization techniques such as Infrared Spectrometry,  $^{13}\text{C}$  NMR, and  $^1\text{H}$  NMR. Also several of the inconclusive experiments did produce ample solid product that had similar physical characteristics as the verified compounds and matched some article description but were insoluble in all attempted solvents. Therefore, no characterization could be performed, but the inconclusive samples are most likely the target compounds as well. Although many of the goals for this research project were accomplished, this project has extensive opportunities for continuation and additional success. The resolution of the ominous solubility issue and/or alternative and more consistent synthesis procedures could easily become the focus of future researchers who could extend this project to the point where the analysis of these complexes' catalytic properties could be thoroughly study and eventually applied to lessen the impact of  $\text{CO}_2$  on the environment and/or benefit further research into artificial enzymes.

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