Synthesis of Scandium and Gallium Metal Complexes for use in the Ring-Opening

Polymerization of Lactide and Propylene Oxide

Honors Research Thesis

Presented in partial fulfillment of the requirements for graduation *with honors research distinction* in Chemistry in the undergraduate colleges of The Ohio State University

by

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Abstract

 As the demand for polymers increases, it is becoming clear that the current methods used to produce polymers and the types of polymers manufactured are not sustainable. Currently, about 99% of plastics produced worldwide are made from petroleum sources. Thus the development of polymers from renewable resources such as biomass and carbon dioxide is increasingly attractive. This project investigates the efficacy of scandium and gallium complexes of tetraphenylporphyrin (TPP) and Jacobsen's ligand (salen) in the polymerization of lactide and the copolymerization of CO_2 and propylene oxide. Thus far (TPP)ScCl, (TPP)GaCl, (salen)ScCl, and (salen)GaCl have been synthesized. These compounds were synthesized from the metal chlorides and protonated ligands using standard Schlenk-line and dry box techniques. Preliminary results show that these complexes are inactive in the homopolymerizations of lactide and propylene oxide. This is likely due to the low nucleophilicity of the chloride anion, which makes it a poor initiator for ring-opening polymerizations. Currently attempts to synthesize the alkoxide derivatives of these compounds are in progress.

1. Polymers in Industry

Since the invention of the first synthetic polymer, Bakelite, in 1907, polymers have swiftly infiltrated almost every aspect of human life. Polymers can be found in clothing, cars, packaging, building materials, electronic devices, or even in biomaterials, such as heart valve or blood vessel replacements. While polymeric materials have a vast range of properties and characteristics, the most widely used polymers can be classed into four major groups: polyesters, polyolefins, polyurethanes, and polycarbonates.

Polyesters are generally used in fabrics and textiles, and account for 80% of all manmade fibers[1]. In 2009 polyester fiber production was 30.77 million tons[2], and is projected to reach 39.3 million tons by 2015[3]. Polyolefins, the most common of which is polyethylene, are used in disposable packaging such as plastic bags, shampoo bottles, and milk containers. In 2007, total polyolefin demand was over 110 million tons, and is projected to be almost 150 million tons by 2012.[4] Polyurethanes are used in plastic foam compounds, such as foam seating, seals and gaskets, upholstery, footwear, and insulation foam. The polyurethane market is projected to reach 9.6 million tons by 2015[5]. Polycarbonates are easily molded and therefore find applications in automobile, aircraft, construction, and electronic industries. In 2009 the global polycarbonate market was 2.9 million tons, and is projected to grow by 6% annually up to 2015, or to about 4 million tons. This brings global production of the four major types of polymers to about 200 million tons by 2015, or 26 kilograms per person worldwide.

2. Sustainability in Industry

As the demand for polymers increases, it is becoming clear that the current methods used to produce polymers and the types of polymers manufactured are not sustainable. Currently, about 99% of plastics produced worldwide are made from petroleum sources[6]. Increasing demand for a limited resource such as oil, especially in an increasingly globalized world with emerging Asian markets, is causing rising prices for polymer feedstock[7]. Additionally, plastics pose a daunting problem for waste management. A large portion of polymers is used for packaging and is discarded after a single use. The United States alone produces 30 million tons of plastic municipal solid waste annually. Plastic waste is generally either incinerated, a process which is uneconomical and environmentally unsound, or it is deposited in landfills where traditional plastics comprise about 25% of total landfill space[8]. Most of the polymers deposited in landfills do not degrade in landfill conditions, causing an incessant accumulation of waste.

Also of concern when evaluating polymer synthesis is the atom economy of the methods used. Of the four major types of polymers, only polyolefins and polyurethanes are made by atom efficient schemes. Polycarbonates and polyesters are generally synthesized via polycondensation reactions. Polycarbonates are formed by reacting diols with phosgenes in a process that is both expensive and hazardous[9] to give the desired polymer and HCl as a byproduct (Scheme 1).

Scheme 1. Synthesis of polycarbonate from bisphenol-A and phosgene[10]
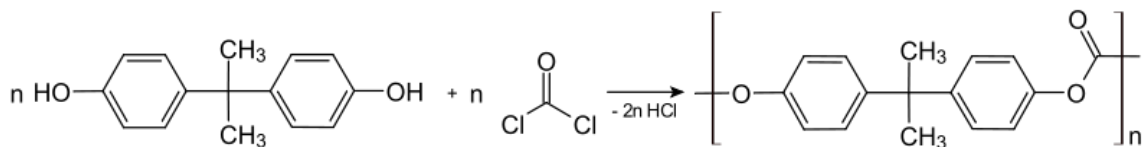
Similarly, current industrial synthesis of polyesters generally involves polycondensation of a diol and a diacid to give the desired polymer and water (Scheme 2).

**Scheme 2.** Synthesis of poly(ethylene terephthalate) from ethylene glycol and terephthalic acid[11]
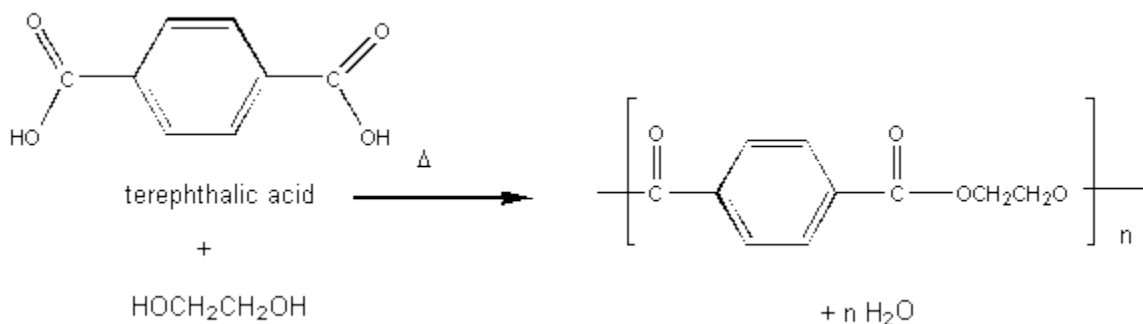
Since esterification is an equilibrium process, polycondensation to form polyesters often requires heating the system to remove water, which requires energy input. Overall, these processes are not considered atom efficient because they produce a significant amount of undesired product.
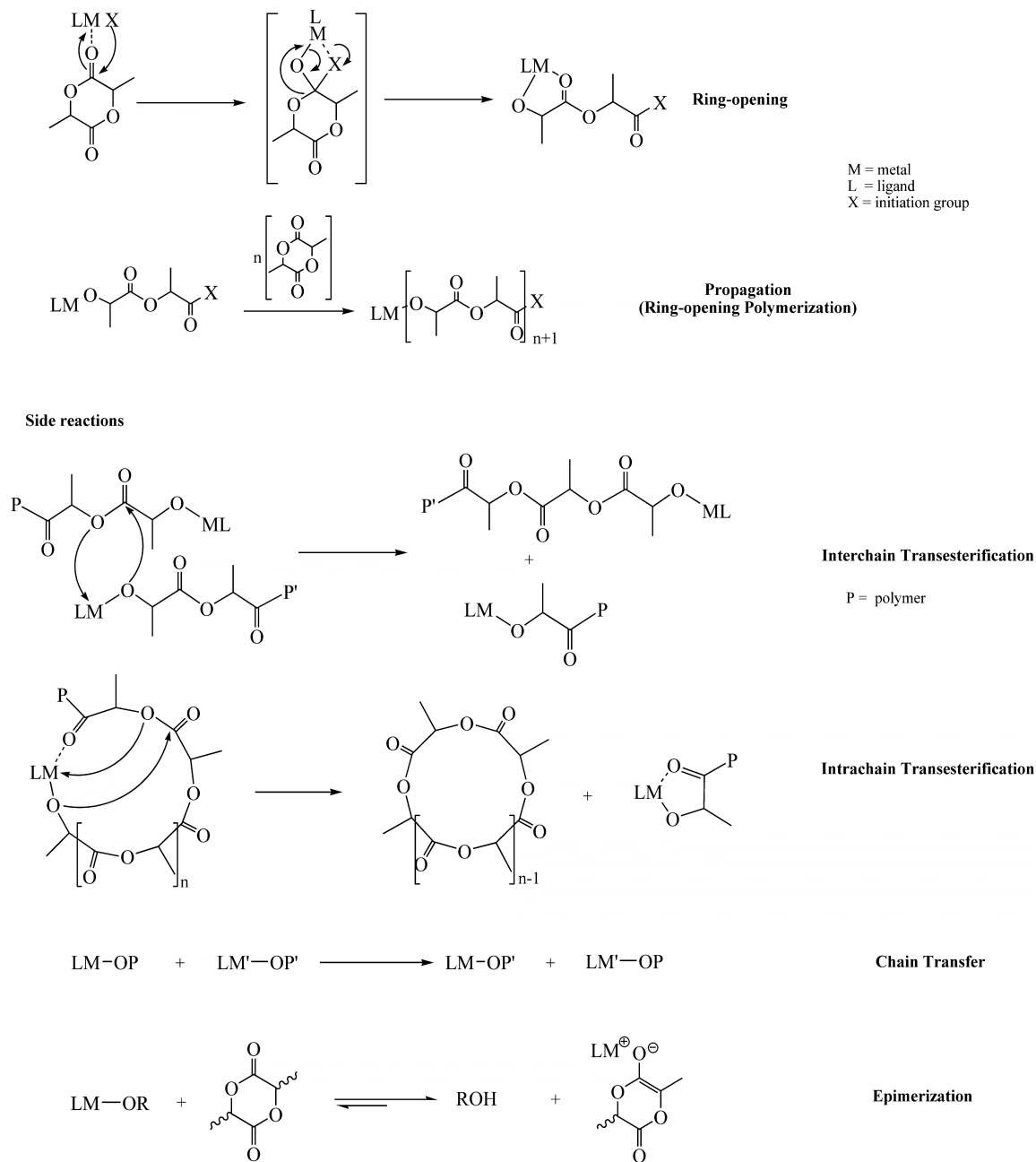
3. Ring-Opening Polymerization

The scientific community has sought to address the issue of sustainable polymerization practices through increasing interest in the development of atom economical reactions to make biodegradable polymers from renewable resources.[12,13] Of particular interest is catalytic ring-opening polymerization (ROP). Ring-opening polymerization is a highly efficient method of synthesizing macromolecules, and as a "living" polymerization mechanism it provides better control over the molecular weight and molecular weight distribution of the products.[14] A living polymerization mechanism is one in which chain transfer and chain termination do not occur, allowing polymerization to continue as long as unreacted monomer is present. Many different types of ROP catalysts have been developed[14], but we will focus on ROP using metal coordination catalysis. In the general mechanism for ring-opening polymerization, an initiator attacks the cyclic monomer, causing the ring to open and forming a new complex that can in turn ring-open another monomer (Scheme 3). ROP can be done using only one monomer, or can be used for copolymerizations or the formation of block copolymers.

Scheme 3. General ring-opening polymerization reactions.
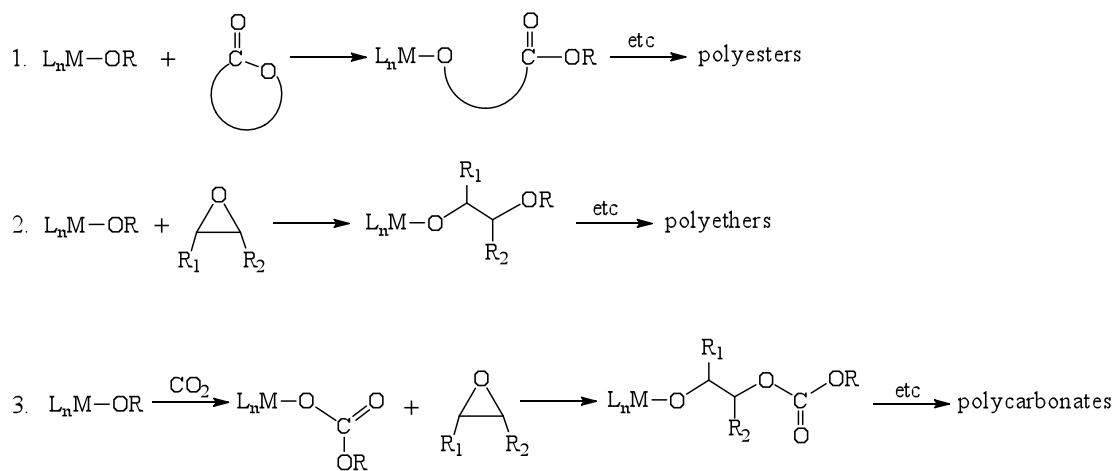
In theory, the initiation rates of ROP reactions are much faster than the propagation rates, and chain transfer or termination does not occur, which leads to narrow molecular weight distributions. In actuality, side reactions such as chain transfer, backbiting, cyclization, and chain termination can occur (Scheme 4). Minimization of these side reactions depends on the selectivity of the catalyst for unreacted monomer.

Scheme 4. ROP and Side Reactions of Lactide using a coordination catalyst.[15]

M = metal
L = ligand
X = initiation group

Ring-opening

**Propagation
(Ring-opening Polymerization)**

Side reactions

Interchain Transesterification

P = polymer

Intrachain Transesterification

LM−OP + LM'−OP' ⟶ LM−OP' + LM'−OP   **Chain Transfer**

LM−OR + ⇌ ROH +   **Epimerization**

The driving force of ring-opening polymerizations is the thermodynamically favorable relief of ring strain. Thus highly strained molecules such as epoxides are often used as monomers. Here we will focus on the ring-opening polymerizations of lactide and propylene oxide.

4. Polylactide and Poly(propylene carbonate) (PPC)

Polylactide (PLA) is a polyester that can be synthesized by the ring-opening polymerization of lactide monomers (Scheme 4). PLA can be used in industrial products such as packaging, disposable tableware, diapers, and home textiles. Due to growing demand for bioplastics, the PLA market is estimated to reach 3 million metric tons by 2020.[16] PLA is economically and environmentally desirable because lactide monomers can be derived from starch and other biomass. Moreover, PLA is biodegradable[12], which not only helps to address the issue of waste management, but also allows for applications in medicine, such as dissolving sutures or drug delivery.[17]

Similarly, the production of polycarbonates from carbon dioxide is both economically and environmentally attractive. Carbon dioxide is a practically omnipresent chemical in the natural world, and is additionally a major byproduct of many industrial processes. Although increased industrial use of CO_2 is not a viable option for significantly decreasing worldwide CO_2 emissions, it provides an application for carbon dioxide isolated by carbon sequestration and storage processes.[18] It also presents a more environmentally sound path to products that would otherwise be synthesized from toxic or environmentally harmful chemicals.[19] However, carbon dioxide is a challenging starting material because it is extremely stable, with a free energy of formation of -394.01 kJ/mol.[29] Thus the use of reactive species as reagents, such as propylene oxide, was developed.

5. Polymerization of PPC

5.1 Early Discoveries

The copolymerization of racemic propylene oxide (PO) and carbon dioxide was first achieved in the 1960s by Inoue *et al*. A 1:1 mixture of diethyl zinc and optically active alcohol was first reported to enantioselectively homopolymerize PO[20], and a few years later a heterogeneous 1:1 mixture of diethyl zinc and water was reported to copolymerize CO_2 and PO.[21] However, the activity of the catalysts was generally low with initial turn-over-frequencies (TOFs) on the order of 0.12 h^{-1}.[29] Further work was done using a variety of systems that were generally composed of $ZnEt_2$ and a co-catalyst containing two labile hydrogens. It was hypothesized that the labile hydrogens are necessary so that $ZnEt_2$ and the co-catalyst react to form a polymeric species containing zinc-oxygen bonds.[22] It was also hypothesized that the polymerizations proceeded by a mechanism of backside attack based on inversion of configuration at the carbon center that is favored for attack in optically active epoxides. The use of strong Lewis bases as solvents slowed the polymerization reactions, from which it was inferred that coordination of the epoxide to the metal center precedes ring opening.[23] However, these first generation catalysts were often insoluble and their structure was poorly defined, which made rigorous mechanistic studies difficult.

The development of zinc bis(phenoxide) complexes in 1995 by Darensbourg and coworkers helped to confirm the inferences made from work with the polymeric zinc oxide species. Studies on binding sites determined that while CO_2 will insert into zinc catalysts without binding sites, at least one binding site is necessary to allow ring opening

epoxide homopolymerization or copolymerization with CO_2 to occur. Also, catalysts with only one binding site showed significantly fewer ether linkages than catalysts with two binding sites.

5.2 Zinc ß-diiminate Catalysts

In 2001, Coates and coworkers reported the copolymerization of CO_2 and epoxides by various new zinc ß-diiminate (BDI) compounds (Figure 1). These compounds were found to be highly active at low CO_2 pressures such as 6.9 bar, and produced polymers with narrow PDIs (1.06 to 1.14).[24] Electronic and steric effects of substituents were investigated and were found to have a profound effect on catalyst activity. For example, at 50 °C and 6.9 bar CO_2 with R^1= H and R^2, R^3=Et a TOF of 239 h^{-1} was obtained. For the same reaction conditions with R^1=CN, R^2= Me, R^3= iPr the TOF was increased to 2290 h^{-1}.[25] Further investigations of BDI catalysts by Coates et al. and Chisholm and coworkers probed the effect of the metal center and initiating species in the polymerization of lactide and will be discussed below.

Figure 1. An example of a typical ZnBDI dimer.[20]
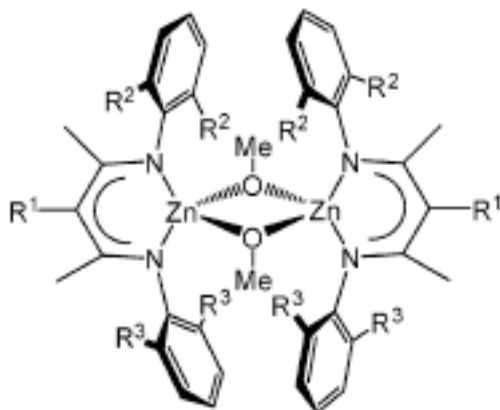
5.3. Metal Salen Catalysts

In 2000, Jacobsen and coworkers published a patent on the copolymerization of racemic 1,2-epoxyhexane with carbon dioxide by a chiral chromium salen (salen= (*R,R*)-(-)-*N,N'*-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamine, Figure 2) complex. The catalyst was found to selectively react with the (*S*)-enantiomer. At that time, the Darensbourg group developed the use of chromium salen catalysts and published a thorough account of their utility in the copolymerization of carbon dioxide and cyclohexene oxide (CHO) in 2002.[25] At 80 °C, 58.5 bar carbon dioxide, and in the absence of a co-catalyst the resulting atactic polymer was found to have an average molecular weight of 8900 g/mol and a TOF of 10.4 h^{-1}. The addition of five equivalents of *N*-methylimidazole as a co-catalyst improved catalyst activity to a TOF of 32.2 h^{-1}. This is generally hypothesized to be due to the co-catalyst binding axial to the initiating group, which would weaken the metal-initiator bond and facilitate monomer insertion. Experimentation with ligand substitutions found that sterically non-encumbering, electron-donating substituents produced the most active catalysts. Replacing the chloride initiator with azide also increased the TOF from 35.7 h^{-1} to 46.9 h^{-1}.[26]

Chromium salen complexes have also been developed for PO and CO_2 copolymerization, with **(2)** (Figure 2, X=N_3) being the most active with a TOF of 192 h^{-1} at 60 °C and 34.5 bar, with 93% copolymer selectivity and 99% carbonate linkages.[19] The use of **(1)** where X= NO_3 with bulky nucleophiles was reported in 2007 to greatly improve the regioselectivity of PO/CO_2 copolymerization, achieving head-tail linkages of up to 93% and copolymer selectivity of 99% with 7-benzyl-1,5,7-triazabicyclo[4.4.0]dec-5-ene as a cocatalyst.[26] Mechanistic studies suggest that the co-catalyst acts as an

initiator instead of coordinating to the metal center, and it was proposed that each catalyst molecule binds two propagating polymer chains.

While chromium salen catalysts have attained a high degree of copolymer selectivity for cyclohexene oxide, their use in the production of poly(propylene carbonate) (PPC) has been problematic largely due to the formation of propylene carbonate (PC). Rate studies have shown that the difference in activation energies between PPC and PC is only 33 kJ/mol, so it is necessary to develop highly active catalysts for PPC production at ambient temperatures in order to achieve high selectivity. Cobalt salen catalysts have shown both improved activity and selectivity in the formation of PPC. Coates first reported a salen cobalt catalyst in 2003 that selectively formed PPC with TOFs around 70 h^{-1} with high catalyst loadings.[19] Further work by Coates and co-workers found that using PPNCl at lower catalyst loadings with (salen)CoOBzF$_5$ produced PPC with a TOF of 620 h^{-1}, molecular weight of 26 800, and a PDI of 1.13. The catalysts were also determined to stereoselectively enchain (S)-PO, with (salen)CoBr showing an increased TOF of 1100 h^{-1} in the production of isotactic PPC when (S)-PO was used instead of rac-PO. GPC analyses also concluded that in the presence of a co-catalyst each cobalt center binds two growing PPC chains, while in the absence of a co-catalyst there is only one growing chain.[19] These catalysts were also shown to homopolymerize PO, producing highly isotactic PPO.

Aluminum(III) salen complexes have shown much lower activity than the Cr(III) and Co(III) analogues with TOFs from 5 to 35 h^{-1}, low molecular weights, and narrow PDIs. Iron, zinc, gallium, and manganese complexes have been shown to be inactive for copolymer formation.[19]

Figure 2. Chromium salen complexes **(1)** and **(2)**.[19]
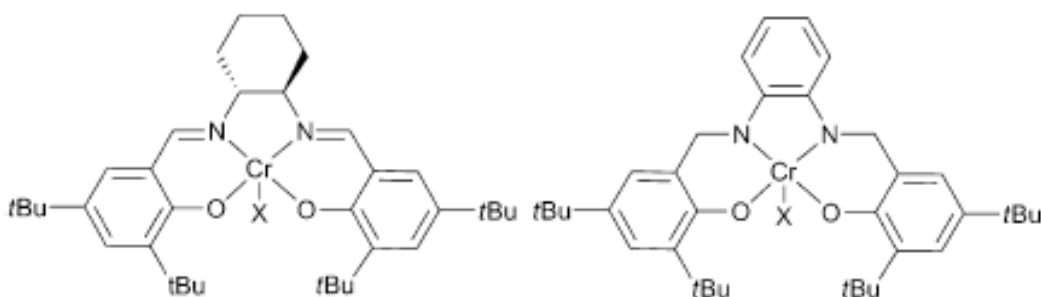
5.4 Metalloporphyrin Catalysts

Aluminum tetraphynylporphyrin (TPP) complexes were reported by Inoue *et al.*
as the first reported single-site catalysts for CO_2/epoxide copolymerization.[27] The
copolymerizations were run in the presence of a quaternary organic salt or
triphenylphosphine system such as $EtPh_3PBr$. The reactions took two to three weeks to
reach completion and produced copolymers with narrow molecular weight distributions
in the range of 1.06 to 1.14. Chisholm and coworkers have since demonstrated that the
the ring-opening of PO by (TPP)AlX (X=Cl, OR, O_2CR) is significantly faster in the
presence of the co-catalyst 4-*N,N*-dimethylaminopyridine (DMAP), and that DMAP's
presence shifts the reversible insertion of CO_2 in favor of the alkylcarbonate. The rate of
ring opening was found to follow the order Cl> OR> O_2CR, but reverses to O_2CR> OR in
the presence of DMAP. In the presence of DMAP, the preferred product was PPC with
few ether linkages, while (TPP)AlX alone gave mainly PPO. In some cases the methine
carbon of PO was shown to be attacked with retention of stereochemistry, strongly
suggesting an S_N1 pathway.[28,29]

Gas phase studies by the Chisholm group have also demonstrated the relative affinities of (TPP)MCl (M= Al, Ga, Cr, and Co) for PO in the gas phase. The cobalt cation showed a very low affinity for PO, and the ease of PO dissociation from the metal center was determined to follow the order (TPP)Ga$^+$ > (salen)Al$^+$ > (TPP)Al$^+$. This reflects the relative Lewis acidities of the compounds, as gallium is a softer element than aluminum, and salen is a stronger donor ligand than TPP.[30]

6. Polymerization of Lactide

The ring-opening polymerization of lactide can be accomplished using organic, enzymatic, or metal coordination catalysts.[31] Metal coordination catalysts have been developed using main group, transition, and lanthanide elements, with varying degrees of stereoselectivity. Ideally these metal catalysts do not cause epimerization of the chiral centers of lactide, which would result in a stereo-random polymer. Metal catalysts are generally considered to impose stereopreference through one of two mechanisms: chain-end control or enantiomorphic control. In chain-end control the chirality of the bound chain end determines which monomer will be preferentially inserted. Enantiomorphic control depends on the chirality of the catalyst. In chain-end control a mistake in the polymerization sequence is propagated, whereas in systems that display enantiomorphic control a mistake is generally corrected so that only isolated monomers are out of sequence.

Varying the tacticity of PLA can greatly affect the physical properties of the polymer. For example, heterotactic PLA has been found to show crystallinity, whereas atactic PLA is amorphous. Therefore, there is considerable interest in studying catalyst effect on tacticity. Monomer enchainment in which two adjacent stereocenters have the same chirality is an isotactic linkage, and enchainment in which two adjacent stereocenters have differing chirality is a syndiotactic linkage. A polymer displaying all isotactic linkages is referred to as an isotactic (*i*) polymer, one with syndiotactic (*s*) linkages is a syndiotactic polymer, and a polymer with a pattern of isi or sis linkages is called a heterotactic polymer. Atactic polymers have a random stereosequence.

Figure 3[32]. Lactide monomers and forms of PLA.

L-lactide   D-lactide   meso-lactide

rac-lactide

iii

iis

sii

isi

sis

ssi

iss

sss
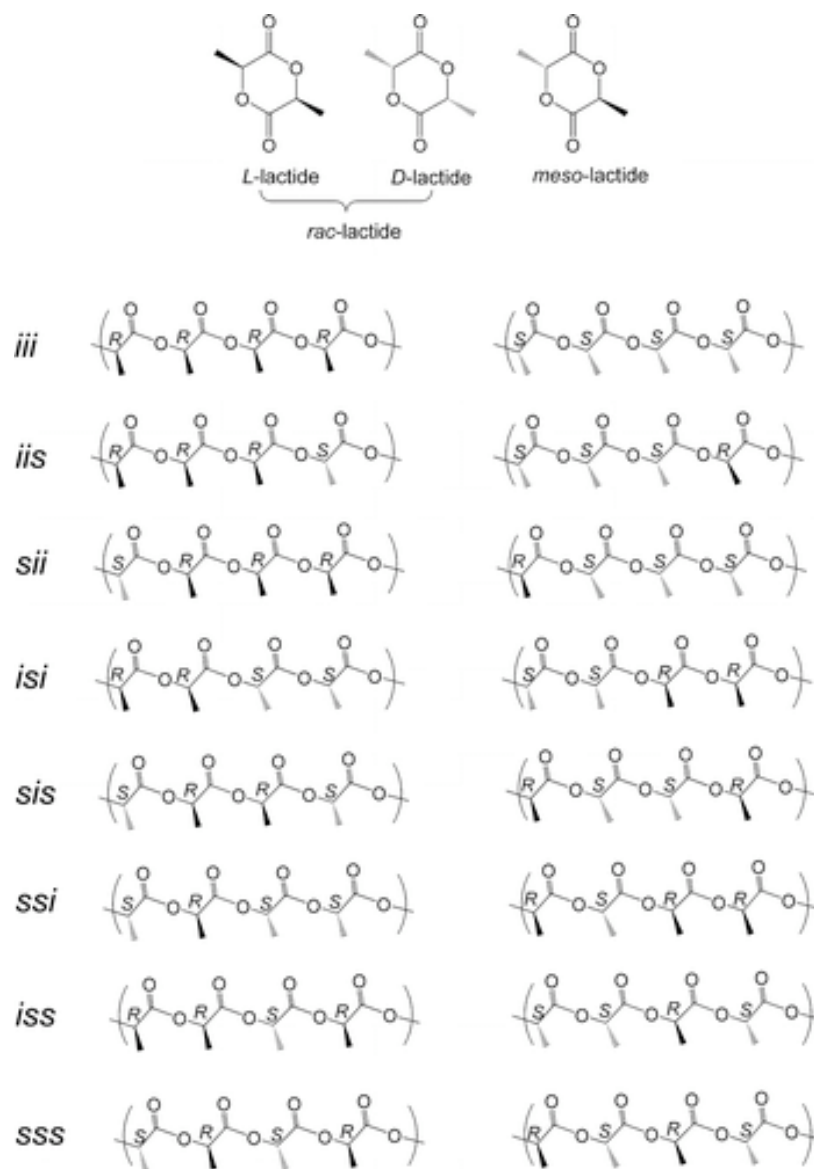
6.1 Metal Salen Catalysts

In 1993, Spassky et al. reported the ROP of *rac*-LA using an enantiomerically pure chiral BINAP-derived salen aluminum. It was discovered that at low conversion the polymer consisted almost exclusively of D-lactide. Ovitt and Coates later demonstrated

the production of syndiotactic PLA from *meso*-lactide using this catalyst, and was

hypothesized to demonstrate enantiomorphic site control based on the chirality of the

ligand.[33] Work by Feijen *et al.* employing (*R,R*-salen)AlOR resulted in preferential

opening of L-LA to give high levels of isotactic enchainment, with a probability of

isotactic enchainment (P_i) of 0.93. Solvent effects were shown to be important in this

system, since in chloroform or toluene monomers with opposite configuration of the

chain end are preferentially inserted, suggesting a chain-end control mechanism.[33]

Variations in stereoselectivity have also been demonstrated for other salen aluminum

catalysts such as (R,R-salen)AlOCH$_2$CH(S)MeCl, suggesting that in some cases both

chain-end control and enantiomorphic site control occur.[34]

Further studies with (salen)AlOR catalysts determined that the salen ligand

chirality was a minimal source of stereocontrol.[32,33] It was also determined that for (*R,R*-

and (*S,S*-salen)AlOEt, chain end exchange is a more rapid process than monomer

enchainment, which confirms Coates' explanation of the formation of heterotactic PLA

from *meso*-LA and racemic binaph Al catalyst.[32] Experimentation with ligand

substitution of the salen backbone found that electron withdrawing substitution increased

the rate of polymerization, and that sterically demanding groups increased selectivity at

the expense of reaction rate.[33] Trans-esterification for this class of catalysts is low,

resulting in polymers with very narrow PDIs. However, these catalysts are water

sensitive, and are kinetically very slow.

Salen yttrium complexes have also been investigated and shown to have higher

kinetic activity than the aluminum analogues. However, PLA from salen yttrium

catalysts tend to be atactic, with some instances of stereoseletivity. Cui et al. reported the

use of salen and salan based yttrium compounds in the polymerization of *rac*-LA to give modestly heteroselective polymer (P_r= 0.69).[33]

6.2. ß-diiminate Catalysts

In 1999, Coates and co-workers reported the heterospecific ROP of *rac*-lactide (P_r= 0.94) at high levels of activity using (BDI)ZnOiPr.[35] Further work with BDI catalysts yielded that ligand substituents control both the rate of polymerization and the degree of stereselectivity. BDI derivatives of Sn(II) and magnesium have also shown stereocontrol in lactide ROP, with the (BDI)Sn(II)OiPr forming slightly heterotactic PLA (P_r=70) and (BDI)Mg complexes in THF giving highly heterotactic polymer (P_r=0.90).[33] Computational studies have indicated that for stereoselective metal BDI catalysts selectivity is attained through a chain-end control mechanism in which both electrostatic and stereoelectronic interactions contribute.[33]

7. Goals of the Research Project

We propose to investigate the efficacy of certain scandium and gallium derivatives of *meso*-tetraphenylporphyrin and salen (Figure 4) in the ring-opening polymerization of PO and lactide. These complexes are expected to be more active than their aluminum counterparts in the polymerization of lactide due to the increased radius of the metal center. The larger metal center is hypothesized to allow for more facile coordination of a large monomer such as lactide. Also, gallium (III) and scandium (III) ions are more electropositive than aluminum (III), which leads to a more polar metal-axial ligand bond. This is expected to increase the ring-opening capability of the axially bonded species. Herein we discuss the synthesis of some of these catalysts as well as preliminary polymerization studies.
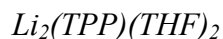
Figure 4. Salen (*R,R*-Jacobsen's ligand) (left) and *meso*-tetraphenylporphyrin (right).
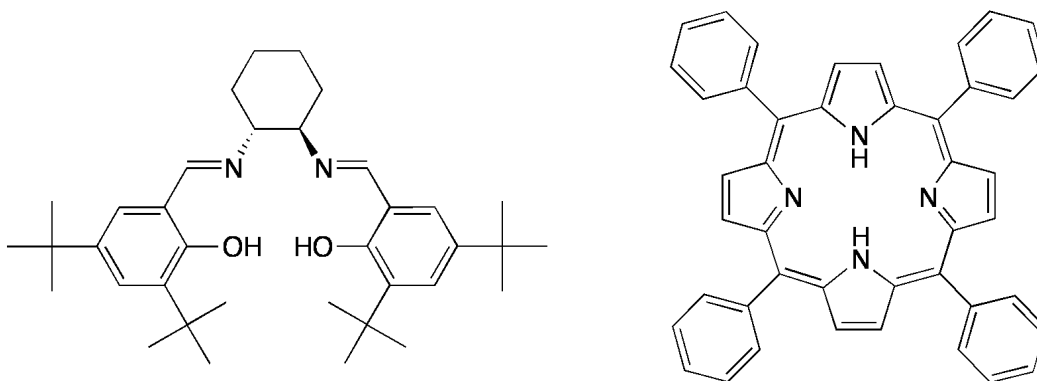
8. Experimental

8.1. Synthesis

All manipulations were carried out under nitrogen atmosphere using standard dry box and Schlenk line techniques. Solvents were dried prior to use, and all reagents were used as received.

Li$_2$(TPP)(THF)$_2$

H$_2$TPP (2.50 g, 4.10 mmol) and LiN(Si(CH$_3$)$_3$)$_2$ (1.40 g, 8.40 mmol) were placed in a Schlenk flask equipped with a magnetic stir bar. To the flask was added 150 mL THF and the solution was refluxed overnight at 90°C to give a deep blue solution. The reaction mixture was cooled to room temperature, filtered, and the solvent was removed under reduced pressure to give a bright violet powder (2.58 g, 82%). ^{1}H NMR (250 MHz, CDCl$_3$): 0.41 (broad, 8H, THF), 0.92 (broad, 8H, THF), 7.70 (m, 12H, -C$_6$H$_5$), 8.15 (m, 8H, -C$_6$H$_5$), 8.73 (s, 8H, -CH-).

Sc(TPP)(C$_6$H$_5$CH$_3$)Cl/Li$_2$TPP (10:1 ratio)

A Schlenk flask was charged with Li$_2$(TPP)(THF)$_2$ (308 mg, 0.40 mmol) and ScCl$_3$ (62.0 mg, 0.41 mmol). Toluene (30 mL) was transferred to the flask and the reaction mixture was refluxed for 8 hrs. The solution was allowed to cool to room temperature and filtered. Hexane (20 mL) was added, the solution was cooled to -25 °C overnight, filtered, and washed with hexane to give purple crystals (760 mg, 24%). ^{1}H NMR (250 MHz, CDCl$_3$): 0.87 (t, 2H, hexane), 1.30 (m, 2H, hexane), 7.30- 7.62 (m, 5H, toluene), 7.65- 7.86 (broad m, 12H, ScTPPCl Ar-H), 8.08 (d, 4H, ScTPPCl Ar-H), 8.18-

8.24 (m, 1.6H, Li_2TPP Ar-H impurities), 8.405 (broad m, 4H, ScTPPCl Ar-H), 8.47 (s, 0.8H, Li_2TPP impurity), 8.83 (s, 0.8H, Li_2TPP impurity), 9.03 (s, 8H, ScTPPCl pyrrolic H).

Ga(TPP)Cl

Ga(TPP)Cl was prepared according to the literature.[31] H_2TPP (250 mg, 0.41 mmol), sodium acetate trihydrate (1.40 g, 9.8 mmol), and $GaCl_3$ (0.21 g, 1.2 mmol) were refluxed in acetic acid (100 mL) overnight. After the removal of the solvent the product was extracted with chloroform and purified by column chromatography with chloroform as the eluent over an alumina column. The product was dried under reduced pressure to give a bright purple solid (146 mg, 50%). ^{1}H NMR (250 MHz, $CDCl_3$): 7.76 (broad m, 12H, Ar-H), 8.00- 8.35 (broad d, 8H, Ar-H), 9.04 (s, 8H, pyrrolic H).

(salen)GaCl[37]

H_2(salen) (260 mg, 0.48 mmol) was dissolved in 25 mL THF in a Schlenk flask. To another Schlenk flask was added NaH (25.0 mg, 1.00 mmol) in 20 mL of THF. The NaH slurry was transferred by cannula to the H_2(salen) solution and the resulting solution was allowed to stir overnight. $GaCl_3$ (0.5 M in pentane, 1.0 mL) was transferred to the salen solution, which was then refluxed for 8 hrs. The solvent was removed under reduced pressure, and the solid was then dissolved in diethyl ether and filtered through a plug of Celite. Recrystallization from diethyl ether yielded the desired product (65.0 mg, 21%). ^{1}H NMR (250 MHz, $CDCl_3$): 1.21 (m, 0.5H, diethyl ether), 1.29 (d, 18H, -C(CH_3)$_3$), 1.52 (d, 18H, -C(CH_3)$_3$), 1.4-1.5 (4H, NCH(CH_2**CH_2****CH_2**CH_2)CHN), 1.82 (m, 0.7H, THF), 2.06 (dd, 2H, NCH($CH_2$$CH_2$$CH_2$$CH_2$)CHN), 2.52 (dd, 2H,

NCH(CH$_2$CH$_2$CH$_2$CH$_2$)CHN), 3.20 (broad t, 1H, NC**H**(CH$_2$CH$_2$CH$_2$CH$_2$)CHN), 3.46 (q, 0.3H, diethyl ether), 3.72 (m, 1.7H, THF and NC**H**(CH$_2$CH$_2$CH$_2$CH$_2$)CHN), 6.98 (dd, 2H, Ar-H), 7.50 (d, 2H, Ar-H), 8.16 (d, 1H, Ar-CH), 8.35 (d, 2H, Ar-CH).

(salen)(THF)ScCl[36]

To a Schlenk flask was added H$_2$(salen) (300 mg, 0.55 mmol) in 10 mL THF. A solution of CaH$_2$ (25 mg, 0.61 mmol) in 10 mL THF was added to the H$_2$(salen) solution and allowed to stir overnight. The solution was transferred to a three-neck round-bottomed flask containing ScCl$_3$ (86.0 mg, 0.57 mmol) in 5 mL THF and refluxed for 6 hrs. The solution was allowed to cool to room temperature and filtered through a plug of Celite. Solvent was removed under reduced pressure to give the product as a yellow solid (0.208 g, 30%). ^{1}H NMR (250 MHz, CDCl$_3$): 1.29 (s, 18H, -C(CH$_3$)$_3$), 1.46 (s, 18H, -C(CH$_3$)$_3$), 1.21-1.50 (7H, NCH(CH$_2$CH$_2$CH$_2$CH$_2$)CHN), 1.70 (broad s, 1H, NCH(CH$_2$CH$_2$CH$_2$CH$_2$)CHN), 1.83 (m, 4H, THF), 1.99-2.07 (broad d, 2H, NC**H**(CH$_2$CH$_2$CH$_2$CH$_2$)C**H**N), 3.73 (m, 4H, THF), 7.10 (broad s, 2H, Ar-H), 7.485 (d, 2H, Ar-H), 8.10-8.40 (broad d, 2H, Ar-CH).

(salen)GaOC(CH$_3$)$_3$

To a Schlenk flask was added (salen)GaCl (65.0 mg, 0.10 mmol) in 15 mL diethyl ether. To another flask was added potassium *tert*-butoxide (15.0 mg, 0.13 mmol) in 10 mL diethyl ether. Both solutions were cooled to -50 °C in an acetone/liquid nitrogen bath and the (salen)GaCl solution was transferred to the KOC(CH$_3$)$_3$ solution *via* cannula. The mixture was stirred overnight and the solvent was removed under reduced pressure to give a bright yellow solid. ^{1}H NMR (250 MHz, C$_6$D$_6$): 1.16 (s, 1H,

$NCH(CH_2CH_2CH_2CH_2)CHN$), 1.23 (d, 1H, $NCH(CH_2CH_2CH_2CH_2)CHN$), 1.32-1.37 (covered d, 2H, $NCH(CH_2CH_2CH_2CH_2)CHN$), 1.39 (s, 18H, $-C(CH_3)_3$), 1.41 (s, 9H, -$OC(CH_3)_3$), 1.46 (m, 2H, $NCH(CH_2CH_2CH_2CH_2)CHN$), 1.82 (broad s, 1H, $NCH(CH_2CH_2CH_2CH_2)CHN$), 1.83-1.96 (broad s, 20H, $NCH(CH_2CH_2CH_2CH_2)CHN$ and $-C(CH_3)_3$), 1.98 (broad t, 1H, $NC\mathbf{H}(CH_2CH_2CH_2CH_2)C\mathbf{H}N$), 3.32 (broad t, 1H, $NC\mathbf{H}(CH_2CH_2CH_2CH_2)C\mathbf{H}N$), 7.055 (d, 2H, Ar-H), 7.56 (d, 1H, Ar-CH), 7.745 (d, 1H, Ar-CH), 7.82 (t, 2H, Ar-H).

8.2 General Polymerization Procedures

Attempted PO Homopolymerization: Racemic propylene oxide (0.30 mL) was added to 0.02 mmol catalyst and 0.02 mmol cocatalyst if applicable, and allowed to stir for 24 hrs at room temperature. Reaction aliquots were analyzed by 250 MHz ^{1}H NMR.

Attempted PO/CO$_2$ Copolymerization: *rac*-PO (0.3 mL) was added to 0.02 mmol catalyst and 0.02 mmol cocatalyst if applicable. Reactions were done in an autoclave pressurized with 45 bar CO_2 at room temperature. Reaction aliquots were analyzed by 250 MHz ^{1}H NMR after 24 hrs.

Attempted Lactide Polymerization: Reactions were performed in deuterated ^{1}H NMR solvents in a J.Young tube using 60.0 mg monomer and 0.02 mmol catalyst. Reaction aliquots were analyzed by 250 MHz ^{1}H NMR.

9. Results and Discussion

Sc(TPP)Cl, Ga(TPP)Cl, (salen)ScCl, and (salen)GaCl were successfully synthesized *via* the deprotonation of the corresponding ligands followed by reaction with the respective metal chlorides (Scheme 5).

The synthesis of Sc(TPP)Cl provided lower yield (24%) and less pure product than is observed for Ga(TPP)Cl and similar compounds in the literature, namely Sc(OEP)Cl (Figure 5).[37] We hypothesize that this is due to scandium's significantly larger ionic radius at 0.745 Å, *versus* gallium's 0.55 Å radius. The larger ionic radius increases the difficulty of inserting the metal into the porphyrin ring, and increases sensitivity to hydrolysis to form the bis(μ-hydroxide) complex (Figure 5).

Figure 5.[38] Sc(OEP)Cl (left) and a general bis(μ-hydroxide) scandium porphyrin (right).
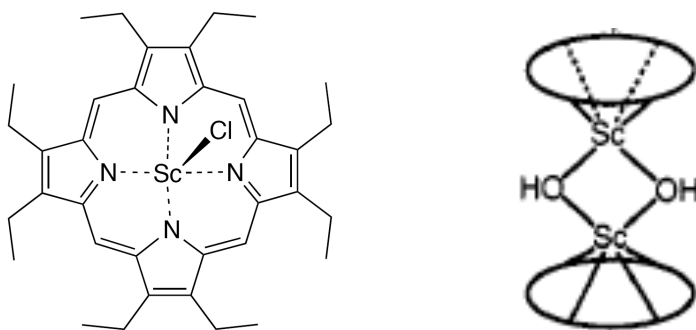
The more facile preparation and purification of the octaethylporphyrin (OEP) complex are hypothesized to be due to the differing electronic and geometric properties of the ligand. In light of scandium's low electronegativity and large radius, the inductive effect of the ethyl groups in OEP could be more favorable for the formation of the

scandium product than the electron-withdrawing properties of the phenyl groups in TPP.

Additionally, Arnold *et. al.* note that the crystal structure of Sc(OEP)Cl shows the

porphyrin to be slightly domed and ruffled, an accommodation that could be less

energetically favorable for a porphyrin such as TPP that has bulky phenyl substituents.

Scheme 5. Synthesis of scandium (III) and gallium (III) metal complexes.
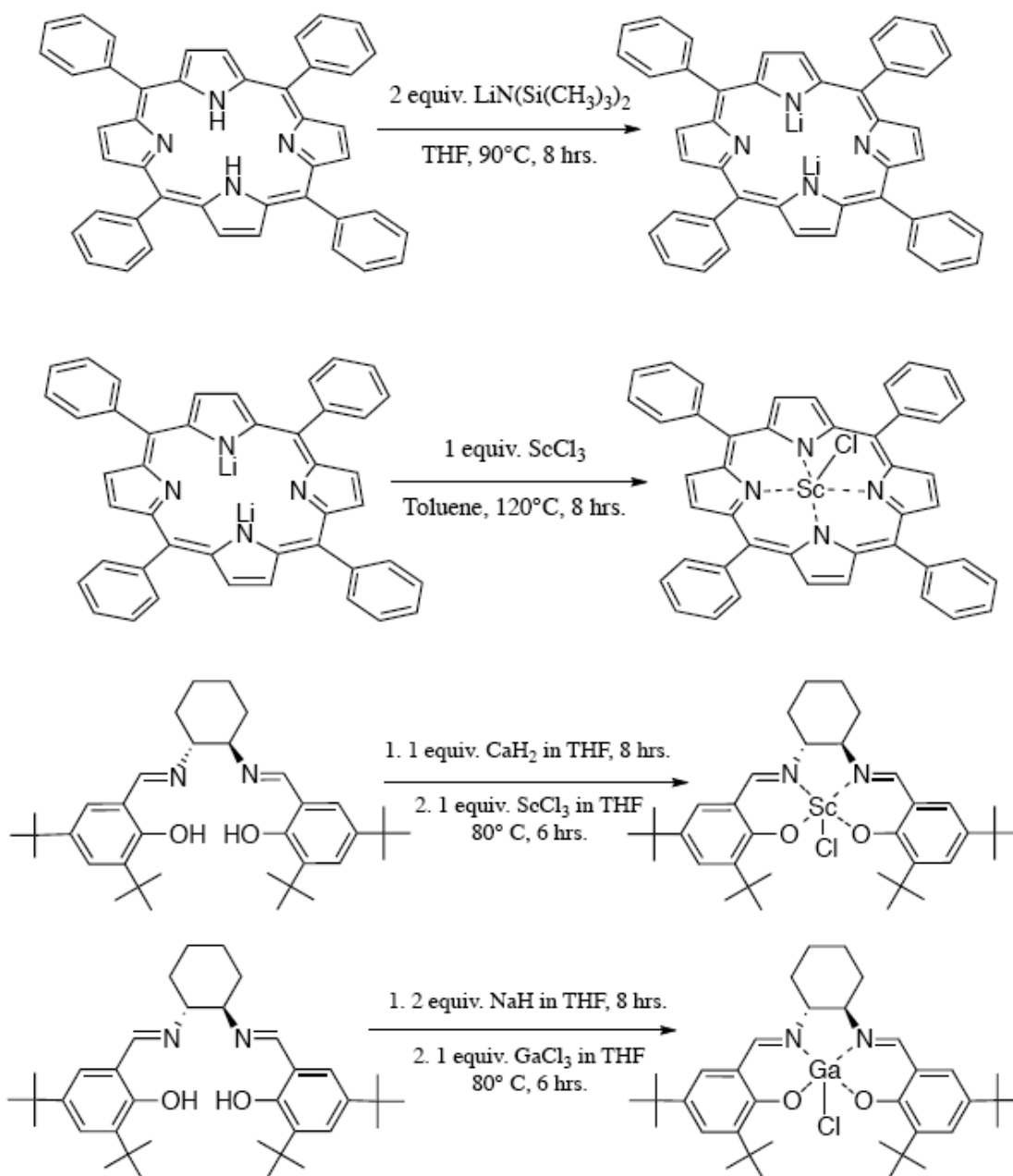
Attempts have been made to exchange the axial chloride ligands with alkyl, amide, or alkoxide groups via salt metathesis reactions with MeLi, ^{n}BuLi, LiN(SiMe$_3$)$_2$, LiN(C$_3$H$_7$)$_2$, LiN(CH$_3$)$_2$, and LiOC(CH$_3$)$_3$. All attempts gave mixtures of products with low conversion to the desired product. However, KOC(CH$_3$)$_3$ was successfully reacted with (salen)GaCl to give (salen)GaOC(CH$_3$)$_3$.

Below are the results of the polymerizations attempted thus far (Table 1). All metal complexes were shown to be inactive in the ring opening of PO and lactide. In the case of the chloride derivatives this is likely due to the poor nucleophilicity of the chloride anion.

Catalyst: Cocatalyst	Monomer(s)	Monomer: Catalyst: Cocatalyst Ratio	CO$_2$ Pressure (bar)	Results
Sc(TPP)Cl	PO	300:01:00	___	Inactive
Sc(TPP)Cl: PPNCl	PO	300:01:01	___	Inactive
Ga(TPP)Cl	PO	300:01:00	___	Inactive
Ga(TPP)Cl:DMAP	PO	300:1:1	___	Inactive
Ga(TPP)Cl	PO/CO$_2$	300:1:0	45	Inactive
Ga(TPP)Cl:DMAP	PO/CO$_2$	300:1:1	45	Inactive
Ga(TPP)Cl	L-Lactide	20:1	___	Lactide coordination[a]
(salen)GaOC(CH$_3$)$_3$	rac-Lactide	20:1	___	Inactive[b]

Table 1: Results of attempted polymerizations. a) Confirmed by presence of two sets of lactide peaks in ^{1}H NMR. b) ^{1}H NMR showed signs of catalyst degradation; inactivity is likely due to catalyst death.

All reactions with PO showed no evidence of PO coordination to the metal center. While Ga(TPP)Cl did not coordinate PO, it was found to coordinate L-lactide. This

result suggests that if the axial chloride could be replaced by an alkoxide that Ga(TPP)OR could be active in the ROP of lactide. Preliminary results from the ROP of lactide using (salen)GaOC(CH$_3$)$_3$ are inconclusive as the ^{1}H NMR showed signs of catalyst degradation. Further work will include attempts to synthesize this catalyst on a larger scale and evaluate its performance in the ROP of lactide.

In conclusion, the salen and gallium metal compounds studied display the potential to coordinate and ring-open lactide as hypothesized, but do not appear to coordinate propylene oxide. Future efforts will be focused on using potassium salts to synthesize the alkoxide derivatives of these compounds.

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