COPOLYMERIZATION OF CO_2 AND EPOXIDES CATALYZED BY

A SCHIFF-BASE CHROMIUM(III) COMPLEX

BY

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ABSTRACT

Global atmospheric carbon dioxide (CO_2) levels have reached a record high in the last century and this is suspected to be a major contributor to climate change due to its effects as a greenhouse gas.[1, 2] Notwithstanding the 200 gigatons (Gt) of CO_2 recycled through the natural carbon cycle each year, there is an excess of approximately 7 Gt of annual, anthropogenic CO_2 emissions.[2] Mitigating this accumulation will require a variety of approaches. One such approach is the capture and utilization of CO_2 as raw material source which may have potential economic viability.[5] In this context, the production of biodegradable polymers, such as polycarbonates, utilizing synthetic techniques which incorporate CO_2 as a C_1 feedstock holds significant interest.[6-8] Ring-strained heterocycles (i.e. epoxides, aziridines, etc.) are known to undergo chemical reactions with CO_2, which is quite stable and fairly inert.[10, 11] On this basis, we sought to design single-site catalysts which facilitate the production of polycarbonates via copolymerization of epoxides and CO_2. Since tetradentate catalysts comprise the great majority of studies and publications in this field, the basis of this study was to synthesize and investigate two tridentate Schiff bases.[12-14] 2-[(2-Hydroxy-2-phenylethylimino)methyl]-4,6-bis(*tert*-butyl)phenol (H_2L^P) and (1*S*,2*R*)-1-[(3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino]-2-indanol, (H_2L^I). Addition of these ligands with an equal amount of $CrCl_3 \cdot 3THF$ complex yielded catalysts $L^PCr^{III}Cl$ and $L^ICr^{III}Cl$ respectively. Of these catalysts, $L^ICr^{III}Cl$ proved to be most effective in the coupling of CO_2 and cyclohexene oxide (CHO) to produce

poly(cyclohexene carbonate) (PCHC). Typical polymerization reactions were carried out in bulk, utilizing a 25-ml stainless steel autoclave reactor, pressurized to ~52 bar with CO_2 maintained at 353K in a temperature-controlled oil bath. Under these conditions, catalyst $L^ICr^{III}Cl$ produced PCHC with a number average molecular weight (M_n) of 3578 Daltons (Da), polydispersity index (PDI) of 5.1, and a turnover frequency (TOF) of 13.82 hr^{-1}. Initial PCHC was observed to have a CO_2-incorporation of approximately 40% based on ^1H NMR spectroscopy. Addition of a neutral phosphine cocatalyst (tricylcohexylphosphine, PCy_3) proved effective at increasing CO_2 incorporation to approximately 78%. Nevertheless, increasing PCy_3 levels resulted in diminished TOF and a linear decrease in M_n to as low as 609 Da. In addition, Schiff base Cr^{III} catalysts have been documented for the asymmetric ring opening of epoxides and aziridines.[15, 16] Catalyst $L^ICr^{III}Cl$ produced PCHC which is atactic as determined by ^{13}C NMR spectroscopy. As such, Catalyst $L^ICr^{III}Cl$ proved effective for the copolymerization of CO_2 and CHO at moderate TOF.

ACKNOWLEDGEMENTS

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"As often observed in scientific research, the step for essential progress is the discovery of unexpected facts or the idea of combining separate facts that could not be correlated before."

~ Dr. Shohei Inoue

APPROVED:

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Chair, Thesis Committee   Date

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Dean, Graduate School   Date

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Dean, Academic College   Date

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LIST OF ABBREVIATIONS

Å   Angstrom (10^{-10} m or 0.1 nanometer)

BPA   bisphenol-A

CaH_2 calcium hydride

CHO   cyclohexene oxide

CO_2 carbon dioxide

Da   Daltons ($1.660539040 \times 10^{-27}$ kg)

DCM   methylene chloride

DMAP   *N,N*-dimethyl-4-aminopyridine

ECH   epichlorohydrin

EO   ethylene oxide

$EtPh_3PBr$ ethyltriphenyl-phosphonium bromide

Gt   gigatons

IBO   isobutylene oxide

K   degrees Kelvin (0 K is equivalent to -273.15 °C)

M_n number average molecular weight

N-MeIm   *N*-methylimidazole

PCHC   poly(cyclohexene carbonate)

PCy_3 tricyclohexylphosphine

PDI   polydispersity index

PO	propylene oxide
PPN	bis(triphenylphosphoranylidene)ammonium
Salen	*N,N'*-bis(salicylidene)ethylenediamine
sc(CO$_2$)	supercritical carbon dioxide
SO	styrene oxide
*t*BME	*t*-butyl methyl ether
THF	tetrahydrofuran
TOF	turnover frequency
TON	turnover number
(tpp)AlCl	aluminum tetraphenylporphyrin

CHAPTER I

INTRODUCTION

1.1 CARBON DIOXIDE CAPTURE AND UTILIZATION

A byproduct of oil and gas refining, low cost petrochemical feedstocks allow plastic production on a vastly efficient and sophisticated scale.[17] However, petroleum resources are predicted to be exhausted within a century at the current rate of consumption.[18] In addition, plastic pollution poses another challenge: Annual production of petroleum-based polymers is 78 million metric tons globally, of which 32% ends up littering the environment, 40% goes to landfills, 14% is incinerated or used for energy recovery, and the remaining 14% is recycled.[19] Owing to this, development of biodegradable or compostable plastics from renewable resources is an area of research that has gained significant interest over the last 40 years.

Another consequence of the widespread use of petroleum is the emission of large amounts of carbon dioxide (CO_2). This is of great concern as CO_2 has long been considered a major contributor to climate change due to its behavior as a "greenhouse gas" and its accumulation in the atmosphere.[2] Indeed, there has been an increase in atmospheric CO_2 from approximately 315 ppm in 1960 to 408.69 ppm as of July 2018.[20] Further, anthropogenic CO_2 emissions are on the rise and expected to expand over the next few decades, largely due to the rise of India and China as major consumers of fossil fuels.[21] To place this in context, 200 Gt (gigatons) of CO_2 is recycled through the natural

carbon cycle each year. However, currently there is an excess of approximately 7 Gt of annual, anthropogenic CO_2 emissions which is not part of the natural carbon cycle and therefore represents a net accumulation.[2] Aggravating this problem, CO_2 emissions are projected to more than double by 2050 according to the International Energy Agency.[22]

Total carbon emissions from fossil fuel consumption and cement production (million metric tons of C)
From 1751 - 2014
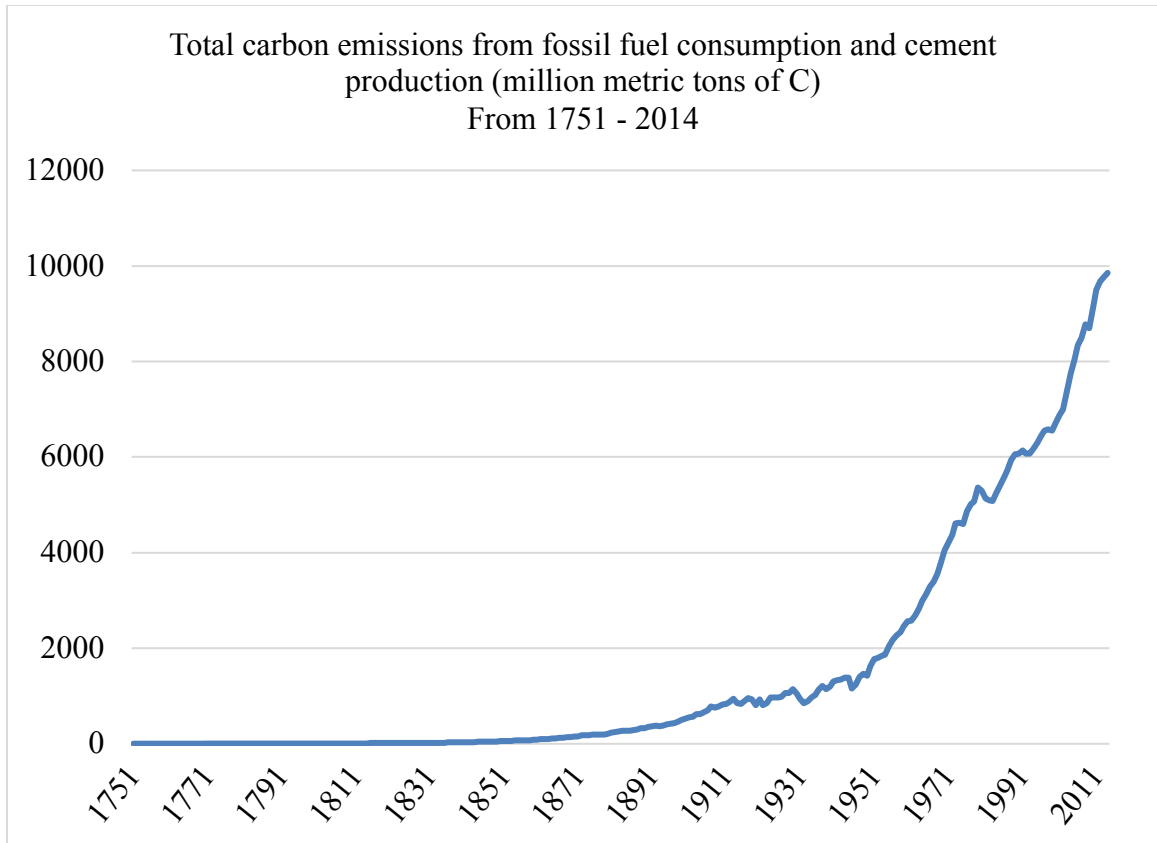
Figure 1.1   The trend in CO_2 emissions from fossil fuel combustion, 1751-2014 (data downloaded from Oak Ridge National Laboratory).[22]

If we are to respond to this persistent and growing problem, we must recognize that the agency to mitigate such a global issue does not exist in any single society, national government, or governmental department. As such, addressing the atmospheric CO_2 accumulation problem will require a variety of approaches/programs which will likely

span across multiple areas of economics and governance. The U.S. Department of Energy has devised one such program, commonly known as CO_2 capture/storage (CCS), and utilization (CCU).[5, 23-29] Solvent-based chemisorption techniques, carbonate looping technology, and oxy-fuel combustion are three of the leading options for carbon capture.[23] Storage of captured CO_2 poses a significant roadblock in that it relies on sequestration in depleted oil/gas reservoirs, deep coal beds, and deep saline aquifers in which leakage is likely to occur. This issue may be curtailed by carbonation of minerals (ex. serpentine) which solves the issue of leakage while creating another of feasibility.[23] Nevertheless, the utilization and storage of captured CO_2 may be accomplished via the manufacture of commodity chemicals, liquid fuels, and polymers. In this context, the production of biodegradable polymers, such as polycarbonates, utilizing synthetic techniques which incorporate CO_2 as a C_1 feedstock holds significant interest.[6-8] Indeed the use of CO_2 as a low cost, renewable, raw material holds tremendous potential and as such, has been a goal of synthetic chemists for many years.[5, 25, 28] Further, ring-strained heterocycles (i.e. epoxides, aziridines, etc.) are known to undergo chemical reactions with CO_2, which is otherwise quite stable and fairly inert.[5]

One example of this is the metal-catalyzed coupling of CO_2 and epoxides to produce cyclic carbonates[30-32] and polycarbonates[33-39] which has been a subject of considerable interest in recent decades. Specifically in the preparation of aliphatic polycarbonates, this represents a possible alternative to petrochemical materials in applications such as films, packaging and rigid plastics.[40] The history and mechanism behind this coupling process known as co-polymerization, is discussed in sections 1.3 and 1.4, respectively.

Scheme 1.1 The interfacial polycondensation of phosgene and bisphenol-A (BPA).
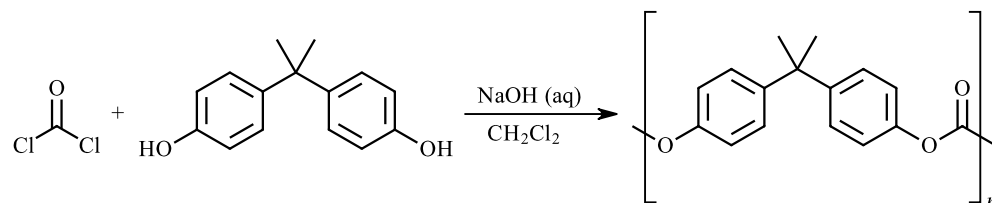
1.2 PRODUCTION OF POLYCARBONATES AND THE PHOSGENE PROCESS

Currently, the large-scale production of polycarbonate is accomplished by what is known as the "Phosgene Process", which utilizes the extremely toxic phosgene precursor as a primary C_1 feedstock (Scheme 1.1).[2] This process is carried out batchwise in stirred tanks or continuously in tubular reactors via an interfacial, biphasic polycondensation of phosgene and diols, most commonly bisphenol-A (BPA). This process typically consists of an aqueous sodium bisphenolate phase mixed with phosgene in a halogenated organic phase (methylene chloride, DCM). During production, a large amount of DCM (10 times by weight of the polycarbonate) must be used. Carbonate oligomers are produced at the interface, which then enter the organic phase and the byproducts (NaCl and Na_2CO_3) enter the aqueous phase. Upon completion, the two phases are separated by centrifugation and the organic phase is subjected to a series of acidic and alkaline washes. In addition to high cost, this method generates a large amount of wastewater contaminated with DCM, sodium carbonate, and sodium chloride. Phosgene, BPA, and DCM are toxic chemicals, the use of which poses safety problems during production as well as waste and leaching problems post-production. Another issue is that DCM has a high affinity for polycarbonate which makes total separation from the final product difficult.

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Another means of producing polycarbonates which would seem to circumvent many of these issues is the "transesterification melt process" depicted in Scheme 1.2.[41] In the presence of a catalyst, bisphenol-A, and diphenyl carbonate undergo an ester-exchange reaction which is carried out under high vacuum and temperature in bulk, polymer melt. At first glance this would seem to alleviate concerns associated with halogenated solvents and the use of phosgene, until it is pointed out that diphenyl carbonate is a derivative of phosgene. Ultimately, this process is plagued by additional issues of cost as well as low molecular weight, phenol separation, and does not address our primary concern of CO_2 utilization in any way.

Scheme 1.2   Melt transesterification of BPA and diphenyl carbonate to form polycarbonate.
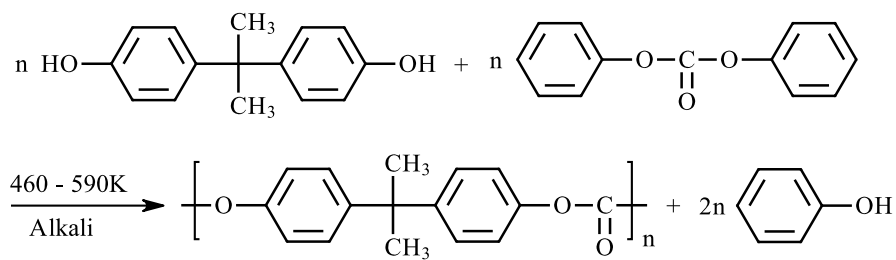
As such, polycarbonate production is currently plagued by problems with primary resources, pollution, consumer safety, as well as the high cost. Owing to this, CO_2 as a carbon resource has gained considerable interest over recent decades. This is particularly due to its low cost, inert nature, and abundance. Therefore, CO_2 lends itself to copolymerization with epoxides under total atom economy while greatly minimizing, or eliminating altogether, the need for dangerous organic solvents.

1.3 CATALYTIC COUPLING OF CO_2 AND EPOXIDES TO PRODUCE CARBONATES AND POLYCARBONATES

The copolymerization of CO_2 and epoxides was first discovered and reported by Inoue and coworkers in 1969.[10] Inoue employed a heterogeneous catalyst, the precise structure of which remains unclear, but is comprised of diethyl zinc ($ZnEt_2$) and water (Scheme 1.3) and was shown to couple propylene oxide (PO) and CO_2 to provide polycarbonate of appreciable molecular weight with a TOF of 0.12 h^{-1} at 353K and 20-50

Scheme 1.3 Inoue's first-generation heterogeneous zinc catalyst.

$$n(C_2H_5)_2Zn \quad + \quad nH_2O \quad \xrightarrow{\quad (2n-1)C_2H_6 \quad} \quad H_3C-\overset{H_2}{\underset{}{C}}-Zn\left(\!\!-O-Zn\!\!-\right)_{n-1}OH$$
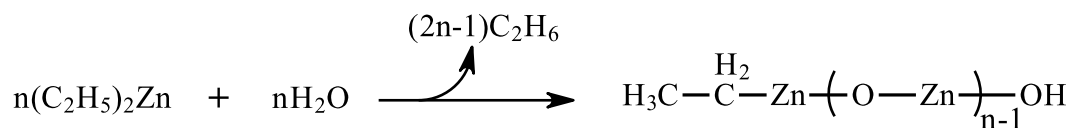
bar in CO_2. Polymer yield was shown to be optimum at a 1:0.9 $H_2O/ZnEt_2$ ratio (Figure 1.4). Further, and in addition to PO, Inoue also reported copolymerizations with ethylene oxide (EO), styrene oxide (STO), epichlorohydrin (ECH), and isobutylene oxide (IBO) (Scheme 1.4).

Scheme 1.4 Structures of epoxides capable of copolymerization via $ZnEt_2/H_2O$.

EO   STO   ECH   IBO
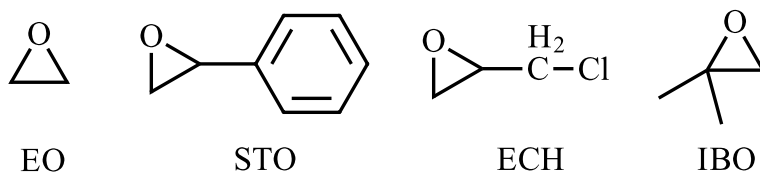
FTIR spectral analysis of the resulting polymers exhibited strong bands at 1750, 1250, and 790 cm^{-1}, which are characteristic of the –O–CO–O– carbonate group.[10] Later, and along this same line of work, Inoue investigated other insoluble zinc catalysts which were derived in an analogous fashion to the original catalyst system. Rather than water, these included other diprotic species such as primary amines, diols and dicarboxylic acids.[42] Despite the importance of this discovery, there were major drawbacks for these early catalysts including broad molecular weight distributions which is likely due to the non-uniform structure of the zinc active-sites as well as the propensity of zinc to catalyze epoxide homopolymerization resulting in low CO_2 incorporation, cyclic carbonate, and unwanted polyether linkages as seen in Scheme 1.5.[43]

Scheme 1.5 Generalized copolymerization of CO_2 and epoxides.

P = 20-50 bar
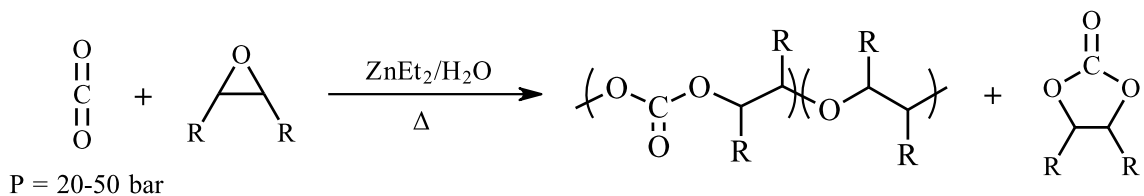
In the mid 70's, following Inoue's lead, Kuran *et al.* investigated diethylzinc catalysts derived from di- and triprotic species such as resorcinol and pyrogallol, respectively (Figure 1.2).[11] Though it was a slight improvement, Kuran's heterogeneous zinc systems were plagued by a number of similar drawbacks. These include the need for high catalyst loadings, poor reproducibility, low turnover numbers (TON), broad molecular weight distributions and again, less than 100% alternating copolymer (low CO_2 incorporation). Addressing such drawbacks through rational catalyst design proved

difficult owing to the uncertainty in defining the precise active-site structure in these alkyl zinc systems, making structure/activity relationships hard to elucidate. This, coupled with the many drawbacks described previously, provided impetus for the development of well-defined, single-site, homogenous catalysts known as the binary second-generation coordination complexes.
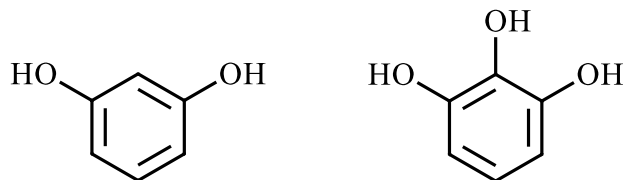
Figure 1.2 Structures of resorcinol (left) and pyrogallol (right).

In 1981, Rokicki and Kuran published a thorough review of these early investigations, as well as the first, most widely accepted mechanistic model of epoxide binding and CO_2 insertion, the coordinative anion insertion mechanism (Scheme 1.6).[44] Three basic steps defined this mechanism. First, there is the binding of the epoxide to the active metal center with concomitant activation of the carbons in the three-membered oxirane ring. Next, the bound and activated epoxide is concertedly ring-opened and inserted into a Zn—O bond. This is followed by rapid CO_2 insertion to form the carbonate functionality. Ideally this last step should be rapid compared to epoxide enchainment if completely alternating copolymer is to be realized as a product. In other words, there are instances wherein epoxide ring-opening and enchainment is rapid and competitive with CO_2 insertion. This can result in the consecutive enchainment of multiple epoxides which is the source of ether linkages in the polymer backbone and

Scheme 1.6 The Mechanism of Epoxide/CO_2 Copolymerization.[13]

Initiation

Metal Alkoxide   Metal Carbonate

Propagation

Copolymerization

Cyclic Carbonate
(Back-biting)
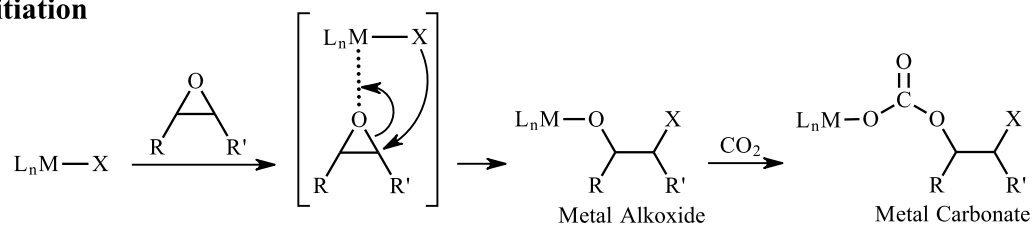
Homopolymerization   Cyclization

Chain Transfer

Metal Alkoxide
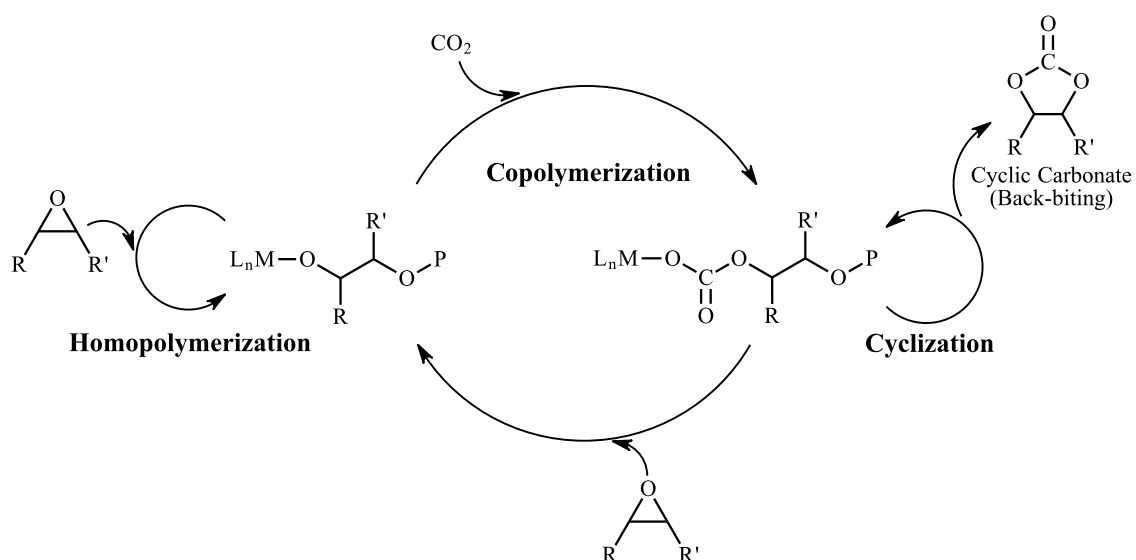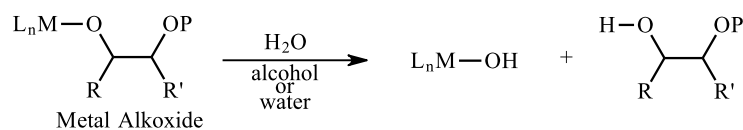
M = metal
L_n = ligand set
X = halide
R = R' = $CH(CH_2)_4CH$

polymer chain = —O—P =
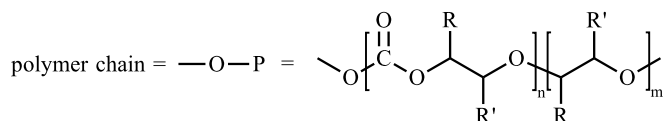
indicative of less efficient CO_2 incorporation. Determination of the relative ratio of ether to carbonate linkages can be made by ^1H NMR spectroscopy and provides a reasonable measure of the relative efficiency of CO_2 incorporation for a given catalyst system under a specific set of conditions.[6]

Concerning homogenous, single-site catalysts, the first of these were reported by Takeda and Inoue in 1978.[3] In these studies, aluminum porphyrin and *N,N'*-bis(salicylidene)ethylenediamine (salen) complexes were investigated.[45] Porphyrin and salen ligands were chosen due to their structural similarity to chlorophyll in the fixation of CO_2 via photosynthesis. Aluminum tetraphenylporphyrin, (tpp)AlCl (Figure 1.3) in the presence of co-catalysts such as quaternary organic salts or neutral phosphines was shown to be active for the copolymerization of CO_2 with EO, CHO, and PO.[37, 45] With ethyltriphenyl-phosphonium bromide (EtPh$_3$PBr) as a cocatalyst, this system yielded copolymers with perfect CO_2 incorporations, narrow polydispersity indices (~1.10 PDI), but with low number average molecular weight (M_n = 3500-6000).[3] Kruper and Dellar in 1995, and Mang and Holmes in 2000 investigated chromium derivatives of the porphyrin catalyst system which were also shown to be effective at copolymerizing CHO and CO_2.[4, 9] Solubility in supercritical carbon dioxide sc(CO_2) was investigated through Mang and Holms' fluorinated analogue. Overall, these catalysts required long reaction times (12-23 days) and harsh conditions such as super critical temperature (383K) and pressure (225 bar).[9]

In 1995, Darensbourg and coworkers synthesized the first highly active, discrete, well-defined, zinc bis-phenoxide complexes as catalysts for CO_2/epoxide copolymerization. These systems were based on 2,6-disubstituted phenols depicted in
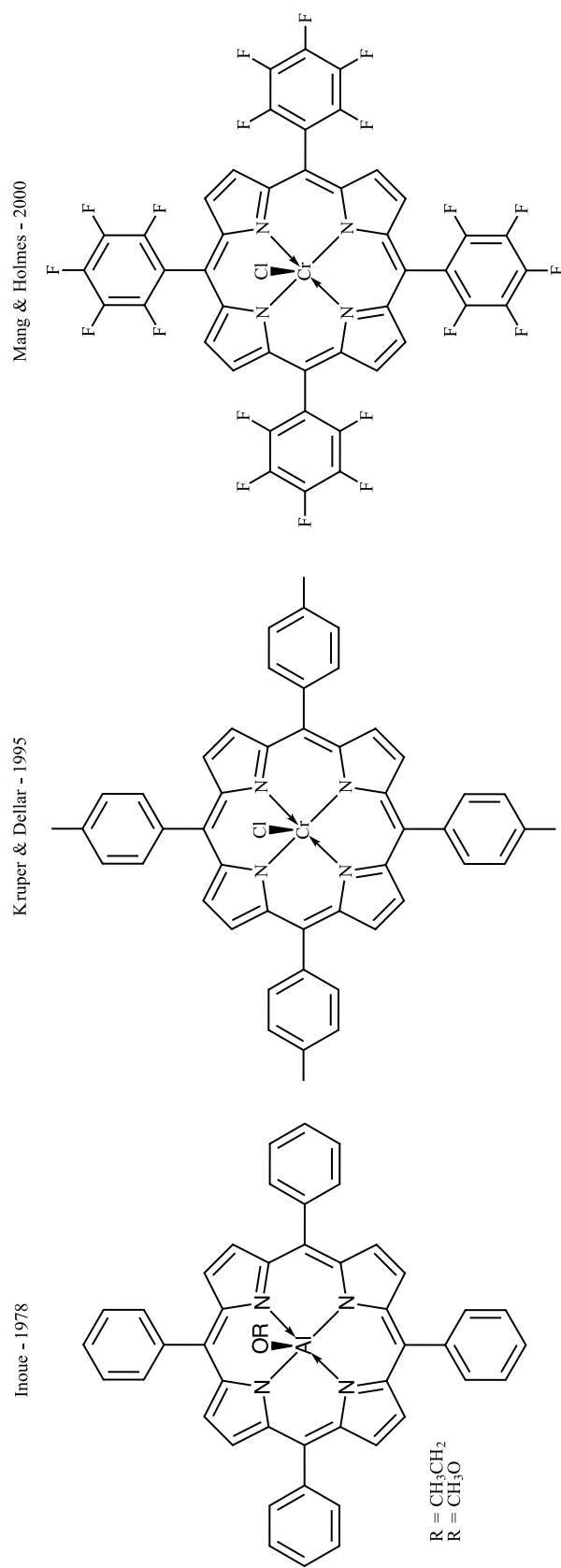
Figure 1.3 Structures of Aluminum and Chromium(III) porphyrin catalysts reported by Inoue (1978)[3], Kruper and Dellar (1995)[4], and Mang and Holmes (2000)[9].
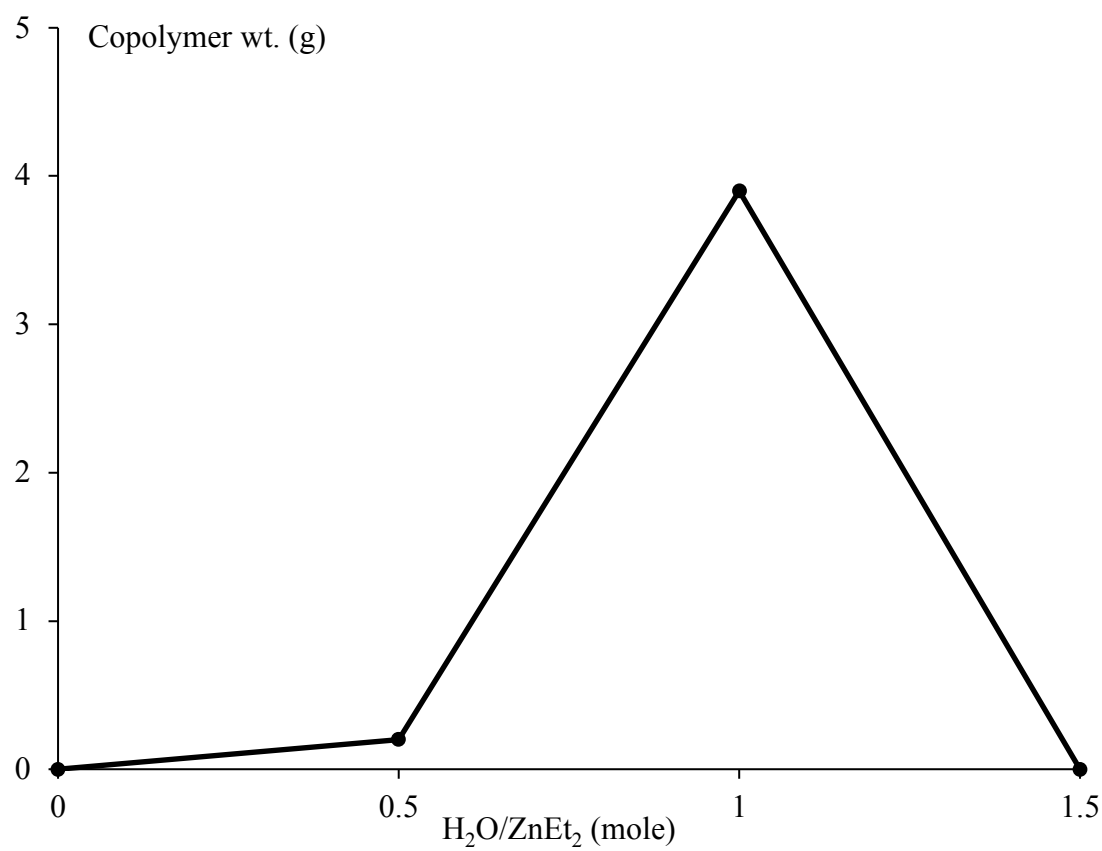
Figure 1.4 The relation between copolymer yield and catalyst composition in the polymerization of PO/CO$_2$ by ZnEt$_2$/H$_2$O system.[10]

(a)   (b)
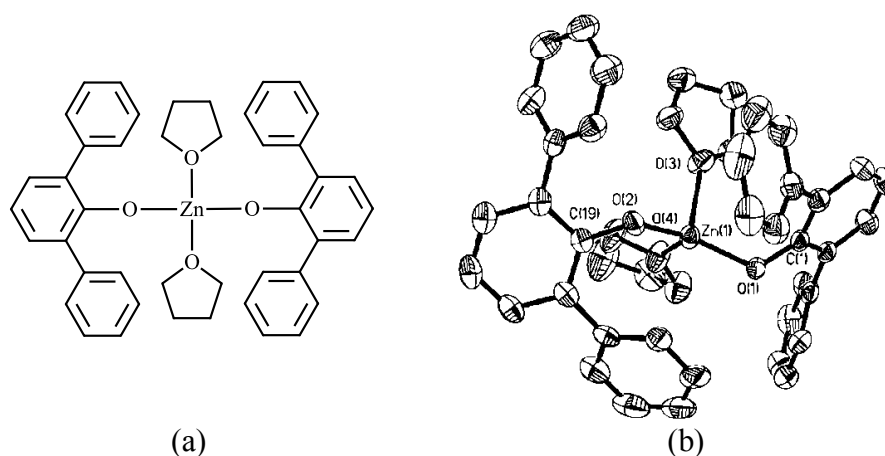
Figure 1.5 Darensbourg's monomeric zinc-*bis*(phenoxide) complex (a) and thermal ellipsoid representation (b). Reprinted (adapted) with permission from Journal of the American Chemical Society, Copyright 1999.[46]

figure 1.5.[46, 47] X-ray diffraction studies showed these complexes to generally exhibit a distorted tetrahedral geometry and where the presence of metal bonded tetrahydrofuran (THF) molecules served as reasonable models of epoxide binding. This facilitated rational, rather than speculative, catalyst design in subsequent studies. By modifying the substituent groups of the *bis*(phenoxide)Zn(THF)$_2$ complex, Darensbourg's group produced polymers with number average molecular weights of up to 38,000. However, it was determined that the phenoxides acted as polymerization initiators, resulting in a rather ill-defined active species, producing polymers with higher polydispersity indices (PDI > 4.0) and lower TOFs of ~10 hr^{-1}.[48] Additionally, zinc bis-phenoxides were active for epoxide homopolymerization, resulting in undesired ether linkages and CO$_2$ incorporations of ~90%. The backbiting tendency of this system was pronounced with PO/CO$_2$ copolymerizations, due to steric considerations and the inherent stability of the monomeric, cyclic propylene carbonate. Owing to this, only a fraction of the product was in the form of polycarbonate.

Following the bis-phenoxide work of Darensbourg, bi-functional, zinc ß-diiminate catalysts (Figure 1.6) were reported by Coates and co-workers in 1998.[49, 50] These catalysts proved to be quite effective, yielding copolymers with CO_2 incorporations of approximately 95-96%, with TOF = 135 to 449 hr^{-1}. Further, these results were obtained under remarkably mild conditions (293-353K; 6.9 bar in CO_2).

(a)   (b)
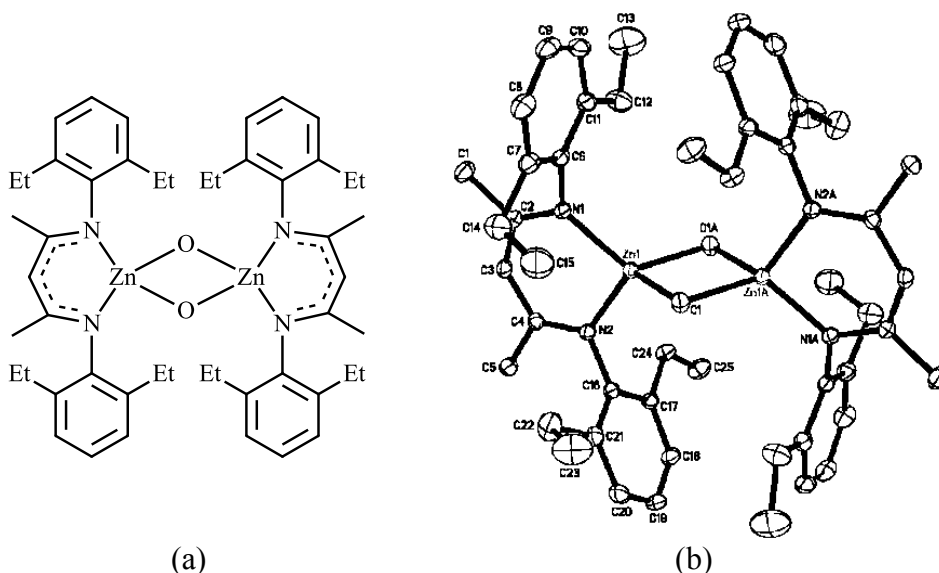
Figure 1.6 Coates' Zinc ß-diiminate complex structure (a) and thermal ellipsoid (b) representation. Reprinted (adapted) with permission from Journal of the American Chemical Society, Copyright 2001.[50]

Coates found that improving catalytic activity of ß-diiminate complexes is accomplished by fine tuning their steric environment to allow for loosely held dimeric structures.[51] Introduction of electron withdrawing substituents such as cyanide increased the activity of these systems as well as the introduction of co-catalysts such as azides, chloride, dinitrophenolate anions, and neutral amines. Complexes with excessively bulky substituents did not allow for monomer coordination at all. This discovery led to the proposal of a bimetallic coordination-insertion pathway in which one metal of the

complex coordinates the monomer while the second metal feeds the growing polymer chain.

Since then, several other transition metals have been investigated for this purpose. Among these are numerous chromium(III) and cobalt(III) coordination compounds based on the well-known Schiff base "salen" ligand and derivatives thereof. The first example of a chromium(III) salen catalyst was reported in the patent literature by Jacobsen and coworkers in February of 2000 without any copolymerization results or claims.[52]

In this account, PCHC was prepared under 1 bar of CO_2 with no other relevant details reported. Independently, and unaware of the patent literature at the time, Darensbourg and Yarbrough, inspired by Jacobsen's elegant work on asymmetric epoxide ring-opening, reported the use of a salen chromium(III) chloride catalyst which exhibited high activity toward copolymerization of CO_2 with cyclohexene oxide resulting in polymer with very uniform molecular weight distributions.[6] Around this same time Nguyen and coworkers at Northwestern University independently reported similar results with Jacobsen's salen chromium(III) chloride catalyst.[53] This sparked a new direction in the investigation of CO_2/epoxide copolymerizations from zinc to chromium(III) and cobalt(III) salen,[54-72] and porphyrin[9, 73, 74] catalysts and related derivatives. Indeed, these have become the mainstay in the CO_2/epoxide work conducted since 2001 as detailed in the literature, including numerous comprehensive reviews on the subject.[13,14,33,35,37,62,75-80]

1.4 MECHANISM, RING OPENING, AND BACKBITING

Alternating copolymerization of CO_2 and epoxides is proposed to occur via a coordination-insertion mechanism shown in Scheme 1.6.[13] For reference, the

transesterification of hydrocarbons involves the formation of a π complex. On the other hand, the coordination-insertion mechanism of heterocyclic and heterounsaturated monomers occurs via covalent σ bond formation. The first step is initiation, in which a Lewis acid metal center coordinates the epoxide (monomer) for subsequent nucleophilic attack by the metal bound nucleophile (halide, alkoxide, etc.) to give a ring-opened alkoxide. In the case of CHO, C—O bond cleavage occurs with inversion of configuration at the site of attack yielding a *trans* ring-opened product. The resulting metal alkoxide is then carboxylated (concerted CO_2 insertion), yielding a metal carbonate bond. The carbonate is then free to act as a nucleophile in the enchainment of another epoxide, resulting in a coordination-insertion cycle. However, the cycle may undergo two unwanted side reactions. One is intermolecular backbiting of a metal-alkoxide to yield cyclic carbonate side-product. The other is a chain transfer reaction with external oxygen/acid which forms a hydroxyl terminated copolymer chain. Some catalysts also homopolymerize epoxides to yield a polymer with more or less polyether character. The repeated, consecutive insertion of CO_2 is thermodynamically disfavored and has not been reported in literature.

1.5 SCOPE

In spite of the inherent versatility in the synthesis of Schiff base ligands, tetradentate salens, porphyrins and derivatives thereof represent the bulk of the chromium(III) and cobalt(III) catalysts employed for this purpose.[76] Relatively few chromium species have been investigated with markedly different ligand architectures. Notable exceptions are the work of Duchateau and coworkers concerning the use of

chromium(III) iminopyrrole, aminopyrrole and aminophosphine complexes[81] as well as that of Kozak and coworkers who have developed chromium(III) diamine bisphenolate catalysts for this purpose (Figure 1.7).[82]
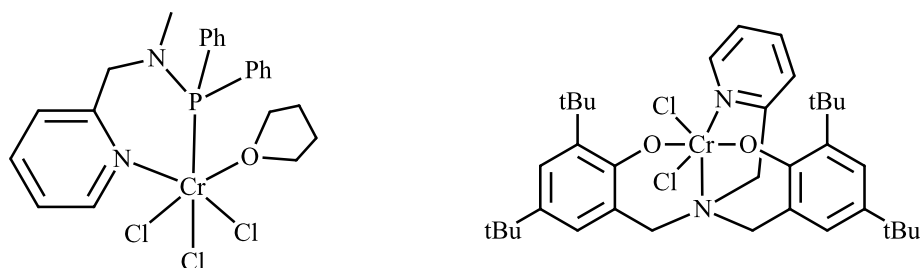
Figure 1.7 Duchateau (left) and Kozak (right) catalysts.

Herein we report the synthesis and characterization of two chromium(III) catalysts using tridentate Schiff base ligands, 2-[(2-hydroxy-2-phenylethyl-imino)methyl]-4,6-bis(tert-butyl)phenol (H$_2$L^P), and (1S,2R)-1-[(3,5-Di-tert-butyl-2-hydroxybenzylidene)amino]-2-indanol (H$_2$L^I). The ligand H$_2$L^I contains 2 chiral centers at the first and second position of the indanol moiety and can be prepared according to a previously published procedure as depicted in Schemes 2.1 and 2.2.[15] Additionally, it is also available commercially from Sigma Aldrich. We report the effectiveness of L^{P}Cr^{III}Cl and L^{I}Cr^{III}Cl as catalysts for the bulk, solventless copolymerization of CO$_2$ and CHO with and without the assistance of a neutral phosphine donor.

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CHAPTER II

MATERIALS AND EXPERIMENTAL PROCEDURES

2.1 MATERIALS AND EQUIPMENT

2.1.1 MATERIALS

All glassware used in this study was thoroughly cleaned via standard acid/base bath procedures, followed by drying for a minimum of 24 hours in a Fischer Scientific Isotemp Oven at 403.15K. Unless otherwise stated, all manipulations were carried out using standard air-free Schlenk techniques or in an argon-filled glovebox with vacuum antechamber. All chemicals were purchased from Sigma Aldrich and used as received unless otherwise stated. Calcium Hydride (CaH_2) was purchased from STREM Chemicals and used as received. Cyclohexene oxide was purchased from ACROS Organics and distilled over CaH_2 prior to use. THF was purified by distillation from sodium ketyl still, degassed and stored for ≥ 12 hours over 4 Å molecular sieves prior to use. Anhydrous Ethanol was purchased from Sigma Aldrich in a bottle equipped with a Sure/Seal™ cap and used as received. Bone dry CO_2 was purchased from Airgas Southwest, Inc. Ultra-High Purity (5.0 UHP) Argon was purchased from Praxair, Inc.
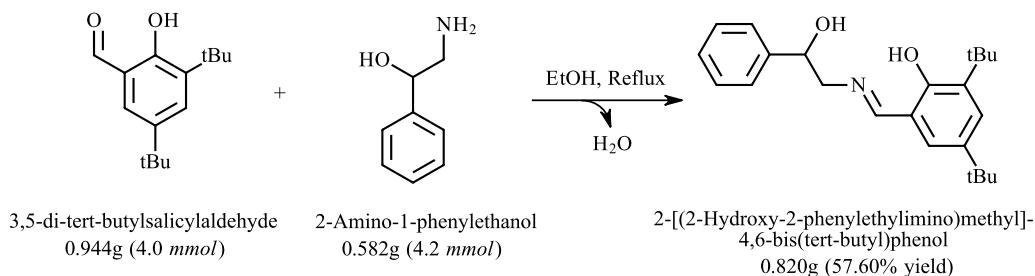
2.1.2 EQUIPMENT

- Glovebox – MBRAUN Labstar[Pro] – Serial No.: 15-087

- Glovebox Vacuum Pump – Edwards Model RV12—Serial No.: 159400620

- Drying Oven – Fischer Scientific 725G – Serial No.: 007N0032

- Vacuum Oven – Napco Model 5831 – Serial No.: 9509-021

- Heating Mantle Power Supply – Staco Energy Products Co. Model 3PN1010B

- Hotplate/Stirrer – VWR 7x7" Ceramic 120V – Serial No.: 150511001

- Balance 1 – OHAUS AR1530 – Serial No.: H181 1203120695 P

- Balance 2 – VWR-363AC – Serial No.: 454089

- NMR – Bruker Magnet System 400'54 Ascend – Serial No.: 749

    o Magnet: BZH 767'400'70I

- FTIR – ThermoFisher Nicolet iS5 – Serial No.: ASB1817506

2.2 EXPERIMENTAL PROCEDURES

Scheme 2.1 Synthesis of 2-[(2-Hydroxy-2-phenylethylimino)methyl]-4,6-bis(*tert*-butyl)phenol, $C_{23}H_{31}NO_2$ (H_2L^P).

3,5-di-tert-butylsalicylaldehyde	2-Amino-1-phenylethanol	2-[(2-Hydroxy-2-phenylethylimino)methyl]-
0.944g (4.0 *mmol*)	0.582g (4.2 *mmol*)	4,6-bis(tert-butyl)phenol
		0.820g (57.60% yield)

2.2.1 SYNTHESIS OF 2-[(2-HYDROXY-2-PHENYLETHYLIMINO)METHYL]-4,6-BIS(*TERT*-BUTYL)PHENOL, $C_{23}H_{31}NO_2$ (H_2L^P)

In a two-necked, 250-ml round bottom flask, 0.944g (4.0 *mmol*) of 3,5-di-tert-butylsalicylaldehyde was dissolved in ~50ml of ethanol equipped with reflux condenser under inert (Argon) conditions. 0.582g (4.2 *mmol*) of 2-amino-1-phenylethanol in ~50ml

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of ethanol was added via cannulan to the round bottom flask. The resulting yellow solution was then allowed to stir at reflux for 3 hours. Upon cooling, a yellow precipitate formed. The solvent by filtration and remaining volatiles removed in vacuo. After drying, the ligand was determined to weigh 0.820g (57.60% yield). ^{1}H NMR (400 MHz, CDCl$_3$, δ) 1.29 (s, 9H, -C(CH$_3$)$_3$), 1.43 (s, 9H, -C(CH$_3$)$_3$), 3.81 (qd, 2H, -CH$_2$-N=CH-), 5.03 (q, 1H, C$_6$H$_5$-CH(OH)-CH$_2$-), 7.09 (d, 1H, Ar), 7.38 (d, 1H, Ar), 7.25-7.35 (m, 5H, Ar).

2.2.2 SYNTHESIS OF (1*S*,2*R*)-1-[(3,5-DI-*TERT*-BUTYL-2-HYDROXY-BENZYLIDENE)AMINO]-2-INDANOL, C$_{24}$H$_{31}$NO$_2$ (H$_2$L^I)

H$_2$L^I was be synthesized in a fashion analogous to that described for H$_2$L^P in the previous section (Scheme 2.2). However, (1*S*,2*R*)-1-[(3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino]-2-indanol (CAS No. 212378-89-7) is commercially available from Sigma Aldrich. In some later syntheses this ligand was purchased and used as received for catalyst synthesis. ^{1}H NMR (400 MHz, CDCl$_3$, δ) 1.32 (s, 9H, -C(C*H*$_3$)$_3$), 1.39 (s, 9H, -C(C*H*$_3$)$_3$), 3.08-3.24 (qd, 2H, C$_6$H$_5$-C*H*$_2$-CH(OH)-), 4.21 (d, 1H, -C*H*-N=), 4.7 (m, 1H, -C*H*(OH)-), 7.19-7.34 (m, 5H, Ar), 7.41 (d, 1H, Ar), 11.86 (s, 1H, Ar-O*H*), 13.94 (s, 1H, -N=C*H*-).

**Scheme 2.2** (1*S*,2*R*)-1-[(3,5-Di-*tert*-butyl-2-hydroxybenzylidene)amino]-2-indanol, C$_{24}$H$_{31}$NO$_2$ (H$_2$L^I).
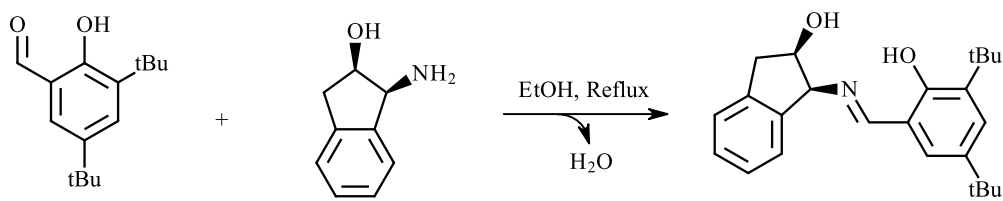
2.2.3 SYNTHESIS OF (C$_{23}$H$_{29}$NO$_2$Cr^{III}Cl), L^{P}Cr^{III}Cl CATALYST

The synthesis of L^{P}Cr^{III}Cl was carried out in a fashion analogous to previously reported procedure.[15] In a 65-ml tear-drop flask, 0.396g (1.1 *mmol*) of H$_2$L^P was dissolved in 15ml of dry, freshly distilled THF under an inert argon atmosphere. The resulting solution was delivered via cannula to a 50-ml round bottom flask containing 0.425g (1.1 *mmol*) of the chromium(III) chloride THF complex, CrCl$_3$•3THF. The resulting dark brown reaction solution was then allowed stir at room temperature for 4 hours under an inert Ar(g) atmosphere. The reaction mixture was diluted to ~250ml with *t*-butyl methyl ether (tBME) and washed several times with saturated brine and water. The organic phase was dried over Na$_2$SO$_4$ overnight, filtered and the solvent removed under reduced pressure. The resulting brown powder was weighed and found to be 0.427g (0.97 *mmol*, 86.8% yield). Despite no single-crystal XRD data, previous characterization of an analogous compound provides sound precedent for a dimeric structure in the solid state.[16]

Scheme 2.3 Synthesis of (C$_{23}$H$_{29}$NO$_2$Cr^{III}Cl) L^{P}Cr^{III}Cl Catalyst.
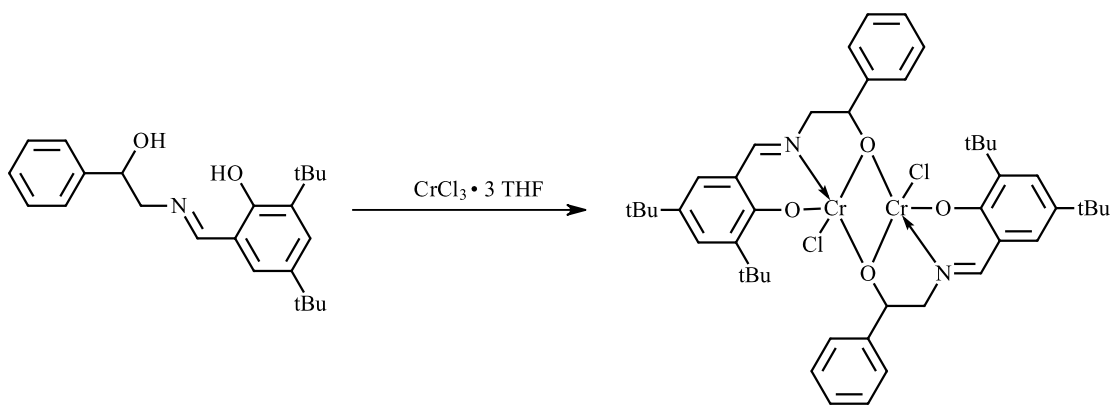
2.2.4 SYNTHESIS OF (C₂₄H₂₉NO₂Cr^III Cl), L^I Cr^III Cl CATALYST

In a 65-ml tear-drop flask, 0.621 g (1.7 *mmol*) of H₂L^I was dissolved in ~ 25 ml of dry, freshly distilled THF under an inert argon atmosphere. The resulting solution was delivered via cannulan to a 100-ml round bottom flask containing 0.637g (1.7 *mmol*) of CrCl₃·3THF dissolved in ~20 ml of THF. The resulting dark brown reaction solution was then allowed stir at room temperature for 3 hours under an inert Ar(g) atmosphere, followed by an additional 12 hours open to air. The reaction mixture was diluted to ~200 ml with tBME and washed several times with saturated brine and water. The organic phase was dried over Na₂SO₄ overnight, filtered and the solvent removed under reduced pressure. The rustling brown powder was weighed and found to be 0.437g (0.97 *mmol*, 57% yield). Despite no single-crystal XRD data, previous characterization of an analogous compound provides sound precedent for a dimeric structure in the solid state.[16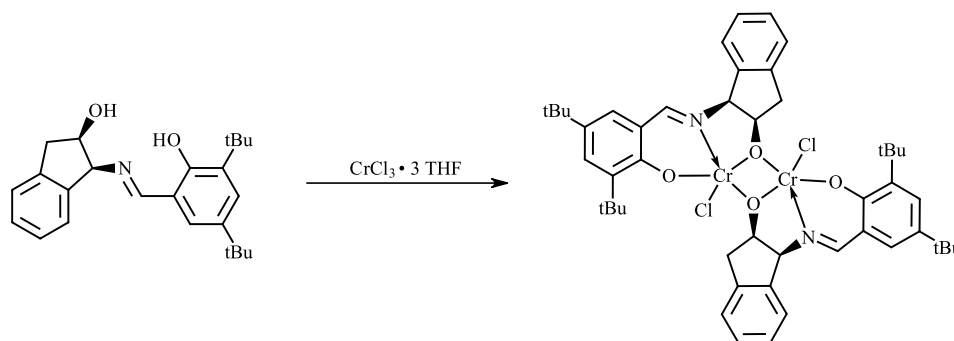] Elemental Analysis calculated for C₂₄H₂₉ClCrNO₂: C, 63.92; H, 6.48; N, 3.11: Found C, 67.29; H, 7.14; N, 2.66. Galbraith Laboratories, Knoxville, TN.

Scheme 2.4. Synthesis of (C₂₄H₂₉NO₂Cr^III Cl) L^I Cr^III Cl Catalyst.

2.2.5 COPOLYMERIZATION OF CYCLOHEXENE OXIDE AND CO_2

Inside an Argon-filled glovebox, freshly distilled CHO (approximately 10-13g) is charged into a 25-ml, stainless-steel reactor equipped with a magnetic stir bar, a two-way inlet valve, and a pressure gauge (Figure 2.1). To this, an appropriate amount (typically ~15mg) of $L^I Cr^{III} Cl$ was added, and when applicable an appropriate quantity of triphenylphosphine (PCy_3) co-catalyst (~4-18 mg). The reactor was then sealed and removed to a fume hood, connected via inlet valve to a purged, "bone-dry" CO_2 line and submerged into a temperature-controlled oil bath. The reactor is then pressurized to approximately 34.5-37.9 bar in CO_2 at ambient temperature. The reactor is then heated to and maintained at 353 K, resulting in an internal pressure of approximately 48.3-57.9 bar. All polymerizations were carried out under these conditions over a reaction time of 18 hours.   Following each polymerization, a small aliquot of the crude reaction mixture was collected and analyzed by FTIR spectroscopy to determine the presence of copolymer and/or monomeric, cyclohexene carbonate, 7,9-dioxabicyclo[4.3.0]nonan-8-one.[6]   The reaction solution is then diluted in DCM and the polymer reprecipitated in cold hexane or methanol. The precipitate was then dried in vacuo and the polymer characterized by ^{1}H and ^{13}C NMR spectroscopy to determine CO_2 incorporation and polymer stereoregularity. Additionally, to determine molecular weight distribution, selected polymer samples were characterized by gel permeation chromatography (GPC). GPC analysis was carried out in THF against polystyrene standards (in duplicate) by EAG Laboratories (Maryland Heights, Missouri).
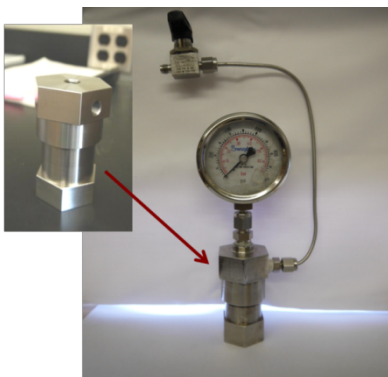
Figure 2.1 The 25-ml, Stainless Steel reactor, equipped with inlet valve and pressure gauge.

CHAPTER III

RESULTS AND DISCUSSION

3.1 SYNTHESIS OF LIGANDS AND CATALYSTS $L^PCr^{III}Cl$ AND $L^ICr^{III}Cl$

Two tridentate Schiff base coordination complexes were synthesized for this project. The catalyst $L^PCr^{III}Cl$ proved to be rather ineffective toward CO_2/CHO copolymerization as indicated by low (approx. ~15%) CO_2 incorporation as detailed in Table 3.1 in the next section. In contrast, $L^ICr^{III}Cl$ yielded copolymers with significantly higher CO_2 incorporations (~45%), for this reason, $L^ICr^{III}Cl$ became the major focus of our efforts.

Scheme 3.1 The copolymerization of CO_2 and cyclohexene oxide, mediated by $L^ICr^{III}Cl$.

$$CO_2\ incorp. = \frac{x}{x + y}$$
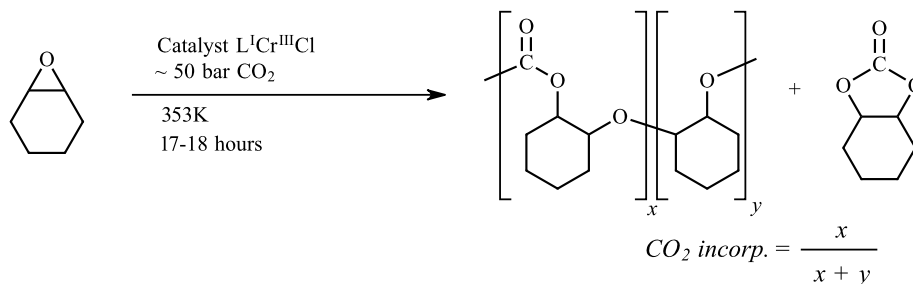
The ligand H_2L^I ($C_{24}H_{31}NO_2$) was synthesized by condensation of (1*S*,2*R*)-1-amino-2-indanol with an equal amount of 3,5-di-*tert*-butyl salicylaldehyde (see Scheme 2.2). The resulting ligand was isolated and characterized by FTIR and ^1H NMR spectroscopy. Following this, the catalyst $L^ICr^{III}Cl$ ($C_{24}H_{29}NO_2Cr^{III}Cl$) was readily synthesized from H_2L^I and $CrCl_3 \cdot 3THF$ as described previously in the literature (Scheme

2.4).[15] Upon binding of H_2L^1 ligand to the metal center, there was a slight shift of the $\nu_{(CN)}$ vibration from 1625 cm^{-1} to lower frequency at 1617 cm^{-1} in the FTIR spectra of the free ligand and complex respectively. This taken with NMR characterization of the ligand as well as elemental analysis data described in the previous chapter provides verification of the isolation of the target complex, $L^1Cr^{III}Cl$.

3.2   CO₂/CHO   COPOLYMERIZATION   RESULTS   FOR   CATALYSTS $L^PCr^{III}Cl$ AND $L^1Cr^{III}Cl$

The $L^1Cr^{III}Cl$ catalyst was found to be an effective catalyst for the coupling of CHO and CO_2 to produce alternating copolymer, poly(cyclohexene carbonate) (Scheme 3.1). At 353K and 50 bar in CO_2, the catalyst exhibited a TON of 249 mol CHO/mol Cr and a TOF of 13.8 hr^{-1} (Table 3.1). Table 3.1 details the results of all polymerizations described herein. Further, following polymerization (in all cases), a sample of the crude reaction mixture was taken, diluted with DCM and analyzed by FTIR spectroscopy to determine the extent of cyclic carbonate formation (Figure 3.1). Based on the FTIR data, $L^1Cr^{III}Cl$ appeared to be nearly 100% selective toward the production of polymer under the reported reactions conditions as evidenced by the intense absorbance observed at approximately $\nu_{(CO_2)}$ = 1750 cm^{-1}. This is assigned to the asymmetric $\nu_{(CO2)}$ stretch of PCHC.[10] Very little, if any signal, was observed for the corresponding band assigned to the cyclic carbonate, 7,9-dioxabicyclo[4.3.0]nonan-8-one, at $\nu_{(CO_2)}$ = 1802 cm^{-1}.[6,10] Figure 3.1 illustrates a representative FTIR spectrum of the products recovered in this study.

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Table 3.1 Copolymerization Data of Cyclohexene Oxide with CO_2.

Catalyst	Entry	Catalyst Loading (mg)	Co-Catalyst Loading PCy$_3$[a] (eq.)	TOF[b] (mol CHO/mol Cr·hr)	CO$_2$ Incorp.[c] (%)
L^{P}Cr^{III}Cl	1	14	0	43.9	14
”	2	36	0	11.8	17
L^{I}Cr^{III}Cl	1	7	0	13.9	49
”	2	15	0	11.7	42
”	3	30	0	13.8	31
”	4	15	0.5	9.6	53
”	5	15	0.5	6.7	49
”	6	15	1	7.36	82
”	7	15	1	7.91	73
”	8	15	1.5	6.27	80
”	9	15	1.5	8.59	67
”	10	15	1.5	6.3	69
”	11	15	2	8.82	73
”	12	15	2	9.38	67
”	13	15	2	7.05	73

All polymerizations were carried out in bulk CHO over 18 hours in a 25-ml stainless steel reactor equipped with a magnetic stir bar, at 353K and under ~52 bar CO$_2$. [a]Tricyclohexylphosphine loadings are given in equivalents relative to catalyst. [b]The turnover frequency is reported as moles of CHO consumed per mole of chromium(III) per hour. [c]CO$_2$ incorporation is calculated by integration of methine resonances in ^{1}H NMR spectra of the polymers (CDCl$_3$, 400 MHz).

1742 cm^{-1}

$\nu_{(CO_2)} = 1742$ cm^{-1}

$\nu_{(CO_2)} = 1802$ cm^{-1}
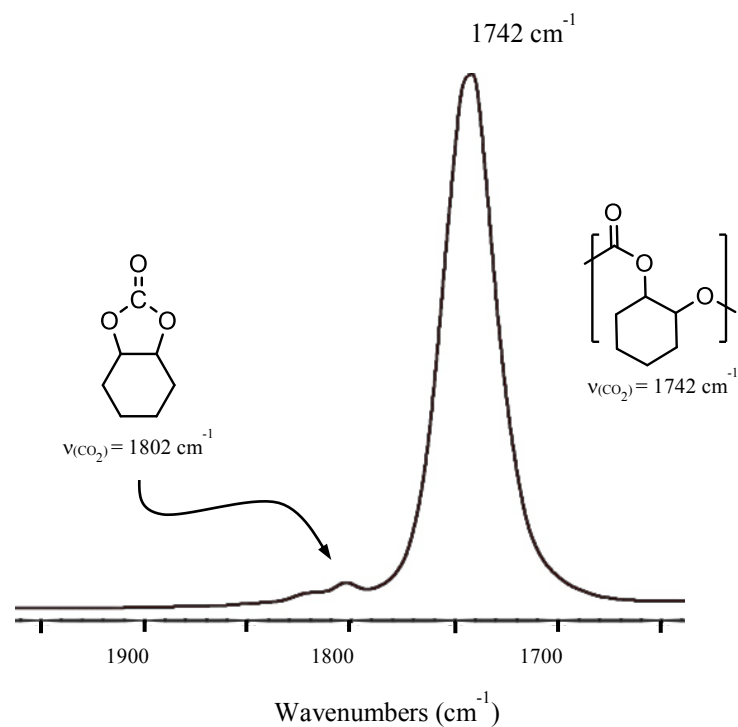
1900   1800   1700

Wavenumbers (cm^{-1})

Figure 3.1 The $\nu_{(CO_2)}$ region of a representative FTIR spectrum of PCHC prepared from copolymerization of CO_2 and CHO mediated by $L^I Cr^{III} Cl$. In some samples, trace amounts of the cyclic carbonate, 7,9-dioxabicyclo[4.3.0]nonan-8-one, are evidenced by a small absorbance at $\nu_{(CO_2)} = 1802$ cm-1.[6, 10]

3.3 EFFECT OF TRICYCLOHEXYLPHOSPHINE (PCy₃) AS A CO-CATALYST – CO₂ INCORPORATION & TOF

Following each polymerization reaction, samples of the PCHC were evaluated as to the degree of CO_2 incorporation into the polymer structure. This was determined by ^{1}H NMR spectroscopy and taken based on relative integrations of the methine chemical shifts centered at δ = 4.6 ppm and δ = 3.4 ppm corresponding to carbonate and ether linkages respectively (Scheme 3.1 and Figure 3.2).[2] While there is some variability concerning CO_2 incorporation, there is an observed trend worthy of remark. The initial CO_2 incorporation was measured to be approximately 42-49% relative to CHO monomer enchainment. However, given the precedent in the literature for the use of N-heterocyclic amines, bulky phosphines (Tolman cone angles[83] – 145°-185°) and salts derived from bis(triphenylphosphine)iminium (PPN⁺), as well as ammonium salts (R₄N⁺),[57, 59, 84] we embarked on a study of the effect of various levels of PCy₃ on the TON and TOF of the polymerizations mediated by $L^I Cr^{III} Cl$. The addition of PCy₃ proved to have a marginal impact on TOF but rather, a significant effect on CO_2 incorporation. As the addition of PCy₃ was increased from 0 to 2 equivalents relative to chromium, CO_2 incorporation was observed to increase from 42% to a maximum of 78% at 1 equivalent PCy₃ relative to chromium. There appears to be no statistically significant change in this value with addition of PCy₃ beyond 1 equivalent (Figure 3.3).

Another important question which presented some potential was that of stereocontrol. Indeed, the ligand, $H_2 L^I$, contains two chiral centers and can be synthesized or purchased in an enantiomerically pure form.[15] To this point, ^{13}C NMR spectroscopy in the carbonate region was employed to evaluate the stereoregularity
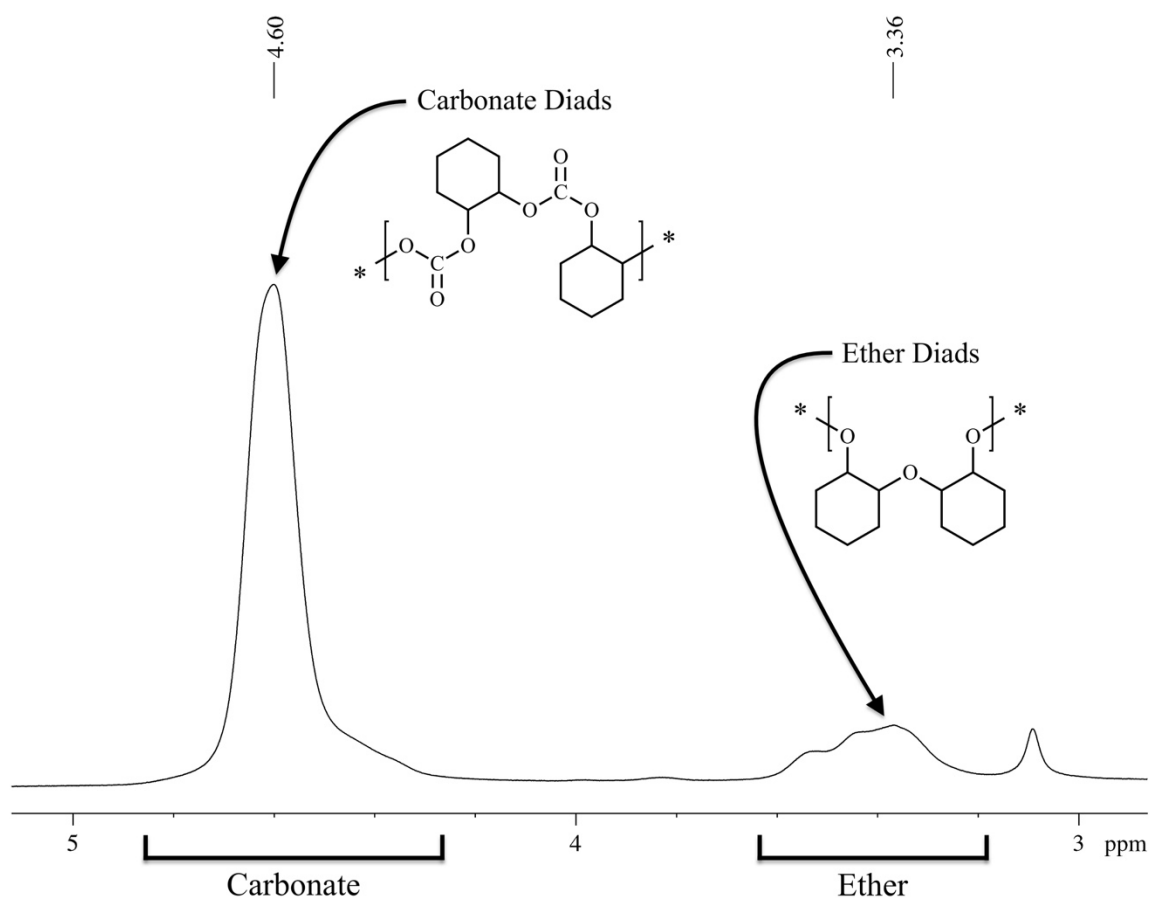
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Figure 3.2 The methine chemical shifts in a representative ^{1}H NMR spectrum of PCHC prepared from copolymerization of CO_2 and CHO mediated by $L^{I}Cr^{III}Cl$. Integration of the shifts centered at δ = 4.6 ppm and δ = 3.4 ppm (Scheme 3.1) provide relative quantification of carbonate and ether linkages respectively.[6]
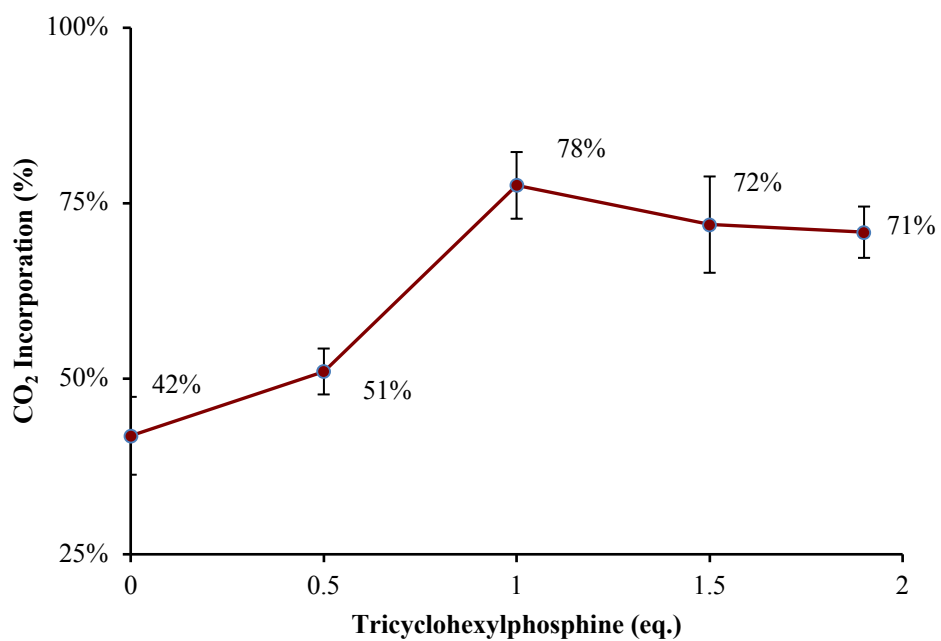
Figure 3.3 Plot of average CO_2 incorporation as determined by ^{1}H NMR spectroscopy with increasing tricyclohexylphosphine. Data reported here are represented as average values for polymerizations carried out with a catalyst loading of 15 mg $L^I Cr^{III} Cl$.

of PCHC recovered from the polymerizations described here. Consistent with previous literature, a complex set of chemical shifts were observed centered at δ = 153.9 ppm and δ = 153.1 - 153.4 ppm which are assigned to isotactic, syndiotactic and heterotactic tetrads within the copolymer microstructure, respectively (Figure 3.4).[85] As such, all polymers were observed to be atactic, indicating a lack of stereocontrol in the ring opening and enchainment of the CHO monomer.

3.4 GEL PERMEATION CHROMATOGRAPHY

Selected polymers were analyzed by gel permeation chromatography (GPC) in order to determine molecular weight distributions. These results are summarized in Table 3.2. Initially, 15 mg of $L^I Cr^{III}Cl$ at 353K and 52 bar CO_2, produced polymer with a number average molecular weight (M_n) of 3578 Da with a corresponding PDI of 5.1. Broad molecular weight distributions were observed for all polymerizations reported herein with the PDI ranging from 3.6 to 5.2. Such broad distributions are in contrast to that typically reported for chromium(III) catalysts in the literature and may be indicative of either slow initiation of the active species or slow deactivation of the catalyst during polymerization. Further, it was also observed there was a fairly linear decrease in the number average molecular weight with the addition of increasing amounts of the cocatalyst, PCy_3 (Table 3.2; Figure 3.5). So, even as additional PCy_3 served to enhance CO_2 incorporation, it appears to have a consistent and measurable negative impact on molecular weight. This trend is opposed to that reported for salen chromium(III) systems.[86] As such, there is insufficient data for a definitive mechanistic explanation of this trend. However, it does suggest there is a consistent inhibition of the rate of CHO

monomer ring-opening and enchainment which would appear to be consistent with both the lower molecular weights as well as the enhanced CO_2 incorporations. It is unlikely that chain-transfer is the case of this observation, as that would also result in narrower molecular weight distributions.

Table 3.2 Gel Permeation Chromatography Data for Selected Copolymers [a]

Entry [b]	PCy_3[c] (eq.)	Mn (Da)	PDI
2	0	3578	5.1
6	1	2993	3.6
7	1	2185	3.7
8	1.5	1239	5.2
11	2	989	4.3
12	2	609	4.1

[a] GPC analysis was conducted in THF against narrow molecular weight polystyrene standards. [b] Selected PCHC samples were prepared from polymerizations performed over 18 hours in a 25-ml stainless steel reactor equipped with magnetic stir bar, at 353K and under ~58 bar CO_2 with a catalyst loading of 15 mg $L^ICr^{III}Cl$. [c] Amounts of PCy_3 are given in equivalents relative to the catalyst ($L^ICr^{III}Cl$).
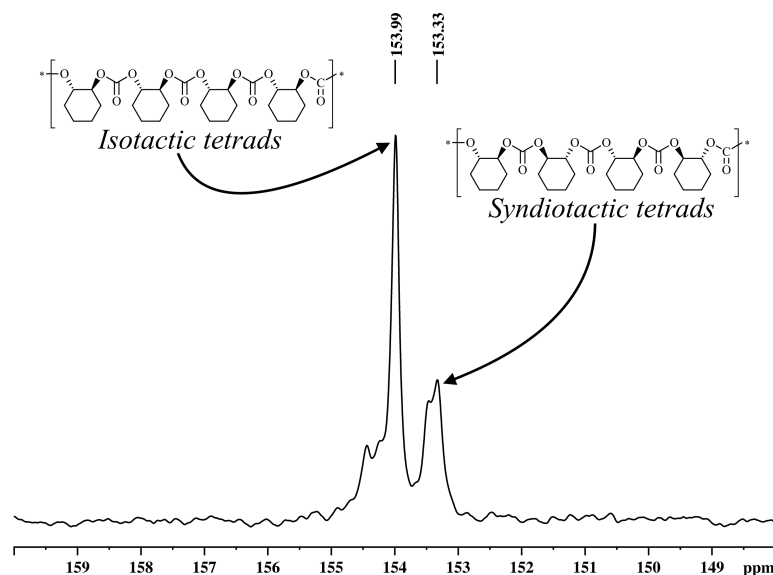

Figure 3.4 The carbonate chemical shifts in a representative ^{13}C NMR spectrum of PCHC prepared from copolymerization of CO_2 and CHO mediated by $L^ICr^{III}Cl$. The *m*-centered (isotactic) and *r*-centered tetrads (syndiotactic) appearing at $\delta = 153.99$ ppm and $\delta = 153.33$ ppm respectively integrate equally.[85]

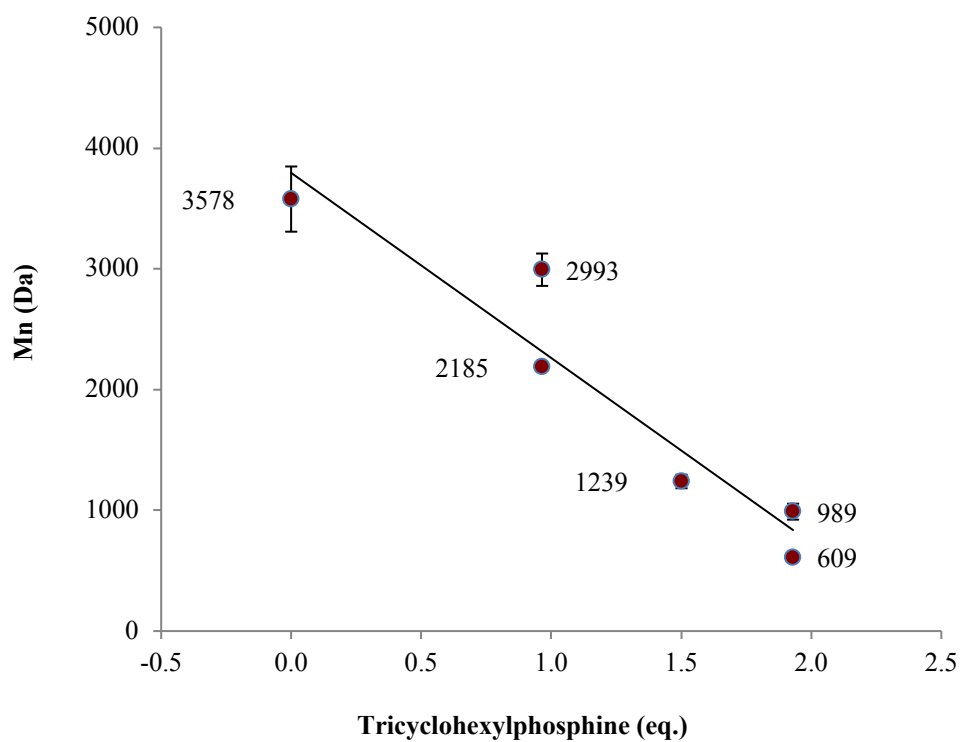**Figure 3.5** Plot of the number average molecular weights of PCHC prepared from copolymerization of CO_2 and CHO mediated by $L^ICr^{III}Cl$, as determined gel permeation chromatography.

CHAPTER IV

CONCLUSIONS

While there is still much work to be done before the coupling of CO_2 and epoxides to produce polycarbonates commercially can be realized on a large scale, considerable progress has been made in the understanding of this process. To that end, two air-stable, tridentate, Schiff-base chromium(III) coordination complexes were synthesized, characterized and shown to be reasonably effective in the coupling of CO_2 and CHO to produce PCHC under readily accessible conditions, as described in the previous chapters of this thesis. Complex $L^I Cr^{III} Cl$ was found to be nearly 100% selective toward polycarbonate as evidenced by the lack of any cyclic carbonate observed in the FTIR spectral data. Addition of PCy_3 as a cocatalyst was shown to enhance the degree of CO_2 incorporation, resulting in polymers which were found to be as high as 82% carbonate in contrast to initial values of ~31-49% carbonate for polymerization carried out in the absence of PCy_3. Nevertheless, number average molecular weight and TOF were highest for polymers prepared in the absence of phosphine ($Mn = 3578$; TOF = 13.9 hr^{-1}). These data indicate enchainment inhibition by PCy_3 rather than unwanted chain transfer which would be accompanied by much narrower molecular weight distributions in addition to the lower M_n values. Future investigations into $L^I Cr^{III} Cl$ may indicate whether similar effects might be observed with addition of PPN+ salts or N-heterocyclic

compounds such as *N*-methylimidazole (*N*-MeIm) and *N,N*-dimethyl-4-aminopyridine (DMAP) derivatives as cocatalysts.

Additionally, as H_2L^I presents a ligand environment with two chiral centers, ^{13}C NMR spectroscopy showed no appreciable stereocontrol for any PCHC sample recovered from the polymerizations described here. As such, all polymers were observed to be atactic and therefore indicating a lack of stereocontrol in the ring opening and enchainment of the CHO monomer. It is apparent that the mechanism is not similar to that of other salen chromium(III) complexes reported in literature. This is not surprising given that the geometries of those ligand architectures are quite different than that reported herein. Nevertheless, future work will likely include examination of catalyst activity at lower temperature, the implementation of additional cocatalysts such as N-methylimidazole or PPN+ salts as well as the effect of reaction time. Also, we continue to work toward structural characterization of the catalysts by single crystal x-ray diffraction. The current system is far from optimized and there is sufficient impetus for these future lines of investigation.

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Figure 1.5 Darensbourgs' monomeric zinc-*bis*(phenoxide) complex.

Figure 1.6 Coates' Zinc ß-diiminate complex structure.