Synthesis, Characterization and Catalytic Activity of Chromium Complexes

Joanna Gurnham

December 20, 2013

Thesis submitted to the

Faculty of Graduate and Postdoctoral Studies

University of Ottawa

For MSc degree in chemistry

Faculty of Science

Ottawa-Carleton Chemistry Institute

Abstract

There has been a growing demand for specific linear alpha olefins in the polyethylene industry in order to control polymer rheology. This growing demand thereby increases the need for highly active and selective ethylene oligomerization catalysts. Chromium-based catalysts continue to be of high interest for this application due to this metal's versatility in both selective and non selective ethylene oligomerization. Ligand design is an important consideration in oligomerization chemistry: the ability of the ligand to stabilize low valent chromium and to support a two-electron redox process will allow the catalytic systems to follow the selective ring expansion mechanism for oligomerization.

Chelating aminophosphane based ligands, previously studied by our group, have been shown to support both tri- and tetramerization of ethylene. We have explored modifications of one of the NP arms by replacing with a different coordinating group in an attempt to further stabilize the monovalent state of chromium and increase selectivity. Other ligands explored in this work are pyrrole based ligands, which have shown high activity and selectivity towards ethylene oligomerization. One example of this is the commercial Chevron-Phillips system.

Recently, the co-polymerization of CO_2 with epoxides has been studied as an environmentally friendly route to convert CO_2 into biodegradable polymers. The first successful catalytic system to achieve these results consisted of a diethyl-zinc complex. More recently, aluminum, chromium, cadmium and cobalt have been studied as polycarbonate catalysts. To date, the only reported chromium catalysts for CO_2-epoxide copolymerization are Cr-salen and Cr-porphyrin complexes, studied by Darrensbourg and Holmes, respectively.

We were particularly interested in finding new chromium-based complexes able to catalyze epoxide/CO_2 copolymerization by using molecules with the nitrogen donor motif embedded in different functions such as neutral pyridines with anionic pendants, pyrroles with either imine or amine pendants, or a combination of these.

Acknowledgements

First and foremost, I would like to express my gratitude to my supervisor Dr. Sandro Gambarotta, for his patience, motivation, enthusiasm and immense knowledge. His help and support have been central in the research and writing of this thesis.

Many thanks to Dr. Robbert Duchateau for giving me the opportunity to work at Eindhoven University of Technology in Holland, and to Lidia Jasinska-Walc for her assistance while I was there. It was a wonderful learning experience and an unforgettable trip. I would also like to thank Dr. Ilia Korobkov for his advice and assistance in obtaining X-ray crystal structures, and the University of Ottawa mass spectrometry team for all of their help.

Finally, I would like to thank all of the current and previous members of the Gambarotta group, particularly Ahmed, Yacoob, Sebastiano and Camilo, for all of their help in starting my degree in chemistry. Coming from a background in biology, their assistance and advice was much needed and very much appreciated.

Thank you!

Table of Contents

Page

Abstract ii

Acknowledgements iii

List of Figures viii

List of Tables x

List of Abbreviations xi

Chapter 1: Introduction

1.1 Preamble 1

1.2 Ethylene Polymerization 2

1.3 Non-Selective Ethylene Oligomerization 4

1.4 Selective Ethylene Oligomerization 7

1.5 Chromium Based Ethylene Tri- and Tetramerization 10

1.6 Polycarbonate Overview 20

1.7 CO_2-Epoxide Copolymerization: Mechanistic Considerations 22

1.8 Epoxide-CO_2 Copolymerization: Catalytic Systems 25

1.9 Zinc Catalysts for CO_2-epoxide Copolymerization 33

Page

1.10 CO_2-epoxide Copolymerization: Bimetallic Mechanism 38

1.11 Thesis Aim 41

1.12 References 42

Chapter 2: Aminophosphine-Chromium Catalysts for Ethylene Tetramerization

2.1 Introduction 50

2.2 Experimental 52

2.2.1 Synthesis of Ligands 53

2.2.2 Synthesis of Complexes 54

2.2.3 Catalytic Test Results 55

2.3 X-Ray Data 56

2.4 Results and Discussion 56

2.5 References 64

Chapter 3: Pyrrole Based Ligands for Chromium Catalyzed Selective Ethylene Trimerization

3.1 Introduction 68

3.2 Experimental 70

Page

3.2.1 Synthesis of Ligands 71

3.2.2 Synthesis of Complexes 73

3.2.3 Catalytic Test Results 75

3.3 X-Ray Data 76

3.4 Results and Discussion 76

3.5 References 90

Chapter 4: Chromium Catalyzed CO_2-Epoxide Copolymerization

4.1 Introduction 92

4.2 Experimental 98

4.2.1 Synthesis of Complexes 98

4.2.2 Polymerization Procedure 98

4.2.3 Analysis of Polymers 99

4.3 Results and Discussion 100

4.4 References 112

Conclusion 114

Appendix A: X-ray Crystallography Procedure 116

Appendix B: NMR Spectra of Synthesized Ligands 117

Appendix C: GC-FID of Select Oligomerization Products 122

Appendix D: MALDI-ToF-MS of Select Polycarbonates 124

Appendix E: GPC of Select Polycarbonates 126

List of Figures

	Page
Figure 1.1: A. Low Density Polyethylene. B. Linear Low Density Polyethylene. C. High Density Polyethylene.	2
Figure 1.2: Bidentate ligands for selective oligomerization developed by Exxon-Mobil.	11
Figure 1.3: Tridentate PNP and SNS ligands developed by Sasol Technology.	12
Figure 1.4: Tridentate ligands for selective ethylene oligomerization.	13
Figure 1.5: BP and Sasol's PNP ligands.	14
Figure 1.6: Modifications of N-substituents in PNP framework ligands.	15
Figure 1.7: Iminodiphosphine ligands for oligomerization.	15
Figure 1.8: Bidentate diphosphine ligands by Sasol Technology.	16
Figure 1.9: Bis-pyridine ligands for tri- and tetramerization.	18
Figure 1.10: N-P ligands with modifications to the donor pendant.	18
Figure 1.11: Aluminum and manganese porphyrin complexes.	25
Figure 1.12: Al-alkoxide complexes for CO_2-epoxide copolymerization.	26
Figure 1.13: Aluminum-salen complexes.	27
Figure 1.14: Chromium-salen complexes.	28
Figure 1.15: Chromium-salen and chromium salan complexes.	28
Figure 1.16: Chromium-salanen complex.	29
Figure 1.17: Early Cobalt-salen complexes.	30
Figure 1.18: Cobalt-salen complexes.	31
Figure 1.19: Chromium and cobalt porphyrin complexes.	32
Figure 1.20: Zinc-phenoxide complexes.	34
Figure 1.21: bis(salicyclaldiminato)-zinc complexes.	34

Page

Figure 1.22: Quinoxaline zinc complexes. 35

Figure 1.23: Pyridinium alkoxy zinc dibromides. 36

Figure 1.24: β-diiminate zinc catalysts. 37

Figure 1.25: Zinc anilidoaldimin complexes. 38

Figure 2.1. Partial thermal ellipsoid drawing of **2.1** at 50% probability. 58

Figure 2.2. Partial thermal ellipsoid drawing of **2.3** at 50% probability. 60

Figure 3.1. Partial thermal ellipsoid drawing of **3.2** at 50% probability. 78

Figure 3.2. Partial thermal ellipsoid drawing of **3.3** at 50% probability. 80

Figure 3.3. Partial thermal ellipsoid drawing of **3.6** at 50% probability. 82

Figure 4.1: Graphical representation of conversion of cyclohexeneoxide (%) as a function of time, catalyzed by complex **3.1**. 105

Figure 4.2: Graphical representation of % carbonate linkages versus % ether linkages as a function of time, catalyzed by complex **3.1.** 105

Figure 4.3: Graphical representation of conversion of cyclohexeneoxide (%) as a function of time, catalyzed by complex **3.3**. 108

Figure 4.4: Graphical representation of % carbonate linkages versus % ether linkages as a function of time, catalyzed by complex **3.3.** 109

List of Tables

Page

Table 1.1: Summary of activity and selectivity of catalysts **7-14**. 13

Table 1.2: Summary of activity and selectivity of ligands **25-31** with chromium. 17

Table 1.3: Summary of activity of ligands **34-38** with chromium. 19

Table 2.1. Table of crystal data and refinements for **2.1** and **2.3**. 56

Table 2.2: Ethylene Oligomerization Results of PyNP Complexes. 63

Table 3.1: Table of crystal data and refinements for **3.1, 3.3** and **3.6**. 76

Table 3.2. Ethylene oligomerization results for **3.1**. 84

Table 3.3. Ethylene oligomerization results of Pyr-N ligand with various chromium sources. 86

Table 3.4. Ethylene oligomerization results for Pyr-N-Py ligand with various chromium sources. 88

Table 3.5. Ethylene oligomerization results for complex **3.6.** 88

Table 4.1: CO_2-epoxide Copolymerization Results of PyNP complexes. 103

Table 4.2: CO_2-epoxide Copolymerization Results for Complex **3.1**. 104

Table 4.3: CO_2-epoxide Copolymerization Results for Complexes **3.2** and **3.3.** 107

Table 4.4: CO_2-epoxide copolymerization results for complexes **3.4-3.6**. 110

List of Abbreviations

bdi	β-diiminate
BPA-PC	Bisphenol A polycarbonate
CHO	Cyclohexene oxide
DEAC	Diethyl aluminum chloride
dMAO	depleted methylaluminoxane
DMAP	4-dimethylaminopyridine
EC	Ethylene carbonate
EDG	Electron donating group
EWG	Electron withdrawing group
HDPE	High density polyethylene
LAO	Linear alpha olefin
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
MAO	Methylaluminoxane
MeIm	Methyl imidazole
MMAO	Modified methylaluminoxane
NMR	nuclear magnetic resonance
PC	Polycarbonate
PCHC	Poly(cyclohexenecarbonate)
PDI	Polydispersity index
PE	Polyethylene
PO	Propylene oxide
PP	Polypropylene

PPC	Poly(propylene carbonate)
PPN^+Cl^-	bis(triphenylphosphine)iminium chloride
PPO	Poly(propylene oxide)
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVC	Polyvinylchloride
S-F	Schulz-Flory
SHOP	Shell higher olefin process
TBD	1,5,7-triazobicyclo-[4,4,0]-dec-5-ene
TEAl	Triethyl aluminum
TIBA	Triisobutyl aluminum
TOF	Turnover frequency
tpp	Tetraphenylporphyrin

Chapter 1: Introduction

1.1 Preamble

Polymers play a key role in our modern society, from natural polymers such as DNA and proteins, to synthetic polymers used for plastics or fabrics. The polymerization process consists of covalent bond formation between monomers to form a chain or network of repeating subunits. The most commonly widespread polymers include: low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polyvinylchloride (PVC), polystyrene (PS), nylon (polyamide), Teflon (polytetrafluoroethylene, PTFE), polyurethane (PU) and polycarbonate (PC). This thesis work will focus on the development of polyethylene and polycarbonate.

There are three different types of polyethylene: high density polyethylene (HDPE), low density polyethylene (LDPE) and linear low density polyethylene (LLDPE), all of which rely on the utilization of α-olefin as co-monomers. PE has a broad range of applications in packaging materials, and industries including construction, automotive, medical, etc.

There are two different types of PC. The most common is synthesized from bisphenol-A and phosgene, according to the GE-Sabic proprietary technology.[1] However, recent work has investigated the use of CO_2 as a renewable, non-toxic monomer for the synthesis of PC when combined with epoxides. The uses for PC range from computer cases and CDs to automotive and aircraft components to toys and baby bottles.

1.2 Ethylene Polymerization

Polyethylene is the most widely used plastic, whose worldwide consumption peaked $45x10^6$ tons in 1995.[2] This is largely due to the fact that PE, as with all polyolefins, is composed solely of carbon and hydrogen, and therefore can easily be recycled or combusted.[3] As mentioned above, there are different types of polyethylene (Figure 1). HDPE has virtually no branching, and is the most widely used type of polyethylene (Figure 1, C). LDPE has a random branching structure (Figure 1, A), and LLDPE contains uniform branches, randomly distributed along the main polyethylene chain (Figure 1, B). HDPE is used for packaging, such as milk jugs, detergent bottles, garbage containers, and has many product applications, from toys to water pipes. LDPE and LLDPE are typically extruded into films, used for plastic bags, plastic wrap, cable coverings, toys, containers and piping.[2] The co-monomers required for the synthesis of branched polyethylene are light weight linear alpha olefins, or LAOs, including 1-butene, 1-hexene and 1-octene (C_4-C_8). Ethylene is a readily available monomer for use in the polymerization process, however, these light LAO fractions are more difficult to acquire.[4]

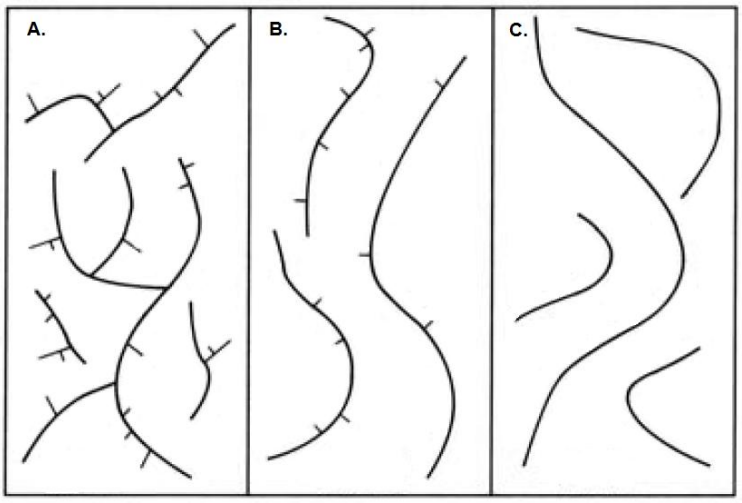
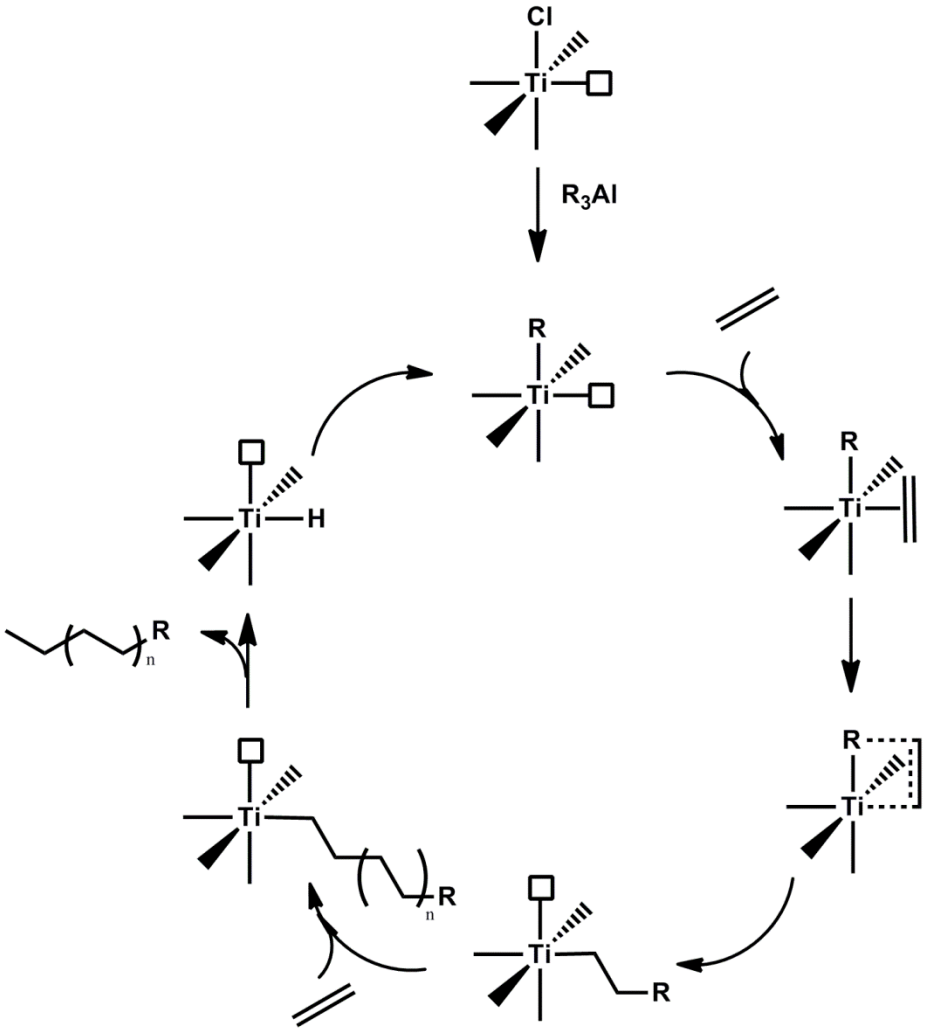


Figure 1.1: A. Low Density Polyethylene. B. Linear Low Density Polyethylene. C. High Density Polyethylene

In 1953, Karl Ziegler of the Max-Planck Institute discovered a titanium tetrachloride catalyst that polymerized ethylene into HDPE when used with diethyl aluminum chloride (DEAC) as a cocatalyst. Shortly after, Giulio Natta of the Polytechnical Institute of Milan discovered a catalyst capable of polymerizing propylene into polypropylene.[3] In 1963, Ziegler and Natta shared the Nobel Prize for Chemistry. Ziegler-Natta polymerization systems are based on titanium and vanadium metal salts[5,6] and alkyl-Aluminum compounds as cocatalysts.[7]

Scheme 1.1



The polymerization process is initiated by an alkyl aluminum reagent which activates the metal centre via alkylation, exchanging the alkyl, R, for the chloride. (Scheme 1.1). An ethylene monomer then coordinates via π-bonding at the vacant site and subsequently inserts into the metal alkyl bond. This leaves the vacant site open for another molecule of ethylene to coordinate and insert. This cycle continues, causing the polymer chain to grow. The cycle is terminated via β-hydride elimination, generating polyethylene and a metal hydride complex, which can undergo ethylene insertion to continue the cycle.[8,9]

The possibility of copolymerizing different α-olefins and thus introducing branching of the appropriate length is central to control the polymer rheology. As briefly mentioned above, co-monomers such as 1-hexene and 1-octene are in high demand, and their extraction from crude oil cannot satisfy the need of the polymer industry. Therefore, there is a need for developing catalytic systems for the production of specific LAOs from ethylene, a relatively inexpensive and largely available source. This is the process of ethylene oligomerization, which today is available as both selective and non-selective processes, including the Chevron Phillips system and the SHOP process, which will be elaborated on in subsequent sections.

1.3 Non-selective Ethylene Oligomerization

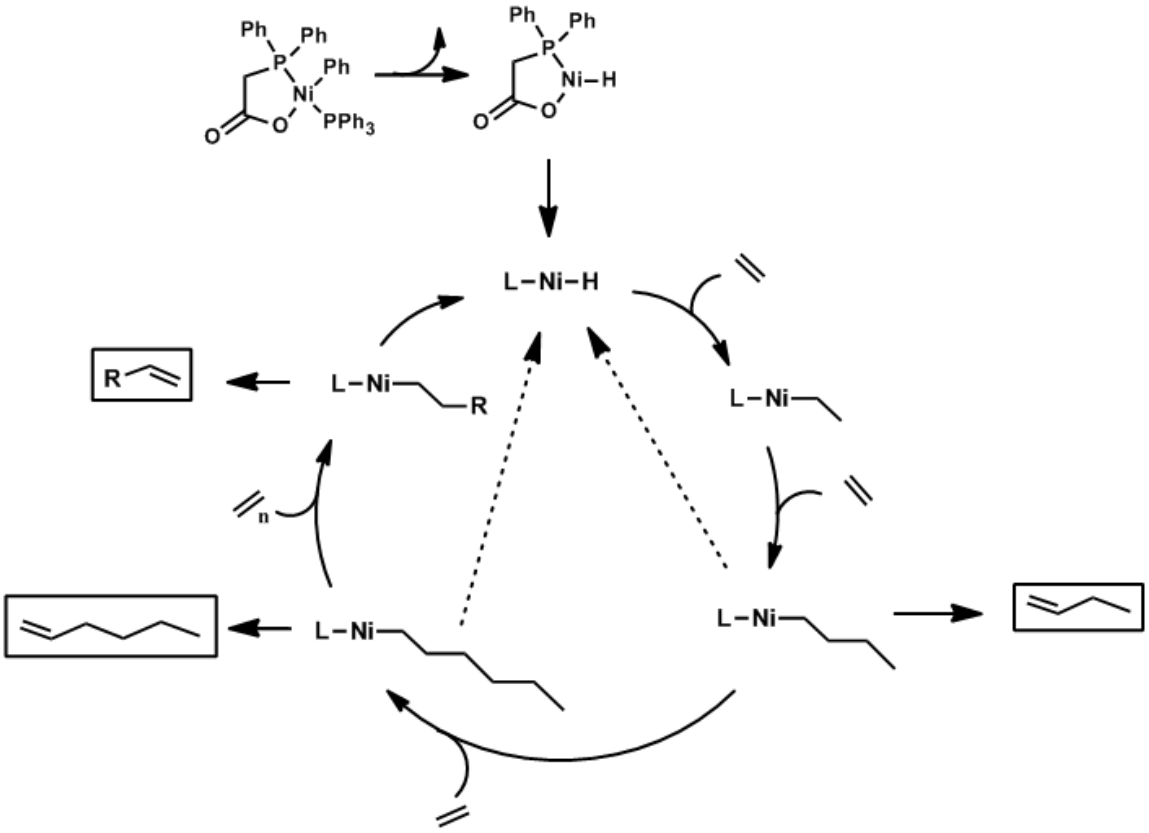
Non-selective ethylene oligomerization is a truncated polymerization process that produces C_4 to $C_{>20}$ molecules with a double bond in the alpha position, also called LAOs. As mentioned, the C_4 to C_8 fractions (1-butene, 1-hexene and 1-octene) are particularly important in the production of HDPE and LLDPE. Heavier fractions of LAOs have specific applications as well: C_{12}-C_{20} fractions are used as surfactants and biodegradable detergents and C_6-C_{10} fractions

are used as plasticizers. LAOs are also used in the production of organo-aluminum compounds, oxo-alcohols, epoxide intermediates, synthetic and wax lubricants, amines and synthetic fatty acids.[4,10–13]

The Shell higher olefin oligomerization process (SHOP) produces nearly half of LAOs used worldwide, close to 1 million tons per year.[13] This process was developed after the discovery that nickel salts significantly enhanced the catalytic activity of the Ziegler system.[14] Other processes for synthesizing LAOs include alcohol dehydrogenation, paraffin-wax cracking and paraffin dehydrogenation, but due to the availability of ethylene and high quality of the products obtained, SHOP continues to be the most widely used preparation method.[13]

The SHOP catalytic cycle follows the Cossee-Arlman chain growth mechanism, producing a statistical distribution of even numbered carbon olefins, also called a Schulz-Flory distribution.[8,9] The Schulz-Flory distribution can be controlled by managing the geometric α-olefin chain growth factor K. A typical K value for industrial processes falls between 0.75 and 0.80, and can be achieved by varying the catalyst structure.[15–17] The mechanism of SHOP oligomerization has been investigated by Keim and co-workers, and it was found to be very similar to polymerization, with the only difference being the chain termination step via β-hydride elimination occurs at an earlier stage for oligomerization.[16,18–26] The chain growth mechanism for SHOP oligomerization is shown in Scheme 1.2.

Scheme 1.2



A nickel chloride salt with a diorganophosphino ligand reduces to a nickel-hydride species at high temperature and pressure in toluene, thus beginning the oligomerization process.[27,28] Ethylene inserts into the metal-hydride bond, forming a metal-alkyl. Subsequent ethylene insertions cause the chain to grow, until the metal-alkyl eliminates an α-olefin via β-hydride elimination and regenerates the metal-hydride. Other metals used for non-selective ethylene oligomerization include Ti, Zr, Pd, Al, Ru and Cr.[29]

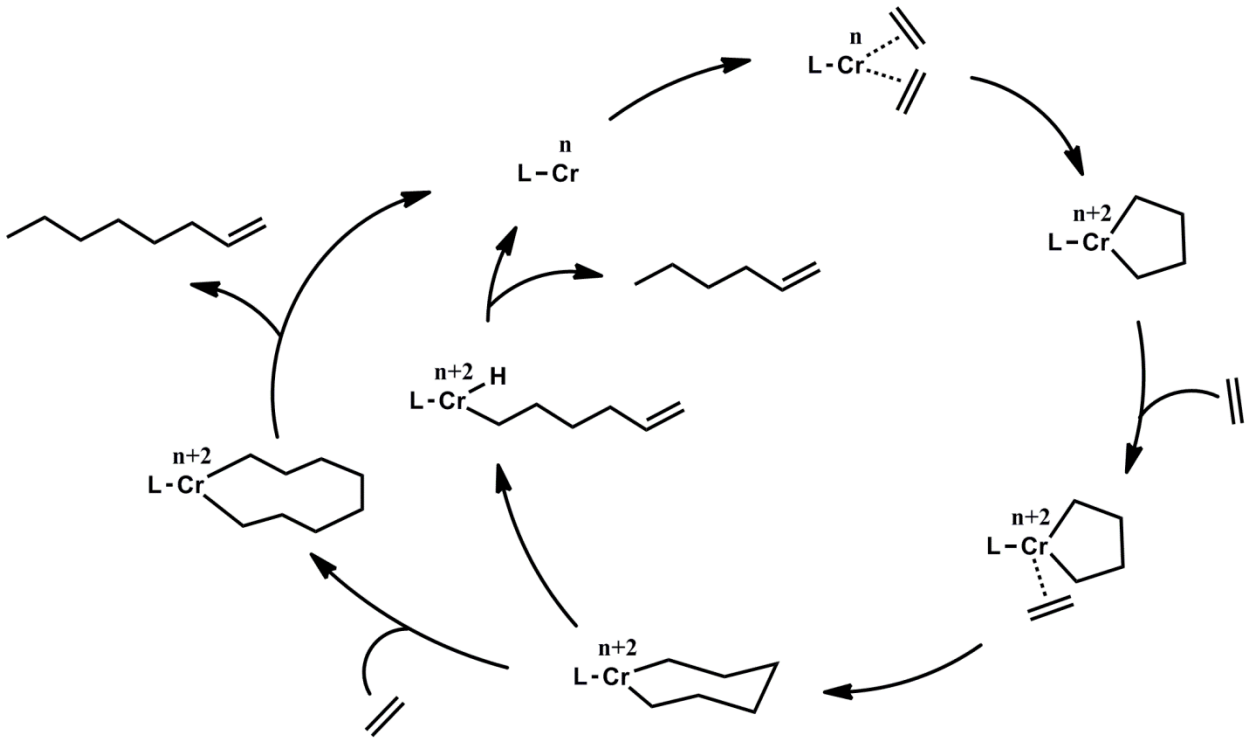
1.4 Selective Ethylene Oligomerization

Because the lighter LAOs are in much higher demand, they can be separated via fractionation. However, this is an energy intensive process, and in order to avoid it, selective oligomerization is desirable. Selective processes for di-, tri- and tetramerization have been developed based on a different mechanistic pathway. A redox mechanism involving metallacyclic intermediates, commonly referred to as the ring expansion mechanism, is responsible for selective oligomerization of 1-hexene and 1-octene.[30–32]

Titanium catalyzed ethylene dimerization was proposed to follow the metallacycle mechanism for the commercial Alphabutol process developed by the French Institute of Petroleum, which produces over 500,000 tons of 1-butene per year.[33–35]

The earliest trimerization catalytic systems used chromium complexes, but other transition metals have also been successful for selective ethylene oligomerization.[31] Nonetheless, chromium remains the most popular metal for oligomerization, largely due to its stability, low-price and ease of activation. The mechanism followed by a selective oligomerization is a redox ring expansion mechanism, as proposed by Manyik and co-workers.[36] (Scheme 1.3)

Scheme 1.3



The process is initiated by the oxidative coupling of two molecules of ethylene, producing a metallocyclopentane complex. Further ethylene insertions result in larger metallacyclic rings. The metallacycle decomposes via β-hydride elimination, followed by reductive elimination, producing the linear alpha olefin and regenerating the lower oxidation state metal complex. The selectivity of this mechanism is believed to be controlled by the stability of the metallacycles: a seven membered ring gives 1-hexene and a nine membered ring gives 1-octene.

The ring expansion mechanism is the generally accepted mechanism for tri- and tetramerization.[12,37–39] It was proposed in the literature that several redox couples as

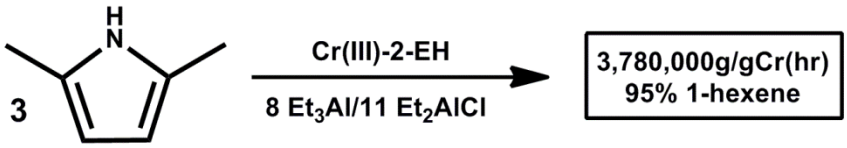
Cr(I)/Cr(III), Cr(II)/Cr(IV) and even Cr(III)/Cr(V) may participate in the metallcycle mechanism. However, work from our lab in recent past has pointed out the first possibility as unequivocally linked to the appearance of selectivity in the catalytic cycle. In particular, this work has also discovered the existence of redox dynamism where the initial chromium precursors are not only generated via spontaneous reduction, but also re-formed via a series of coproportionations and disproportionations. Clearly the ligand plays a central role in the occurrence and extent of redox dynamism, thus in the end determining the outcome of the catalytic cycle (selective vs. non-selective).[40–48] The monovalent state of chromium seems to be the crucial oxidation state responsible for the selective oligomerization. The most effective synthetic route to reach this highly reactive state is to perform in situ two electron reductions of the trivalent state. This bypasses the divalent state which is thought to be responsible for non-selective behavior and whose high thermodynamic stability may pose serious selectivity problems.[49]

The chromium reduction is achieved via alkyl-aluminum based cocatalysts. The most common of these is methylaluminoxane (MAO), which is synthesized via hydrolysis of Me_3Al. The role of MAO is to enhance the Lewis acidity of the metal centre, thereby making it electrophilic towards ethylene coordination. MAO is a solution in toluene, and contains some free Me_3Al. To use this cocatalyst with an aliphatic solvent, it needs to be in the form of Me_3Al-depleted-MAO (dMAO). This is achieved by removal of solvent and Me_3Al at elevated temperatures and *in vacuo*.

1.5 Chromium Based Ethylene Tri- and Tetramerization

The discovery of the first major catalyst for selective ethylene trimerization was made by Phillips Petroleum scientists and later implemented and commercialized by Chevron Phillips. The original system had a respectable activity of 1.5 $x10^5$ g/gCr/h, but was further improved by Mitsibushi Chemical Corporation. The greatness of the catalytic cycle lies in its simplicity. The catalyst consists of a mixture of a near to stoichiometric amount of 2,5-dimethyl pyrrole ligand with chromium octanoate in the presence of diethyl aluminum chloride (DEAC) and triethyl aluminum (TEAl) as cocatalysts, forming 1-hexene with high selectivity (>95%) and activity (3.78 $x10^6$ g/gCr/h). The Chevron-Phillips system is the largest commercial system for ethylene trimerization, currently producing over 50,000 tons of 1-hexene per year.[50]

Scheme 1.4



Since the ligand system plays such a central role in the performance of selective oligomerization catalysts, it comes as no surprise that a considerable amount of ligand systems based on the largest possible variety of donor atoms have been screened. Ligand denticity is also an important issue given the particular dynamisn of this family of catalysts. The other issue is selection of appropriation functions and donor atoms for the stabilization of the lower oxidation states. To this end, many bidentate ligand systems have been studied for chromium based oligomerization. The simplest ligand is a dimethoxyethane in combination with chromium

tris(adamantanecarboxylate), aluminum *t*-butoxide and triisobutylaluminum, as developed by Briggs and coworkers of Union Carbide Corporation. Although it proved to be a trimerization catalyst, this system had low selectivity and activity and therefore was not commercialized.[51,52] Ackerman and coworkers of Exxon-Mobil also developed several bidentate ligands used with chromium showing varying degrees of activity and selectivity (Figure 1.2). Ligands **5** and **6** with methyl chromium dichloride, activated with MMAO gave both 1-hexene and 1-octene with selectivities C_6:C_8 53.4/45.7% and 63.5/35.4%, respectively. Ligands **1-4** produced 1-hexene with high selectivity as well as moderate to high activity, the highest having been observed from ligand **4**. Unfortunately, in all cases (Ligands **1-6**), a high amount of unwanted PE wax was produced, preventing the commercialization of these systems as well.[53–58] The formation of solid materials results in reactor fouling and consequent downtime and increase in operating costs, making these systems less than ideal for commercialization.

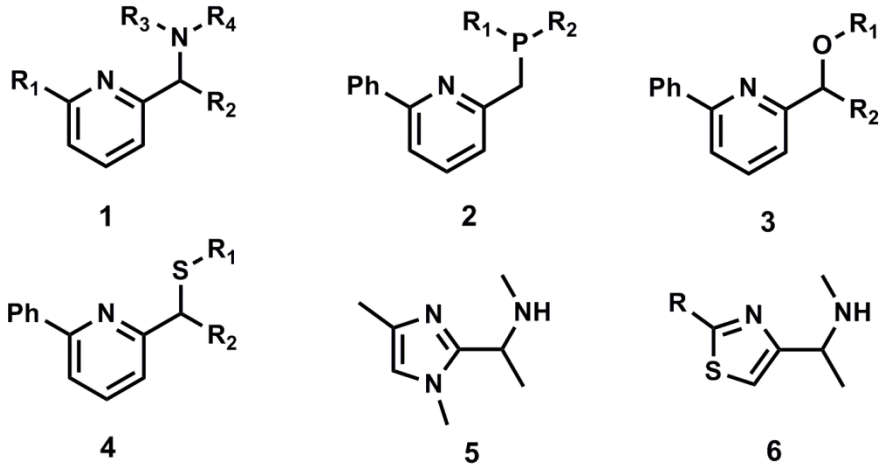


Figure 1.2: Bidentate ligands for selective oligomerization developed by Exxon-Mobil.

Highly selective oligomerization systems have been obtained by using tridentate, facial ligands. McGuinness and co-workers have reported a series of catalysts containing PNP or SNS ligand frameworks that form an octahedral geometry upon complexation with chromium

trichloride (Figure 1.3**, 7, 8**). Upon activation with MAO, these systems were found to be selective for 1-hexene (93-98%) with high activity. The SNS catalytic system showed higher selectivity (98%) and was four times as active as the PNP system. An analogue of **7** was prepared containing N-alkyl functions (**9**), however, activity and selectivity for 1-hexene decreased, indicating that the N-H function is responsible for the promising activity shown by complexes **7** and **8**. It has been suggested that the N-H function is deprotonated during activation, generating a monoanionic ligand.[40,59]

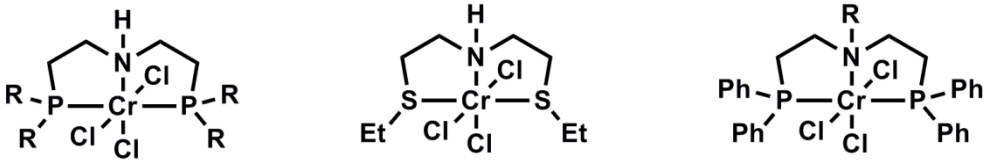


Figure 1.3: Tridentate PNP and SNS ligands developed by Sasol Technology.

The high selectivity and activity demonstrated by the SNS ligand with chromium created high interest in developing tridentate sulfur based ligands. McGuinness and co-workers have also probed variations on the PNP and SNS ligands (**7** and **8**), by preparing PSP and SPS ligand frameworks. (Figure 1.4, **10, 11**). Unfortunately, these modifications showed no improvement over the original complexes, **7** and **8.**[60] Evans and co-workers have further modified the ligand framework to contain all sulfur heteroatoms (**12**). However this too displayed lower activity and lower selectivity towards 1-hexene than Sassol's original ligands (**7** and **8**).[61] A tridentate ligand containing all phosphorous heteroatoms was developed by Amoco corporation (**13**), showing higher selectivity and activity than the previous modifications (**9-12**), however, not as high as the original SNS system (**8**). In addition, the high cost and difficulties associated with the synthesis of this ligand prevented commercialization.[62]

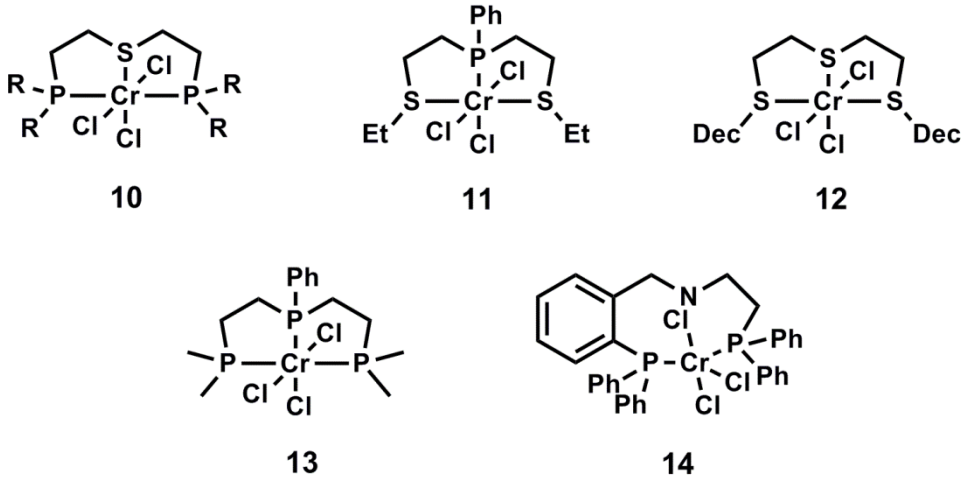


Figure 1.4: Tridentate ligands for selective ethylene oligomerization.

Bluhm and co-workers reported a tridentate PNP ligand containing a phenyl bridge between two donor atoms (**14**). When activated with MAO, very high selectivity for 1-hexene was observed (>99%), however the activity was quite low. In addition, 40% unwanted PE wax was also produced.[63] The activity of complexes **7-14** is summarized in Table 1.1.

Table 1.1: Summary of activity and selectivity of catalysts **7-14**.

#	Donor atoms	Activity (g/gCr(h))	Selectivity C_6 (%)	Reference
7	PNP	37,400	93	[40]
8	SNS	160,840	98	[40]
9	PN(R)P	920	>99	[59]
10	PSP	5,130	26	[60]
11	SPS	7,140	40	[60]
12	SSS	6,330	70	[61]
13	PPP	33,930	97	[62]
14	PNP	5,740	83	[63]

In 2002, British Petroleum reported a highly active ethylene trimerization catalyst based on a PNP ligand framework (Figure 1.5, **15)**. It was proposed that the ortho-methoxy substituents on the phenyl pendants help to stabilize monovalent chromium, allowing for this system to follow the Cr (I)/(III) dynamism, resulting in selective oligomerization (90% 1-hexene, 1,033,200 g/gCr(h)).[64] Sasol Technology investigated this system further, and found that by removing the *ortho* substituents from the phenyl groups (**16**), the selectivity of this system can be switched to 60% 1-octene, with the major by-product 1-hexene (16%).[65] Further investigation by Sasol revealed that the controlling factor in determining the C_6 *versus* C_8 selectivity was the steric interaction. The *ortho* substituents on the phenyl pendants restrict ring growth beyond the 7-membered metallacycle, resulting in only 1-hexene formation. When these substituents are removed, the 9-membered metallacyle can be form, affording 1-octene.[66]

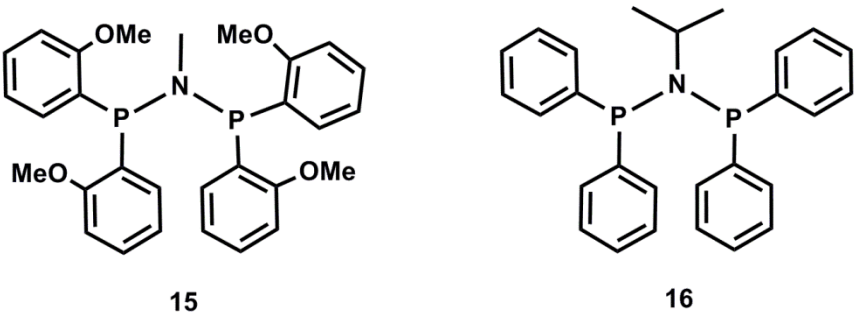


Figure 1.5: BP and Sasol's PNP ligands.

The PNP ligand framework has been further modified by altering the substituent at the central nitrogen atom (Figure 1.6). The selectivity displayed by these ligands followed the same trend: the increased steric bulk on the nitrogen atom shifted selectivity towards trimerization. Complexes **17-20** selectively produced 1-hexene, however, when the N-alkyl substituent contained branching in the α-position (**21**) the selectivity changed to 1-octene.[67–69]

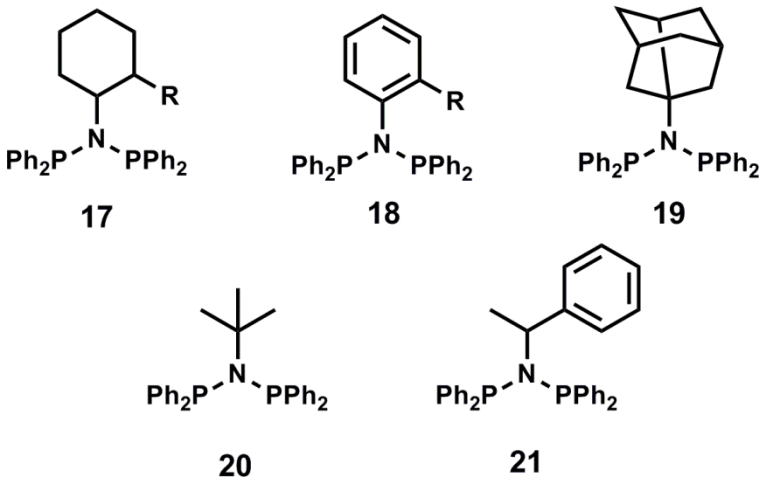


Figure 1.6: Modifications of N-substituents in PNP framework ligands.

Shell Chemicals prepared iminodiphosphine ligands which, in combination with chromium and MAO, were active tri- and tetramerization catalysts (Figure 1.7). Iminodiphosphines are known to rearrange to the PNP structure upon coordination to transition metals.[70] It was thought that this isomerisation occurred upon coordination to chromium, however, there was no improvement in selectivity or activity with this type of ligand (**22**). When an N-H group is present on one phosphorous, selective oligomerization was observed, and selectivity for 1-hexene or 1-octene was found to be dependent on the other substituent at the phosphorous. In the case of the bulky phenyl group, trimerization was observed (**23:** 87% C_6), but with the smaller group, methyl, tetramerization occurred (**24:** 82% C_8).[71,72]

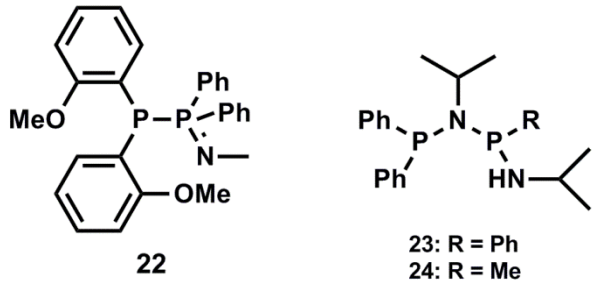


Figure 1.7: Iminodiphosphine ligands for oligomerization.

Because of the success of diphosphinoamine ligands in tetramerization, simple bidentate diphosphines were studied in combination with chromium. Figure 1.8 shows some of the diphosphine ligands developed by Sasol Technology.

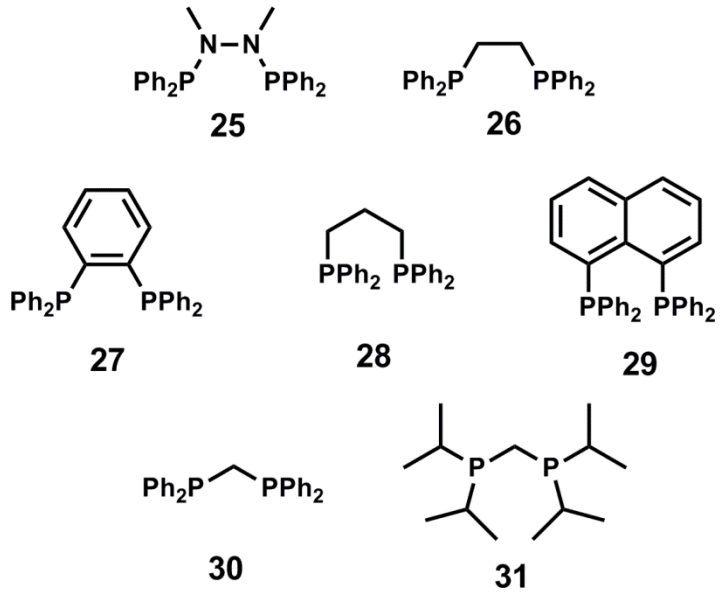


Figure 1.8: Bidentate diphosphine ligands by Sasol Technology.

The diphosphine ligand that most closely resembles the diphosphinoamine framework is ligand **30**, due to the bite angle between the phosphorous atoms. However this ligand was not effective for selective oligomerization, yielding a Schulz-Flory distribution of oligomers. This is attributed to the acidic methylene protons on the carbon bridging the two phosphorous atoms. Ligand **31**, also with a 1-carbon bridge and a bite angle comparable to that of the PNP systems, has less acidic methylene protons, and was active for tetramerization. When a 2 carbon or 2 nitrogen bridge links the phosphorous atoms (**25-27**), selectivity remained in favour of 1-octene. When the carbon bridge was increased to three carbons (**28-29**), both activity and selectivity

towards 1-octene decreased. This indicates that the length of the carbon bridge, which controls the P-Cr-P angle, influences the selectivity of a system: smaller bite angles give rise to tetramerization systems. The activity and selectivity of these diphosphine ligands is summarized in Table 1.2.

Table 1.2: Summary of activity and selectivity of ligands **25-31** with chromium.

	Activity (g/gCr(h))	**Selectivity C_6 (%)**	**Selectivity C_8 (%)**	**Reference**
25	26, 200	25	59	[73]
26	144,000	16	60	[73]
27	2,240,000	13	57	[74]
28	13,000	9	30	[74]
29	70,000	62	31	[74]
30	21,000	Schulz-Flory		[74]
31	174,000	14	62	[74]

Another bidentate ligand with two nitrogen donors was developed by our group in 2010 (Figure 1.9). The 2,2'-dipyridylamine ligand with an alkylated central nitrogen atoms shows 99% selectivity for 1-octene (**32**). Regrettably, polyethylene wax remained the major product.[75]

The original ligand was modified by adding methyl substituents at the ortho position of the pyridine rings (**33**). This modification caused the selectivity to change entirely towards 1-hexene, with the major product still PE wax.[75] This could be due to steric interactions preventing the ring growth to the 9-membered metallacycle.

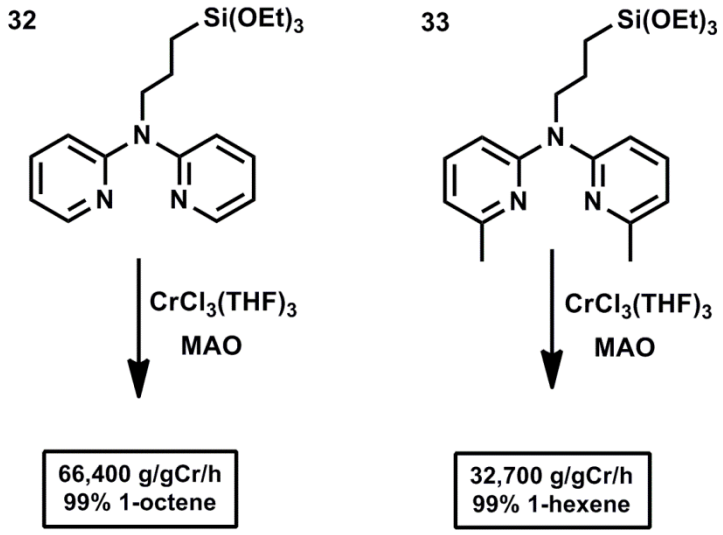


Figure 1.9: Bis-pyridine ligands for tri- and tetramerization.

Due to the high interest in PNP based ligands, recent work by our group has focused on phosphorous and nitrogen donor atoms with various pendants (Figure 1.10). Ligand **34**, with chromium and depleted MAO (dMAO), appeared to be a tri- and tetramerization system, giving C_6:C_8 = 70:30. When the carbon bridge connecting the N-P fragments was extended from 2C to 3C (**35**), the selectivity changed to 89% 1-octene.[76] Although intermediate structures were not isolated, this change in selectivity could be attributed to the decreased steric hindrance, allowing for a larger metallacycle to form.

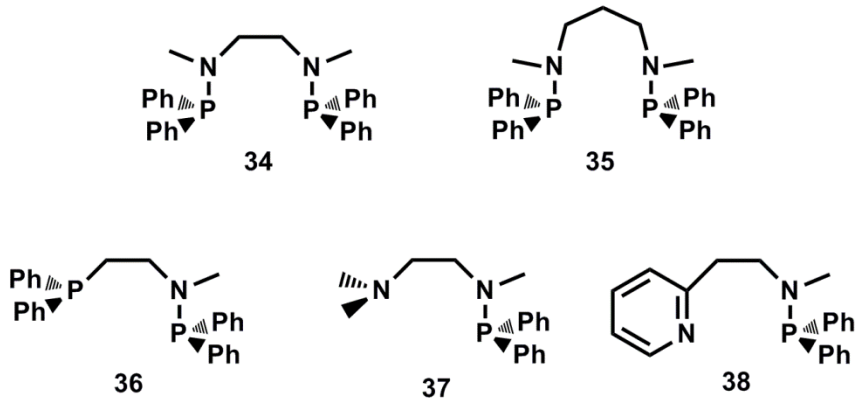


Figure 1.10: N-P ligands with modifications to the donor pendant.

In a subsequent work, while maintaining one N-P fragment, the second donor pendant was changed to diphenyl phosphine, dimethyl amine and pyridine (Figure 1.10). In the case of the phosphorous pendant (**36**), with chromium and dMAO activation, a Schulz-Flory distribution enriched in the C_6 and C_8 fragments was observed. Both nitrogen containing pendants (dimethyl amine, **37**, and pyridine, **38**), showed selective behaviour towards 1-octene, with **37** displaying the highest activity. The lower activity of **38** could be due to the high stability of the pyridine donor.[77] Oligomerization activity for ligands **34-38** is summarized in Table 1.3.

Table 1.3: Summary of activity of ligands **34-38** with chromium.

	Activity (g/gCr(h))	**Selectivity C_6 (%)**	**Selectivity C_8 (%)**	**Reference**
34	7, 200	10	89	[76]
35	6,900	70	30	[76]
36	6,700	39	32	[77]
37	12,500	11	89	[77]
38	4,500	25	75	[77]

Although there are a few catalysts for ethylene trimerization of high selectivity, there is a striking lack of tetramerization systems with comparable selectivity. Among the few known tetramerization systems, the best selectivity has been observed for aminophosphine based systems[73,77,78] as well as pyridine containing systems.[75,77] As such, we focused on developing novel aminiphosphine based or pyridine containing chromium complexes for use in selective oligomerization. In addition, the knowledge that monovalent chromium is the active species in

the redox mechanism for selective oligomerization leads to very specific ligand requirements, and so monoanionic ligands were investigated as well.

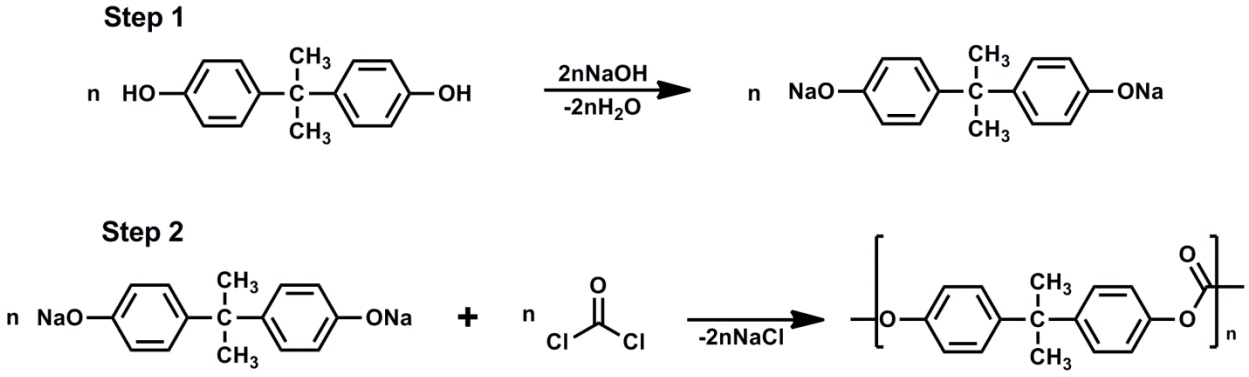
1.6 Polycarbonate overview

As mentioned in the previous section, chromium complexes are the most versatile for olefin oligomerization. On the other hand, the same category has been used for entirely different catalytic purposes such as the formation of polycarbonates via CO_2-epoxide copolymerization. Therefore, as a part of this thesis, it was thought that the same catalytic systems capable of performing ethylene oligomerization could also be screened for polycarbonate chemistry.

Polycarbonates are widely used polymers with exceptional properties. The global demand for polycarbonates exceeded 1.5 million tons in 2008, the most common type of polycarbonate being bisphenol-A polycarbonate (BPA-PC).[79]

BPA-PC was discovered in 1953 independently by both Schnell at Bayer, and Fox at General Electric.[80,81] The synthesis of BPA-PC follows the interfacial polycondensation mechanism shown in Scheme 1.5. Bisphenol A is deprotonated by NaOH, and subsequently treated with phosgene ($COCl_2$), producing a chloroformate, which is attacked by another phosgene as polymerization continues.

Scheme 1.5:



PC-BPA is a strong, stiff, hard and transparent polymer that displays high thermal stability. It maintains rigidity up to 140^{o}C and toughness down to -20^{o}C. It is an amorphous polymer with high tensile strength, up to 80 N/mm^{2}. These extraordinary characteristics make BPA-PC widely applicable for many uses.[82]

The largest application of BPA-PC is in the optical media market, including the production of computers and CDs. This is followed by sheeting and glazing applications, and electronics such as mobile phones, electrical chargers and coverings and housings for power distribution. BPA-PC has also found employment in the transportation industry for the synthesis of automotive head lamp lenses, air bag compartments, dashboards, bumpers, body panels, etc. Polycarbonates are used in household appliances, packaging materials, furniture, sporting goods and medical applications. BPA-PC is commonly used in blends, as it has a high compatibility with a range of polymers.[79]

Recently, consumer awareness has halted the use of BPA-PC in household items, from baby bottles to water dispensers, due to potential health hazards. The possibility of BPA

leaching into water at room temperature has increased the demand for an alternative to BPA-PC. In addition, the synthesis of BPA-PC is done with highly toxic phosgene which has a sinister reputation as a chemical weapon.[82,83]

The concern for environmental conservation is another factor that has influenced industrial production of many polymers. The increased consumer demand for biodegradable or recyclable products has led to the development of PC from the copolymerization of CO_2 and epoxides. This synthesis is of high interest due to the use of CO_2, an abundant, renewable, non-toxic C1 feedstock. So far, PC synthesized from the copolymerization of CO_2 and epoxides cannot match the properties of BPA-PC. However these polymers still have a variety of applications in packaging, thermoplastics, resins, safety glass, elastomers, adhesives and antifoam agents.[84,85]

1.7 CO_2-Epoxide Copolymerization: Mechanistic Considerations

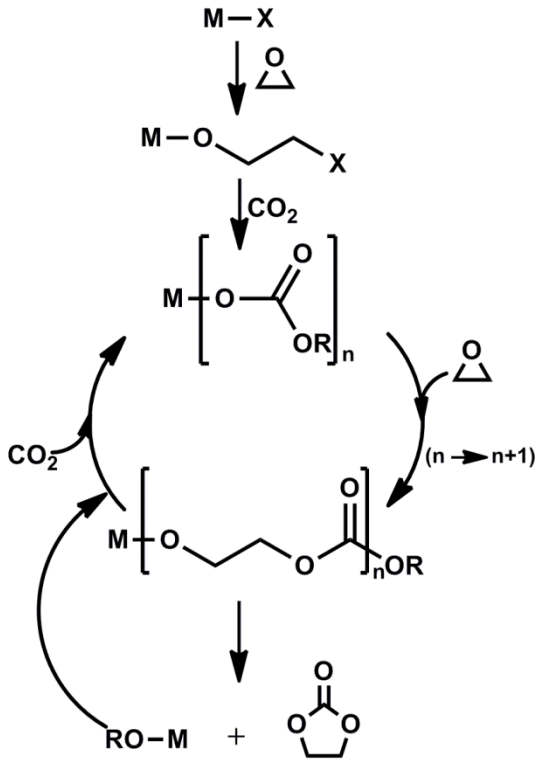
Consumer pressure for non-toxic, renewable polymeric materials has led to the development of a new synthetic procedure for PC: the copolymerization of CO_2 and epoxides. CO_2 is non-toxic, non flammable, and an abundant C1 resource, making it an ideal reagent. However, it is a thermodynamically stable molecule, a severely limiting factor for its employment. In order to overcome this obstacle, CO_2 is reacted with high-energy content reagents, including strained heterocycles such as epoxides.[85]

The reaction between CO_2 and an epoxide, propylene oxide (PO), was first discovered by Inoue and coworkers in 1969. They observed that $ZnEt_2$ in combination with a protic solvent was active for the catalysis of an alternating copolymerization reaction. The original CO_2-epoxide coupling system displayed very low activity, giving a TOF of only $0.12h^{-1}$ at 80^oC under

50 atm CO_2.[86] Inoue et. al. further investigated the $ZnEt_2$ catalyst with other solvents and cocatalysts, and were able to improve the activity only slightly, observing a TOF of 0.43 h^{-1}.[87]

Although the discovery of a catalyst for the alternating copolymerization of CO_2 and epoxides was a significant finding, the active species for the polymer formation remains unknown. Several mechanistic studies support the coordination-insertion mechanism catalyzed by Lewis acidic metal complexes, shown in Scheme 1.6. The metal halide, aryl/alkoxide or carboxylate complex initiates the copolymerization by coordinating the epoxide and opening the ring via nucleophilic attack by the initiating group, X. This results in the formation of a metal bound alkoxide. CO_2 inserts into the metal alkoxide to form a metal carbonate. The cycle propagates by the nucleophilic attack of the metal bound carbonate to a coordinated epoxide, producing a new metal alkoxide, into which CO_2 can be inserted. Multiple repetitions of this cycle leads to a copolymer with carbonate linkages.[84,85,88–91] The cycle is terminated by hydrolysis of the polymer with a proton originating from quenching with HCl/MeOH.[92] A common side reaction seen with the copolymerization of CO_2 and epoxides is the formation of cyclic polymers via the backbiting of a metal alkoxide into a carbonate linkage. (Scheme 1.6) Systems can be tuned to favour cyclic species formation by altering reaction conditions such as temperature, CO_2 pressure, cocatalyst additives and epoxide concentration.[93,94]

Scheme 1.6:

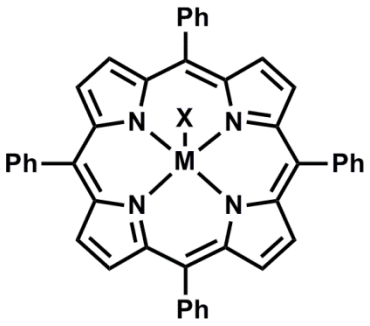


Other mechanistic considerations include regio-selectivity, stereochemistry, and polymer linkages. Ring opening of the epoxide is usually favored at the less hindered C-O bond, although regio-irregular polymers are often produced due to ring opening at either C-O bond. Ring opening usually occurs in an S_N2 type reaction resulting in an inversion of configuration and a *trans* product, although there are no reported catalysts that generate tactic polymer.[85,95,96] Ether linkages are observed as a result of two consecutive epoxide molecules inserting in a polymer chain. Catalytic systems can be tuned to favor carbonate linkages via CO_2 incorporation by changing CO_2 pressure and epoxide concentration.[85]

To date, only a few metals have been found to be active for polycarbonate catalysis, including Al, Cr, Co, Mg, Zn, Cu and Cd. Large differences in their activity have been attributed to the ligand framework.

1.8 Epoxide-CO_2 Copolymerization: Catalytic Systems

As previously mentioned, the first known catalyst for CO_2-epoxide copolymerization was the simple diethyl zinc system discovered by Inoue et al in 1969.[86] Starting in 1978, Inoue developed a series of Al and Mn catalysts with a tetraphenylporphyrin (tpp) ligand framework. (Figure 1.11).



39: M = Al, X = Cl
40: M = Al, X = OMe
41: M = Mn, X = OAc

Figure 1.11: Aluminum and manganese porphyrin complexes.

The complexes with chloride and methoxy initiating functions (**39** and **40**) reacted with PO to form poly(propylene oxide) (PPO) and poly(propylene carbonate) (PPC), respectively. The chloride derivative ring opened the epoxide at the least hindered C-O bond, giving a regio-regular polymer. When activated in the presence of ammonium or phosphonium salts, complex **39** produced a low molecular weight PPC with a narrow PDI displaying >99% carbonate linkages. Complex **40** also produced low molecular weight PPC with a narrow PDI with 40% carbonate linkages. Although these complexes had low TOFs (0.18-0.30 h^{-1}), they show the earliest example of a monodisperse polymer with a low PDI.[97]

Inoue and coworkers later developed a similar porphyrin system replacing aluminum with manganese as the active metal centre (**41**). This system reacted with cyclohexene oxide and

CO_2 to produce poly(cyclohexene carbonate) (PCHC) with a low PDI and moderate TOF of 16.3 h^{-1}. Additives to this system, such as PPh_3 or MeIm, reduced the polymerization rate of PCHC.[98]

In 2000, Beckmann and coworkers developed a series of Al-alkoxide catalysts (Figure 1.12 **42-44**) that reacted with CHO and CO_2, producing PCHC with only 20% carbonate linkages with a TOF of 2.7 h^{-1}.[99–101]

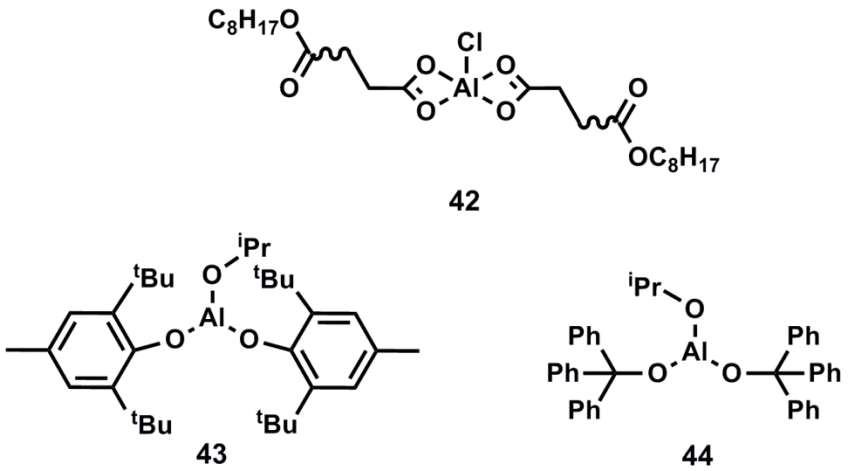


Figure 1.12: Al-alkoxide complexes for CO_2-epoxide copolymerization.

The most recent aluminum catalysts developed for CO_2-epoxide copolymerization utilize a salen ligand framework (Figure 1.13). The salen-aluminum complex **45** was able to catalyze the alternating copolymerization of ethylene oxide and CO_2 to ethylene carbonate. When quarternary ammonium salts were used as cocatalysts, the activity could be greatly improved, giving TOFs as high as 2220 h^{-1}.[102,103] In 2005, Darensbourg and coworkers investigated the activity of salen-Al complexes bearing different substituents towards propylene oxide and CO_2 copolymerization. Complex **46**, bearing electron-withdrawing nitro groups, in the presence of 4-dimethylaminopyridine (DMAP), demonstrated the highest activity for the formation of propylene carbonate, with a TOF of 32 h^{-1}.[104]

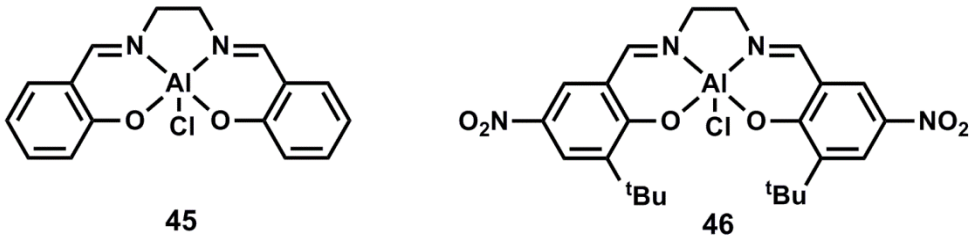


Figure 1.13: Aluminum-salen complexes.

Although aluminum complexes are active for the copolymerization of CO_2 and epoxides, they exhibit low activities and high percentages of ether linkages. The highest activity came from the salen-Al complex, and so the salen ligand was investigated further for its activity in polycarbonate chemistry.

In addition to aluminum, the salen framework has been investigated with cobalt and chromium. In 1999, Jacobsen and coworkers worked on chiral chromium-salen complexes that were effective polycarbonate catalysts for PPC.[105] Darensbourg and coworkers continued work on salen-chromium complexes, investigating a wide variety of substituents, initiating groups and cocatalysts (Figure 1.14). Chiral complexes were investigated in the hope of finding a stereoselective PC catalyst. Complex **47** was able to copolymerize CO_2 and CHO in the presence of a nucleophilic cocatalyst, MeIm. Replacing the chloride initiation group with an azide, complex **48**, improved the activity, resulting in a TOF of 1153 h^{-1}. These complexes, **47** and **48**, were also active for the copolymerization of PO and CO_2. Complex **50** showed activity towards the reaction between PO and CO_2 only, with the highest TOF of the three complexes, 192 h^{-1}. An increase in stereoselectivity was seen in the coupling of PO and CO_2 by complex **49** when activated in the presence of bulky nucleophiles such as 1,5,7-triazabicyclo-[4,4,0]-dec-5-

enes (TBDs). It is suggested that the TBD cocatalysts play a role in the ring opening of the epoxide.[89,106–108]

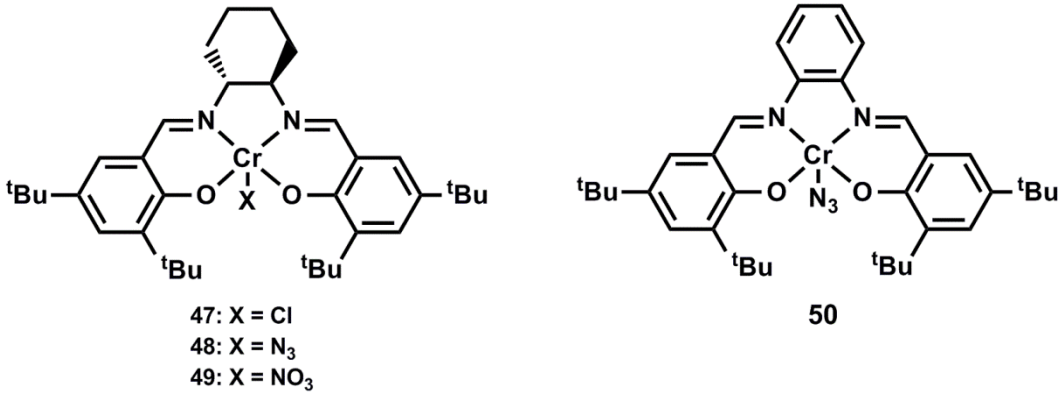


Figure 1.14: Chromium-salen complexes.

Rao and coworkers reported that reduced salen-Cr, or salan-Cr complexes, were more effective catalysts for CO_2-epoxide coupling than the corresponding salen complexes. (Figure 1.15) When activated with DMAP, the salan-Cr complexes, **52a-d**, showed up to 30 times higher activity. This difference is attributed to the reduced electrophilicity of the chromium centre due to the sp^3 hybridization of the amino donors in the salan ligand. This allows for reversible epoxide/DMAP binding.[109,110]

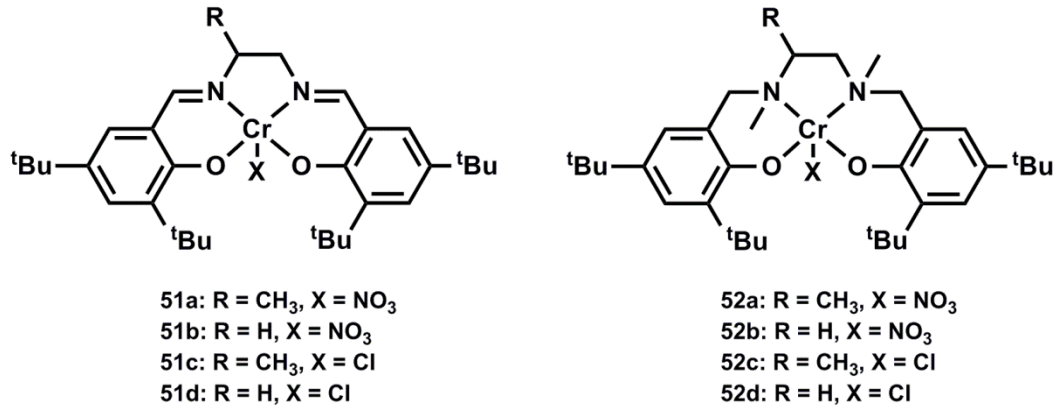
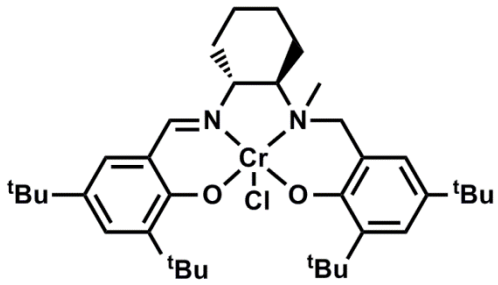


Figure 1.15: Chromium-salen and chromium salan complexes.

Because of the success of both salen-Cr and salan-Cr complexes for catalyzing copolymerization reactions, a half reduced salalen-Cr complex was investigated (Figure 1.16). When activated with cocatalyst bis(triphenylphosphine)iminium chloride ([PPN]Cl), complex **53** reacted with CHO to form PCHC with a TOF of 230 h^{-1} under 34 atm of CO_2. When the CO_2 pressure was reduced to just 1 atm, the TOF remained high, at 100 h^{-1}, an excellent activity for such mild conditions. This is likely due to the flexibility of the ligand framework, which, unlike the rigid salen ligands, can bind in both axial and equatorial sites, allowing for bidentate binding of the polymer chain, thus reducing the energy required for CO_2 insertion.[111]

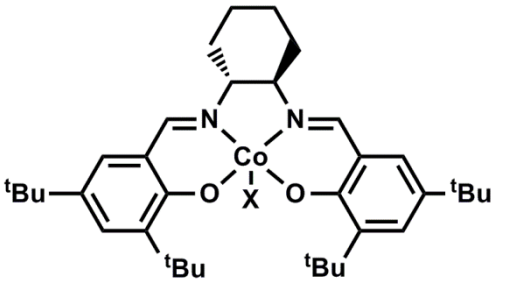


53

Figure 1.16: Chromium-salanen complex.

Chromium-salen and chromium-salan complexes have shown higher activity towards CO_2-epoxide alternating copolymerization than the aluminum complexes previously discussed, but the TOFs for these chromium complexes are considered to be moderate. Substituting chromium for cobalt as the active metal in the salen ligand framework has resulted in an increase of copolymerization activity.

The first cobalt catalyst supported by a salen ligand framework was reported by Coates and coworkers in 2003 (Figure 1.17, **54a**). The catalyst produced PPC with >99% carbonate linkages with a TOF of 70 h^{-1}. This number could be increased significantly with the addition of cocatalysts. Coates and coworkers further studied the effect of cocatalysts using complexes **54a-c.** When tested in the absence of cocatalysts, the activity was dependent on the X group to activate polymerization. The highest activity was observed from complex **54c**, a TOF of 90h^{-1}. When cocatalyst [PPN]Cl was added to the reaction mixture, the TOF increased to 620 h^{-1}. Based on GPC analysis, Coates concluded that without cocatalysts, only one polymer chain grew per cobalt centre, but when [PPN]Cl was added, two polymer chains grew per cobalt centre, due to initiation from the cocatalyst.[112,113]



54a: X = OAc
54b: X = pentafluorobenxoate
54c: X = Br

Figure 1.17: Early Cobalt-salen complexes.

High TOFs were observed from complexes **55-58** (Figure 1.18). In the presence of DMAP, complex **55** polymerized CO_2 and PO with a TOF of 501 h^{-1}, producing a polymer with a low PDI.[114] Complexes **57a-c** contain four tertiary amine cations, where complex **56** contains only two. The tertiary amine cations on pendant arms were designed to keep the anionic copolymer chains close to the metal centre, essentially incorporating a cocatalyst into the ligand

framework. These thermally robust complexes were active at high temperatures, up to 80°C. When complexes **56** and **57a-c** were tested under the same conditions, complex **57c** showed the highest activity, producing a PPC with a TOF of 26 000 h^{-1}, where as **56** had a TOF of only 3300 h^{-1}. When the loading of complex **56** was quadrupled, the activity was comparable to that of **57c**, with a TOF of 22 000 h^{-1}.[115,116] Complex **58** also demonstrated high activity for the production of PPC with a TOF of 10 880 h^{-1}. This high activity is attributed to the ability of the pendant groups to stabilize the active cobalt centre and preventing decomposition to inactive Co(II) species. With this simple modification, decomposition was prevented even at temperatures up to 100°C.[117]

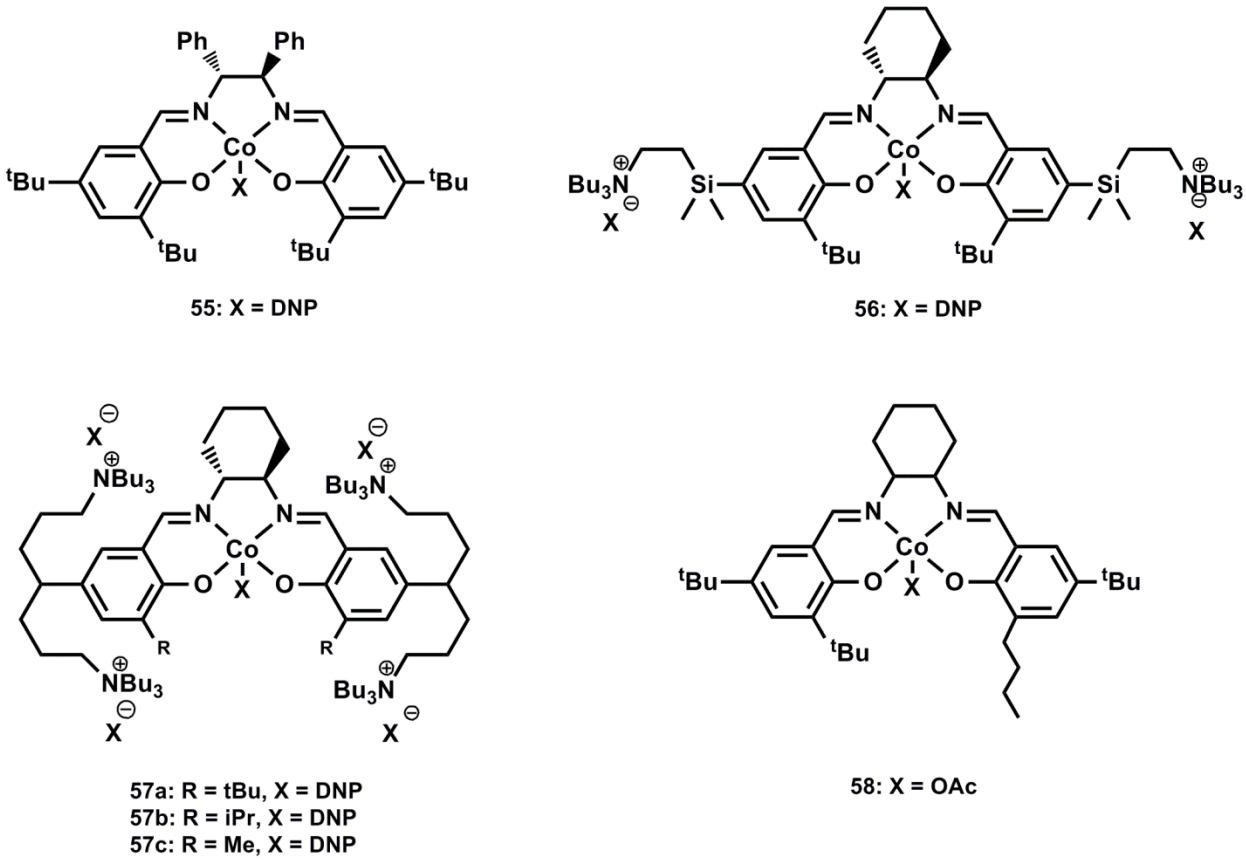


Figure 1.18: Cobalt-salen complexes

Both cobalt and chromium salen complexes showed higher polymerization activity than their aluminum counterparts, with cobalt being the most active of the three. The only other ligand frameworks that have been investigated for CO_2-epoxide copolymerizaton using cobalt or chromium as the active metal centre are porphyrin systems (Figure 1.19). Although active in the presence of DMAP, the cobalt porphyrin complex **59** was not as active as cobalt supported by salen ligands, and produced PCHC with 96% carbonate linkages with a TOF of only 21 h^{-1}. The chromium porphyrin complexes, **60a-c**, showed activity comparable to that of the chromium-salen catalysts when activated with DMAP, producing PCHC with 97% carbonate linkages at TOFs as high as 173 h^{-1}.[84,85]

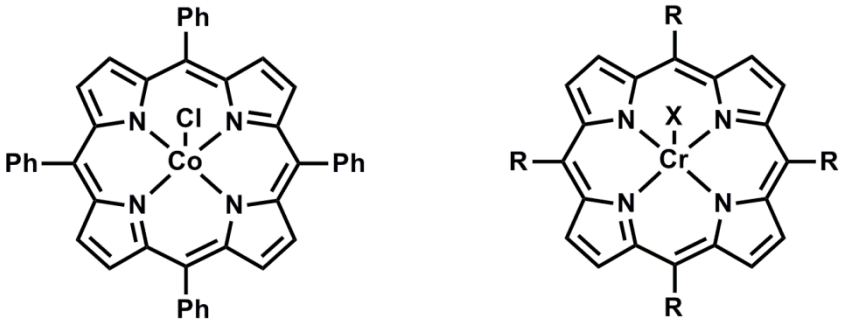


Figure 1.19: Chromium and cobalt porphyrin complexes.

Chromium and cobalt catalysts have shown much promise in the development of polycarbonate chemistry, though much further research needs to be done to find ligand frameworks capable of supporting these active metals and producing high activity. So far, the most extensively studied metal is zinc, and the ligands combined with this active metal could give some insight into ligand design for polycarbonate catalyst synthesis.

1.9 Zinc Catalysts for CO_2-epoxide Copolymerization

Since the development of the first heterogeneous zinc catalyst for polycarbonate synthesis, many other zinc complexes have been investigated, including a heterogeneous $Zn(OH)_2$/glutaric acid complex. This system is able to produce PPC at a TOF of 7.7 h^{-1}.[118] These heterogeneous systems are not easily reproducible and afford non-uniform polymeric materials, and so homogeneous catalysis is ideal for polycarbonate synthesis.[85]

A series of soluble zinc phenoxide complexes were synthesized in order to address the issues with heterogeneous catalysis (Figure 1.20). Complex **61a**, bis((2,6-diphenyl)phenoxy) zinc, produced PCHC with 91% carbonate linkages at 80^{o}C. Although the TOF was moderate, 2.4 h^{-1}, a high PDI was observed, 4.5. Subsequent work on this ligand framework investigated the steric influences of bulky substituents on copolymerization of CHO and CO_2. Studies with complexes **61b-d** revealed that bulky substituents at the *ortho* position were not required for high copolymerization activity. Complex **61d** showed the highest activity with a TOF of 9.6 h^{-1}.[119,120] Three-coordinate zinc phenoxides were investigated, **62a, b,** producing PCHC with 100% carbonate linkages and TOFs around 7.6 h^{-1}.[121] Thus, these studies showed the effectiveness of homogeneous zinc catalysts in producing polymers with high percentages of carbonate linkages and moderate TOFs, leading to the development of other soluble zinc catalysts.

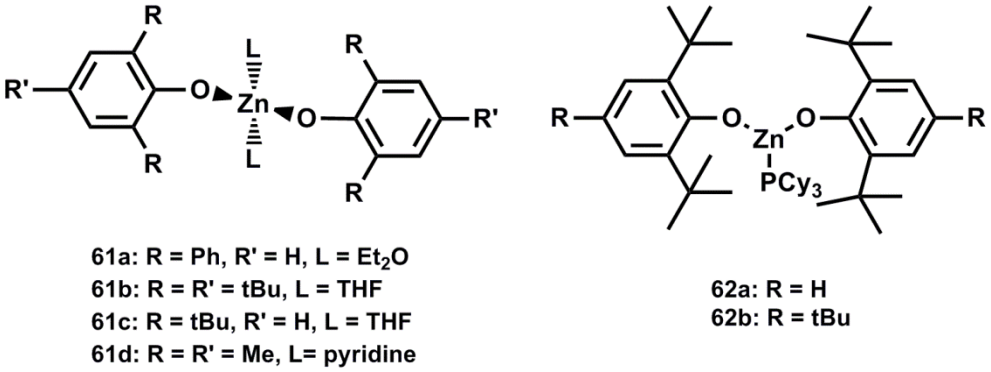


Figure 1.20: Zinc-phenoxide complexes.

The success of the zinc-phenoxide compounds in CO_2-epoxide copolymerization led Darensbourg and coworkers to develop a series of bis(salicyclaldiminato)-zinc complexes (Figure 1.21). Complex **63a** displayed the highest activity for the copolymerization of CHO and CO_2, producing PCHC with >99% carbonate linkages and moderate TOF, 6.9 h^{-1}, but unfortunately with a high PDI, 10.3.[122]

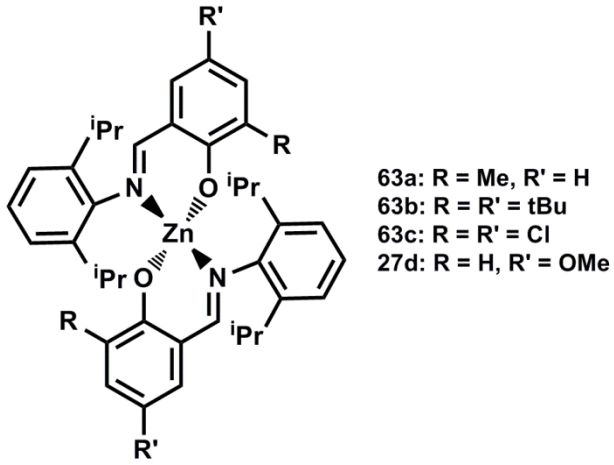


Figure 1.21: bis(salicyclaldiminato)-zinc complexes.

Hampel and coworkers reported complexes of quinoxaline-derivative of zinc, (Figure 1.22) once again, the success of the zinc phenoxide complexes having been the rationale for these attempts. However, the activities with TOFs of 4.9 and 3.6 h^{-1}, respectively were disappointingly low.[85]

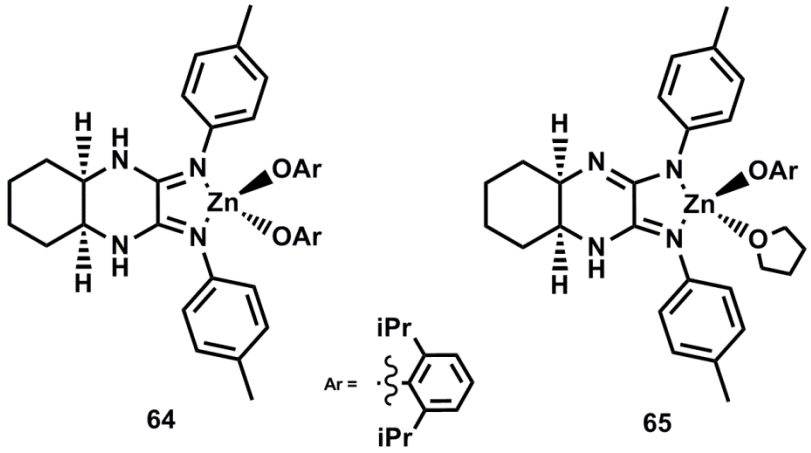


Figure 1.22: Quinoxaline zinc complexes.

In 2000, Kim and coworkers developed dimeric pyridinium alkoxy zinc dibromides (Figure 1.23) which converted PO and CO_2 to cyclic PC with high TOFs 340 and 530 h^{-1}, respectively. These complexes were also able to convert EO and CO_2 to cyclic EC with high TOFs of 1200 and 1450 h^{-1}, respectively. Complex **66c** investigated the effect of electron withdrawing groups on the complex, and it was discovered that while EWG decreased catalytic activity, EDG promoted polymerization. (Me > H > Cl) Complexes **67a** and **b** showed almost identical catalytic activity as **66a** and **b** for both PC and EC, indicating the same active species for both complexes.

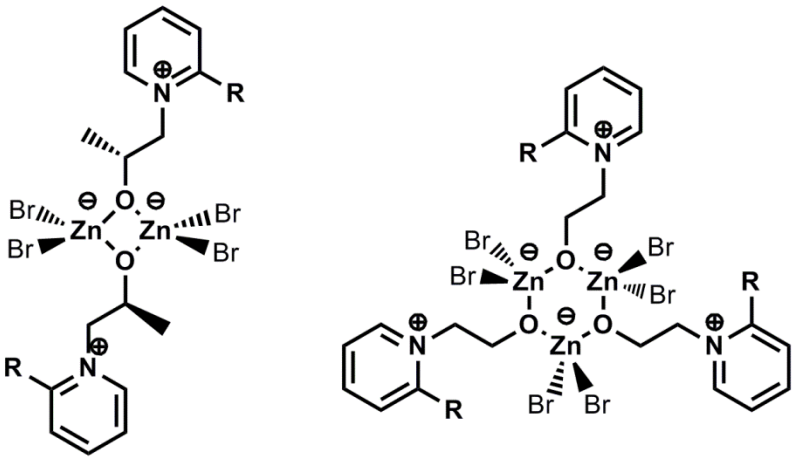
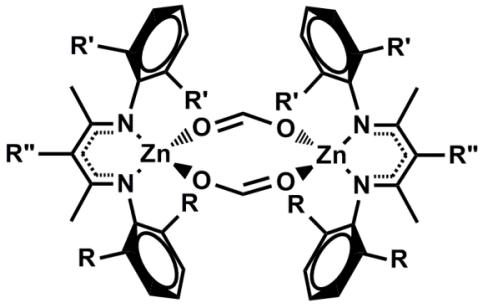


Figure 1.23: Pyridinium alkoxy zinc dibromides.

Coates et al developed a series of β-diiminate (bdi) zinc catalysts (Figure 1.24) that are highly active for epoxide-CO_2 copolymerization at low pressures and temperatures (7 atm, 50^{o}C). Several features were incorporated into the ligand design, including initiator groups, and steric and electronic properties. Solution state ^{1}H NMR studies have shown that compounds **68a** and **69b** were in equilibrium between the monomeric and dimeric state, which **68b, 69a** and **69c** were exclusively dimeric.[123,124] In addition, they found that modifications at the *ortho* substituents influenced polymerization activity greatly. Bulkier groups at the *ortho* position resulted in higher activity. The unsymmetrical *β*-diiminate zinc complexes, **68c** and **d,** were highly active polymerization catalysts, and the asymmetric ligand combined with an electron withdrawing *cyano* substituent, produced PCHC with 90% carbonate linkages with the highest TOF, 917 h^{-1}.[125]



68a: R = R' = iPr, R" = H
68b: R = R' = Et, R" = H
68c: R = iPr, R' = Et, R" = H
68d: R = iPr, R' = Et, R" = CN

69a: R = Et, R' = Me
69b: R = iPt, R' = iPr
69c: R = Et, R' = iPt

Figure 1.24: β-diiminate zinc catalysts

In 2005, Lee and coworkers developed a series of zinc anilidoaldimin complexes (Figure 1.25) based on the bdi complexes of Coates et al. Bulky R groups on the terminal phenyl rings (**70c** and **e**) increased polymerization activity, a finding consistent with that of the bdi complexes. A fluorinated analogue, **70g**, was later synthesized, showing 2.5 times greater activity, with a high TOF of 785 h^{-1}. This increase in activity is attributed to the electron withdrawing effect of the fluorine, thereby reducing the electron density at the zinc centre, facilitating the bonding of CO_2 and epoxides.[126]

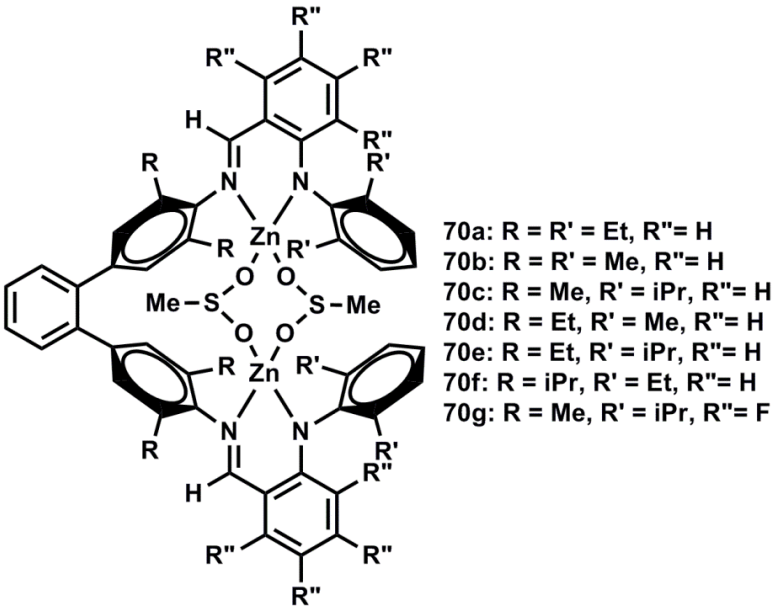


Figure 1.25: Zinc anilidoaldimin complexes.

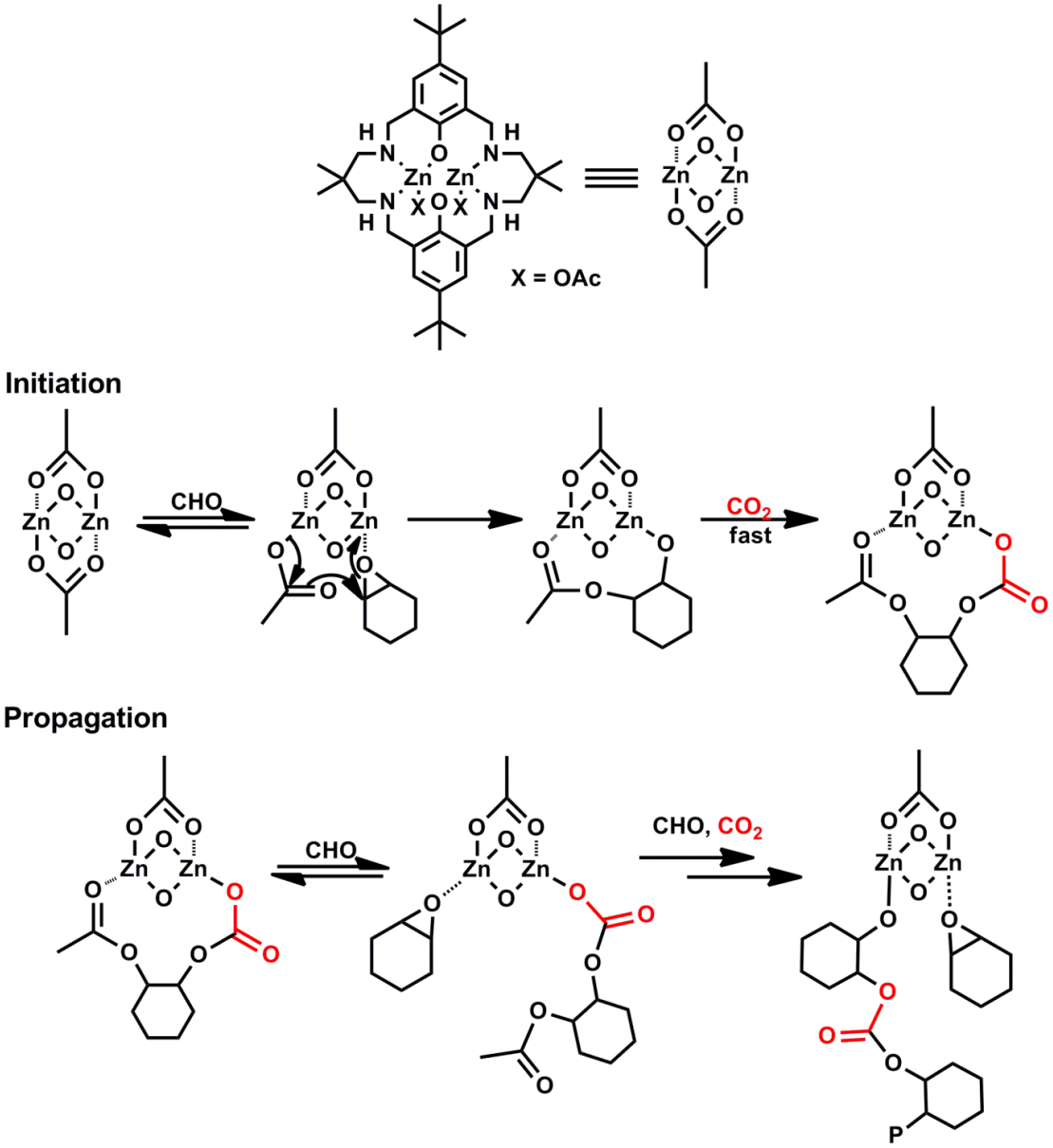
Because of the high activities of many bimetallic zinc species, a bimetallic mechanism for the copolymerization of CO_2 and epoxides was hypothesized. Williams and coworkers have championed this field by developing a dizinc complex and thoroughly elucidating the mechanism.

1.10 CO_2-epoxide Copolymerization: Bimetallic Mechanism

A dizinc complex supported by a macrocyclic ligand as highlighted in Scheme 1.7, shows a record activity for the copolymerization of CO_2 and CHO at low CO_2 pressures. The polymer produced contained >99% carbonate linkages, a narrow PDI and the system had TOFs up to 140 h^{-1}.[127] Recent studies with bimetallic species, particularily dizinc systems, have shown excellent activity for CO_2-epoxide copolymerization, leading to the hypothesis of a bimetallic mechanism. Ancillary ligands that are capable of binding two active metals in close proximity are naturally of

great interest for this purpose, and Williams and coworkers have carried out extensive experimental and computational investigations of a particular dizinc complex in order to gain firm mechanistic insight. Based on these studies, and particularly on kinetic evidences,[128,129] they have proposed a bimetallic mechanism illustrated in Scheme 1.7. The process is initiated by the coordination of cyclohexene oxide at one of the zinc centres. This is the rate determining step. Nucleophilic attack of the initiating group, in this case an acetate ligand, opens the CHO ring, forming a zinc alkoxide species. A molecule of CO_2 then inserts into the Zn-alkoxide bond to form Zn-carbonate in a subsequent rapid step. The second acetate ligand is bonded to both zinc centres and functions to keep the active metal sites in an octahedral geometry and maintain a neutral charge balance for the duration of the reaction. The polymerization continues with the carbonate species ring opening another coordinate CHO, forming a new Zn-alkoxide. Again, CO_2 rapidly inserts into the Zn-alkoxide, thus closing the catalytic cycle.[129]

Scheme 1.7



Cocatalysts play an important role in both the monometallic and bimetallic proposed mechanisms. A strongly donating cocatalyst coordinates to the metal centre, weakening the Cr-Nu bond, and promoting dissociation of the anionic ligand, a step required for the initiation of polymerization. Neutral cocatalysts, such as 4-dimethylaminopyridine (DMAP) or N-methylimidazole (MeIm) weakly coordinate to the metal centre, while anionic cocatalysts, such

as bis(triphenylphosphine)iminim chloride (PPN^+Cl^-), give strong binding. In addition, anionic cocatalysts are able to participate in the ring opening of a coordinated epoxide via nucleophilic attack. For this reason, anionic cocatalysts are often more effective for CO_2-epoxide copolymerization.[106,107,130]

1.11 Thesis Aim

This thesis work focuses on the development of chromium catalysts with the potential for selective ethylene tetramerization by using aminophosphine based or pyridine containing ligands. As seen in the literature, these types of ligands have shown promising activity towards selective oligomerization.[73,75,77,78,131] In addition, monoanionic ligands with chromium have been investigated in an attempt to stabilize the monovalent chromium active species in the redox mechanism for selective ethylene oligomerization. These catalysts were tested, and their oligomerization activity and selectivity will be described in Chapters 2-3.

So far, catalysts for the copolymerization of CO_2 and epoxides are scarce, but effective. Cr-porphyrin[132] and cr-salen complexes[88] are the only reported chromium catalysts for polycarbonate synthesis from CO_2 and epoxides. These catalysts have shown promising activity, producing polycarbonates with high %carbonate linkages, moderate to high TOFs and molecular weights in the low-moderate range. Because chromium catalysts have been promising thus far in the literature, the chromium catalysts developed for ethylene oligomerization were screened for this type of polymerization as well. These catalysts showed promising activity, as outlined in Chapter 4, and have indicated that chromium complexes should be explored further for the copolymerization of CO_2 and epoxides.

1.12 References

(1) Bhat, S.; Rai, R.; Krishnamurthy, S.; Tyagi, S.; Volkers, A. (SABIC). WO2009057025, 2009.

(2) Ullmann, F. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley Online Library, 1985.

(3) Kaminsky, W. *Catalysis Today* **2005**, *62*, 23–34.

(4) McGuinness, D. S. *Chemical Reviews* **2011**, *111*, 2321–2341.

(5) Tornqvist, E. G. M.; Richardson, J. T.; Looney, R. W.; Wilchinsky, Z. W. *Journal of Catalysis* **1967**, *8*, 189–196.

(6) Natta, G.; Corradini, P.; Allegra, G. *Journal of Polymer Science* **1961**, *51*, 399–410.

(7) Chen, E. Y.; Marks, T. J. *Chemical Reviews* **2000**, *100*, 1391–1434.

(8) Arlman, E. J.; Cossee, P. *Journal of Catalysis* **1964**, *3*, 99–104.

(9) Cossee, P. *Journal of Catalysis* **1964**, *3*, 80–88.

(10) Albahily, K.; Licciulli, S.; Gambarotta, S.; Korobkov, I.; Chevalier, R.; Schuhen, K.; Duchateau, R. *Organometallics* **2011**, *30*, 3346–3352.

(11) Agapie, T. *Coordination Chemistry Reviews* **2011**, *255*, 861–880.

(12) Tomov, A. K.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. J. *Journal of the American Chemical Society* **2006**, *128*, 7704–7705.

(13) Vogt, D. In *Applied Homogeneous Catalysis with Organometallic Compounds*; Cornils, B., Herrmann, W. A., Ed.; Wiley Online Library: Weinheim, Germany, 2000; pp. 245–258.

(14) Wilke, G. *Angewandte Chemie International Edition* **1988**, *27*, 185–206.

(15) Schulz, G. . *Zeitschrift für physikalische Chemie* **1935**, *30*, 379–398.

(16) Keim, W.; Schulz, R. P. *Journal of Molecular Catalysis* **1994**, *92*, 21–33.

(17) Flory, J. *Journal of the American Chemical Society* **1936**, *58*, 1877–1885.

(18) Keim, W. *Angewandte Chemie International Edition* **1990**, *29*, 235–244.

(19) Bestrnann, H. J.; Lienerr, J.; Mott, L.; Liehigs, J.; Chem, A.; Keim, B. W.; Kowaldt, F. H.; Goddard, R.; Kriiger, C. *Angewandte Chemie International Edition* **1978**, *06*, 466–467.

(20) Miiller, U.; Keim, W.; Kriiger, C.; Betz, P. *Angewandte Chemie International Edition* **1989**, *8*, 1011–1013.

(21) Köhn, R. D.; Haufe, M.; Kociok-Köhn, G.; Grimm, S.; Wasserscheid, P.; Keim, W. *Angewandte Chemie International Edition* **2000**, *39*, 4337–4339.

(22) Keim, B. W.; Appel, R.; Storeck, A.; Kriiger, C.; Goddard, R. *Angewandte Chemie International Edition* **1981**, *20*, 116–117.

(23) Keim, W. *Annals New York Academy of Science* **1983**, 191–200.

(24) Keim, W.; Behr, A.; Limbacker, B. *Angewandte Chemie International Edition* **1983**, *95*, 655–660.

(25) Keim, W.; Behr, A.; Gruber, B.; Hoffrnann, B.; Kowaldt, F. H.; Kurschner, U.; Limbacker, B.; Sistig, F. P. *Organometallics* **1986**, *5*, 2356–2359.

(26) Keim, W. *Journal of Molecular Catalysis* **1989**, *52*, 19–25.

(27) Lutz, E. F. (Shell Oil). US4528416A, 1985.

(28) Lutz, E. F.; Gautier, P. A. (Shell Oil). EP0177999A1, 1986.

(29) Skupinska, J. *Chemical Reviews* **1991**, *91*, 613–648.

(30) Wass, D. F. *Dalton Transactions* **2007**, 816–819.

(31) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *Journal of Organometallic Chemistry* **2004**, *689*, 3641–3668.

(32) Briggs, J. R. *Journal of the Chemical Society Chemical Communications* **1989**, 674.

(33) Chauvin, Y. *Angewandte Chemie International Edition* **2006**, *45*, 3740–3747.

(34) Tobisch, S. *Organometallics* **2007**, *26*, 6529–6532.

(35) Tobisch, S. *Dalton Transactions* **2008**, 2120–2127.

(36) Manyik, R.; Walker, W.; Wilson, T. *Journal of Catalysis* **1977**, *47*, 197–209.

(37) Agapie, T.; Labinger, J. a; Bercaw, J. E. *Journal of the American Chemical Society* **2007**, *129*, 14281–95.

(38) Agapie, T.; Schofer, S. J.; Labinger, J. a; Bercaw, J. E. *Journal of the American Chemical Society* **2004**, *126*, 1304–5.

(39) McGuinness, D. S.; Suttil, J. a.; Gardiner, M. G.; Davies, N. W. *Organometallics* **2008**, *27*, 4238–4247.

(40) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chemical Communications* **2003**, *49*, 334–335.

(41) Zhang, J.; Braunstein, P.; Hor, T. S. A. *Organometallics* **2008**, *27*, 4277–4279.

(42) Peitz, S.; Peulecke, N.; Aluri, B. R.; Hansen, S.; Müller, B. H.; Spannenberg, A.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M.; Wöhl, A.; Müller, W. *European Journal of Inorganic Chemistry* **2010**, *8*, 1167–1171.

(43) Aluri, B. R.; Peulecke, N.; Peitz, S.; Spannenberg, A.; Müller, B. H.; Schulz, S.; Drexler, H.-J.; Heller, D.; Al-Hazmi, M. H.; Mosa, F. M.; Wöhl, A.; Müller, W.; Rosenthal, U. *Dalton Transactions* **2010**, *39*, 7911–7920.

(44) Trimerization, C. E.; Rensburg, W. J. Van; Steynberg, J. P.; Stark, K. B.; Huyser, J. J.; Steynberg, P. J. *Organometallics* **2004**, *23*, 1207–1222.

(45) Elowe, P. R.; McCann, C.; Pringle, P. G.; Spitzmesser, S. K.; Bercaw, J. E. *Organometallics* **2006**, *25*, 5255–5260.

(46) Bhaduri, S.; Mukhopadhyay, S.; Kulkarni, S. a. *Journal of Organometallic Chemistry* **2009**, *694*, 1297–1307.

(47) Beweries, T.; Fischer, C.; Peitz, S.; Burlakov, V. V; Arndt, P.; Baumann, W.; Spannenberg, A.; Heller, D.; Rosenthal, U. *Journal of the American Chemical Society* **2009**, *131*, 4463–9.

(48) Emrich, R.; Heinemann, O.; Jolly, P. W.; Kru, C.; Verhovnik, G. P. J. *Organometallics* **1997**, *16*, 1511–1513.

(49) Vidyaratne, I.; Nikiforov, G. B.; Gorelsky, S. I.; Gambarotta, S.; Duchateau, R.; Korobkov, I. *Angewandte Chemie International Edition* **2009**, *48*, 6552–6556.

(50) Araki, Y.; Nakamura, K.; Nanba, Y.; Okano, T. (Mitsubishi Chemical Corporation). US 5856612, 1999.

(51) Briggs, J. R. (Union Carbide Corporation). US4668838, 1987.

(52) Levine, Isaac, J.; Karol, F. J. (Union Carbide Corporation). US4777315, 1988.

(53) Ackerman, L. J.; Diamond, G. M.; Hall, K. A.; Longmire, J. M.; Micklatcher, M. (Exxon-Mobil). WO2008085655, 2008.

(54) Ackerman, L. J.; Diamond, G. M.; Hall, K. A.; Longmire, J. M.; Murphy, V. J.; Nava-Salgado, V. . (Exxon-Mobil). WO2008085653, 2008.

(55) Ackerman, L. J.; Diamond, G. M.; Hall, K. A.; Longmire, J. M.; Murphy, V. J.; Verdugo, D. (Exxon-Mobil). WO2008085659, 2008.

(56) McConville, D. H.; Ackerman, L. J.; Li, R. T.; Bei, X.; Kuchta, M. C.; Boussie, T. R.; Walzer, J. F.; Diamond, G. M.; Rix, F. C.; Hall, K. A.; La Pointe, A. M.; Longmire, J. M.; Murphy, V. J.; Sun, P.; Verdugo, D.; Schofer, S.; Dias, E. (Exxon-Mobil). WO2006099053, 2006.

(57) Ackerman, L. J.; Bei, X.; Boussie, T. R.; Diamond, G. M.; Hall, K. A.; La Pointe, A. M.; Longmire, J. M.; Murphy, V. J.; Verdugo, D.; Schofer, S.; Dias, E.; McConville, D. H.; Li, R. T.; Walzer, J. F.; Rix, F. C.; Kuchta, M. C. (Exxon-Mobil). WO2006096881, 2006.

(58) Ackerman, L. J.; Diamond, G. M.; Hall, K. A.; Longmire, J. M.; Murphy, V. J.; Verdugo, D. (Exxon-Mobil). WO2008085658, 2008.

(59) Mcguinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552–556.

(60) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *Journal of the American Chemical Society* **2003**, *125*, 5272–5273.

(61) Moulin, J. O.; Evans, J.; McGuinness, D. S.; Reid, G.; Rucklidge, A. J.; Tooze, R. P.; Tromp, M. *Dalton Transactions* **2008**, *3*, 1177–1185.

(62) Wu, F.-J. (Amoco Corporation). US5811618, 1998.

(63) Bluhm, M. E.; Walter, O.; Döring, M. *Journal of Organometallic Chemistry* **2005**, *690*, 713–721.

(64) Carter, A.; Cohen, S. a; Cooley, N. a; Murphy, A.; Scutt, J.; Wass, D. F. *Chemical Communications* **2002**, *3*, 858–9.

(65) Blann, K.; Bollmann, A.; Dixon, J. T.; Neveling, A.; Morgan, D. H.; Maumela, H.; Otto, S.; Pepler, L.; Killian, E.; Hess, F. M.; Mahomed, H.; Overett, M. J. (Sasol Technology). WO2004056479A1.

(66) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. *Chemical Communications* **2005**, 620–1.

(67) Blann, K.; Bollmann, a; Debod, H.; Dixon, J.; Killian, E.; Nongodlwana, P.; Maumela, M.; Maumela, H.; Mcconnell, a; Morgan, D. *Journal of Catalysis* **2007**, *249*, 244–249.

(68) Killian, E.; Blann, K.; Bollmann, A.; Dixon, J. T.; Kuhlmann, S.; Maumela, M. C.; Maumela, H.; Morgan, D. H.; Nongodlwana, P.; Overett, M. J.; Pretorius, M.; Höfener, K.; Wasserscheid, P. *Journal of Molecular Catalysis A: Chemical* **2007**, *270*, 214–218.

(69) Jiang, T.; Zhang, S.; Jiang, X.; Yang, C.; Niu, B.; Ning, Y. *Journal of Molecular Catalysis A: Chemical* **2008**, *279*, 90–93.

(70) Fei, Z.; Scopelliti, R.; Dyson, P. J. *European Journal of Inorganic Chemistry* **2004**, *2004*, 530–537.

(71) Fritz, P. M.; Bolt, H.; Wohl, A.; Muller, W.; Winkler, F.; Wellenhofer, A.; Rosenthal, U.; Hapke, M.; Peulecke, N.; Al-Hazmi, M. H.; Aliyev, V. O.; Mosa, F. M. (Linde and Sabic). WO2009006979, 2009.

(72) Aliyev, V. O.; Al-Hazmi, M. H.; Mosa, F. M.; Rosenthal, U.; Muller, B. H.; Hapke, M.; Peulecke, N.; Wohl, A.; Fritz, P. M.; Bolt, H.; Muller, W.; Winkler, F.; Wellenhofer, A. (Linde and Sabic). WO2009121456, 2009.

(73) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.; Wasserscheid, P.; Kuhlmann, S. *Journal of the American Chemical Society* **2004**, *126*, 14712–14713.

(74) Overett, M. J.; Blann, K.; Bollmann, A.; De Villiers, R.; Dixon, J. T.; Killian, E.; Maumela, M. C.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Rucklidge, A.; Slawin, A. M. Z. *Journal of Molecular Catalysis A: Chemical* **2008**, *283*, 114–119.

(75) Licciulli, S.; Thapa, I.; Albahily, K.; Korobkov, I.; Gambarotta, S.; Duchateau, R.; Chevalier, R.; Schuhen, K. *Angewandte Chemie International Edition* **2010**, *49*, 9225–9228.

(76) Shaikh, Y.; Albahily, K.; Sutcliffe, M.; Fomitcheva, V.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angewandte Chemie International Edition* **2012**, *51*, 1366–1369.

(77) Shaikh, Y.; Gurnham, J.; Albahily, K.; Gambarotta, S.; Korobkov, I. *Organometallics* **2012**, *31*, 7427–7433.

(78) Dulai, A.; McMullin, C. L.; Tenza, K.; Wass, D. F. *Organometallics* **2011**, *30*, 935–941.

(79) (British Plastics Organization) In *Plastepedia*; 2008.

(80) Christopher, W. F.; Fox, D. W. *Polycarbonates*; Reinhold Publishing: New York, 1962.

(81) Schnell, H. In *Polymer Reviews*; Interscience Publishers: New York, 1964.

(82) Ullmann, F. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley Online Library, 1985; pp. 603–611.

(83) Crandall, J. . Phosgene Toxicity http://emedicine.medscape.com/article/832454-overview (accessed Jun 8, 2013).

(84) Kember, M. R.; Buchard, A.; Williams, C. K. *Chemical Communications* **2011**, *47*, 141–163.

(85) Coates, G. W.; Moore, D. R. *Angewandte Chemie International Edition* **2004**, *43*, 6618–6639.

(86) Inoue, S.; Tsuruta, T.; Koinuma, H. *Journal of Polymer Science Part B* **1969**, *7*, 287–292.

(87) Kobayashi, M.; Inoue, S.; Tsuruta, T. *Journal of Polymer Science Chemical Edition* **1973**, *11*, 2383–2385.

(88) Darensbourg, D. J. *Chemical Reviews* **2007**, *107*, 2388–410.

(89) Darensbourg, D. J.; Yarbrough, J. C. *Journal of the American Chemical Society* **2002**, *124*, 6335–6342.

(90) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Journal of the American Chemical Society* **1998**, *120*, 11018–11019.

(91) Clements, J. H. *Industrial & Engineering Chemistry Research* **2003**, *42*, 663–674.

(92) Van Meerendonk, W. J.; Duchateau, R.; Koning, C. E.; Gruter, G.-J. M. *Macromolecules* **2005**, *38*, 7306–7313.

(93) Gorecki, P.; Kuran, W. *Journal of Polymer Science Part C* **1985**, *23*, 299–304.

(94) Kuran, W.; Listos, T. *Macromolecular Chemistry and Physics* **1994**, *195*, 1011–1015.

(95) Kuran, W.; Listos, T. *Macromolecular Chemistry and Physics* **1994**, *195*, 977–984.

(96) Inuoe, S.; Koinuma, H.; Yokoo, Y.; Tsuruta, T. *Macromolecular Chemistry* **1971**, *143*.

(97) Takeda, N.; Inoue, S. *Macromolecular Chemistry* **1978**, *179*, 1377–1381.

(98) Sugimoto, H.; Ohshima, H.; Inoue, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2003**, *41*, 3549–3555.

(99) Sarbu, T.; Styranec, T.; Beckman, E. J. *Nature* **2000**, *405*, 165–168.

(100) Sarbu, T.; Beckman, E. J. *Macromolecules* **1999**, *32*, 6904–6912.

(101) Sarbu, T.; Styranec, T.; Beckman, E. J. *Industrial & Engineering Chemistry Research* **2000**, *39*, 4678–4683.

(102) Lu, X.; Feng, J.; He, R. *Applied Catalysis A: General* **2002**, *234*, 25–33.

(103) Lu, X.; He, R.; Bai, C. *Journal of Molecular Catalysis A: Chemical* **2002**, *186*, 1–11.

(104) Darensbourg, D. J.; Billodeaux, D. R. *Inorganic chemistry* **2005**, *44*, 1433–42.

(105) Jacobsen, E.; Tokunaga, M.; Larrow, J. Chiral Chromium salen for PPC. WO 0094632000, 1999.

(106) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorganic Chemistry* **2004**, *43*, 1831–3.

(107) Darensbourg, D. J.; Mackiewicz, R. M. *Journal of the American Chemical Society* **2005**, *127*, 14026–14038.

(108) Darensbourg, D. J.; Mackiewicz, R. M.; Billodeaux, D. R. *Organometallics* **2005**, *24*, 144–148.

(109) Li, B. O.; Wu, G.; Ren, W.; Wang, Y.; Rao, D.; Lu, X. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, *46*, 6102–6113.

(110) Rao, D.-Y.; Li, B.; Zhang, R.; Wang, H.; Lu, X.-B. *Inorganic chemistry* **2009**, *48*, 2830–6.

(111) Nakano, K.; Nakamura, M.; Nozaki, K. *Macromolecules* **2009**, *42*, 6972–6980.

(112) Qin, Z.; Thomas, C. M.; Lee, S.; Coates, G. W. *Angewandte Chemie (International ed. in English)* **2003**, *42*, 5484–5487.

(113) Lu, X.-B.; Wang, Y. *Angewandte Chemie (International ed. in English)* **2004**, *43*, 3574–3577.

(114) Niu, Y.; Zhang, W.; Pang, X.; Chen, X.; Zhuang, X.; Jing, X. *Journal of Polymer Science Part A: Polymer Chemistry* **2007**, *45*, 5050–5056.

(115) Noh, E. K.; Na, S. J.; S, S.; Kim, S.-W.; Lee, B. Y. *Journal of the American Chemical Society* **2007**, *129*, 8082–8083.

(116) Na, S. J.; S, S.; Cyriac, A.; Kim, B. E.; Yoo, J.; Kang, Y. K.; Han, S. J.; Lee, C.; Lee, B. Y. *Inorganic chemistry* **2009**, *48*, 10455–10465.

(117) Ren, W.-M.; Liu, Z.-W.; Wen, Y.-Q.; Zhang, R.; Lu, X.-B. *Journal of the American Chemical Society* **2009**, *131*, 11509–11518.

(118) Ree, M.; Bae, J. Y.; Jung, J. H.; Shin, T. J. *Journal of Polymer Science Part A: Polymer Chemistry* **1998**, *37*, 1863–1876.

(119) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. a.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *Journal of the American Chemical Society* **1999**, *121*, 107–116.

(120) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *Journal of the American Chemical Society* **2000**, 12487–12496.

(121) Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. *Inorganic Chemistry* **2000**, *39*, 1578–1585.

(122) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. *Inorganic Chemistry* **2001**, 986–993.

(123) Cheng, M.; Darling, N. a.; Lobkovsky, E. B.; Coates, G. W. *Chemical Communications* **2000**, 2007–2008.

(124) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *Journal of the American Chemical Society* **2001**, *123*, 8738–8749.

(125) York, N.; Bastide, J.; Hamelin, J.; Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angewandte Chemie International Edition* **2002**, *41*, 2599–2602.

(126) Lee, B. Y.; Kwon, H. Y.; Lee, S. Y.; Na, S. J.; Han, S.-I.; Yun, H.; Lee, H.; Park, Y.-W. *Journal of the American Chemical Society* **2005**, *127*, 3031–3037.

(127) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angewandte Chemie International Edition* **2009**, *48*, 931–933.

(128) Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K. *Macromolecules* **2012**, *45*, 6781–6795.

(129) Jutz, F.; Buchard, A.; Kember, M. R.; Fredriksen, S. B.; Williams, C. K. *Journal of the American Chemical Society* **2011**, *133*, 17395–17405.

(130) Klaus, S.; Vagin, S. I.; Lehenmeier, M. W.; Deglmann, P.; Brym, A. K.; Rieger, B. *Macromolecules* **2011**, *44*, 9508–9516.

(131) McGuinness, D. S.; Gibson, V. C.; Steed, J. W. *Organometallics* **2004**, *23*, 6288–6292.

(132) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303–308.

Chapter 2: Aminophosphine-Chromium Catalysts for Ethylene Tetramerization

2.1 Introduction

The demand for 1-hexene and 1-octene by the petrochemical industry is constantly growing, making the development of selective ethylene oligomerization catalysts of particular importance.[1–7] As a result of a large body of research in this field, several highly active trimerization systems have been discovered with chromium-based catalysts, with selectivity up to 99.9%.[1–3,8–14] The process of tetramerization remains instead somewhat more elusive and certainly less developed, since the commercially available systems provide only selectivity below 70%. A PNP system from Sasol,[15] and a dppe ligand from SK Energy are the only existing examples of commercial tetramerization systems (selectivity: 70% and 69% respectively).

Chromium complexes usually are the most preferred catalysts for selective and non selective ethylene oligomerization.[2,10,11,14,18–28] Their popularity is mainly due, in addition to good performances, to the simplicity of their preparation, ease of activation and usually low-cost. The fact that the organometallic chemistry of trivalent chromium shows a general inclination toward homolytic fission of the Cr-C bond, with consequent one-electron reduction of the metal center, has raised questions in the mechanistic debate revolving around the selectivity of these catalysts.[10,14,19,20,26,27,29,30] A main issue was the identity of the metal oxidation state responsible for the selective versus unselective and polymerization behavior. An air stable chromium trivalent precursor is normally the starting point for the catalytic cycle. Activation

with alkyl-aluminum cocatalysts reduce the metal to the divalent state and sometimes to the monovalent state.[31] The monovalent chromium intermediate is the catalytically active species undergoing oxidative addition of two molecules of ethylene, affording a metallocyclopentane intermediate. Subsequent ethylene insertion causes the ring to expand to the 7-membered metallocycle, which produces 1-hexene via reductive elimination. Another additional insertion of ethylene is believed to produce a 9-membered metallacycle, which upon reductive elimination, selectively produces 1-octene.[21,22,29,32–35] Because of the nature of this mechanism, 1-hexene and 1-octene are often produced in a mixture. This has triggered the debate about whether an alternative mechanism, such as the so-called dimetallic mechanism,[36] might be able to boost the selectivity to levels comparable to that of 1-hexene.

The divalent chromium complexes have been shown to be responsible for a statistical distribution of oligomers (Schulz-Flory distribution), according to the Cossee-Arlman chain growth mechanism.[37,38] These species may also be produced via a one-electron reduction from the trivalent state by alkyl aluminum activators. On the other hand, chromium in the trivalent state is responsible for the production of polyethylene wax.[26,27] Because chromium can readily interconvert between the mono-, di- and trivalent state via reductions and dis- and co-proportionations, it is not unusual to obtain a complex mix of products that includes a Schulz-Flory distribution enriched in 1-hexene and 1-octene, as well as polyethylene wax. This is not a desirable scenario and therefore ligands should be tuned to stabilize the appropriate oxidation state of the specific target process.

Ligand design plays an important role in ethylene oligomerization, as it is the ligand that controls the steric and electronic environment of the transition metal, and therefore determines the resting oxidation state of the catalytic centre, and ultimately influences the mechanism and

selectivity of a catalytic cycle. Aminophosphine based ligands with chromium have demonstrated high selectivity for ethylene oligomerization.[7,14,15,17,18,39–41] Previous work in our group has focused on bidentate NP based ligands, which have been shown to support both tri- and tetramerization of ethylene. Both the Pyridine-NP and the PNP ligands afford high selectivity for 1-octene (75% and 89% respectively) when activated with DMAO and Et_3Al.[42,43]

Other pyridine based ligands have shown high selectivity towards ethylene oligomerization as well.[1,2,25,27,44] Of particular interest is the bipyridyl ligand with an alkylated bridging nitrogen developed by our group. This catalytic system, when activated with methylaluminoxane, produces pure 1-octene (99.9%) although polyethylene wax was the major product.[25]

Given the promising behavior shown by both the NP and pyridine-containing systems highlighted above, we have now considered a new pyridine-NP ligand [$Ph_2PN(Me)CH_2Py$].

We herein report the synthesis of chromium and chromium-zinc complexes with a $Ph_2PN(Me)CH_2Py$ (**PyNP**) ligand and a study on their catalytic behavior for ethylene oligomerization.

2.2 Experimental

All manipulations were carried out under inert nitrogen atmosphere using Schlenk glassware or in a dry-box. Solvents were dried using aluminum oxide purification system. Chemicals were used from commercial sources and used as received. Et_3Al was purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albemarle Corporation. Me_3Al depleted MAO (DMAO) was prepared by removing (*in vacuo* 2

mmHg) all volatiles under moderate heating (40 ˚C) for 6 hours. CHNS elemental analyses were carried out by using a Micro Cube elemental analyzer made by "Elementar". Magnetic susceptibilities were measured using Johnson Matthey magnetic susceptibility balance at room temperature; sample preparation was performed inside a dry-box using calibrated, sealed tubes. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on Bruker Avance 400 MHz spectrometer.

2.2.1 Synthesis of Ligand

Preparation of $Ph_2PN(Me)CH_2Py$ (PyNP)

A solution of 2-[(methylamino)methyl]pyridine (5.0 g, 40.9 mmol) in THF (100 mL) was cooled to 0^oC and Et_3N (6.6 mL, 47.1 mmol) was added. Chlorodiphenylphosphine (7.6 mL, 40.93 mmol) was added slowly and the resulting mixture was stirred at room temperature for 48h. The resulting suspension was filtered, and the solvent removed *in vacuo*. The product (PyNP) was obtained as a sufficiently pure orange oil and used as is. (10.1g, 33.0 mmol, 81%) ^1H NMR (400 MHz, $CDCl_3$) δ: 8.51-7.07 (m, 14H (Ph and Py H's)), 4.38 (d, J = 9.2 Hz, 2H), 2.51 (d, J = 6.4, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 160.1, 149.1, 139.0, 136.5, 132.2, 128.6, 128.2, 122.0, 121.9, 62.4, 37.4. ^{31}P NMR (300 MHz, $CDCl_3$) δ: 67.54 (s).

2.2.2 Synthesis of Complexes

Preparation of (PyNP)$CrCl_3$(THF) (2.1)

A suspension of $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) in toluene (5 mL) was treated with **PyNP** (0.15 g, 0.5 mmol). The suspension turned green in colour immediately and stirring was continued for 12 hours. The insoluble complex was collected by centrifugation and redissolved in THF (5 mL). The turquoise solution was cooled to -35^{o}C and allowed to stand undisturbed for 3 days. X-ray quality crystals were isolated, washed with cold hexane (2 x 2 mL) and dried *in vacuo* (0.22 g, 0.4 mmol, 82%). μ_{eff} = 3.71 μ_B. Elemental Analysis % calculated for $C_{23}H_{27}Cl_3CrN_2OP$ (found): C 51.46 (52.23), H 5.07 (5.34), N 5.22 (5.80).

Preparation of (PyNP)$MeCrCl_2$(THF) (2.2)

A suspension of $MeCrCl_2(THF)_3$ (0.18 g, 0.5 mmol) in toluene (5 mL) was treated with **PyNP** (0.15 g, 0.5 mmol). The suspension turned dark green immediately and stirring was continued for 12 additional hours. The insoluble complex was collected by centrifugation and redissolved in THF (5 mL). The olive green solution was layered with heptane (2 mL). The crystalline mass was washed with cold hexane (2 x 2 mL) and dried *in vacuo* (0.19 g, 0.37 mmol, 74%). μ_{eff} = 3.76 μ_B. Elemental Analysis % calculated for $C_{24}H_{30}Cl_2CrN_2OP$ (found): C 55.82 (55.34), H 5.86 (5.46), N 5.42 (5.39).

Preparation of (PyNZn(CH_2CH_3)Cr(CH_2CH_3)Cl_2 (2.3)

A solution of **2.1** (0.27 g, 0.50 mmol) in toluene (5 mL) was cooled to -30 ˚C for about 5 min, then $Zn(CH_2CH_3)_2$ was added drop-wise (0.31 g, 2.5 mmol) and the resultant dark green solution

was stirred at room temperature for 20 min. The insoluble solid material was discarded by centrifugation and the resulting solution was cooled to -30 ˚C for 4 days. Blue block-shaped crystals of **2.3** were isolated and washed with cold hexanes (3 x 2 mL) and dried (0.19 g, 0.26 mmol, 52%). μ_{eff} = 3.88 μ_B. Elemental Analysis % calculated for $C_{22}H_{38}Cl_4Cr_2N_4Zn_2$ (found): C 35.94 (36.69), H 5.21 (4.22), N 7.62 (7.06).

2.2.3 Catalytic Tests.

Oligomerization experiments were carried out in a 200 mL pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in toluene (100mL) under nitrogen prior to loading into the reaction Bessel. Solutions were heated using a thermostatic bath and charged with ethylene, maintain pressure throughout the run. Reaction mixtures were quenched by cooling to 0^oC, releasing the pressure, and adding MeOH/HCl (80% MeOH solution). The total yield of oligomers was determined by ^1H NMR by integrating the intensity of the olefinic multplets against the solvent resonances. The composition of the mixture of oligomers was determined by GC/MS and the quantification of each oligomer was carried out by GC by using an FID detector. The alpha value was measured with $C_{(n+2)}/C_n$ ratio for the range C_6-C_{20}.

2.3 X-Ray Data

Table 2.1. Table of crystal data and refinements for **2.1** and **2.3**.

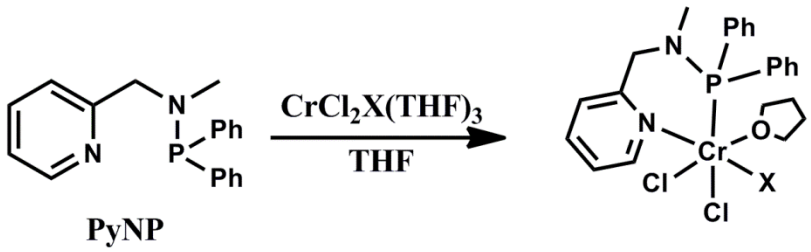
	2.1	**2.3**
Formula	$C_{23}H_{27}Cl_3CrN_2OP$	$C_{22}H_{38}Cl_4Cr_2N_4Zn_2$
Mw	536.80	735.13
Space group	Monoclinic, P 2(1)/n	Monoclinic, P 2(1)/n
***a* (Å)**	11.5191(8)	11.0631(4)
***b* (Å)**	17.7924(11)	11.8885(5)
***c* (Å)**	14.4355(10)	11.2893(5)
α, (deg)	90	90
β, (deg)	106.654(4)	93.596(2)
γ, (deg)	90	90
***V* (Å^3)**	2834.5(3)	1481.89(11)
Z	4	2
Radiation	0.71073	0.71073
T (K)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.342	1.647
μ_{calcd} (mm^{-1})	0.765	2.692
***F*$_{000}$**	1188	748
***R*, *Rw*^{2a}**	0.0653, 0.1590	0.0157, 0.0449
GoF	1.030	1.003

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. $Rw = [\Sigma(|F_o| - |F_c|)2/\Sigma wF_o2]^{1/2}$

2.4 Results and Discussion

The $PyCH_2N(CH_3)PPh_2$ ligand was synthesized by condensation of 2-[(methylamino)methyl] pyridine with chlorodiphenylphosphine. This ligand was then complexed with chromium trichloride (Scheme 2.1) to afford a turquoise crystalline material (**2.1**). The X-ray crystal structure determination confirmed the anticipated ligand coordination (Figure **2.1**).

Scheme 2.1



PyNP

2.1: X = Cl
2.2: X = Me

The crystal structure of **2.1** (Figure 2.1) displays the typical octahedral geometry of Cr(III). A six-membered chelate is formed with the bidentate **PyNP** ligand, which occupies two coordination sites around chromium, binding through the N of the pyridine moiety and the phosphorous atom. Three chlorine atoms occupy three meridional coordination sites, while the last coordination site is occupied by one molecule of THF. All bond lengths and bond angles are within the expected range.

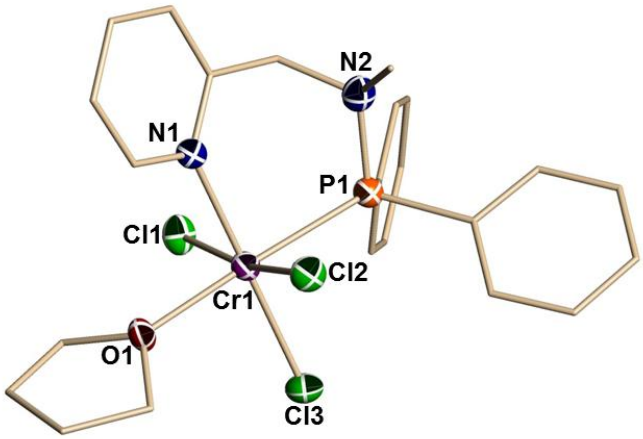
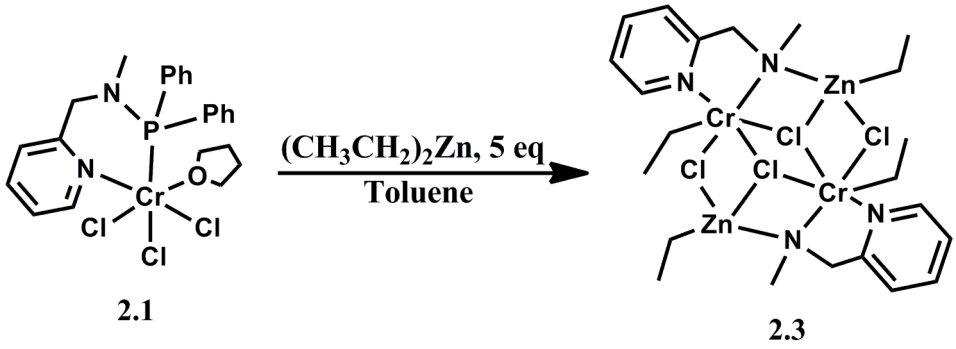


Figure 2.1. Drawing of **2.1** with thermal ellipsoids drawn at 50% probability. Select bond lengths (Å) and angles (deg) of **2.1**: Cr1-P1 2.432(2), Cr1-N1 2.164(6), Cr-Cl1 2.317(2), Cr1-Cl3 2.301(2), Cr1-O1 2.121(5); P1-Cr1-N1 92.15(16), P1-Cr1-Cl3 89.78(8), N1-Cr1-Cl3 87.09(15), N1-Cr1-Cl1 83.37(15), P1-Cr1-Cl2 88.80(8), O1-Cr1-Cl3 91.72(14).

To assess the stability of the Cr-C bond presumably formed as a result of preliminary activation, the **PyNP** ligand was complexed with methyl chromium dichloride. A green, microcrystalline material was obtained (Scheme 2.1). Regrettably, the crystal shape was not suitable for undertaking X-ray diffraction analysis. However, on the grounds of analytical and chemical degradation data, we propose a structure with the same octahedral geometry and group distribution as **2.**1.

Scheme 2.2



2.1 **2.3**

Complex **2.1** was treated with a variety of aluminum alkyl reagents, systematically affording ill-defined materials. We have also explored the reaction with diethyl zinc, a possible alternative alkylating agent (Scheme 2.2). Blue block shaped crystals were obtained in this case and the connectivity was determined by X-ray crystal structure characterization (Figure 2.2). The structure is tetrametallic with two trivalent organochromium centers and two zinc moieties, all interconnected by bridging chlorides. The unusual elongation of the Cr1-Cl1 bond [2.7097(3)Å], attributed to the carbon atom in the *trans* position, indicates distorted octahedral geometry around each chromium centre. The Ph_2P unit of the ligand has been eliminated during the alkylation process, most likely as a result of the nucleophilic attack of one diethyl zinc unit. Having lost this phosphine residue, the ligand became monoanionic. Albeit surprising, this transformation has been observed before by others and us.[42,45] The chromium centre has retained the trivalent state and, even more surprising, formed a seemingly stable bond with an ethyl group. This group is coplanar with the Cr_2Cl_2 core.

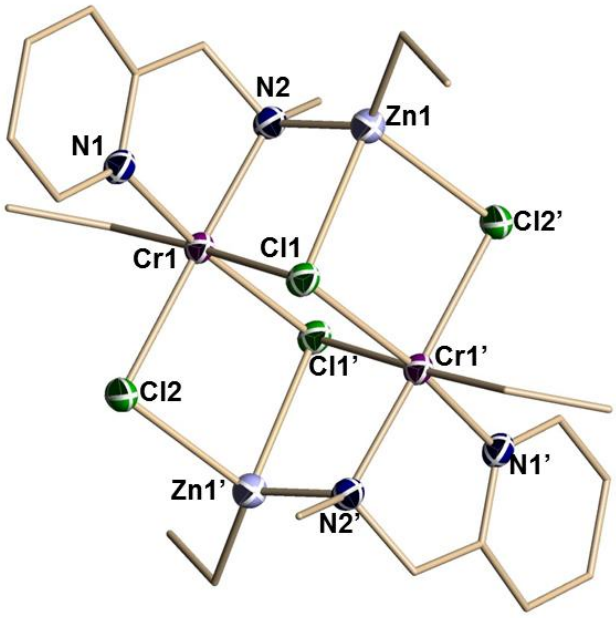


Figure 2.2. Drawing of **2.3** with thermal ellipsoids drawn at 50% probability. Select bond lengths (Å) and angles (deg) of **2.3**: Cr1-Cl1 2.3931(3), Cr1-Cl1' 2.7097(3), Cr1-Cl2 2.4122(3), Cr1-C8 2.068(1), Cr1-N1 2.0535(9), Zn1-Cl1 2.5389(3), Zn1-N2 2.032(1); Cl1'-Cr1-Cl1 87.62(1), Cl2-Cr-Cl1 85.53(1), C8-Cr-Cl1 94.43(4), N1-Cr-N2 81.24(4), Cl2'-Zn-Cl1 85.14(1), N2-Zn1-Cl1 92.62(3).

Ethylene oligomerization experiments were performed on analytically pure, isolated complexes. When the complexes **2.1** – **2.3** were tested in toluene using MAO (methylaluminoxane) as an activator, a non-selective, statistical distribution of α-olefins was obtained, with high activity (Table 2.2, entries 1, 5, 9). Because the divalent state is thought to be responsible for non-selective behavior, a one-electron reduction of the trivalent precatalyst likely occurred *in-situ* upon activation with methylaluminoxane. Non-selective ethylene oligomerization follows the Cossee-Arlman chain growth mechanism[37,38] as indicated by the presence of 1-butene. In support to the hypothesis that a divalent species was responsible for this catalytic behavior, it should be noticed that, in this case the oligomerization experiments have been carried out in toluene. Aromatics are well known to have a poisoning effect on selective

trimerization catalysts, given that the monovalent species, responsible for selective behavior, forms stable and inert π-complexes with them.[46]

In order to prevent the stabilizing effect of toluene, catalytic tests were also conducted in aliphatic solvents, such as methylcyclohexene or heptane. For solubility reasons, the activator used was dMAO (toluene and TMA depleted MAO). Under these conditions, a remarkable change in catalytic behavior was observed. The former non-selective oligomerization was replaced by a distribution enriched in 1-hexene and 1-octene for complexes **2.1** and **2.2**. Unfortunately, the activity was low and unwanted polyethylene waxes were also formed. The observed enriched distribution, as well as the production of polymer, suggests the presence of more than one catalytically active species with different oxidation states of chromium. This is once again supportive of the redox dynamism of chromium in the presence of reducing agents, as each oxidation state is expected to be responsible for a specific catalytic behavior.[26,27,29]

Complex **2.1** showed the highest activity as a non-selective catalyst, producing over 50 g of α-olefins contaminated by a significant amount of polymer (Table 2.2, entry 1). When the trichloro derivative (**2.1**) was activated with DMAO in methylcyclohexene, the selectivity changed, producing only 1-hexene and 1-octene (C_6:C_8 = 49:51). As commonly observed, there was also a significant drop in activity as a possible result of poor solubility of the catalyst precursor (entry 2). When tested for oligomerization activity in the presence of other activators, such as Et_3Al and DMAO, or MMAO, complex **2.1** showed similar selectivity towards the 1-hexene and 1-octene fractions, unfortunately the activity remained low (entries 3-4).

Complex **2.2** showed a similar trend: high activity for non-selective behaviour in toluene when activated with MAO, and an increased selectivity for 1-hexene and 1-octene fractions

when tested in methylcyclohexene with DMAO as an activator (C_6:C_8:C_{10-18} = 20:67:13) (Table 2.2, entry 6). The activity of complex **2.2** was slightly higher than its trichloro derivative, likely due to the increased solubility in aliphatic solvents as introduced to the Cr-alkyl function. On the other hand, the poor stability of this function allows for easier reduction to the divalent state, accounting for the increase in the C_{10} to C_{18} fractions.

Complex **2.3**, obtained from the treatment of **2.1** with Et_2Zn, was tested in the absence of activators in the pursuit of a self-activating catalyst (Table 2.2, entry 10). Unfortunately, no production of oligomers was observed, and only trace amounts of polymers were obtained. When tested in methylcyclohexane and activated with DMAO, again, no production of oligomers was observed, even when the temperature was increased to 100^{o}C (Entries 11, 12). This disappointing behaviour can be attributed to the lack of any significant solubility of this robust dimeric complex in aliphatic solvents.

Table 2.2: Ethylene Oligomerization Results of PyNP Complexes[a]

Entry	catalyst	Co-catalyst (equiv)	alkenes (g)	PE (g)	activity (g/g Cr . h)	linear alpha olefins (mol %)							
						C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
1	**2.1**[b]	MAO (500)	51	1.9	67, 048	8	24	22	16	12	8	6	4
2	**2.1**[c]	DMAO (500)	Trace	2.0	2, 603	0	49	51	0	0	0	0	0
3	**2.1**[c]	DMAO/Et_3Al (500/15)	Trace	1.1	1, 346	14	24	34	5	5	5	8	5
4	**2.1**[c]	MMAO (300)	Trace	2.1	2, 692	18	45	10	8	6	5	4	4
5	**2.2**[b]	MAO (500)	32	0.7	40, 734	5	23	23	17	13	9	6	4
6	**2.2**[c]	DMAO (500)	1.5	3	5, 012	2	18	67	3	2	2	3	3
7	**2.2**[c]	DMAO/Et_3Al (500/15)	Trace	2	3, 506	11	24	41	5	5	4	5	5
8	**2.2**[c]	DMAO/Me_3Al (500/15)	Trace	1.3	1, 641	0	17	29	4	4	4	36	6
9	**2.3**[b]	MAO (500)	26	2.3	34, 981	4	16	19	17	14	12	10	8
10	**2.3**[b]	--	0	0.3	359	-	-	-	-	-	-	-	-
11	**2.3**[c]	DMAO (500)	0	7.3	9, 308	-	-	-	-	-	-	-	-
12	**2.3**[c,d]	DMAO (500)	0	1.1	1, 526	-	-	-	-	-	-	-	-

[a]Conditions: Loading 30 μmol of complex, 60 ˚C temperature, 40 bar (ethylene), 30 min reaction time. [b]100 mL of toluene. [c]100 mL of methylcyclohexane. [d]100˚C. DMAO = Me_3Al depleted MAO; MMAO = modified Me_3Al

In conclusion, this work was advised by previous results from our group on the pyridine-NP ligand containing a two carbon linker, and which showed selectivity towards 1-octene greater than 75%.[42] Thus, by removing one carbon, we hoped to increase selectivity towards 1-octene. To our surprise, we have only observed highly active Schulz-Flory behaviour. Complex **2.2** instead displayed more selective behavior possibly due to its increased solubility. Complex **2.3** showed low reactivity due to the stability of the robust, dimeric structure. Further catalytic activity of these complexes was explored and it will be discussed in Chapter 4.

2.5 References

(1) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *Journal of Organometallic Chemistry* **2004**, *689*, 3641–3668.

(2) McGuinness, D. S. *Chemical Reviews* **2011**, *111*, 2321–2341.

(3) Bluhm, M. E.; Walter, O.; Döring, M. *Journal of Organometallic Chemistry* **2005**, *690*, 713–721.

(4) Blann, K.; Bollmann, a; Debod, H.; Dixon, J.; Killian, E.; Nongodlwana, P.; Maumela, M.; Maumela, H.; Mcconnell, a; Morgan, D. *Journal of Catalysis* **2007**, *249*, 244–249.

(5) Blann, K.; Bollmann, A.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M. J. *Chemical Communications* **2005**, 620–1.

(6) Walsh, R.; Morgan, D. H.; Bollmann, A.; Dixon, J. T. *Applied Catalysis A: General* **2006**, *306*, 184–191.

(7) Overett, M. J.; Blann, K.; Bollmann, A.; De Villiers, R.; Dixon, J. T.; Killian, E.; Maumela, M. C.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Rucklidge, A.; Slawin, A. M. Z. *Journal of Molecular Catalysis A: Chemical* **2008**, *283*, 114–119.

(8) Abbott, R. G.; Kreischer, B. E.; Baralt, E. J.; Small, B. L.; Knudsen, R. D.; (Chevron Phillips Chemical Company, L. (Chevron Phillips). US2007043181A1, 2007.

(9) Reagan, W. (Phillips Petroleum Company). EP 0417477, 1991.

(10) Peitz, S.; Peulecke, N.; Aluri, B. R.; Hansen, S.; Müller, B. H.; Spannenberg, A.; Rosenthal, U.; Al-Hazmi, M. H.; Mosa, F. M.; Wöhl, A.; Müller, W. *European Journal of Inorganic Chemistry* **2010**, *8*, 1167–1171.

(11) Agapie, T. *Coordination Chemistry Reviews* **2011**, *255*, 861–880.

(12) Schofer, S. J.; Day, M. W.; Henling, L. M.; Labinger, J. A.; Bercaw, J. E. *Organometallics* **2006**, *25*, 2743–2749.

(13) Mcguinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552–556.

(14) Carter, A.; Cohen, S. a; Cooley, N. a; Murphy, A.; Scutt, J.; Wass, D. F. *Chemical Communications* **2002**, *3*, 858–9.

(15) Bollmann, A.; Blann, K.; Dixon, J. T.; Hess, F. M.; Killian, E.; Maumela, H.; McGuinness, D. S.; Morgan, D. H.; Neveling, A.; Otto, S.; Overett, M.; Slawin, A. M. Z.;

Wasserscheid, P.; Kuhlmann, S. *Journal of the American Chemical Society* **2004**, *126*, 14712–14713.

(16) Han, T. K.; Chae, S. S.; Kang, S. O.; Wee, K. R.; Kim, S.-K. (SK Energy Corporation). 2009/022770, 2009.

(17) Kim, S.-K.; Kim, T.-J.; Chung, J.-H.; Hahn, T.-K.; Chae, S.-S.; Lee, H.-S.; Cheong, M.; Kang, S. O. *Organometallics* **2010**, *29*, 5805–5811.

(18) Dulai, A.; McMullin, C. L.; Tenza, K.; Wass, D. F. *Organometallics* **2011**, *30*, 935–941.

(19) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chemical Communications* **2003**, *49*, 334–335.

(20) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *Journal of the American Chemical Society* **2003**, *125*, 5272–5273.

(21) Wass, D. F. *Dalton Transactions* **2007**, 816–819.

(22) Dulai, A.; De Bod, H.; Hanton, M. J.; Smith, D. M.; Downing, S.; Mansell, S. M.; Wass, D. F. *Organometallics* **2009**, *28*, 4613–4616.

(23) Vidyaratne, I.; Nikiforov, G. B.; Gorelsky, S. I.; Gambarotta, S.; Duchateau, R.; Korobkov, I. *Angewandte Chemie International Edition* **2009**, *48*, 6552–6556.

(24) Thapa, I.; Gambarotta, S.; Korobkov, I.; Duchateau, R.; Kulangara, S. V.; Chevalier, R. *Organometallics* **2010**, *29*, 4080–4089.

(25) Licciulli, S.; Thapa, I.; Albahily, K.; Korobkov, I.; Gambarotta, S.; Duchateau, R.; Chevalier, R.; Schuhen, K. *Angewandte Chemie International Edition* **2010**, *49*, 9225–9228.

(26) Temple, C.; Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angewandte Chemie International Edition* **2006**, *45*, 7050–7053.

(27) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Journal of the American Chemical Society* **2006**, *128*, 9238–9247.

(28) Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* **2006**, *25*, 715–718.

(29) Jabri, A.; Mason, C. B.; Sim, Y.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angewandte Chemie International Edition* **2008**, *47*, 9717–9721.

(30) Elowe, P. R.; McCann, C.; Pringle, P. G.; Spitzmesser, S. K.; Bercaw, J. E. *Organometallics* **2006**, *25*, 5255–5260.

(31) Albahily, K.; Shaikh, Y.; Sebastiao, E.; Gambarotta, S.; Korobkov, I.; Gorelsky, S. I. *Journal of the American Chemical Society* **2011**, *133*, 6388–95.

(32) Agapie, T.; Schofer, S. J.; Labinger, J. a; Bercaw, J. E. *Journal of the American Chemical Society* **2004**, *126*, 1304–5.

(33) Tomov, A. K.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. J. *Journal of the American Chemical Society* **2006**, *128*, 7704–7705.

(34) Agapie, T.; Labinger, J. a; Bercaw, J. E. *Journal of the American Chemical Society* **2007**, *129*, 14281–95.

(35) McGuinness, D. S.; Suttil, J. a.; Gardiner, M. G.; Davies, N. W. *Organometallics* **2008**, *27*, 4238–4247.

(36) Peitz, S.; Aluri, B. R.; Peulecke, N.; Müller, B. H.; Wöhl, A.; Müller, W.; Al-Hazmi, M. H.; Mosa, F. M.; Rosenthal, U. *Chemistry (Weinheim an der Bergstrasse, Germany)* **2010**, *16*, 7670–6.

(37) Arlman, E. J.; Cossee, P. *Journal of Catalysis* **1964**, *3*, 99–104.

(38) Cossee, P. *Journal of Catalysis* **1964**, *3*, 80–88.

(39) Fei, Z.; Scopelliti, R.; Dyson, P. J. *European Journal of Inorganic Chemistry* **2004**, *2004*, 530–537.

(40) Kuhlmann, S.; Blann, K.; Bollmann, a; Dixon, J.; Killian, E.; Maumela, M.; Maumela, H.; Morgan, D.; Pretorius, M.; Taccardi, N. *Journal of Catalysis* **2007**, *245*, 279–284.

(41) Jiang, T.; Zhang, S.; Jiang, X.; Yang, C.; Niu, B.; Ning, Y. *Journal of Molecular Catalysis A: Chemical* **2008**, *279*, 90–93.

(42) Shaikh, Y.; Gurnham, J.; Albahily, K.; Gambarotta, S.; Korobkov, I. *Organometallics* **2012**, *31*, 7427–7433.

(43) Shaikh, Y.; Albahily, K.; Sutcliffe, M.; Fomitcheva, V.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angewandte Chemie International Edition* **2012**, *51*, 1366–1369.

(44) Albahily, K.; Shaikh, Y.; Ahmed, Z.; Korobkov, I.; Gambarotta, S.; Duchateau, R. *Organometallics* **2011**, *30*, 4159–4164.

(45) Albahily, K.; Ahmed, Z.; Gambarotta, S.; Koc, E.; Duchateau, R. *Organometallics* **2011**, *30*, 6022–6027.

(46) Calucci, L.; Englert, U.; Grigiotti, E.; Laschi, F.; Pampaloni, G.; Pinzino, C.; Volpe, M.; Zanello, P. *Journal of Organometallic Chemistry* **2006**, *691*, 829–836.

(47) Briggs, J. R. *Journal of the Chemical Society Chemical Communications* **1989**, 674.

Chapter 3: Pyrrole Based Ligands for Chromium-Catalyzed Selective Ethylene Trimerization

3.1 Introduction

Because polyethylene is the most widely used plastic,[1] the demand for light linear alpha olefin fractions, as critical ingredients to control polymer rheology, is continually increasing. The C_6 and C_8 fractions are particularly important in the production of branched polyethylene, which has applications in plastic films used in plastic bags, wraps, containers, toys, etc. This vast list of applications, and consequent need for C_6 and C_8 branching comonomers, stimulates the research for new venues to obtain them via selective oligomerization catalysts.[2]

Selective ethylene oligomerization, which produces the most industrially relevant oligomers (1-hexene and 1-octene), follows a redox ring expansion mechanism.[3,4] Chromium is the most preferred metal due to ease of activation, stability of the catalyst precursors and low preparation costs. An important characteristic of this metal is its ability to readily convert between the +1, +2 and +3 oxidation states under catalyst activation conditions, and which may favorably or unfavorably interfere with the outcome of the selective oligomerization mechanism.[2,4–10] Each of the chromium oxidation states has been linked to different products, as discussed in chapter 2.[5–14] The monovalent state in particular is responsible for selective oligomerization behaviour.[8] For this reason, monoanionic ligands are of particular interest when developing catalytic systems for ethylene oligomerization.

In addition to its ability to stabilize monovalent chromium, the coordination fashion of a ligand is an important characteristic. An octahedral six-coordinated chromium centre with three donor atoms can coordinate in a meridional or facial configuration. Luo and co-workers have

proposed that facial coordination of the ligand to a chromium center may be the key to a more active catalytic species due to an increased ligand steric flexibility.[4,15,16]

This type of facial, tridentate ligands have been successfully implemented by McGuiness and co-workers of Sasol Technology with the PNP and SNS ligands. With these systems, it was possible to obtain complexation with chromium in a facial configuration, forming 5-membered chelates with octahedral geometry around a trivalent chromium centre.[17,18] Besides interesting activity, these catalysts have shown up to 98% selectivity towards 1-hexene.

Although the Sasol system has a very interesting level of activity, the most active selective oligomerization system remains the landmark Chevron-Phillips catalyst, capable of producing over 50,000 tons of 1-hexene per year.[19] The Phillips system is based on a 2,5-dimethylpyrrole ligand which coordinates in a 3:1 ratio with a non-chlorinated chromium source. By introducing chlorine to the system via a chlorinated alkylating agent, also referred to as "Phillips conditions", a substantial increase in activity was achieved.[15] The chloro compound was observed to promote a facial geometry complex, which, as previously mentioned, is a favorable conformation for catalytic activity.[16] Other pyrrole based ligands have shown similarly high activity towards ethylene oligomerization, including bulky derivatives of the Phillips system investigated by our group.[7,8] Computational studies, also based on pyrrole ligands for ethylene oligomerization, have provided supporting results.[20,21]

As demonstrated by the Chevron-Phillips system, along with others, pyrrole based ligands have the highest activity toward selective ethylene trimerization. This is attributed to the ability of pyrrole based ligands to alternate between η^1 and η^5coordination throughout the

catalytic process, accounting for changes in the coordination environment of the chromium centre.[2]

We herein report the synthesis of three pyrrole containing ligands containing pendants with different donor functions: PyrCHN(^{n}Bu) (**Pyr=N**), PyrCH$_2$NH(^{n}Bu) (**PyrN**) and PyCH$_2$N(^{n}Bu)CH$_2$Pyr (**PyNPyr**). These ligands were complexed with different chromium sources, and their activity towards ethylene oligomerization tested.

3.2 Experimental

All manipulations were carried out under inert nitrogen atmosphere using Schlenk glassware or in a dry-box. Solvents were dried using aluminum oxide purification system. Chemicals were used from commercial sources and used as received. Et_3Al was purchased from Strem and used as received. Methylaluminoxane (MAO, 20% in toluene) was purchased from Albemarle Corporation. Me_3Al depleted MAO (DMAO) was prepared by removing all volatiles *in vacuo* (2 mmHg) and under moderate heating (40 ˚C) for 6 hours. CHNS elemental analyses were carried out by using a Micro Cube elemental analyzer made by "Elementar". Electrospray Ionization was done using an ESI Micromass Q-ToF-1. Magnetic susceptibilities were measured using a Johnson Matthey magnetic susceptibility balance at room temperature; sample preparation was performed inside a dry-box using calibrated, sealed tubes. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with a Bruker Kappa APEXII CCD diffractometer. NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer.

3.2.1 Synthesis of Ligands

Preparation of *N*-Butyl-*N*-(1H-pyrrolemethylidene)amine (Pyr=N)

A solution of 1*H*-pyrrole-2-carboxaldehyde (9.5g, 100 mmol) in THF (100 mL) was cooled to 0^oC and butylamine (10.9 mL, 110 mmol) was added dropwise. The solution was stirred at 0^oC for 15 minutes, then warmed to room temperature and stirred for an additional 12 hours. Evaporation of the solvent *in vacuo* afforded the product as a dark red oil (14.9g, 100 mmol, 100%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 11.37 (s, 1H, N-H), 8.16 (s, 1H), 6.91 (s, 1H), 6.57 (d, J = 2.4 Hz, 1H), 6.29 (t, J = 3.0 Hz, 1H), 3.64 (t, J = 6.8, 2H), 1.68 (m, 2H), 1.44 (m, 2H), 0.98 (t, J = 7.4, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 152.1, 130.3, 122.0, 114.2, 109.4, 60.5, 33.3, 20.3, 13.4. These values are in agreement with literature data.[22]

Preparation of 1*H*-pyrrol-2-ylmethylbutylamine (Pyr-N)

A solution of *N*-Butyl-*N*-(1H-pyrrolemethylidene)amine (8.0 g, 53.6 mmol) in distilled methanol (80 mL) was cooled to 0^oC, and excess $NaBH_4$ (4.0 g, 105 mmol) was added slowly. Gas evolution was observed. The resulting brown suspension was stirred at room temperature overnight, and then concentrated to 50 mL *in vacuo*. The excess $NaBH_4$ was quenched with 50 mL of water, and the aqueous solution was extracted three times with diethyl ether (3x30 mL). The combined Et_2O fractions were dried over $MgSO_4$, filtered, and the solvent evaporated *in vacuo* affording the product as a red-orange oil (6.89 g, 45.6 mmol, 70%). %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.04 (s, 1H N-H pyrrole), 6.76 (s, 1H), 6.21 (s, 1H), 6.15 (s, 1H), 3.86 (s, 2H), 2.74 (t, J = 7.2 Hz, 2H), 1.60 (m, 2H), 1.46 (m, 2H), 1.03 (t, J = 7.2, 3H). ^{13}C NMR (400 MHz,

$CDCl_3$) δ: 130.4, 117.5, 107.8, 106.4, 49.2, 46.7, 32.0, 20.5, 14.0. These values are in agreement with literature data.[22]

Preparation of *N*-Butyl-*N*-(2-pyridylmethyl)-*N*-*(*1*H*-2-pyrrolylmethyl)amine (Py-N-Pyr)

A suspension of Na_2CO_3 (7.7 g, 4.0 mmol) in water (12 mL) was added to 100 mL of cooled methanol. To the resulting suspension, picolyl chloride hydrochloride (3.8 g, 23 mmol) was added and stirred at 0°C for 2 hours while a pink coloured suspension was formed. Neat 1*H*-pyrrol-2-ylmethylbutylamine (3.5 g, 23 mmol) was added to the pink coloured suspension, and stirring was continued at room temperature for 5 days. The colour slowly changed from pink to pale orange. The suspension was filtered and the filtrate collected and concentrated *in vacuo*. The resulting solution was washed with chloroform (3x15 mL) and the chloroform fractions combined and dried over $MgSO_4$. After filtration and solvent evaporation *in vacuo*, a yellow oil was obtained and purified by column chromatography over silica-60H with 10% MeOH/$CHCl_3$ (1.73g, 7.13 mmol, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.82 (broad s, NH), 8.55 (d, J = 4 Hz, 1H), 7.66 (m, 1H), 7.42 (d, J = 8, 1H), 7.18 (m, 1H), 6.78 (m, 1H), 6.13 (m, 1H), 6.03 (s, 1H), 3.89 (s, 2H), 3.58 (s, 2H), 2.48 (t, J = 6.4, 2H), 1.53 (m, 2H), 1.30 (m, 2H), 0.88 (t, J = 7.2, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ: 159.4, 148.8, 136.7, 128.1, 124.1, 122.2, 117.3, 107.7, 107.6, 58.9, 54.0, 49.3, 29.4, 20.6, 14.1. These values are in agreement with literature data.[22]

3.2.2 Synthesis of Complexes

Preparation of $(Pyr{=}N)_2CrCl(THF)$ (3.1)

A solution of **Pyr=N** (0.15 g, 1 mmol) in THF (5.0 mL) was treated with KH (0.04 g, 1.1 mmol) and the mixture stirred at room temperature for 12 hours. The resulting pale red suspension was treated with $CrCl_3(THF)_3$ (0.19 g, 0.5 mmol) and stirred at room temperature for 12 hours. The colour changed to dark red. The crude material was dried *in vacuo*, redissolved in hexane (5.0 mL) and separated from KCl via centrifugation. The product was recrystallized from hexane at -35°C yielding small red crystals of **3.1** suitable for X-ray analysis (0.18g, 0.4 mmol, 53%). μ_{eff} = 3.78 μ_B. Elemental Analysis % calculated for $C_{27}H_3CrN_6$ (found): C 64.91 (64.08), H 7.87 (7.33), N 16.82 (15.93).

Preparation of $(PyrN)CrCl_2(THF)_2$ (3.2)

A solution of **PyrN** (0.15 g, 1 mmol) in THF (5.0 mL) was treated with KH (0.09 g, 2.2 mmol) and the mixture was stirred at room temperature for 12 hours. The resulting peach suspension was treated with $Cr(acac)_3$ (0.35 g, 1.0 mmol) and stirred at room temperature for 12 hours. The colour changed to dark red-brown. The crude material obtained upon drying the reaction mixture *in vacuo* was redissolved in toluene (5.0 mL) and separated from KCl via centrifugation. The product was recrystallized from toluene at -35°C yielding red crystals of **3.2** (0.31 g, 0.67 mmol, 67%). μ_{eff} = 3.63 μ_B. ESI-MS calculated (found): 420.1380 (420.2056) Elemental Analysis % calculated for $C_{17}H_{31}Cl_2CrN_2O_2$ (found): C 49.04 (49.86), H 7.02 (7.17), N 6.73 (7.29).

Preparation of (PyrN)Cr(acac)$_2$ (3.3)

A solution of **PyrN** (0.23 g, 1.5 mmol) in THF (7.0 mL) was treated with KH (0.13 g, 3.3 mmol) and the mixture was stirred at room temperature for 12 hours. The resulting golden yellow suspension was treated with Cr(acac)$_3$ (0.52 g, 1.5 mmol) and stirred at room temperature for 12 hours. The colour changed to dark red-brown and the mixture evaporated to dryness. The crude material was further dried *in vacuo*, redissolved in toluene (5.0 mL) and separated from K(acac) via centrifugation. The product was recrystallized from toluene at -35^{o}C yielding red crystals of **3.3** suitable for X-ray diffraction (0.21g, 0.5mmol, 35%). μ_{eff} = 3.62 μ_B. Elemental Analysis % calculated for $C_{19}H_{28}CrN_2O_4$ (found): C 56.85 (55.95), H 7.28 (7.09), N 6.98 (7.35).

Preparation of (PyrNPy)CrCl$_2$(THF) (3.4)

A solution of **PyrNPy** (0.97 g, 4.0 mmol) in THF (20.0 mL) was treated with KH (0.18 g, 4.4 mmol) and the mixture was stirred at room temperature for 12 hours. The resulting dark red-brown solution was treated with $CrCl_3(THF)_3$ (1.5 g, 4.0 mmol) and stirred at room temperature for 12 hours, while the colour changed to dark green. The material was dried *in vacuo*, the residue redissolved in toluene (12.0 mL) and separated from KCl via centrifugation. The product was recrystallized from toluene at -35^{o}C yielding small green crystals of **3.4** (0.87g, 2.0 mmol, 50%). μ_{eff} = 3.83 μ_B. ESI-MS calculated (found): 367.1716 (367.2263). Elemental Analysis % calculated for $C_{21}H_{31}Cl_3CrN_2OP$ (found): C 52.30 (52.97), H 6.24 (6.15), N 9.63 (9.02).

Preparation of (PyrNPy)Cr(acac)$_2$ (3.5)

A solution of **PyrNPy** (0.24 g, 1 mmol) in THF 8.0 mL) was treated with KH (0.04 g, 1.1 mmol) and the mixture was stirred at room temperature for 12 hours. The resulting dark red-brown solution was treated with Cr(acac)$_3$ (0.35 g, 1.0 mmol) and stirred at room temperature for 12

hours, while the colour changed to dark brown. The crude material was dried *in vacuo*, redissolved in toluene (6.0 mL) and separated from K(acac) via centrifugation. The product was recrystallized from toluene at -35^{o}C yielding small brown crystals of **3.5** (0.31g, 0.63 mmol, 63%). μ_{eff} = 3.73 μ_B. ESI-MS calculated (found): 491.1877 (491.3080). Elemental Analysis % calculated for $C_{21}H_{31}Cl_3CrN_2OP$ (found): C 60.96 (60.50), H 6.96 (6.76), N 8.53 (7.91).

Preparation of Complex 3.6

A suspension of 3.4 (0.35g, 0.8 mmol) in toluene (5 mL) was cooled to -35^{o}C and cold Et_3Al (0.27 g, 2.4 mmol) was added drop-wise. The resulting dark green solution was stirred for 30 minutes, after which time it was centrifuged and the supernatant solution cooled to -35^{o}C for 3 days, yielding dark green crystals of **3.6** suitable for X-ray analysis (0.28 g, 0.3 mmol, 38%). μ_{eff} = 3.10 $\mu_{B.}$ Elemental Analysis % calculated for $C_{40}H_{68}Al_2Cl_4Cr_2N_6$ (Found): C 51.51 (51.02), H 7.35 (6.92), N 9.01 (8.71).

3.2.3 Catalytic Test Results

Oligomerization experiments were carried out in a 200 mL pressure Büchi reactor containing a heating/cooling jacket. A pre-weighed amount of catalyst was dissolved in toluene (100mL) under nitrogen prior to loading into the reaction Bessel. Solutions were heated using a thermostatic bath and charged with ethylene, maintain pressure throughout the run. Reaction mixtures were quenched by cooling to 0^{o}C, releasing the pressure, and adding MeOH/HCl (80% MeOH solution). The total yield of oligomers was determined by ^{1}H NMR by integrating the intensity of the olefinic multplets against the solvent resonances. The composition of the mixture of oligomers was determined by GC/MS and the quantification of each oligomer was

carried out by GC by using an FID detector. The alpha value was measured with $C_{(n+2)}/C_n$ ratio for the range C_6-C_{20}.

3.3 X-Ray data:

Table 3.1: . Table of crystal data and refinements for **3.1, 3.3** and **3.6**.

	3.1	**3.3**	**3.6**
Formula	$C_{27}H_{37}CrN_6$	$C_{19}H_{28}CrNO_4$	$C_{38}H_{60}Al_2Cl_4Cr_2N_6$
Mw	497.63	400.43	900.68
Space group	Orthorhombic, Pcba	Triclinic, P-1	Monoclinic, P2 (1)/n
***a* (Å)**	15.4907(10)	8.1225(4)	8.8410(2)
***b* (Å)**	15.9467(10)	12.0983(6)	12.4365(3)
***c* (Å)**	22.5005(15)	12.2994(5)	20.7462(5)
α, (deg)	90	62.611(3)	90
β, (deg)	90	78.758(3)	93.4350(10)
γ, (deg)	90	73.791(3)	90
***V* (Å^3)**	5558.2(6)	1027.36(8)	2276.97(9)
Z	8	2	2
Radiation	0.71073	0.71073	0.71073
T (K)	200(2)	200(2)	200(2)
D_{calcd} (g cm^{-3})	1.189	1.294	1.314
μ_{calcd} (mm^{-1})	0.436	0.581	0.784
***F*$_{000}$**	2120.0	424.0	944.0
***R, Rw*^{2a}**	0.0702, 0.1649	0.0515, 0.1280	0.0341, 0.0729
GoF	1.030	1.020	1.027

[a] $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. $Rw = [\Sigma(|F_o| - |F_c|)2/\Sigma wF_o2]^{1/2}$

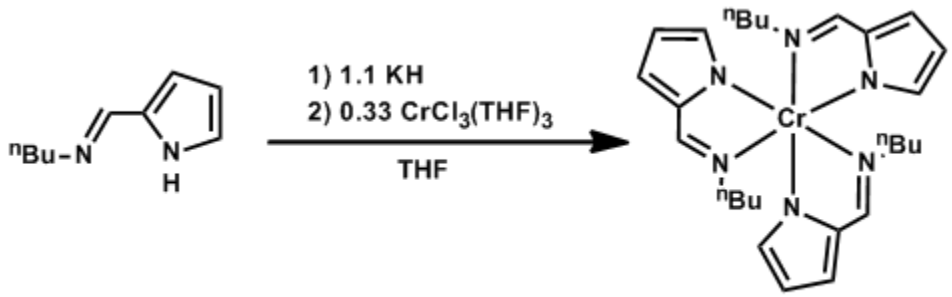
3.4 Results and Discussion

The ligands used in this work started with the preparation of $Pyr(CH)N(CH_2)_3CH_3$ (**Pyr=N)** via condensation of 1*H*-pyrrole-2-carboxaldehyde with butylamine. Subsequent

reduction with $NaBH_4$ afforded $Pyr(CH_2)NH(CH_2)_3CH_3$ (**Pyr-N**). In turn, treatment of the **Pyr-N** ligand with Na_2CO_3 and picolyl chloride hydrochloride afforded $Py(CH_2)N(butyl)(CH_2)Pyr$ (**Py-N-Pyr).**

Pyr=N was complexed with chromium trichloride (Scheme 3.1) to form a red crystalline material (**3.1**). The X-ray crystal structure determination revealed coordination of this species in a Ligand:Chromium ratio of 3:1. (Figure 3.1).

Scheme 3.1:



3.1

Each ligand is monoanionic and contains two donor nitrogen atoms, resulting in a typical octahedral geometry of Cr(III). When the reaction was carried out with L:Cr ratios of 1:1 and 2:1, complex **3.1** was the only characterized product. All bond lengths and angles of this chlorine-free complex are within the expected range.

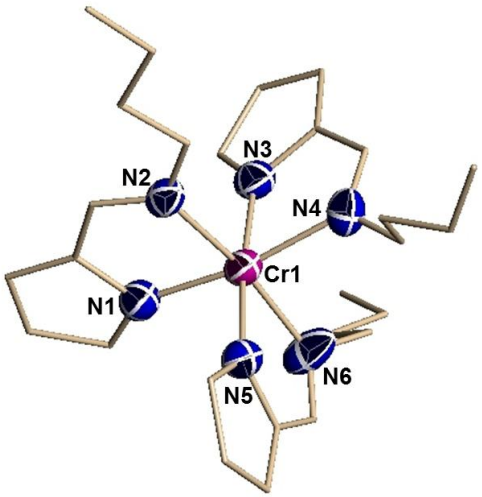
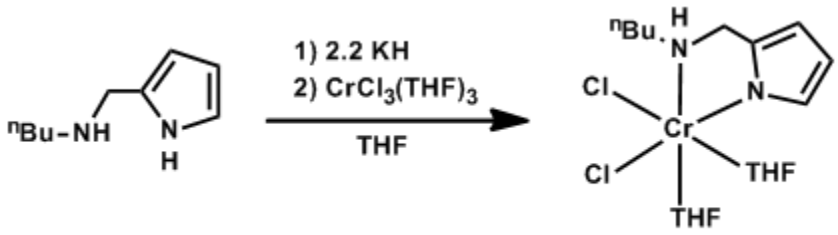


Figure 3.1. Partial thermal ellipsoid drawings for **3.1** at 50% probability. Select bond lengths (Å) and angles (deg) of **3.1**: Cr1-N3 2.006(5), Cr1-N5 2.028(5), Cr1-N6 2.055(5), Cr1-N2 2.069(5), Cr1-N4 2.070(5), N3-Cr1-N1 89.8(2), N3-Cr1-N5 174.6(2), N1-Cr1-N5 93.9(2), N3-Cr1-N6 96.0(2), N5-Cr1-N6 79.8(2).

When **Pyr-N** was complexed with chromium trichloride, a brown, microcrystalline material unsuitable for X-ray analysis was obtained (Scheme 3.2). Characterization was therefore carried out with ESI-MS, IR and magnetic susceptibility measurements (**3.2**), indicating the presence of a singly deprotonated ligand on a chromium metal centre, with two chlorine atoms (thus maintaining the +3 oxidation state) and two molecules of THF to complete the coordination sphere.

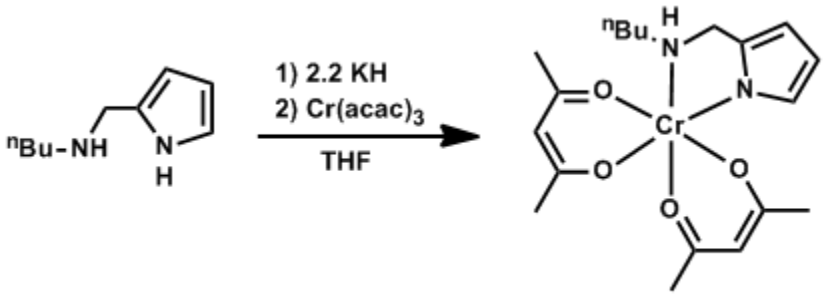
Scheme 3.2



3.2

The reaction of the potassium salt of **Py-N** with a different chromium source, $Cr(acac)_3$ in THF afforded a red-brown crystalline material (Scheme 3.3). The crystal structure determination showed ligand coordination via the two nitrogen donors, and the chromium coordination sphere completed by two molecules of acetylacetenoate (Figure 3.2).

Scheme 3.3:



3.3

The pyramidal geometry of the nitrogen atom indicates that no deprotonation occurred. Accordingly, the I.R. spectrum shows a small peak was at 3176 cm^{-1}, confirming the presence of

the N-H. Furthermore, the magnetic susceptibility measurement showed chromium in the +3 oxidation state. All bond lengths and bond angles were within the expected range

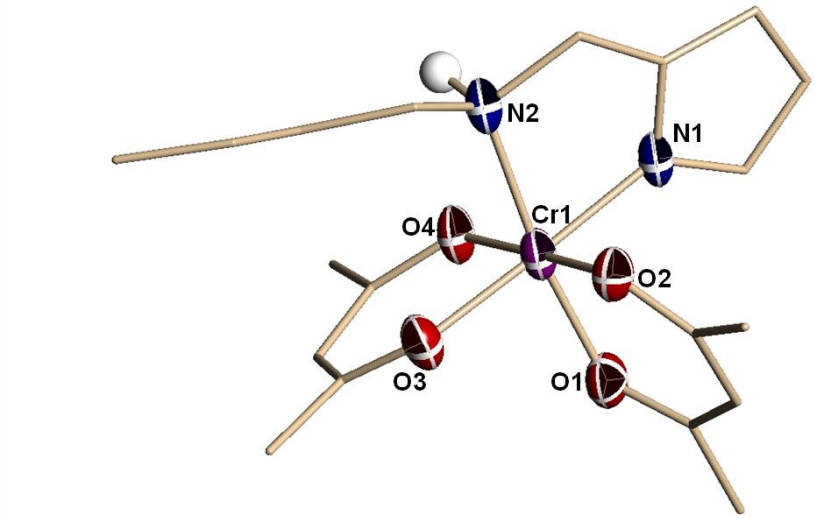
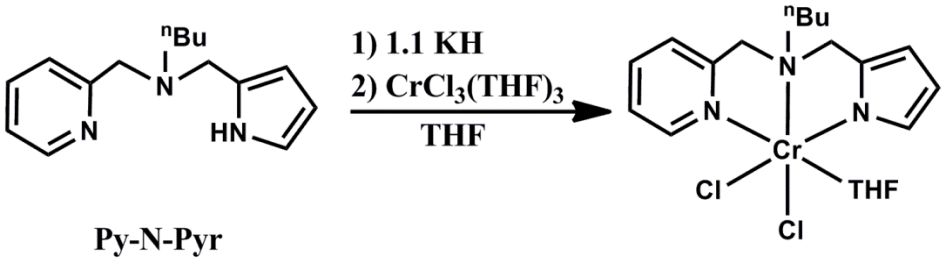


Figure 3.2. Partial thermal ellipsoid drawings for **3.3** at 50% probability. Select bond lengths (Å) and angles (deg) of **3.3**: Cr1-O1 1.952(3), Cr1-O2 1.958(3), Cr1-N1 1.991(3), Cr1-N2 2.120(4), O1-Cr1-O2 91.91(13), O2-Cr1-O4 176.57(12), O1-Cr1-N1 92.18(14), O3-Cr1-N1 175.7(15), O3-Cr1-N2 96.55(13), N1-Cr1-N2 80.04(15).

Scheme 3.4



Py-N-Pyr **3.4**

The reaction of the potassium salt of Py-N-Pyr with $CrCl_3(THF)_3$ in THF afforded a green microcrystalline material. Unfortunately, reiterate attempts to grow suitable crystals for X-ray diffraction were unsuccessful, however, we propose structure **3.4** on the grounds of analytical and magnetic data (Scheme 3.4). Furthermore, the Py-N-Pyr ligand shows similarities to Sasol's PNP and SNS systems, also tridentate, monoanionic ligands with 2 carbon bridges between the donor atoms. Because of these similarities, we suggest that coordination will occur in the same way providing analogous facial configuration, and with a 5-membered chelating ligand surrounding an octahedral, trivalent chromium.[17,18,23]

When complex **3.4** was treated with Et_3Al, a crystalline product was obtained **(3.6)** and its structure determined via X-ray analysis (Figure 3.3).

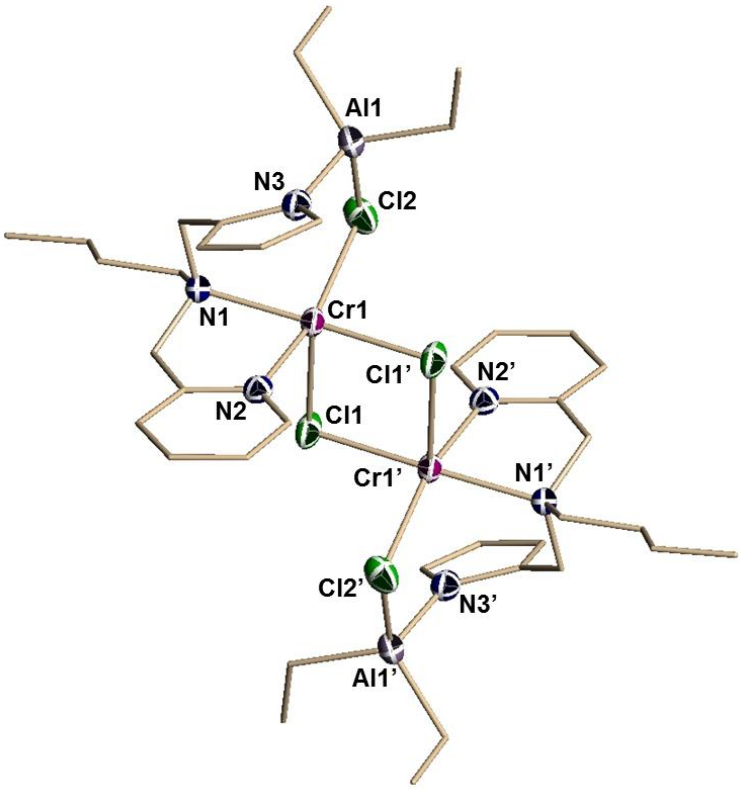
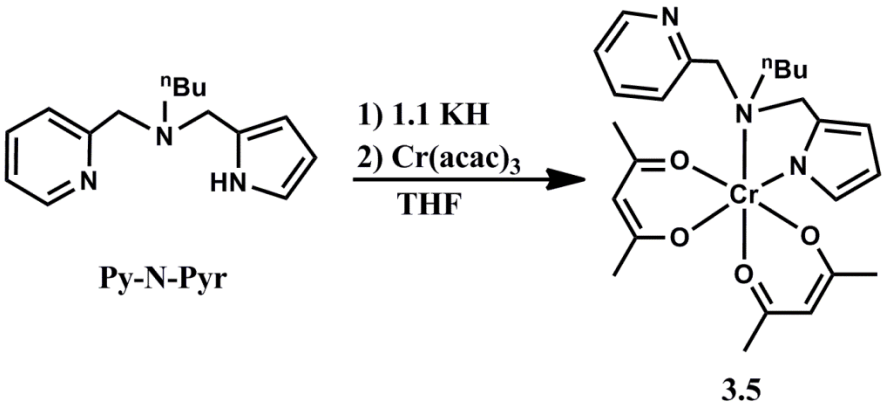


Figure 3.3. Partial thermal ellipsoid drawings for **3.6** at 50% probability. Select bond lengths (Å) and angles (deg) of **3.6**: Cr1-N1 2.1799(13), Cr1-N2 2.0911(14), Cr1-Cl1 2.3812(5), Cr1-Cl3 2.4403(6), Cr1-Cl2 2.6842(5), N2-Cr1-N1 80.82(5), N2-Cr1-Cl1 93.95(4), N2-Cr1-Cl2 163.40(4), Cl1-Cr1-Cl1' 90.515(16), Cl2-Cr1-Cl1' 104.563(18).

This complex is dimeric with each ligand chelating a chromium centre and the two metal-containing units linked by two bridging chlorine atoms. Two nitrogen donors chelate each chromium atom [N1-Cr1-N2 = 82.82(5)^{o}].

The chromium centre is present in its divalent state. The metal reduction resulting from the treatment with an alkylating agent is a rather common occurrence in chromium chemistry.[6,13,24,25]

Scheme 3.5



Py-N-Pyr **3.5**

The reaction of the potassium salt of Py-N-Pyr with a different chromium source, $Cr(acac)_3$ in THF afforded a brown microcrystalline material, which we proposed to have the structure **3.5**. Analytical data were in agreement with the proposed formuation (Scheme 3.5).

Ethylene oligomerization experiments were performed using analytically pure complexes **3.1**-**3.6**. When complex **3.1** was tested in toluene using MAO (methylaluminoxane) as an activator, a non-selective, statistical distribution of α-olefins was obtained with high activity (Table 3.2, Entry 1). When the solvent and activator were changed (Entry 2), a switch in selectivity was observed, the system now favoring the formation of 1-hexene. We can attribute this behaviour to the solvent effect discussed in Chapter 2.[26] Unfortunately, the activity of this selective system was very low, producing only trace amounts of 1-hexene. This again might be the result of very poor solubility of the catalyst precursor in aliphatic solvents.

The reaction conditions employed for testing complex **3.1** were similar to those of the Phillips system based on a 2,5-dimethylpyrrole.[19] The commercial system is well known to be

very sensitive to the so-called chlorine effect. When a halogenated cocatalyst, such as diethyl aluminum chloride (DEAC), is added to the Phillips system, an increase in catalyst activity and selectivity towards 1-hexene was obtained.[15] This was explained by Luo and coworkers, who proposed that chlorinated alkylating agents are able to influence the coordination of the chromium species, allowing for favourable geometry in the catalytic process.[16] In an effort to boost the activity, the selective catalyst **3.1** was therefore tested with a chlorinated alkylating agent, DEAC, in combination with Et_3Al (Entry 3). However, no increase in either selectivity or activity of this system was observed. For comparison purposes, a reaction following the identical Phillips conditions, using the 2,5-dimethylpyrrole catalyst, was carried out. We found that the activity obtained was approximately 33% lower than that of the optimized, commercial system. Therefore, we can conclude that after optimization, our systems will show significantly higher activity.

Table 3.2. Ethylene oligomerization results for **3.1**.[a]

Entry	Catalyst	co-catalyst (equiv)	alkenes (g)	PE (g)	activity (g/g Cr . h)	linear alpha olefins (mol %)							
						C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
1	**3.1**[b]	MAO (500)	33	0.8	41, 290	12	18	18	15	13	10	8	6
2	**3.1**[c]	DMAO (500)	Trace	1.0	1,256	-	99	-	-	-	-	-	-
3	**3.1**[c]	Et_2AlCl/Et_3Al (15/15)	Trace	0.3	321	-	99	-	-	-	-	-	-
4	**3.1**[c]	DMAO (500); Et_2AlCl/Et_3Al (15/15)	1	1.1	2,326	2	45	6	5	8	9	12	13
5	**DMP-Cr(EH)**	Et_2AlCl/Et_3Al (8/11) DMAO (500)	22	1.62	29,538	-	81	8	2	7	1	1	-

[a]Conditions: catalyst (30 μmol), solvent (100 mL), 80 ˚C, ethylene (40 bar), 30 min. [b]Toluene as solvent. [c]Heptane as solvent. PE = polyethylene.

Complexes **3.2** and **3.3** were highly active for non-selective oligomerization when tested in toluene and activated with MAO, following the Cosee-Arlman chain growth mechanism (Table 3.3, entries 1 and 7).[27,28] Because the divalent state is thought to be responsible for non-selective behaviour, a one-electron reduction of the trivalent catalyst precursor likely occurred *in-situ* upon activation with methylaluminoxane. In heptane with dMAO as activator, the selectivity changed to 1-hexene, again reiterating the poisoning effect of toluene on selective catalysts.[26]

Complex **3.2** showed 80% selectivity for 1-hexene when activated with dMAO, displaying moderate activity (Entry 2). When TEAl was used as the only cocatalyst, the selectivity was improved, but at the expense of activity, which decreased significantly. (Entry 3) A combination of dMAO and TEAl resulted in higher activity with the selectivity maintained (84-85% for 1-hexene). This system was tested at a various temperatures, and the highest activity was observed at 100^{o}C (Entries 4-6).

Complex **3.3** showed 97% selectivity towards 1-hexene and displayed good activity when activated with dMAO (Table 3.3, entry 8). Because there is no chlorine present in the precatalyst, this system was tested under "Phillips conditions". Under these conditions, the system was inactive (Entry 9). When tested with these same conditions as well as dMAO, the activity could be improved and selectivity towards 1-hexene remained high, 93% (Entry 10).

Table 3.3. Ethylene oligomerization results of Pyr-N ligand with various chromium sources.[a]

Entry	catalyst	co-catalyst (equiv)	alkenes (g)	PE (g)	activity (g/g Cr . h)	linear alpha olefins (mol %)							
						C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
1	**3.2**[b]	MAO (500)	44	4.6	59, 905	9	17	17	15	14	11	9	8
2	**3.2**[c]	DMAO (500)	5	3.0	10, 089	3	80	4	3	3	3	2	2
3	**3.2**[c]	Et_3Al (15)	2	0.1	2, 849	4	82	5	3	3	2	1	0
4	**3.2**[c]	DMAO/Et_3Al (500/15)	8	2.3	12, 405	2	82	3	3	3	2	2	2
5	**3.2**[c,d]	DMAO/Et_3Al (500/15)	11	4.8	19, 572	1	85	3	3	2	2	2	2
6	**3.2**[c,e]	DMAO/Et_3Al (500/15)	4	1	6, 459	0	83	5	3	3	2	2	2
7	**3.3**[b]	MAO (500)	19	2.6	25, 800	6	17	18	16	14	12	9	8
8	**3.3**[c]	DMAO (500)	9	1.8	13, 228	0	97	3	0	0	0	0	0
9	**3.3**[c]	Et_2AlCl/Et_3Al (15/15)	0	0.4	51	-	-	-	-	-	-	-	-
10	**3.3**[c]	DMAO (500); Et_2AlCl/Et_3Al (15/15)	13	3	19, 921	0	93	2	1	1	1	1	1
11	**3.3**[b]	DMAO (500)	20	2	27, 574	7	16	17	15	14	12	10	9
12	**3.3**[c]	DMAO (500); Me_3Al (15)	7	0.6	9, 628	0	95	5	0	0	0	0	0

[a]Conditions: catalyst (30 μmol), solvent (100 mL), 80 ˚C, ethylene (40 bar), 30 min. [b]Toluene as solvent. [c]Heptane as solvent. [d] 100°C. [e] 60°C. PE = polyethylene.

When tested in toluene with MAO as an activator, both **3.4** and **3.5** gave a statistical distribution of oligomers with good activity (Table 3.4, entries 1 and 6). In both cases, when the solvent was changed to heptane and the activator was dried completely, thereby depleting MAO of any toluene or free TMA, the selectivity changed from a Shultz-Flory distribution to 90% and 94% 1-hexene for complexes **3.4** and **3.5**, respectively (Entries 2 and 7). Once again, this behaviour is attributed to the solvent effect, where the aromatic ring of toluene coordinates strongly with the chromium, forming a stable complex and poisoning the monovalent state.[26] When activated with solely alkyl aluminum reagents, the activity of complex **3.4** decreased slightly, (Entries 3,4) but the selectivity of each system remained the same, indicating that dMAO is important as a cocatalyst for oligomerization. When complex **3.4** was activated with both dMAO and an alkyl aluminum reagent, Et_3Al, (Entry 5) the activity and selectivity

remained unaltered. Interestingly, the production of unwanted polyethylene wax decreased, indicating that the alkyl aluminum reagent is likely responsible for reducing chromium to the di- or monovalent state, thereby eliminating the trivalent state, which is expected to produce polyethylene.[7]

Alkyl aluminum activators, responsible for reducing the trivalent chromium complex to the di- or monovalent state, easily extract oxygenated ligands from the chromium complex, due to the extreme oxophilicity of the aluminum atom. Therefore, it was thought that using an oxygenated chromium source could help to improve the activity of this system. Chromium tris(acetylacetonate) was used as the chromium source to prepare **3.5**. This species showed similar activity to the chlorinated complex **3.4**, but with an increased selectivity, from 90% to 95% (Table 3.4). When testing complex **3.5** with alkyl aluminum activators under identical "Phillips conditions", there was a very slight increase in selectivity. Regrettably, the activity dropped significantly (Entry 8). When Phillips conditions were used in addition to dMAO, the activity was tripled, with a desirable 91% selectivity towards 1-hexene. However, the formation of polyethylene also increased (Entry 9).

Table 3.4. Ethylene oligomerization results for Pyr-N-Py ligand with various chromium sources.[a]

Entry	catalyst	co-catalyst (equiv)	alkenes	PE	activity	linear alpha olefins (mol %)							
			(g)	(g)	(g/g Cr . h)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
1	**3.4**[b]	MAO (500)	14	1.0	18, 431	6	19	18	16	14	11	9	7
2	**3.4**[c]	DMAO (500)	16	3.0	23, 205	1	90	2	2	2	1	1	1
3	**3.4**[c]	Et_3Al (15)	4	0.03	4, 615	3	89	6	1	1	0	0	0
4	**3.4**[c,d]	Et_3Al (15)	8	0.2	9, 478	7	80	6	3	2	1	1	0
5	**3.4**[c]	DMAO/Et_3Al (500/15)	14	0.6	18, 187	0	90	2	1	2	2	2	1
6	**3.5**[b]	MAO (500)	13	0.9	16. 754	5	18	18	17	14	11	9	8
7	**3.5**[c]	DMAO (500)	8	1.5	11, 979	0	94	2	1	1	1	1	0
8	**3.5**[c]	Et_2AlCl/Et_3Al (15/15)	1	0.1	1, 031	0	95	5	0	0	0	0	0
9	**3.5**[c]	DMAO (500); Et_2AlCl/Et_3Al (15/15)	26	3.0	35, 641	0	91	2	1	1	1	2	2

[a]Conditions: catalyst (30 μmol), solvent (100 mL), 80 ˚C, ethylene (40 bar), 30 min. [b]Toluene as solvent. [c]Heptane as solvent. [d] 100°C. PE = polyethylene.

Complex **3.6** also showed a marked solvent effect (Table 3.5). Although the selectivity was very high (Table 3.5, entries 2 and 3), the activity of this complex was much lower than its precursor, **3.4**, indicating that this dinuclear species is not the catalytically active species for this system.

Table 3.5. Ethylene oligomerization results for complex **3.6.**

Entry	catalyst	co-catalyst	alkenes	PE	activity	linear alpha olefins (mol %)							
		(equiv)	(g)	(g)	(g/g Cr . h)	C_4	C_6	C_8	C_{10}	C_{12}	C_{14}	C_{16}	C_{18}
1	**3.6**[b]	MAO (500)	20	3.0	28, 395	6	16	20	15	13	12	10	8
2	**3.6**[c]	DMAO (500)	2	0.8	3, 746	0	97	3	0	0	0	0	0
3	**3.6**[c]	-	1	0.1	992	0	99	1	0	0	0	0	0

[a]Conditions: catalyst (30 μmol), solvent (100 mL), 80 ˚C, ethylene (40 bar), 30 min. [b]Toluene as solvent. [c]Heptane as solvent. PE = polyethylene.

In conclusion, three new ligands were developed and, with different chromium sources, produced six new oligomerization catalysts. In the case of the pyrrole-imine ligand, non-selective behaviour was observed. Instead, the pyrrole-amine and pyridine-amino-pyrrole ligands were able to produce selective systems for 1-hexene. The highest selectivity towards 1-hexene was observed in the case of an alkyl-aluminum intermediate, complex **3.6**, albeit with low activity due to its poor solubility. Complexes **3.4** and **3.5**, containing the pyridine-amino-pyrrole ligand, showed much higher activities with selectivity for 1-hexene up to 94%.

The employment of an oxygenated chromium source for complexes **3.2** and **3.5** showed an increase in activity and selectivity. This can be attributed to the easier extraction of the acac ligands by aluminum alkyl activators. Further catalytic activity of these complexes was explored and will be discussed in Chapter 4.

3.5 References

(1) Ullmann, F. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley Online Library, 1985.

(2) McGuinness, D. S. *Chemical Reviews* **2011**, *111*, 2321–2341.

(3) Skupinska, J. *Chemical Reviews* **1991**, *91*, 613–648.

(4) Agapie, T. *Coordination Chemistry Reviews* **2011**, *255*, 861–880.

(5) Crewdson, P.; Gambarotta, S.; Djoman, M.-C.; Korobkov, I.; Duchateau, R. *Organometallics* **2005**, *24*, 5214–5216.

(6) Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Organometallics* **2006**, *25*, 715–718.

(7) Jabri, A.; Mason, C. B.; Sim, Y.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angewandte Chemie International Edition* **2008**, *47*, 9717–9721.

(8) Vidyaratne, I.; Nikiforov, G. B.; Gorelsky, S. I.; Gambarotta, S.; Duchateau, R.; Korobkov, I. *Angewandte Chemie International Edition* **2009**, *48*, 6552–6556.

(9) Zhang, J.; Li, A.; Hor, T. S. A. *Organometallics* **2009**, *28*, 2935–2937.

(10) Thapa, I.; Gambarotta, S.; Korobkov, I.; Duchateau, R.; Kulangara, S. V.; Chevalier, R. *Organometallics* **2010**, *29*, 4080–4089.

(11) Tomov, A. K.; Chirinos, J. J.; Long, R. J.; Gibson, V. C.; Elsegood, M. R. J. *Journal of the American Chemical Society* **2006**, *128*, 7704–7705.

(12) Jiang, T.; Zhang, S.; Jiang, X.; Yang, C.; Niu, B.; Ning, Y. *Journal of Molecular Catalysis A: Chemical* **2008**, *279*, 90–93.

(13) Temple, C.; Jabri, A.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Angewandte Chemie International Edition* **2006**, *45*, 7050–7053.

(14) Vidyaratne, I.; Scott, J.; Gambarotta, S.; Duchateau, R. *Organometallics* **2007**, *26*, 3201–3211.

(15) Dixon, J. T.; Green, M. J.; Hess, F. M.; Morgan, D. H. *Journal of Organometallic Chemistry* **2004**, *689*, 3641–3668.

(16) Luo, H.-K.; Li, D.-G.; Li, S. *Journal of Molecular Catalysis A: Chemical* **2004**, *221*, 9–17.

(17) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Hu, C.; Englert, U.; Dixon, J. T.; Grove, C. *Chemical Communications* **2003**, *49*, 334–335.

(18) Mcguinness, D. S.; Wasserscheid, P.; Morgan, D. H.; Dixon, J. T. *Organometallics* **2005**, *24*, 552–556.

(19) Abbott, R. G.; Kreischer, B. E.; Baralt, E. J.; Small, B. L.; Knudsen, R. D.; (Chevron Phillips Chemical Company, L. (Chevron Phillips). US2007043181A1, 2007.

(20) Skobelev, I. Y.; Panchenko, V. N.; Lyakin, O. Y.; Bryliakov, K. P.; Zakharov, V. a.; Talsi, E. P. *Organometallics* **2010**, *29*, 2943–2950.

(21) Trimerization, C. E.; Rensburg, W. J. Van; Steynberg, J. P.; Stark, K. B.; Huyser, J. J.; Steynberg, P. J. *Organometallics* **2004**, *23*, 1207–1222.

(22) Bruin, B. De; Kicken, R. J. N. A. M.; Suos, N. F. A.; Gelder, D.; Donners, M. P. J.; Reijer, C. J. Den; Sandee, A. J.; Smits, J. M. M.; Gal, A. W.; Spek, A. L. *European Journal of Inorganic Chemistry* **1999**, 1581–1592.

(23) McGuinness, D. S.; Wasserscheid, P.; Keim, W.; Morgan, D.; Dixon, J. T.; Bollmann, A.; Maumela, H.; Hess, F.; Englert, U. *Journal of the American Chemical Society* **2003**, *125*, 5272–5273.

(24) Jabri, A.; Temple, C.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Duchateau, R. *Journal of the American Chemical Society* **2006**, *128*, 9238–9247.

(25) Albahily, K.; Koç, E.; Al-Baldawi, D.; Savard, D.; Gambarotta, S.; Burchell, T. J.; Duchateau, R. *Angewandte Chemie International Edition* **2008**, *47*, 5816–9.

(26) Calucci, L.; Englert, U.; Grigiotti, E.; Laschi, F.; Pampaloni, G.; Pinzino, C.; Volpe, M.; Zanello, P. *Journal of Organometallic Chemistry* **2006**, *691*, 829–836.

(27) Cossee, P. *Journal of Catalysis* **1964**, *3*, 80–88.

(28) Arlman, E. J.; Cossee, P. *Journal of Catalysis* **1964**, *3*, 99–104.

Chapter 4: Chromium Catalyzed CO_2-Epoxide Copolymerization

4.1: Introduction

The increasing environmental concern about the negative impact of non-degradable polyolefins is providing a potent stimulus to find bio-degradable polymers of comparable physical properties. Of particular interest are of course polymers from other sources, especially renewable materials. Polycarbonates from the copolymerization of CO_2 and epoxide precisely fall in this category.[1–8] As highlighted below, these bio-degradable polymers are very useful and already rapidly supplanting non-degradable polyethylene for a range of applications. In addition, the use of CO_2 in industrial processes is highly attractive as CO_2 is an abundant, renewable C_1 feedstock and may be obtained at very low cost and high purity directly from the exhausts of methane-fired power plants. Because it is a gas, CO_2 as a comonomer is compatible with several current polymerization processes.[1,9]

Polycarbonate is a plastic consumed in large quantities, as it has applications in automotive, mobile phones, laptops, electronics, data storage and everyday objects including telephone keyboards. This high consumption of polycarbonate, and more importantly, increase in demand, are largely due to its properties: high impact and heat resistance, transparency, strength, good electrical insulation and durability.[2,4] It can be also co-extruded in polyethylene films used for wrappings in food industry due to the excellent oxygen barrier properties introduced by the PC component.

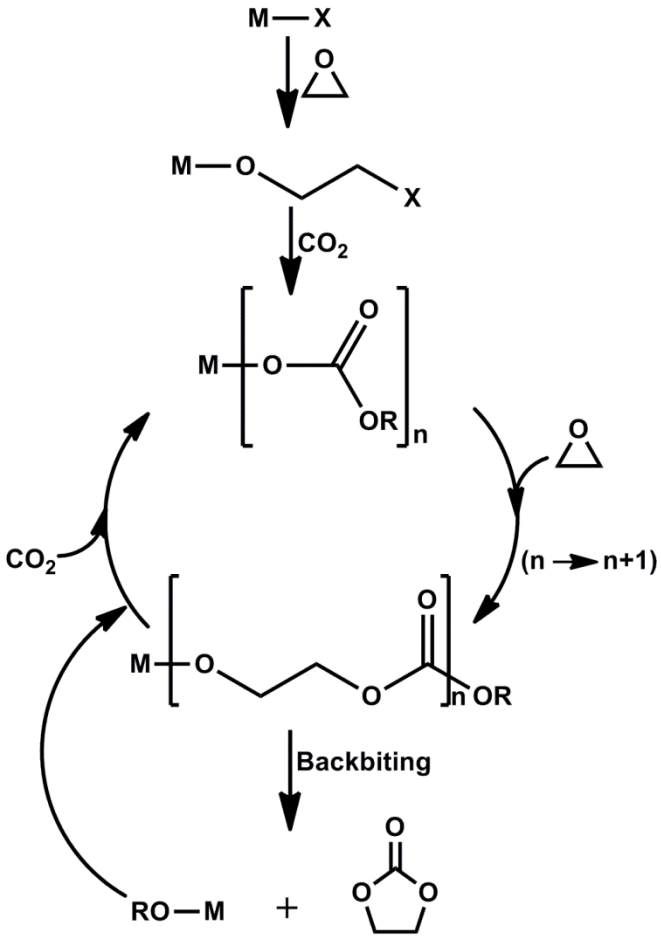
Most polycarbonates are produced via the phosgene method: a reaction between bisphenol A (BPA) and phosgene ($COCl_2$). There are many drawbacks to this synthetic method,

including the toxicity of phosgene, BPA leaching, as well as the difficulty of proper waste disposal.[4]

So far, the properties of polycarbonate synthesized from CO_2 and epoxides cannot match that of conventional BPA-polycarbonate, however they still have a wide variety of applications including packaging materials, thermoplastics and resins, safety glass, adhesives, antifoam agents and plasticizers.[1] Therefore, there is an increase of research effort worldwide for finding more efficient and performing catalysts.

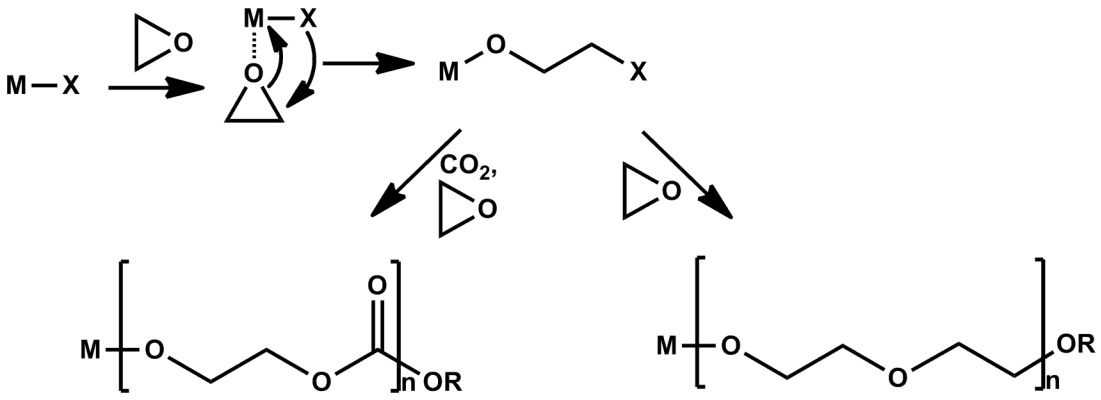
The copolymerization of CO_2 and epoxides is catalyzed by Lewis acidic metal complexes with coordinated halides, carboxylates, alkoxides or aryloxides. The transformation is proposed to occur via a coordination-insertion mechanism, requiring a coordinated group to act as an efficient initiator. The epoxide coordinates to the metal centre, and is opened by the nucleophilic attack of the coordinated initiator function. The resulting unit subsequently inserts CO_2 into the metal-OR bond thus starting the growth of the carbonate polymeric chain. A CO_2 monomer inserts into the metal alkoxide, forming a metal carbonate. Multiple repetitions of this cycle afford a linear polycarbonate. Cyclic polycarbonates, however, may be formed during the chain growth via a backbiting mechanism, where a metal alkoxide attacks a carbonate linkage, forming a truncated metal alkoxide and a cyclic polycarbonate.[3] This mechanism is shown in Scheme 4.1, and can also be found in Chapter 1.

Scheme 4.1:



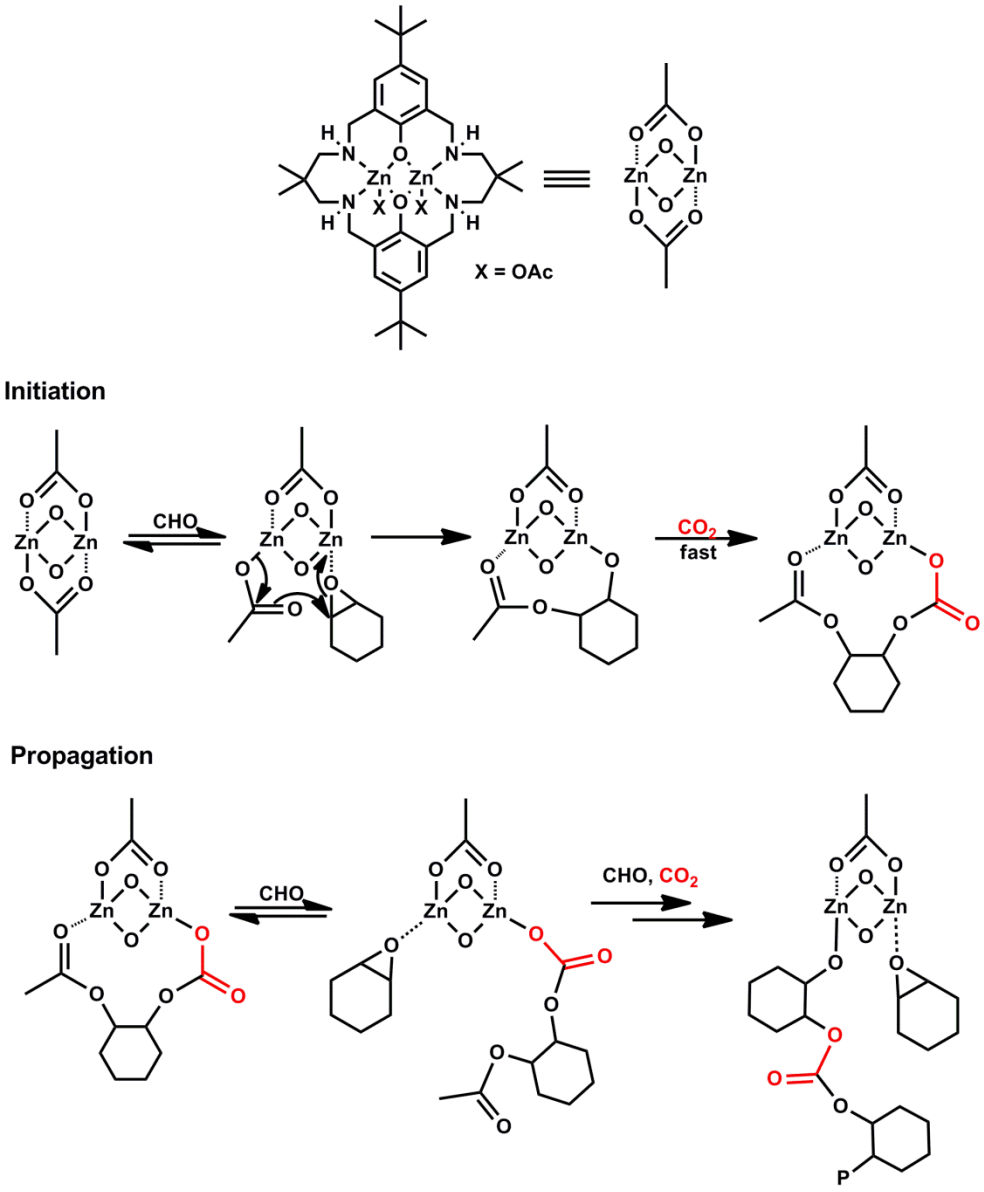
A mechanistic consideration with very important practical repercussions is the formation of carbonate linkages versus ether linkages. CO_2 is a stable molecule that is difficult to activate, while epoxides are highly reactive due to the strain of the ring. For this reason, CO_2 is not always incorporated into the polymer chain, and it is common to find ether linkages along with carbonate linkages (Scheme 4.2). Polyethers have hardly any interest and therefore their formation is regarded as an undesirable parallel feature of the copolymerization reaction.

Scheme 4.2



Zinc is the most studied metal for polycarbonate synthesis, largely due to the discovery in 1969 that a simple diethyl zinc complex may act as a catalytic system. This original diethyl zinc catalyst produced only low conversion of epoxide to polymer.[8,10] Since then, many other zinc complexes have been developed with much higher conversion of epoxide to polycarbonate,[11–19] including several dimetallic complexes.[20–27] Coates and coworkers developed a series of dimeric zinc β-diiminate (BDI) complexes producing moderate weight polymers with TOFs around 2200 h^{-1} and with up to 90% carbonate linkages.[24] The success of these dimeric BDI complexes led to the question of a bimetallic mechanism instead of the monometallic coordination-insertion mechanism previously described in Chapter 1 (Scheme 4.3). This question was elegantly answered by Williams and coworkers, who developed a macrocylic di-zinc complex and, through experimental and computational studies, showed that a bimetallic mechanism is indeed a plausible route.[28,29]

Scheme 4.3



Although many promising results stemmed from the study of zinc catalysts for CO_2-epoxide copolymerization, other transition metals have been investigated as well, including chromium. Chromium porphyrin complexes were developed by Holmes and coworkers to produce low molecular weight polymers with moderate TOFs (around 170 h^{-1}) and up to 97% carbonate linkages.[30] Chromium *salen* complexes, worked on extensively by Darensbourg and

coworkers, have shown excellent activity, with 99% carbonate linkages and high TOFs (1100 h^{-1}).[31] To date, these are the only reported chromium catalysts for the conversion of CO_2 and epoxides to cyclohexenoxide.

We were particularly interested in finding new chromium-based complexes able to catalyze epoxide/CO_2 copolymerization. Since the *salen* type of derivatives, so successfully studied by Darensbourg, and the Cr-porphyrin complexes studied by Holmes and coworkers, appear to be the only existing chromium-based catalysts, we have thus decided to probe complexes of different ligands. In this broad-scope exploratory study, we have used molecules with the nitrogen donor motif embedded in different functions such as neutral pyridines with aminophosphine pendants (**2.1-2.2**), pyrroles with either imine or amine pendants (**3.1-3.3**) and a combination of them (**3.4-3.5**). The reason behind this choice was to use robust ligand systems with little possibility to be leached out or being involved in the reactivity of target molecules. Also the possibility of tuning steric features was regarded as a bonus in case of necessity to reduce backbiting during the copolymerization cycle. Finally, hetero-polymetallic systems such as **2.3** and **3.6** were regarded as of interest *vis-a-vis* the possibility of promoting multi-metallic copolymerization. Given that these complexes were available from the oligomerization work illustrated in the previous chapters, we have decided to test them also for activity in epoxide/CO_2 copolymerization.

We herein describe the catalytic activity of the chromium complexes **2.1-2.3** and **3.1-3.6** for the copolymerization of CO_2 and epoxides to polycarbonates.

4.2 Experimental

All manipulations were carried out under inert nitrogen atmosphere using Schlenk glassware or in a dry-box. Solvents were dried using aluminum oxide purification system. Chemicals were used from commercial sources and used as received. DMAP was purchased from Strem and used as received. PPN^+Cl^- was purchased from Sigma and used as received. Elemental analyses were carried out by using Perkin-Elmer 2400 CHN analyzer. Magnetic susceptibilities were measured using Johnson Matthey magnetic susceptibility balance at room temperature; sample preparation was performed inside a dry-box using calibrated, sealed tubes. X-ray crystal data were determined using a Bruker diffractometer equipped with a Smart CCD area detector and with Bruker Kappa APEXII CCD diffractometer. NMR spectra of ligands were recorded on Bruker Avance 400 MHz spectrometer.

4.2.1: Synthesis of Complexes

Complexes **2.1**-**2.3** and **3.1**-**3.6** are described and characterized in chapter 2 and 3 respectively.

4.2.2: Polymerization Methods

The copolymerizations were performed in both bulk and toluene with a [Cyclohexeneoxide:Catalyst:Cocatalyst] ratio of [500:1:1], unless stated otherwise.

Bulk: A mixture of CHO (5.09 mmol) and catalyst (10.19 μmol) and cocatalyst (10.19 μmol) was reacted in a 5 mL glass sleeve equipped with a stir bar and placed inside a bomb reactor and pressurized with 50 bar CO_2. The reactor was placed in an oil bath on a stirrer/heating plate.

The polymerization was conducted at 80^{o}C, unless stated otherwise. All analyses were performed on crude samples.

Solution: A 5 mL glass sleeve equipped with a stirring bar was placed inside a bomb reactor and charged with a mixture of CHO (5.095 mmol), catalyst (10.19 µmol) and cocatalyst (10.19 µmol) in toluene (1 mL) and pressurized with 50 bar CO_2. The reactor was placed in an oil bath and mounted on top of a stirrer/heating plate. Polymerization was conducted at 80^{o}C, unless stated otherwise. All analyses were performed on crude samples.

4.2.3: Analysis of Polymers

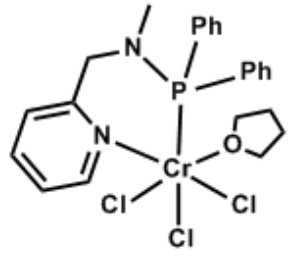
NMR spectra were recorded on a Varian Mercury V*x* (400 MHz) spectrometer at 25^{o}C in chloroform-d_1, and ^{1}H NMR spectra were referenced internally using residual solvent proton signals. SEC analysis was carried out using a Waters 2695 separations module, a model 2414 refractive index detector (at 40^{o}C), and a model 486 UV detector (at 254 nm) in series. Injections were done by a Waters model WISP 712 auto-injector, using an injection volume of 50 μL. The columns used were a PLgel guard (5 um particles) 50 x 705 mm column, followed by two PLgel mixed-C (5 um particles) 300 x 7.5 mm columns at 40^{o}C in series.

All MALDI-ToF-MS spectra were recorded from the crude products. In-house developed software was used to characterize the polymers in detail and allowed elucidation of the individual chain structures, the copolymer's chemical composition, and topology.

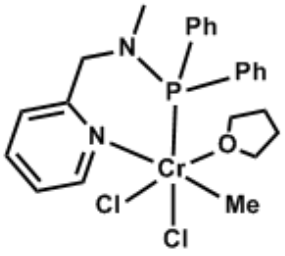
4.3 Results and Discussion

As discussed earlier, polycarbonate synthesis requires Lewis acidic catalysts with a nucleophilic initiator group to aid in a coordination-insertion mechanism of epoxide and CO_2[1–3,7]. The chromium-alkyl function present in complexes **2.2** and **2.3** provides a good nucleophilic initiator that can dissociate from the metal centre as well as facilitate the epoxide's ring opening. Chromium complexes have previously been used as Lewis acidic polycarbonate catalysts,[30,31]

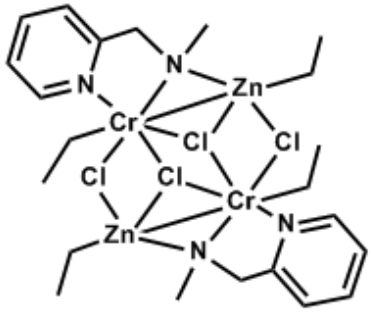
Scheme 4.4



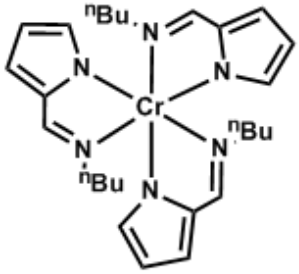
2.1



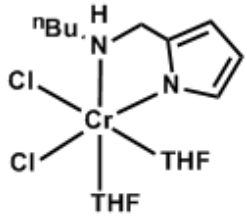
2.2



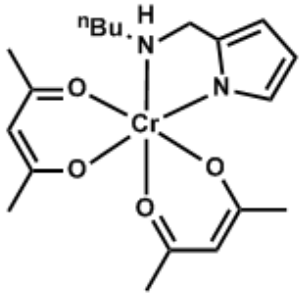
2.3



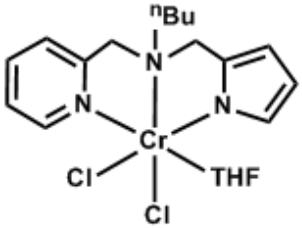
3.1



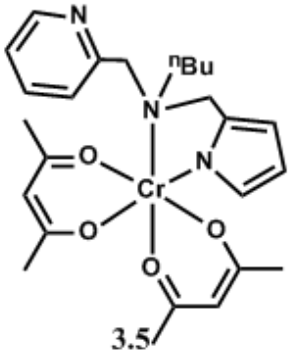
3.2



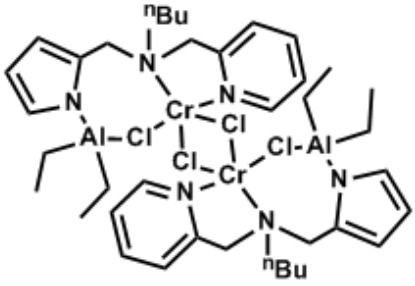
3.3



3.4



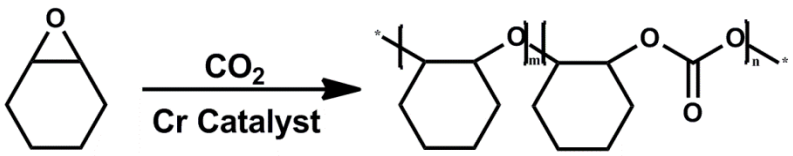
3.5



3.6

however the most popular metal used for such reactions remains zinc[2,13–21,23,25–27,29] Therefore, the combination of both chromium and zinc in a multi-metallic cluster, as seen with complex **2.3**, seemed likely to be able to both participate in a bimetallic mechanism and have a metal-alkyl initiating function.

Scheme 4.5



Upon testing the analytically pure isolated complexes for polycarbonate synthesis from cyclohexene oxide and CO_2 (Scheme 4.5), we found complexes **2.1** and **2.2** to show some degree of polymerization, producing a low molecular weight polycarbonate with moderate TOFs. Disappointingly, complex **2.3** showed no conversion of cyclohexene oxide to polycarbonate, even under various conditions (Table 4.1, entries 1-5). When tested in THF (Entry 6), there was an increase in conversion due to higher solubility, however only 11% carbonate linkages were produced, indicating that this is mainly a polyether catalyst.

Complex **2.2** contains a chromium-alkyl function, and upon testing in toluene using bis(triphenylphosphine)iminium chloride as a cocatalyst, up to 76% conversion of cyclohexene oxide to polycarbonate was obtained (Table 4.1, entry 10). When the reaction using bis(triphenylphosphine) iminium chloride as a cocatalyst was performed in the absence of solvent, there was still 60% conversion of cyclohexene oxide to polycarbonate (Entry 7). When

the reaction time was shortened from 18 hours to only 4, no conversion of cyclohexeneoxide was observed, even when the equivalents of epoxide were increased (Entries 8, 9) indicating an induction time of at least 4 hours.

With either a neutral or a charged catalyst, complex **2.1** showed the highest degree of polymerization of the pyridine-NP based catalysts, with up to 90% conversion of cyclohexene oxide to a low molecular weight polycarbonate (Table 4.1, Entries 12, 14). In the absence of cocatalysts, complex **2.1** still showed 76% conversion of cyclohexene oxide to low weight polycarbonate (Entry 16).

Complex **2.1** and **2.2** both produced similar, low molecular weight polymers with low PDIs. Both complexes displayed the same selectivity toward polycarbonate production, but complex **2.2** exhibited lower activity, likely due to the instability of the chromium-alkyl, which could have decomposed in situ or via reaction with the cocatalyst.

Table 4.1: CO_2-epoxide Copolymerization Results of PyNP complexes[a]

Entry	Catalyst	Cocat.	Reaction time (h)	Solvent	Conversion CHO (%)[b]	M_n (g/mol)[c]	PDI[c]	% Carbonate[b]	TOF (h^{-1})[b]
1	**2.3**	DMAP	18	-	-	-	-	-	-
2	**2.3**	PPN^+Cl^-	18	-	-	-	-	-	-
3	**2.3**	PPN^+Cl^-	4	-	-	-	-	-	-
4	**2.3**	PPN^+Cl^-	18	PhMe	1	-	-	-	-
5[d]	**2.3**	PPN^+Cl^-	18	PhMe	-	-	-	-	-
6	**2.3**	PPN^+Cl^-	4	THF	22	24240	3.65	11	28
7	**2.2**	DMAP	18	-	14	1220	1.25	90	4
8	**2.2**	PPN^+Cl^-	18	-	60	1380	1.26	90	17
9	**2.2**	PPN^+Cl^-	4	PhMe	-	-	-	-	-
10[d]	**2.2**	PPN^+Cl^-	4	PhMe	-	-	-	-	-
11	**2.2**	PPN^+Cl^-	18	PhMe	76	1350	1.34	82	21
12[d]	**2.2**	PPN^+Cl^-	18	PhMe	31	1600	1.30	65	17
13	**2.1**	DMAP	18	PhMe	90	1910	1.39	94	25
14	**2.1**	PPN^+Cl^-	18	-	63	1450	11.41	91	18
15	**2.1**	PPN^+Cl^-	18	PhMe	90	1250	1.31	94	25
16[d]	**2.1**	PPN^+Cl^-	18	PhMe	81	1630	1.43	93	23
17	**2.1**	-	18	PhMe	76	934	1.28	82	21

[a]Conditions: Loading 10 μmol of complex, 80˚C, 50 bar (CO_2). DMAP = 4-dimethylaminopyridine, PPN^+Cl^- = bis(triphenylphosphine) iminium chloride. [CHO]:[Cat]:[Cocat] = 500:1:1. [b]Calculated from ^{1}H NMR spectra. [c]SEC performed in THF against PS standards. [d][CHO]:[Cat]:[Cocat] = 1000:1:1.

Upon testing the chlorine-free catalyst **3.1** for polymerization activity, it was observed that it produced polycarbonates in a higher molecular weight range (3,600 g/mol) than **2.1-2.3** (Table 4.2).

Table 4.2: CO_2-epoxide Copolymerization Results for Complex **3.1**.[a]

Entry	Catalyst	Cocat.	Reaction time (h)	Solvent	Conversion CHO (%)[b]	M_n (g/mol)[c]	PDI[c]	% Carbonate[b]	TOF (h^{-1})[b]
1	**3.1**	PPN^+Cl^-	4	PhMe	33	819	1.07	53	42
2	**3.1**	PPN^+Cl^-	4	-	52	3364	1.53	89	65
3	**3.1**	PPN^+Cl^-	8	PhMe	45	1472	1.48	66	29
4	**3.1**	PPN^+Cl^-	8	-	65	2665	1.26	87	40
5[d]	**3.1**	PPN^+Cl^-	8	-	75	3674	1.93	91	47
6[e]	**3.1**	PPN^+Cl^-	8	-	52	1301	1.42	84	33
7	**3.1**	DMAP	8	-	60	2102	1.20	90	38
8[f]	**3.1**	PPN^+Cl^-	4	-	14	1390	1.50	85	34
9	**3.1**	PPN^+Cl^-	16	PhMe	65	1963	1.17	69	21
10	**3.1**	PPN^+Cl^-	32	PhMe	74	2239	1.18	74	12
11	**3.1**	PPN^+Cl^-	72	PhMe	74	2475	1.16	74	12

[a]Conditions: Loading 10 μmol of complex, 80˚C, 50 bar (CO_2). DMAP = 4-dimethylaminopyridine, PPN^+Cl^- = bis(triphenylphosphine) iminium chloride. [CHO]:[Cat]:[Cocat] = 500:1:1. [b]Calculated from ^{1}H NMR spectra. [c]SEC performed in THF against PS standards. [d]T = 100°C. [e]T = 60°C. [f][CHO]:[Cat]:[Cocat] = 1000:1:1.

After 4 hours, a low weight polymer was produced with only 50% carbonate linkages and low conversion of CHO (Table 4.3, entry 1), but when the reaction time was increased to 8 hours, TOF, molecular weight and % carbonate linkages all increased. When the reaction time was extended even further, we observed an increase in the conversion of CHO to polymer, until 32 hours, at which time the conversion plateaus at 74%, indicating that the catalyst is no longer active (Figure 4.1). Figure 4.2 shows the increase in % carbonate linkages over time of reaction, again reaching a plateau after 32 hours.

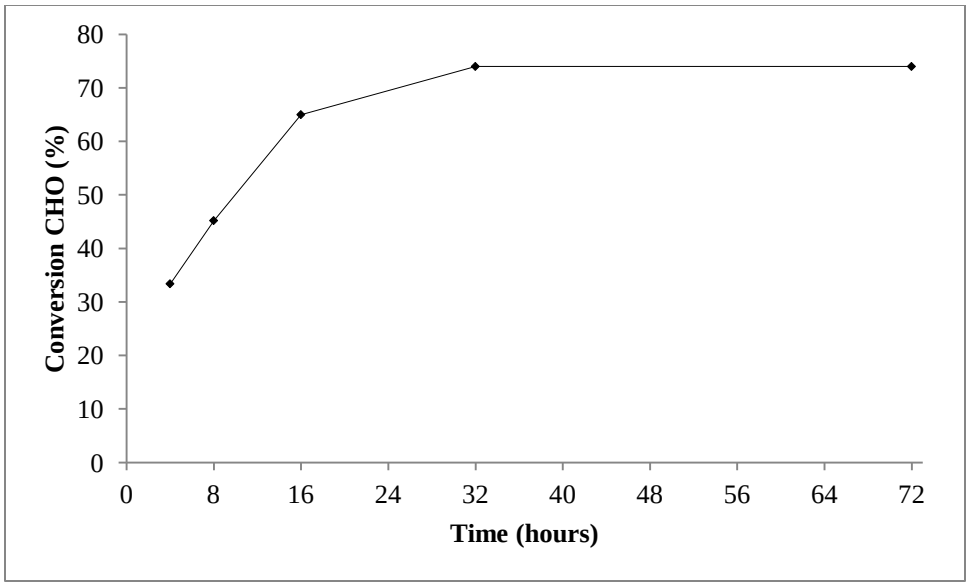


Figure 4.1: Graphical representation of conversion of cyclohexeneoxide (%) as a function of time, catalyzed by complex **3.1**. Reactions run in toluene at 80°C and 50 bar CO_2 with PPN^+Cl^- as a cocatalyst. [CHO:Catalyst:Cocatlyst] = [500:1:1].

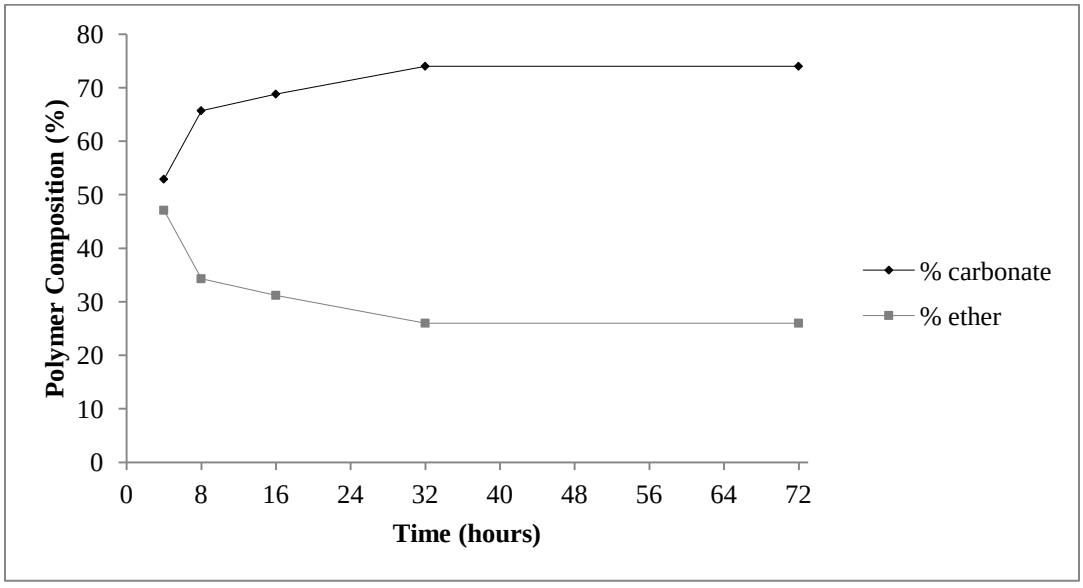


Figure 4.2: Graphical representation of % carbonate linkages versus % ether linkages as a function of time, catalyzed by complex **3.1.** Reactions run in toluene at 80°C and 50 bar CO_2 with PPN^+Cl^- as a cocatalyst. [CHO:Catalyst:Cocatlyst] = [500:1:1].

When the temperature was lowered to 60^{o}C (Table 4.2, entry 6), we observed a decrease in TOF, while at 100^{o}C (Entry 5) there was an increase in TOF and molecular weight. Unfortunately, at this elevated temperature, there was significant production of cyclic polycarbonate. Other changes to reaction conditions were tested, including different CHO:catalyst:cocatalyst ratios and different cocatalysts, but no significant changes were observed. (Entries 7 and 8)

Table 4.3: CO_2-epoxide Copolymerization Results for Complexes **3.2** and **3.3.**[a]

Entry	Catalyst	Cocat.	Reaction time (h)	Solvent	Conversion CHO (%)[b]	M_n (g/mol)[c]	PDI[c]	% Carbonate[b]	TOF (h^{-1})[b]
1	**3.2**	PPN^+Cl^-	4	PhMe	18	1464	1.29	54	30
2	**3.2**	PPN^+Cl^-	4	-	17	1042	1.10	55	29
3	**3.2**	PPN^+Cl^-	8	PhMe	18	1533	1.27	72	17
4	**3.2**	PPN^+Cl^-	8	-	65	1622	1.57	70	46
5	**3.2**	DMAP	8	-	-	-	-	-	-
6[d]	**3.2**	PPN^+Cl^-	8	-	75	3799	3.25	92	48
7[e]	**3.2**	PPN^+Cl^-	8	-	2	1081	1.29	94	2
8[f]	**3.2**	PPN^+Cl^-	4	-	4	1036	1.21	61	5
9	**3.3**	PPN^+Cl^-	4	PhMe	43	2695	1.65	77	55
10	**3.3**	PPN^+Cl^-	4	-	71	2440	1.36	88	88
11	**3.3**	PPN^+Cl^-	8	PhMe	79	6008	1.71	83	51
12	**3.3**	PPN^+Cl^-	8	-	81	4067	1.65	90	52
13[d]	**3.3**	PPN^+Cl^-	8	-	84	4043	1.84	90	53
14[e]	**3.3**	PPN^+Cl^-	8	-	6	1026	1.28	66	6
15	**3.3**	DMAP	8	PhMe	2	695	1.07	52	2
16[f]	**3.3**	PPN^+Cl^-	8	PhMe	49	8626	1.59	96	63
17	**3.3**	PPN^+Cl^-	4	THF	53	3181	1.36	78	67
18	**3.3**	-	4	PhMe	-	-	-	-	-
19	**3.3**	PPN^+Cl^-	16	PhMe	83	5973	1.42	87	26
20	**3.3**	PPN^+Cl^-	32	PhMe	99	6552	2.78	93	15

[a]Conditions: Loading 10 μmol of complex, 80˚C, 50 bar (CO_2). DMAP = 4-dimethylaminopyridine, PPN^+Cl^- = bis(triphenylphosphine) iminium chloride. [CHO]:[Cat]:[Cocat] = 500:1:1. [b]Calculated from ^{1}H NMR spectra. [c]SEC performed in THF against PS standards. [d]T = 100°C. [e]T = 60°C. [f][CHO]:[Cat]:[Cocat] = 1000:1:1.

Complexes **3.2** and **3.3** are synthesized from the same amino-pyrrole ligand with different chromium sources with purpose of obtaining chlorine free materials. Complex **3.2** produced low molecular weight polycarbonates (Table 4.3, entries 1-8). When the temperature was increased

to 100°C, the molecular weight increased to 3800 g/mol (Entry 6), however the PDI increased as well. In all cases, the polymers synthesized by catalyst **3.2** contained over 50% carbonate linkages.

Catalyst **3.3**, similar to catalyst **3.1**, contains no chlorine. Upon testing, we obtained higher molecular weight polymers than the chlorinated analogue, as well as higher TOFs. When the polymerization reaction proceeded for 8 hours (Table 4.3, entry 11), high conversion of CHO to polymer was observed, producing polymer with molecular weight 6000 g/mol with 83% carbonate linkages. The reaction time was extended, and after 32 hours, there was complete conversion of CHO to polycarbonate, as depicted in Figure 4.3. The percentage of carbonate linkages is also increasing over time, reaching 93% after 32 hours (Figure 4.4).

.

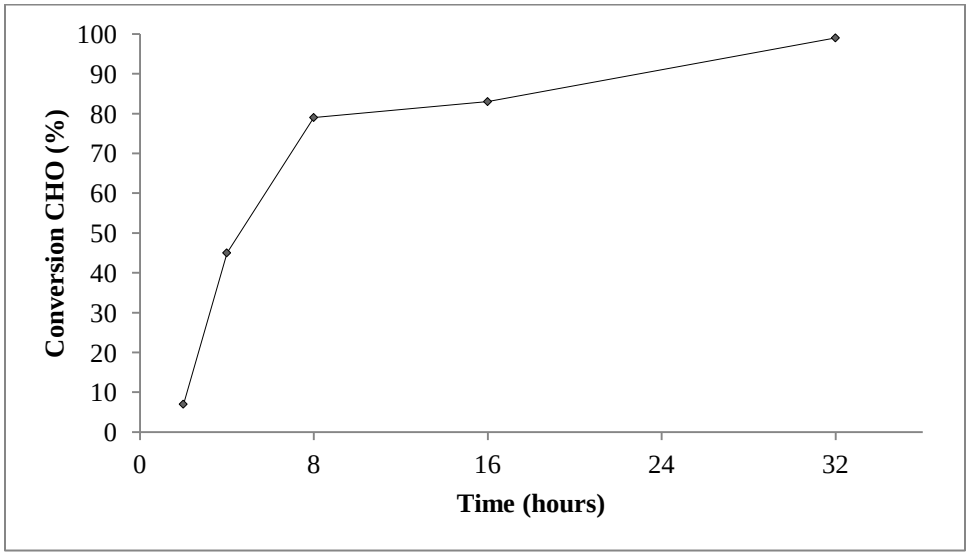


Figure 4.3: Graphical representation of conversion of cyclohexeneoxide (%) as a function of time, catalyzed by complex **3.3**. Reactions run in toluene at 80°C and 50 bar CO_2 with PPN^+Cl^- as a cocatalyst. [CHO:Catalyst:Cocatlyst] = [500:1:1].

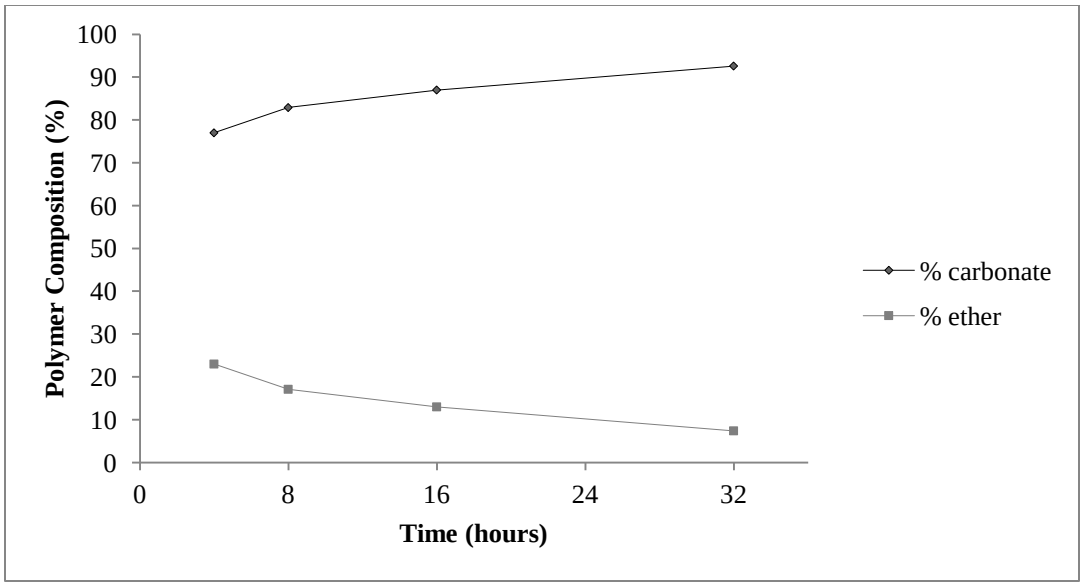


Figure 4.4: Graphical representation of % carbonate linkages versus % ether linkages as a function of time, catalyzed by complex **3.3.** Reactions run in toluene at 80^{o}C and 50 bar CO_2 with $PPN^{+}Cl^{-}$ as a cocatalyst. [CHO:Catalyst:Cocatlyst] = [500:1:1].

Complexes **3.4** and **3.5** are both based on the same pyridine-amino-pyrrole ligand, and, similar to complexes **3.2** and **3.3**, were complexed with different chromium sources producing both chlorinated and chlorine free chromium catalysts. Contrary to our expectations for similar results, we obtained much lower activity (Table 4.4). Both catalysts produced only low-weight products, and, in the case of catalyst **3.5**, the products were just oligomers. In addition, the conversion of CHO to polymer was low. When tested in THF, (Entries 5 and 10), the conversion increased due to higher solubility, and molecular weight increased from the oligomer range to low molecular weight polymer.

The heterodimetallic **3.6**, was a potential candidate for the bimetallic mechanism proposed by Williams and coworkers.[5,26,28,29] Upon testing, we found a disappointingly low conversion of CHO to polymer. When tested in THF, the complex was more soluble but no increase in conversion was observed, and only 25% carbonate linkages were formed.

Table 4.4: CO_2-epoxide copolymerization results for complexes **3.4-3.6**.[a]

Entry	Catalyst	Cocat.	Reaction time (h)	Solvent	Conversion CHO (%)[b]	M_n (g/mol)[c]	PDI[c]	% Carbonate[b]	TOF (h^{-1})[b]
1	**3.4**	PPN^+Cl^-	4	PhMe	6	785	1.27	50	19
2	**3.4**	PPN^+Cl^-	4	-	-	-	-	-	-
3	**3.4**	PPN^+Cl^-	8	PhMe	29	1684	1.29	72	24
4	**3.4**	PPN^+Cl^-	8	-	-	-	-	-	-
5	**3.4**	PPN^+Cl^-	4	THF	67	2426	1.16	71	84
6	**3.5**	PPN^+Cl^-	4	PhMe	2	523	1.01	70	18
7	**3.5**	PPN^+Cl^-	4	-	9	653	1.32	55	39
8	**3.5**	PPN^+Cl^-	8	PhMe	5	578	1.05	55	10
89	**3.5**	PPN^+Cl^-	8	-	11	622	1.12	62	12
10	**3.5**	PPN^+Cl^-	4	THF	52	1746	1.19	81	65
11	**3.6**	PPN^+Cl^-	4	PhMe	8	-	-	-	10
12	**3.6**	PPN^+Cl^-	4	-	-	-	-	-	-
13	**3.6**	PPN^+Cl^-	8	PhMe	9	798	1.11	69	16
14	**3.6**	PPN^+Cl^-	8	-	-	-	-	-	-
15	**3.6**	PPN^+Cl^-	4	THF	7	34686	2.70	25	9

[a]Conditions: Loading 10 μmol of complex, 80˚C, 50 bar (CO_2). DMAP = 4-dimethylaminopyridine, PPN^+Cl^- = bis(triphenylphosphine) iminium chloride. [CHO]:[Cat]:[Cocat] = 500:1:1. [b]Calculated from ^{1}H NMR spectra. [c]SEC performed in THF against PS standards.

In conclusion, we have surveyed a few chromium complexes of pyrrole and pyridine-based ligand systems or activity as CO_2-epoxide copolymerization catalysts finding that they may act as catalysts with in some case interesting catalytic behavior. It should be reiterated that to date, there have been very few examples of chromium catalysts for polycarbonate synthesis in the literature. In particular, complexes **3.1** and **3.3** showed the best activity, producing moderate-molecular weight polymers with high-percent carbonate linkages and moderate TOFs. Interestingly, these two catalysts contained no chlorine, and therefore the only chlorine in the

system was introduced by the cocatalyst. Further investigation needs to be done to determine the effect of chlorinated versus non-chlorinated catalysts in the copolymerization of CO_2 and epoxides.

4.4: References

(1) Kember, M. R.; Buchard, A.; Williams, C. K. *Chemical Communications* **2011**, *47*, 141–163.

(2) Darensbourg, D. J. *Chemical Reviews* **2007**, *107*, 2388–410.

(3) Coates, G. W.; Moore, D. R. *Angewandte Chemie International Edition* **2004**, *43*, 6618–6639.

(4) Fukuoka, S.; Fukawa, I.; Tojo, M.; Oonishi, K.; Hachiya, H.; Aminaka, M.; Hasegawa, K.; Komiya, K. *Catalysis Surveys from Asia* **2010**, *14*, 146–163.

(5) Kember, M. R.; Williams, C. K. *Journal of the American Chemical Society* **2012**, *134*, 15676–15679.

(6) Nelson, A. M.; Long, T. E. *Polymer International* **2012**, *61*, 1485–1491.

(7) Klaus, S.; Lehenmeier, M. W.; Anderson, C. E.; Rieger, B. *Coordination Chemistry Reviews* **2011**, *255*, 1460–1479.

(8) Inoue, S.; Tsuruta, T.; Koinuma, H. *Journal of Polymer Science Part B* **1969**, *7*, 287–292.

(9) Bolm, C.; Beckmann, O.; Dabard, O. a. G. *Angewandte Chemie International Edition* **1999**, *38*, 907–909.

(10) Takeda, N.; Inoue, S. *Macromolecular Chemistry* **1978**, *179*, 1377–1381.

(11) Holtcamp, M. W.; Darensbourg, D. J. *Macromolecules* **1995**, *28*, 7577–7579.

(12) Darensbourg, D. J.; Holtcamp, M. W.; Struck, G. E.; Zimmer, M. S.; Niezgoda, S. a.; Rainey, P.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. *Journal of the American Chemical Society* **1999**, *121*, 107–116.

(13) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C.; Reibenspies, J. H. *Journal of the American Chemical Society* **2000**, 12487–12496.

(14) Darensbourg, D. J.; Zimmer, M. S.; Rainey, P.; Larkins, D. L. *Inorganic Chemistry* **2000**, *39*, 1578–1585.

(15) Darensbourg, D. J.; Yarbrough, J. C. *Journal of the American Chemical Society* **2002**, *124*, 6335–6342.

(16) Dinger, M. B.; Scott, M. J. *Inorganic Chemistry* **2001**, *40*, 1029–1036.

(17) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C. *Inorganic Chemistry* **2002**, *41*, 973–980.

(18) Darensbourg, D. J.; Rainey, P.; Yarbrough, J. *Inorganic Chemistry* **2001**, 986–993.

(19) Cheng, M.; Moore, D. R.; Reczek, J. J.; Chamberlain, B. M.; Lobkovsky, E. B.; Coates, G. W. *Journal of the American Chemical Society* **2001**, *123*, 8738–8749.

(20) Darensbourg, D. J.; Wildeson, J. R.; Yarbrough, J. C. *Organometallics* **2001**, *20*, 4413–4417.

(21) Darensbourg, D. J.; Lewis, S. J.; Rodgers, J. L.; Yarbrough, J. C. *Inorganic chemistry* **2003**, *42*, 581–589.

(22) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Journal of the American Chemical Society* **1998**, *120*, 11018–11019.

(23) Cheng, M.; Darling, N. a.; Lobkovsky, E. B.; Coates, G. W. *Chemical Communications* **2000**, 2007–2008.

(24) York, N.; Bastide, J.; Hamelin, J.; Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Angewandte Chemie International Edition* **2002**, *41*, 2599–2602.

(25) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *Journal of the American Chemical Society* **2002**, *124*, 14284–14285.

(26) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *Journal of the American Chemical Society* **2003**, *125*, 11911–11924.

(27) Allen, S. D.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *Journal of Organometallic Chemistry* **2003**, *683*, 137–148.

(28) Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K. *Macromolecules* **2012**, *45*, 6781–6795.

(29) Kember, M. R.; Knight, P. D.; Reung, P. T. R.; Williams, C. K. *Angewandte Chemie International Edition* **2009**, *48*, 931–933.

(30) Mang, S.; Cooper, A. I.; Colclough, M. E.; Chauhan, N.; Holmes, A. B. *Macromolecules* **2000**, *33*, 303–308.

(31) Darensbourg, D. J.; Mackiewicz, R. M. *Journal of the American Chemical Society* **2005**, *127*, 14026–14038.

Conclusion

This thesis work has provided several examples of the immense effect of minor ligand modifications on the selectivity and activity of ethylene oligomerization systems. Using the aminophosphine ligand, based on previous work by our group, we observed that by changing a two-carbon linker to one-carbon, the selectivity changed from approximately 75% towards 1-octene to a Schulz-Flory distribution of oligomers. With the pyrrole-imine ligand, we observed some selectivity, however the activity of this complex was very low. By saturating the C-N double bond, we were able to synthesize a more soluble, and therefore more active catalyst, displaying similar selectivity. Finally, by adding a pyridine pendant to this ligand moiety we hoped to increase the selectivity of this system, as pyridine based ligands has shown high selectivity in ethylene oligomerization. This last ligand modification improved the selectivity, producing the highest percentage of 1-hexene of the catalysts described.

Another important modification we noted was the use of different chromium sources. Both chromium trichloride and chromium tris(acetylacetonate) were used with these ligands, and it was observed that catalysts synthesized with the oxygenated chromium source proved to have increased selectivity and activity over the chlorinated analogues. This change in activity can be attributed to the easier extraction of the acac ligands by aluminum alkyl activators.

In addition, we investigated another important polymerization process: the copolymerization of CO_2 and epoxide. As previously discussed, there have been very few examples of chromium catalysts for polycarbonate synthesis in the literature. The ligands used in the oligomerization study contained neutral pyridines with aminophosphine pendants, pyrroles with either imine or amine pendants, as well as the combination of these features. Testing these

catalysts based on these ligands for their activity in the copolymerization of CO_2 and epoxide allowed us to investigate the effect of nitrogen donor motifs in chromium complexes. We have shown that chromium complexes are effective catalysts in this type of polymerization. Interestingly, the catalysts that showed the best activity, producing moderate molecular weight polymers with high-percent carbonate linkages and moderate TOFs, were chlorine-free catalysts; the only chlorine in the system was introduced by the cocatalyst.

Because alkyl aluminum activators are used in the ethylene oligomerization process, treatment of precatalysts with alkyl aluminum reagents can lead to the isolation of the catalytically active species involved in the oligomerization process. Treatment of the selective oligomerization catalysts described in this work could provide such information, and provide important mechanistic insights. With this information, ligand modifications, such as alterations of carbon bridges or changing pendants to include phosphines, could be made that would lead to a change in selectivity from tri- to tetramerization.

In order to gain more insight into finding effective polycarbonate catalysts, the existing systems outlined in this work should be optimized. In addition, the effect of chlorinated versus non-chlorinated catalysts was briefly alluded to, however more investigation of these types of systems needs to be done before any generalizations can be made. Chlorinated versus non-chlorinated cocatalysts also should be tested in order to gain more insight as to the effect of chlorine on these polycarbonate catalysts.

Appendix A

X-ray Crystallography Procedure

Suitable crystals were selected, mounted on a thin, glass fiber with paraffin oil, and cooled to the data collection temperature. Data were collected on a Bruker AXS SMART 1 k CCD diffractometer. Data collection was performed with three batch runs at phi = 0.00 deg (600 frames), at phi = 120.00 deg (600 frames), and at phi = 240.00 deg (600 frames). Initial unit-cell parameters were determined from 60 data frames collected at different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied. The systematic absences and unit-cell parameters were consistent for the reported space groups. The structures were solved by direct methods, completed with difference Fourier syntheses, and refined with full-matrix least-squares procedures based on *F*2. All non-hydrogen atoms were refined with anisotropic displacement parameters. When it was not possible to locate them, the hydrogen atoms were treated as idealized contributions.

Appendix B

NMR Spectra of Synthesized Ligands

The following series of NMR spectra were recorded on Bruker Avance 400 MHz spectrometer, using $CDCl_3$ as the solvent.

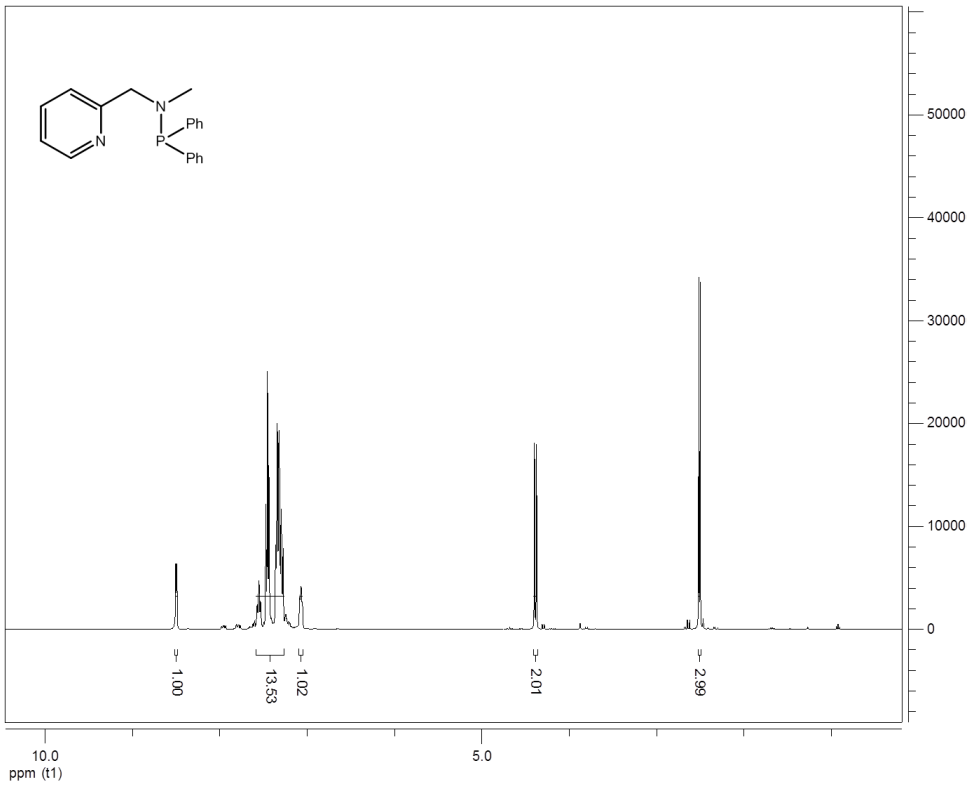


Figure 1a: ^{1}H NMR of **PyNP**.

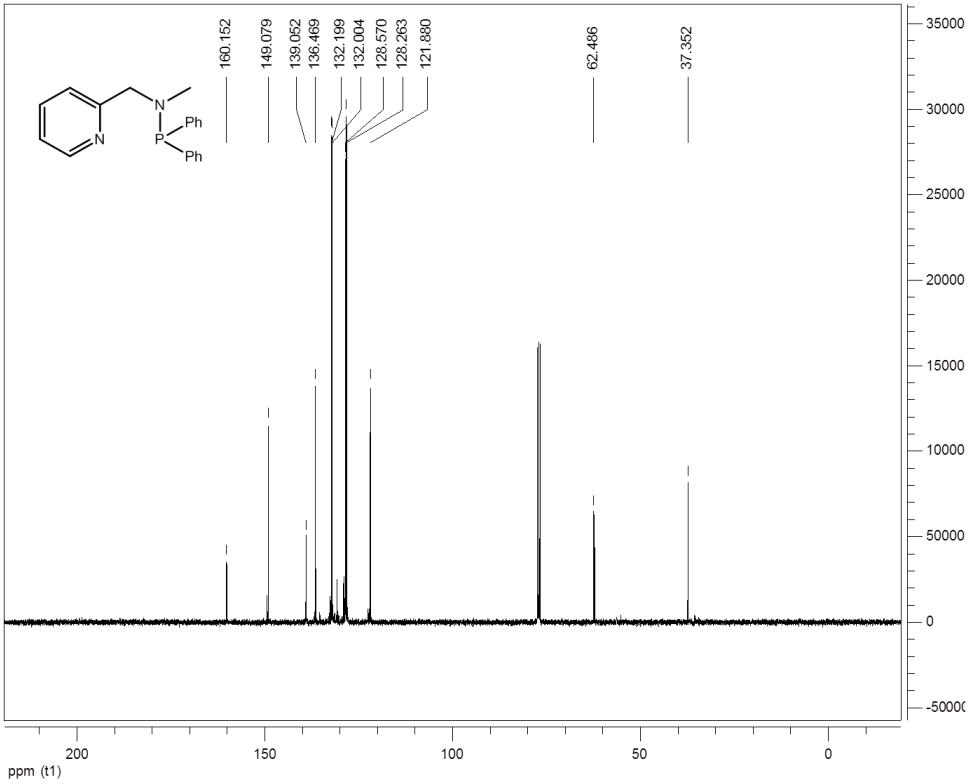


Figure 1b: ^{13}C NMR of **PyNP**.

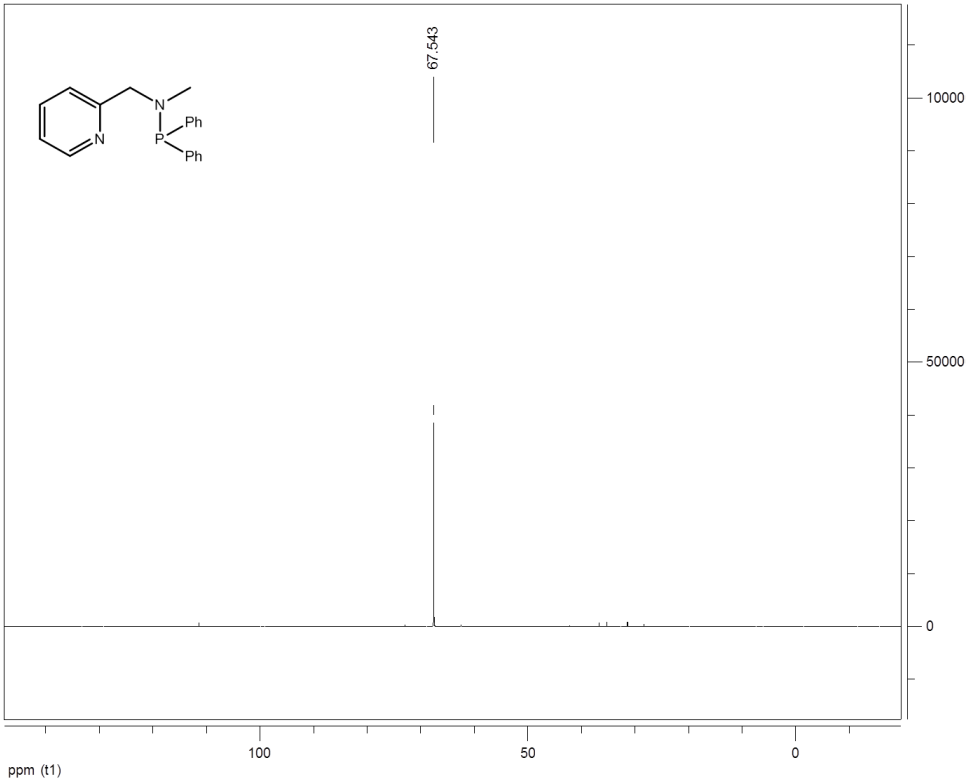


Figure 1c: ^{31}P NMR of **PyNP.**

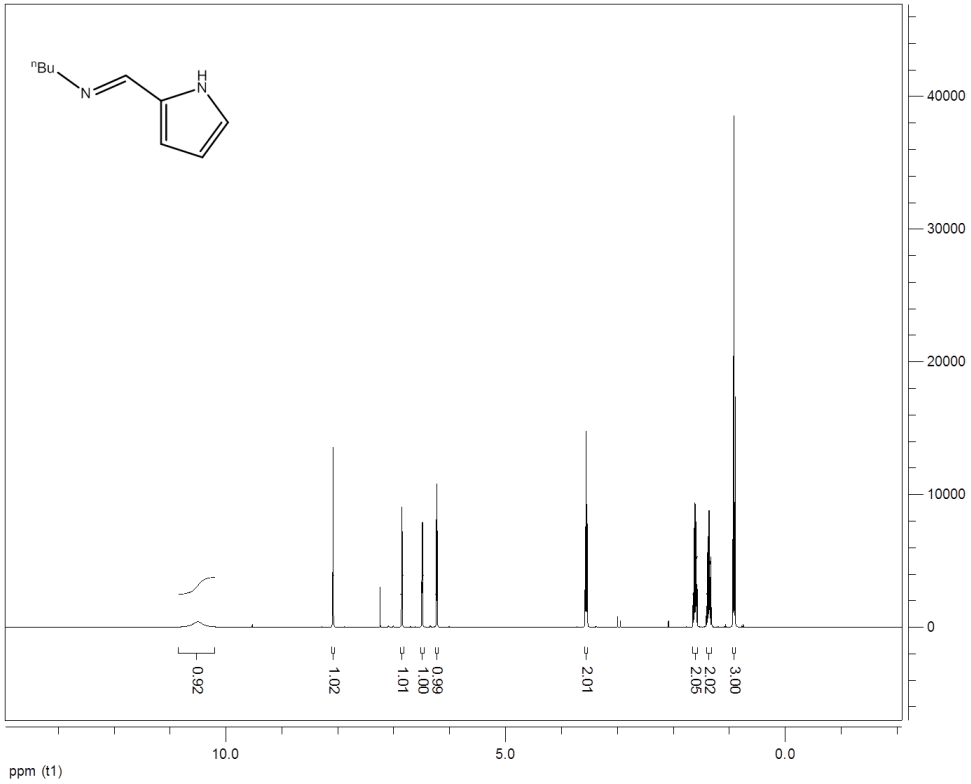


Figure 2a: ^{1}H NMR of **Pyr=N.**

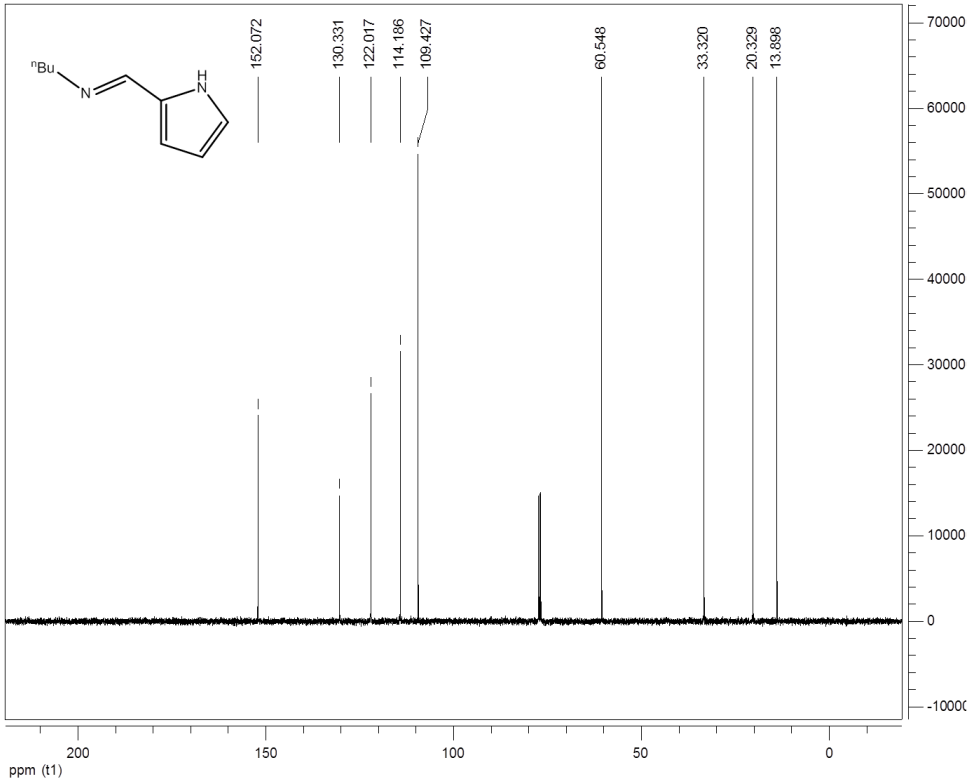


Figure 2b: ^{13}C NMR of **Pyr=N**.

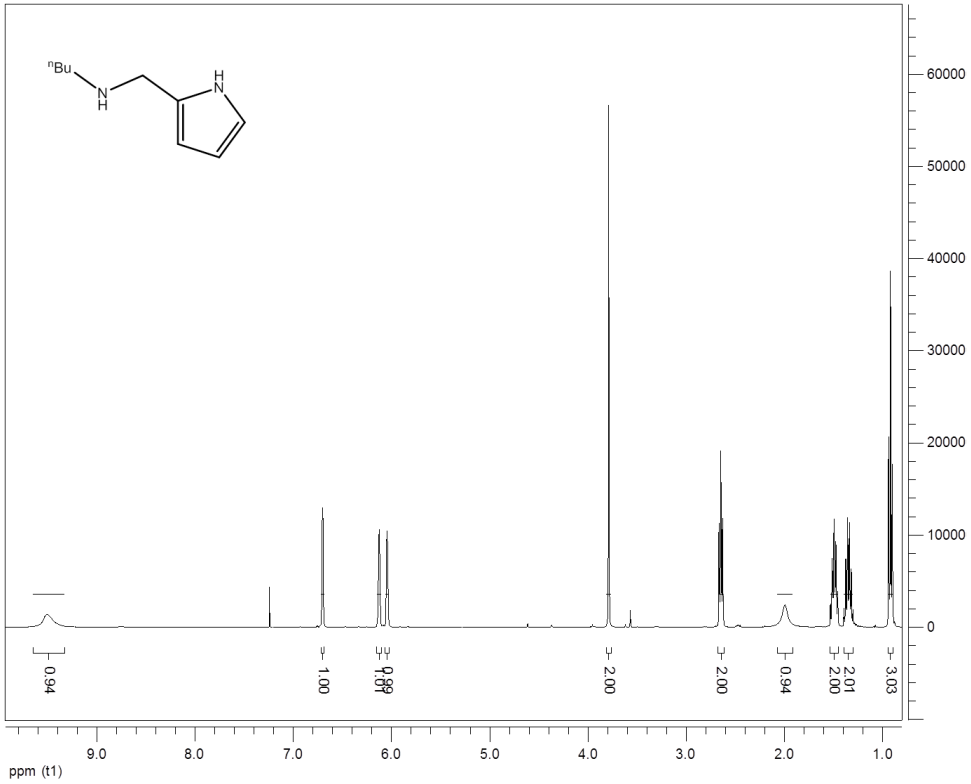


Figure 3a: ^{1}H NMR of **PyrN**.

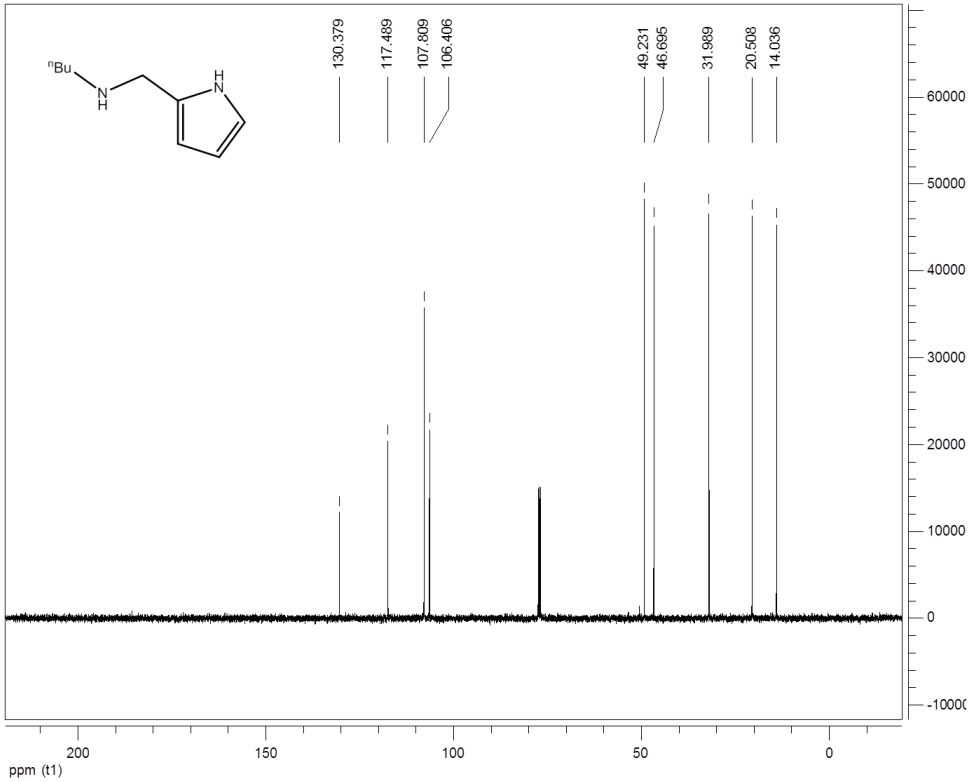


Figure 3b: ^{13}C NMR of **PyrN.**

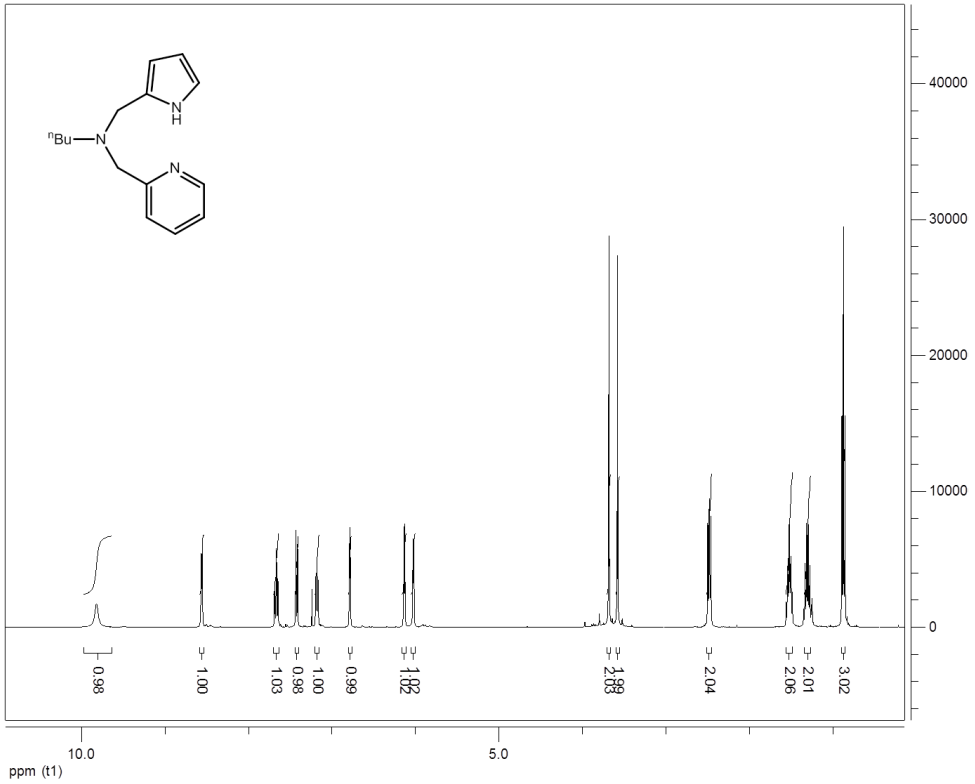


Figure 4a: ^{1}H NMR of **PyNPyr**.

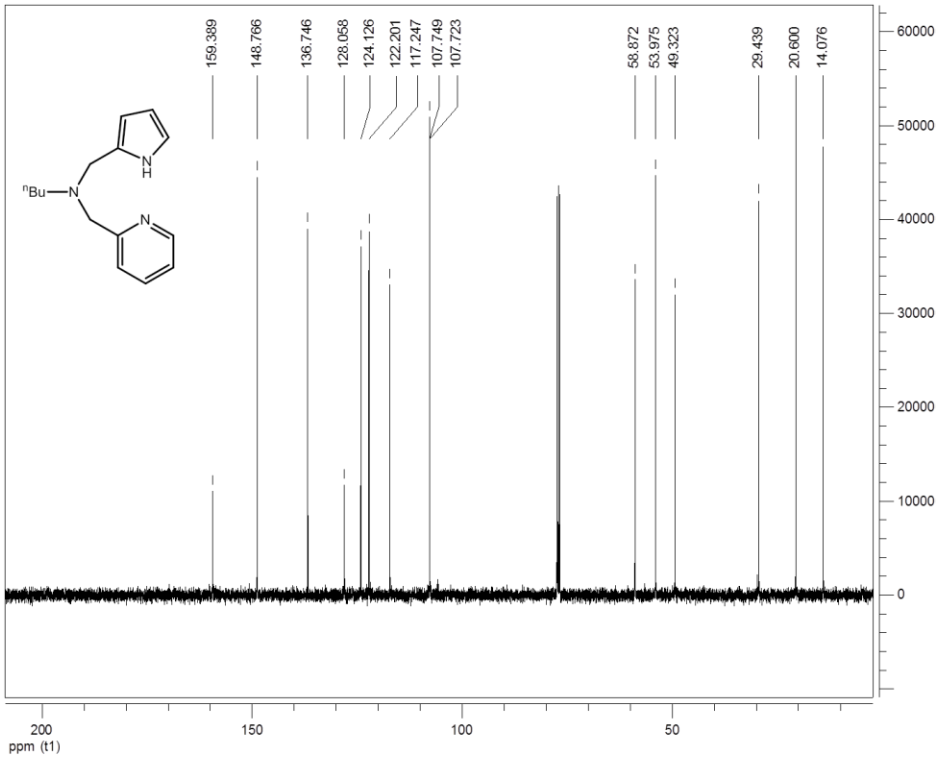
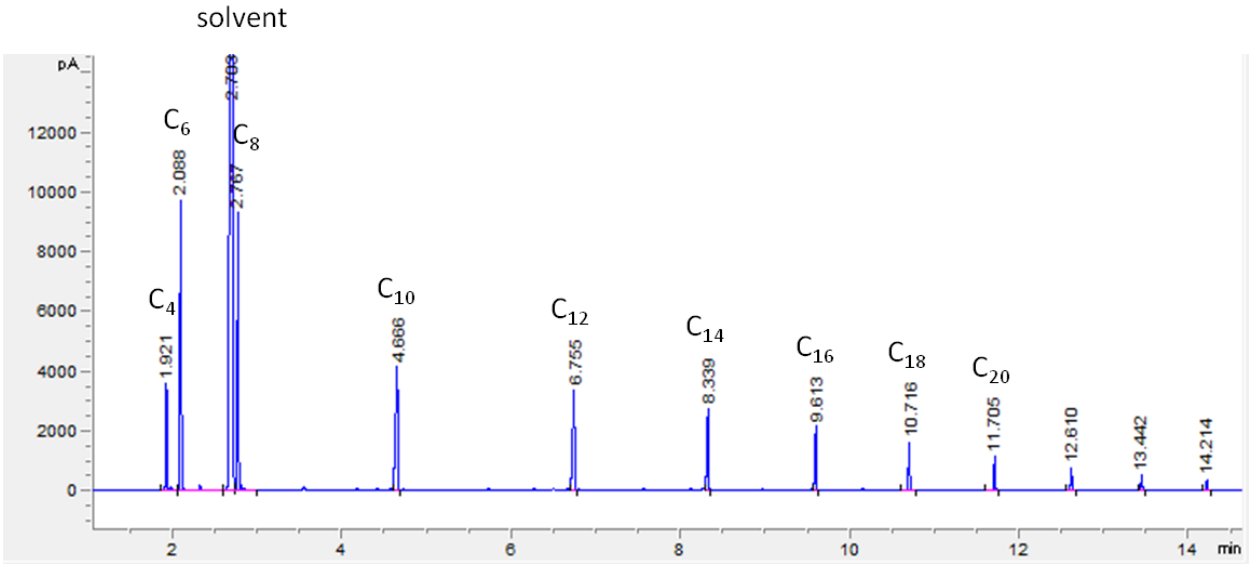
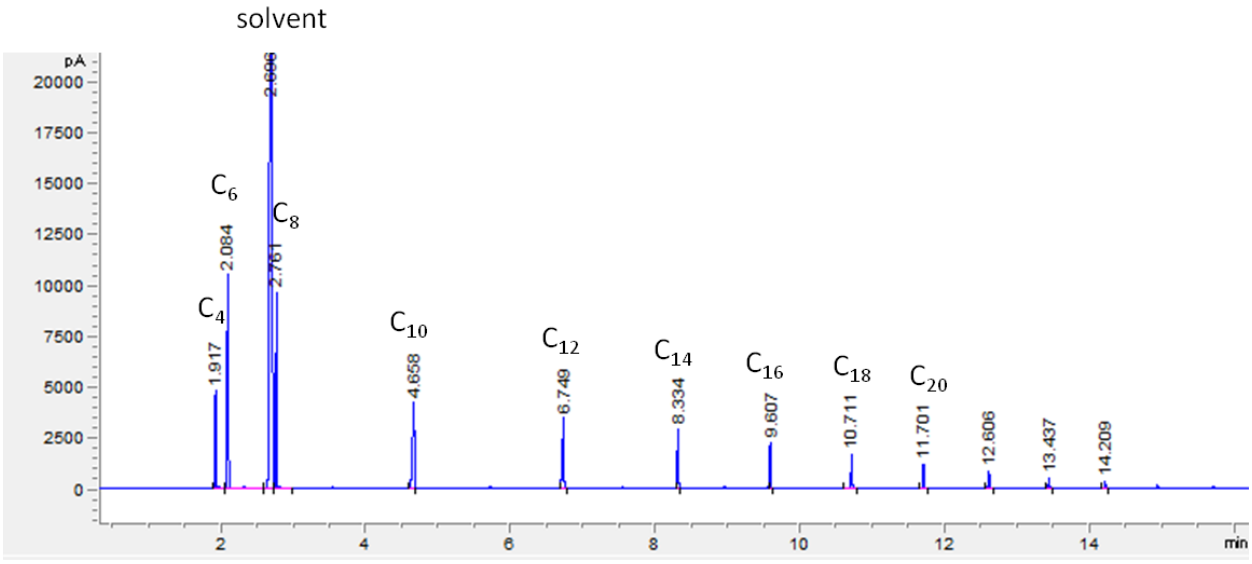


Figure 4b: ^{13}C NMR of **PyNPyr.**

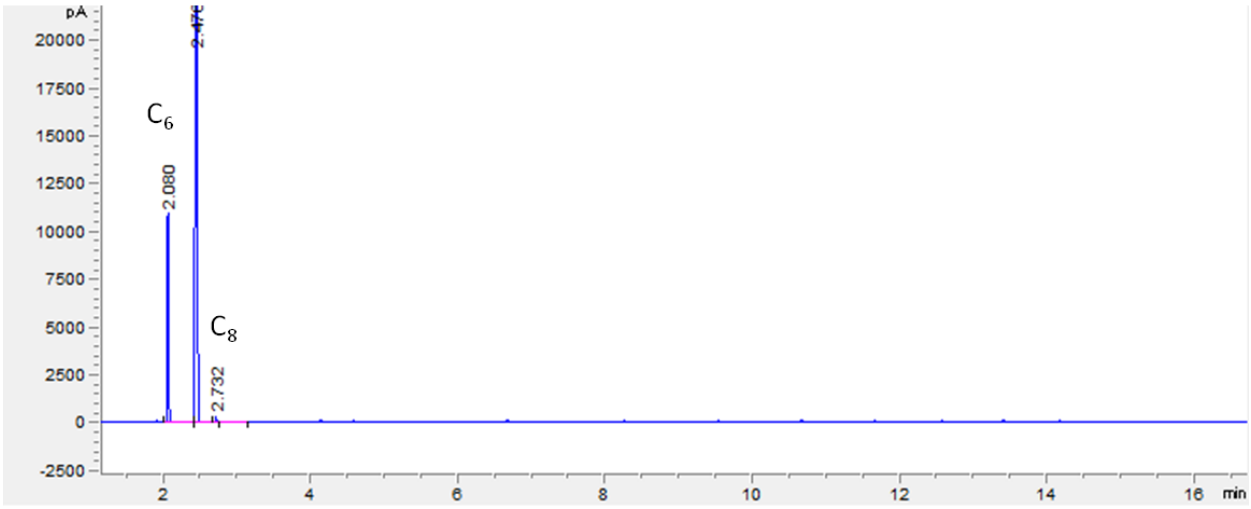
Appendix C

GC-FID of select Oligomerization Products

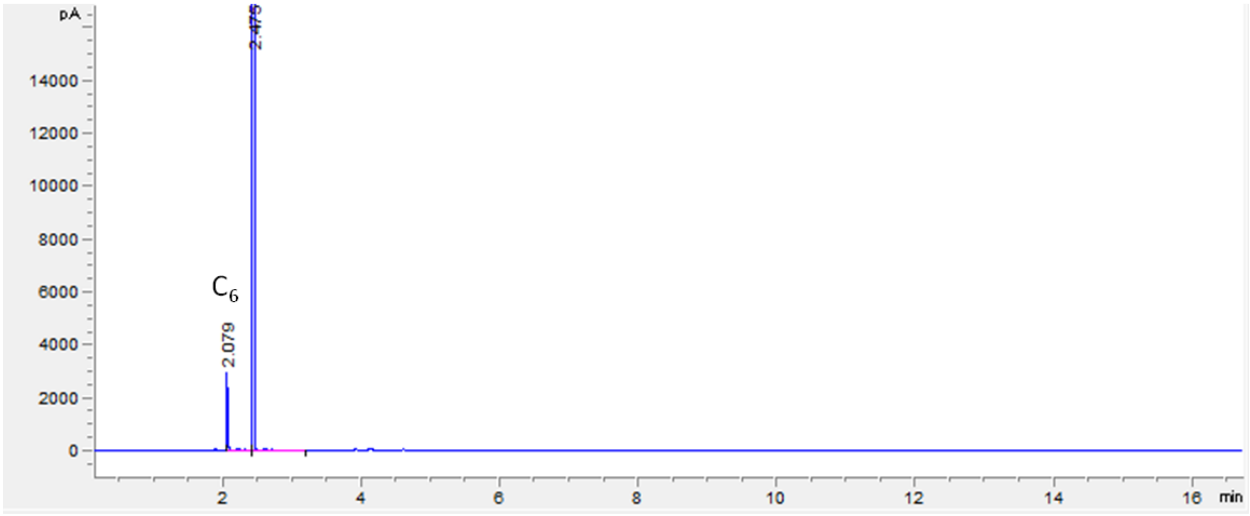




solvent

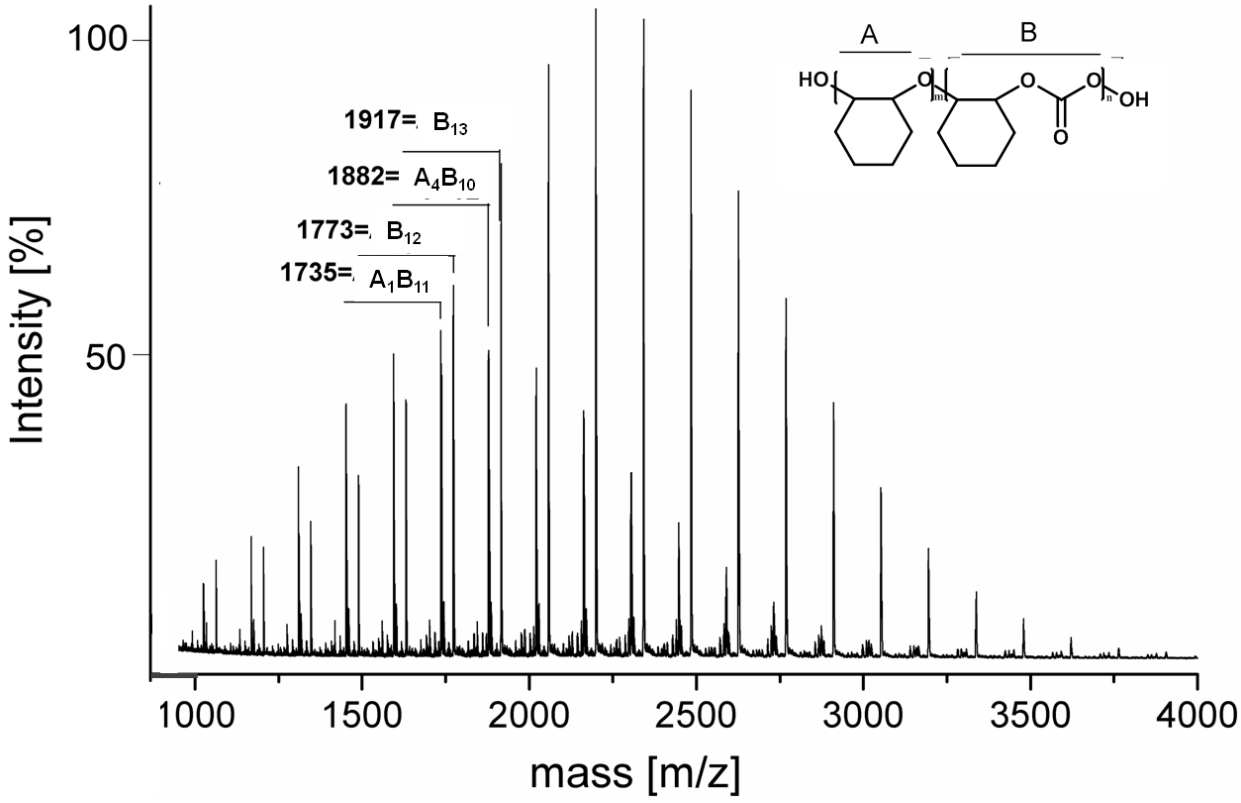


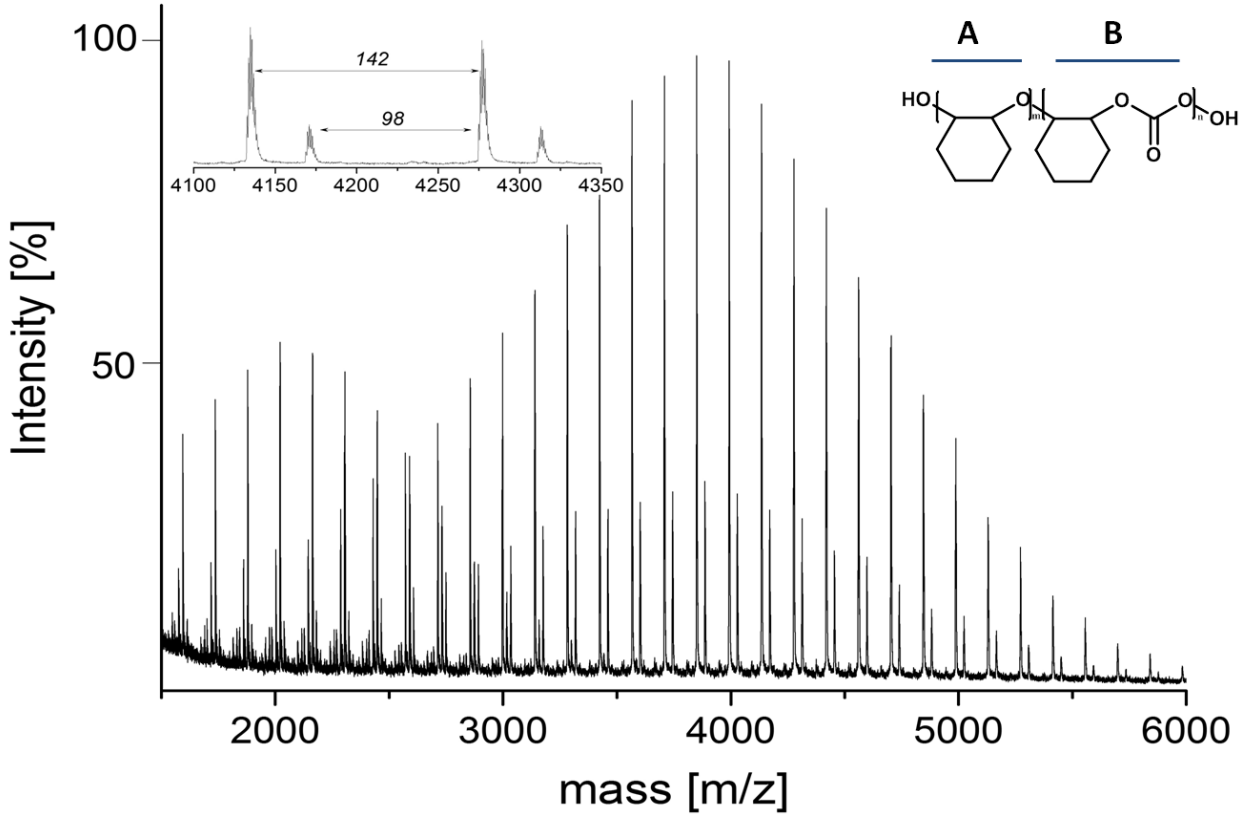
solvent

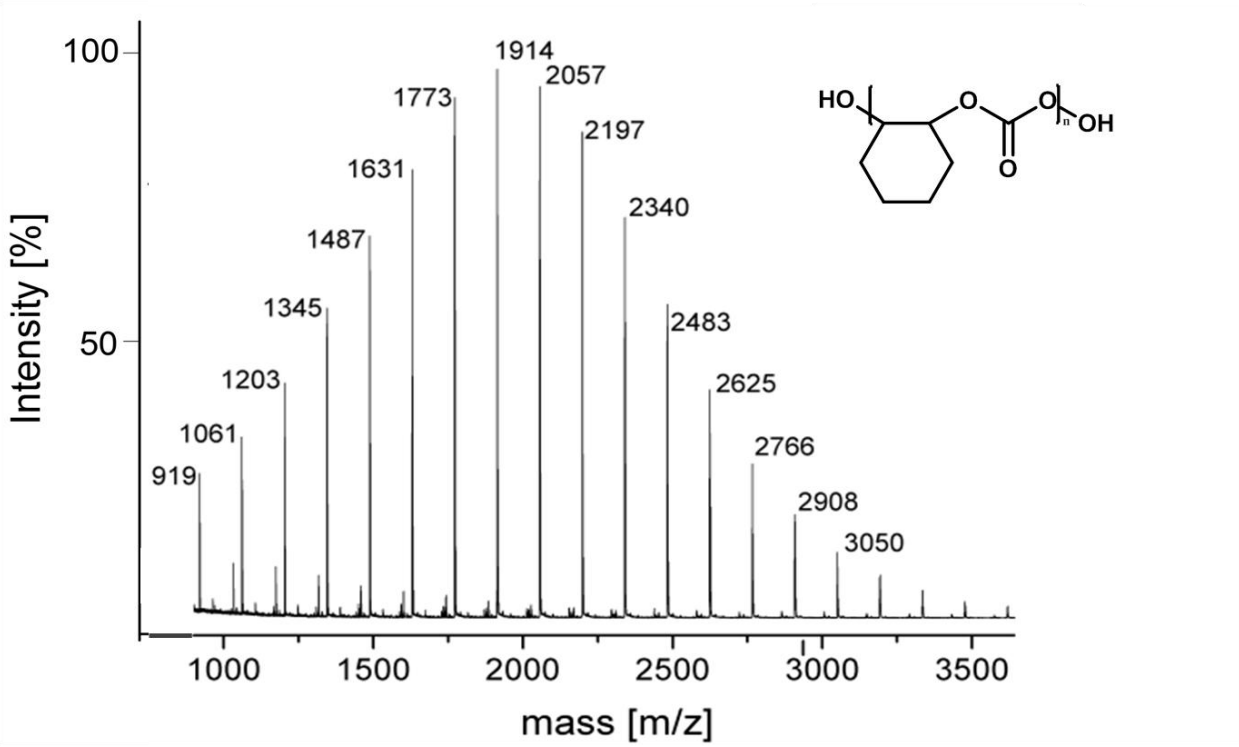


Appendix D

MALDI-ToF-MS of Select Polycarbonates

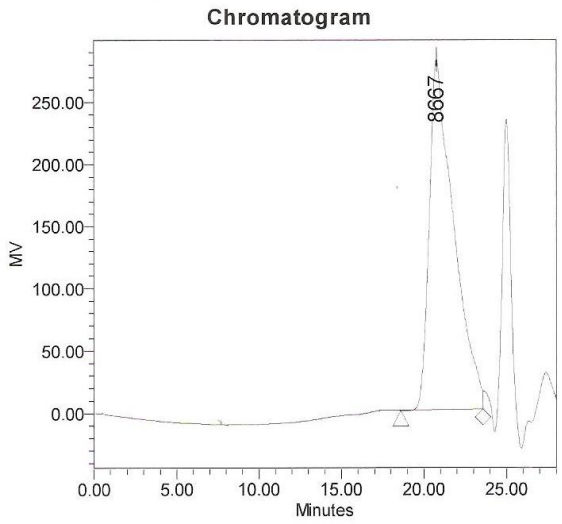


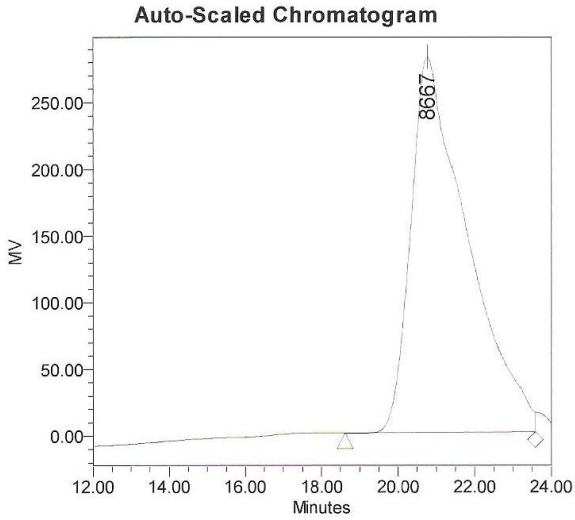

100
50
Intensity [%]
2000
3000
4000
5000
6000
mass [m/z]
142
98
4100
4150
4200
4250
4300
4350
A
B
HO
OH
O


100
50
Intensity [%]
1000
1500
2000
2500
3000
3500
mass [m/z]
919
1061
1203
1345
1487
1631
1773
1914
2057
2197
2340
2483
2625
2766
2908
3050
HO
OH
O

Appendix E

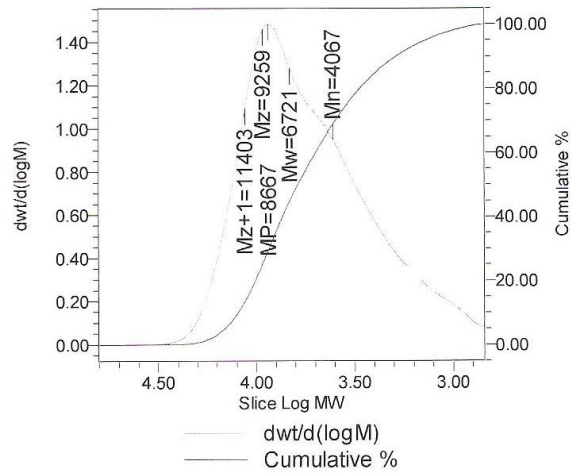
GPC of Select Polycarbonates

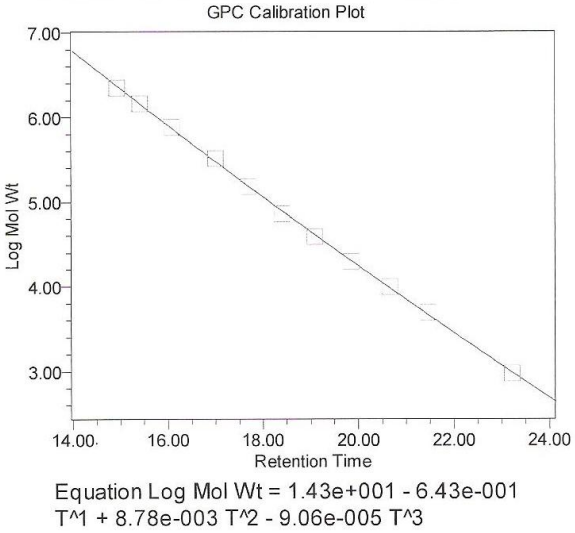


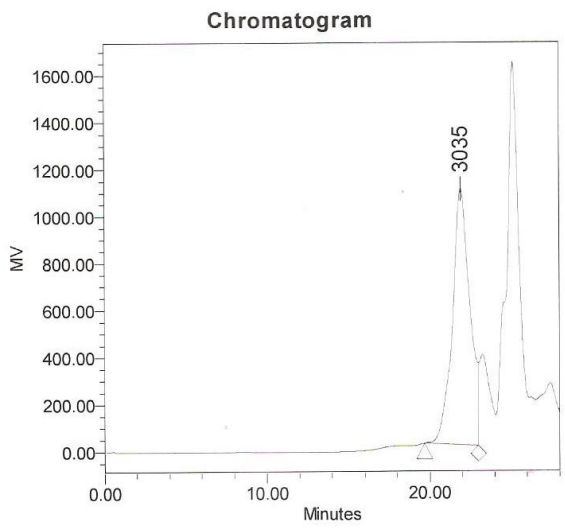


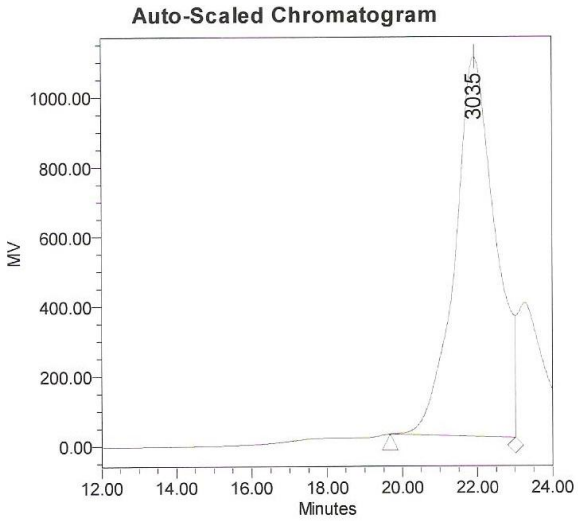
GPC Results

	Time (min)	Adjusted RT (min)	Mn	Mw	Mp	Mz	Mz+1	PDI	Area (µV*sec)	Baseline End (min)	Baseline Start (min)	Data Start (Minutes)	Data End (Minutes)
1		20.770	4067	6721	8667	9259	11403	1.652526	28912702	29.667	18.617	0.0	30.0



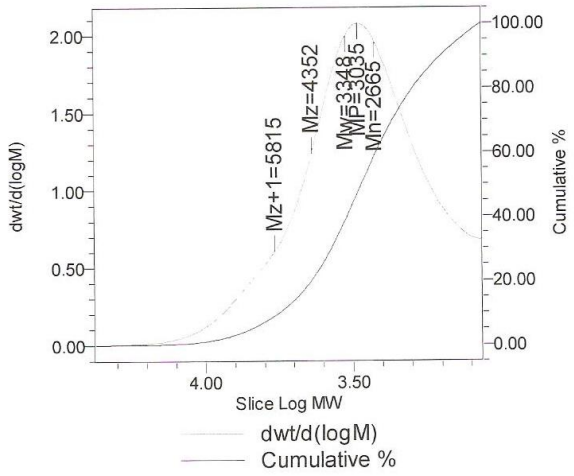


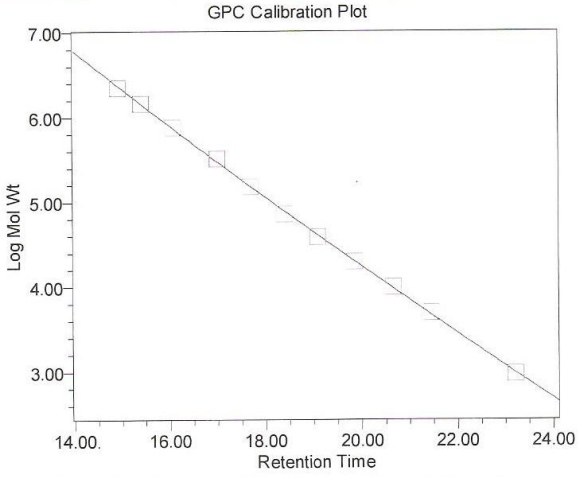




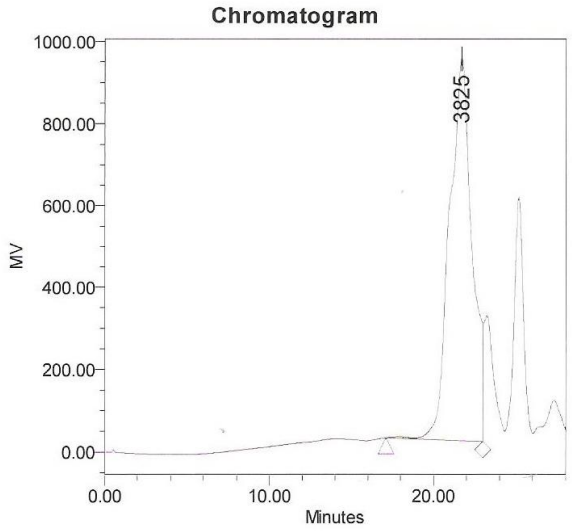
GPC Results

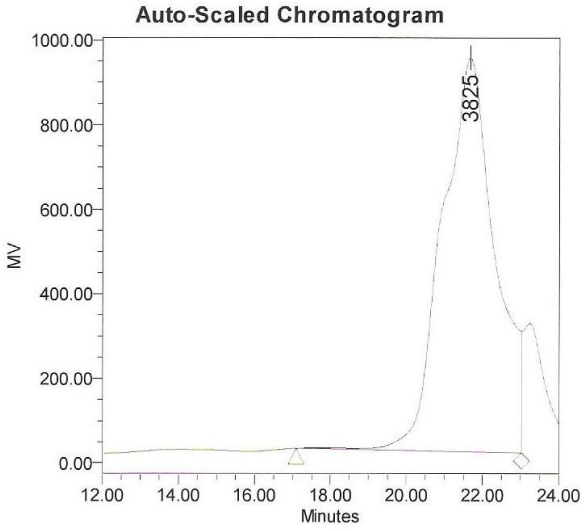
	Time (min)	Adjusted RT (min)	Mn	Mw	Mp	Mz	Mz+1	PDI	Area (µV*sec)	Baseline End (min)	Baseline Start (min)	Data Start (Minutes)	Data End (Minutes)
1		21.933	2665	3348	3035	4352	5815	1.256102	81359989	29.883	19.667	0.0	30.0





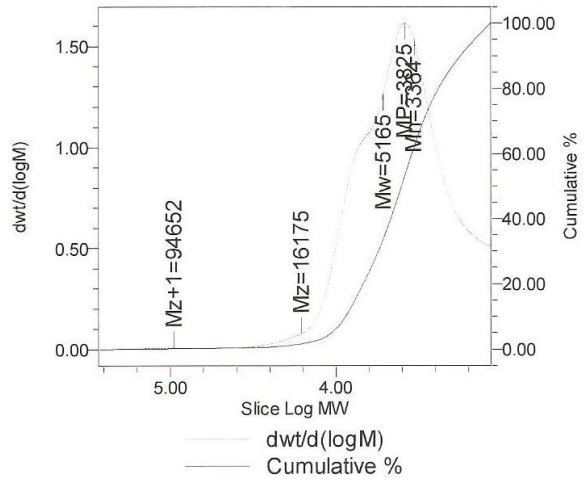
Equation Log Mol Wt = 1.43e+001 - 6.43e-001 T^1 + 8.78e-003 T^2 - 9.06e-005 T^3

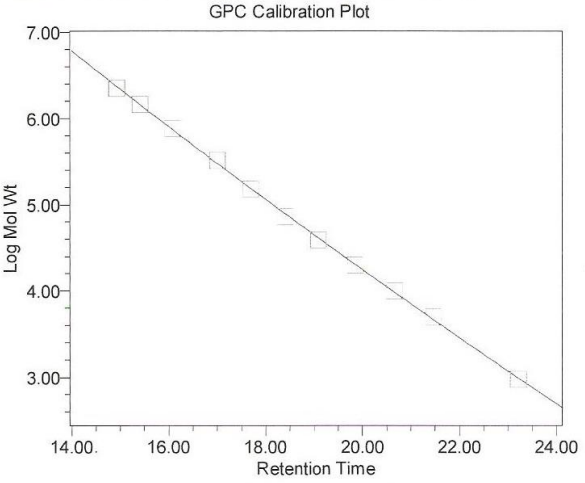




GPC Results

	Time (min)	Adjusted RT (min)	Mn	Mw	Mp	Mz	Mz+1	PDI	Area (µV*sec)	Baseline End (min)	Baseline Start (min)	Data Start (Minutes)	Data End (Minutes)
1		21.675	3364	5165	3825	16175	94652	1.535374	89105331	29.633	17.100	0.0	30.0





Equation Log Mol Wt = 1.43e+001 - 6.43e-001 T^1 + 8.78e-003 T^2 - 9.06e-005 T^3