Three-Coordinate Aluminum Alkyl Complexes for Applications in the Polymerization of Cyclic Esters

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Saskatoon

By

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ABSTRACT

Bulky 1,4-diamines 1,2-[2,4,6-$(CH_3)_3$-C_6H_3NH-$CH_2]_2$-C_6H_4 and 1,2-(2,6-$^{i}Pr_2C_6H_3NHCH_2)_2$-C_6H_4 were utilized as pro-ligands for the formation of novel three-coordinate aluminum alkyl compounds with the general formula [(1,4-diamido)AlR], where R = Me or Et. The synthesis of analogous aluminum hydrides was also explored resulting in the formation of four-coordinate complexes incorporating bridging hydrides.

The three-coordinate aluminum complexes were developed as single-component catalysts in the ring opening polymerization of cyclic esters. The main focus was on caprolactone polymerization, but other monomers were explored, including lactide, butyrolactone, cis-cyclooctene, and diphenylacetylene. The mechanism of polymerization with caprolactone was also studied.

The coordination chemistry of other metals and non-metals with the 1,4-diamido ligands were also investigated. Phosphorus, boron, zinc, and zirconium were the main focus. [(1,4-diamido)PCl] complexes were successfully synthesised as precursors to the formation of cationic phosphenium species, $[(1,4\text{-diamido})P]^{+}$.

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CHAPTER 1: INTRODUCTION

1.1 Polymerization

1.1.1 Cyclic Ester Polymerization

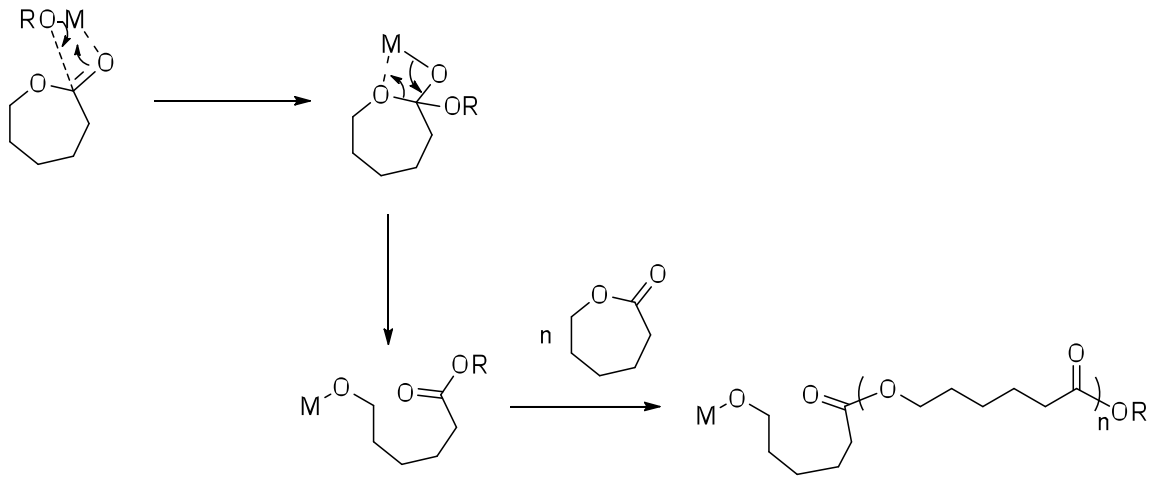
Plastics are an important aspect in the way the world functions. They are found in many materials such as packaging, textiles, and electronics.[1] Major polymers already in use are made from olefins such as ethylene and propylene. Unfortunately, these polyolefins are not very biodegradable and are expensive to process.[2] Hence, there is a need to create original polymers that are more biodegradable and cheaper to create, while still maintaining similar polymer characteristics to those already present in known polymers.[3] There is a current attention around polylactide, polycaprolactone and copolymers of these.[4] This is due to their biodegradable properties and their potential to be synthesized from renewable resources.[5]

1.1.2 Polymerization Mechanism

Polyesters can be synthesized through ring opening polymerization (ROP) of cyclic esters. Organometallic catalysts are the most effective polymerization catalysts with organoaluminum compounds being seen as the more advantageous catalyst for ROP of cyclic esters.[6] Single-site catalysts play an important role in the polymerization

mechanism as it facilitates monomer insertion by containing an open site susceptible for insertion.

It is known in literature that ROP of cyclic esters occurs through a coordination-insertion mechanism with an organometallic catalyst (see Scheme 1-1). An initial coordination of the carbonyl oxygen (found in the monomer), to the metal center is followed by insertion of the monomer into the catalyst. Previous research has shown that this insertion occurs into the aluminum-oxide bond via nucleophilic addition. This causes ring opening to occur and allows propagation of the polymer chain.[7]



Scheme 1-1: Coordination-insertion mech. shown with a general metal alkoxide complex for the polymerization of caprolactone.[7]

1.2 Three-Coordinate Aluminum Complexes

Three coordinate aluminum complexes are relatively rare compared to 4-coordinate or higher analogues.[8] Although relatively rare, these aluminum complexes have some appealing qualities, making them of interest to synthesize. A three coordinate environment around the aluminum centre creates a more lewis acidic aluminum center than that found in the four coordinate aluminum analogue.[9] This greater lewis acidity will play an important role in its catalytic reactivity. Unfortunately, four-coordinate aluminum species are much more common than their three-coordinate counterparts. To create a three-coordinate aluminum species requires the use of bulky ligands. These bulky ligands create steric hinderance around the metal centre, which prevent dimerization or coordination of neutral molecules, allowing a three coordinate center to occur. Bulky substituents are needed to inhibit the formation of a four coordinate species.

One example of a three-coordinate aluminum complex that exists incorporates phenols into its structure. Phenol ligands typically lead to bridging compounds that bridge through the oxygens found in the phenoxide group. However, steric bulky phenols result in the formation of monomeric complexes. 2,6-di-tert-butyl-substituted phenols are known to create such complexes (see Figure 1-1). These compounds are utilized in the preparation of Ziegler-Natta catalysts.[10]

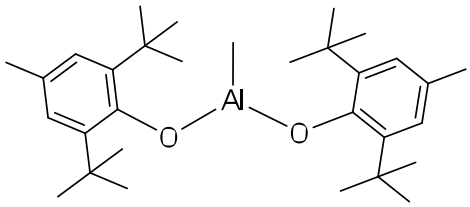


Figure 1-1: $AlMeBHT_2$ complex showing a three coordinate aluminum centre containing BHT ligands.[10]

One known three coordinate diamido aluminum alkyl species is shown in Figure 1-2; a (1,3-diamido)AlMe. This catalyst was used in caprolactone polymerization, and it was found that monomer insertion occurs between the Al-N bond.[11] The main focus of our research is to successfully synthesize new 3-coordinate diamido aluminum species with larger chelate rings to explore the effects of ring size on aluminum coordination environment and catalysis. There is little known about the catalytic activities of such complexes, and we intend to explore the reactivity and stability of these relatively unknown catalysts.

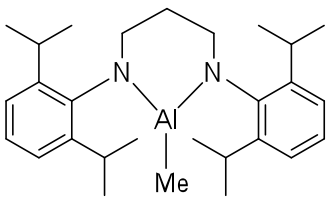


Figure 1-2: Only known 3-coordinate diamide aluminum alkyl complex.[11]

1.3 Diamido Ligands

Diamido ligands are becoming a popular ligand for early transition metals, however, their application in late transition and main group elements remain limited. They have many properties that make them valuable especially in homogeneous catalysis and organometallic chemistry.[12] Diamido ligands act as a bidentate, dianionic ligand that can be sterically and electronically adjusted. By varying the substituents on the nitrogen atoms, you can tune your ligand to perform in a wide array of reactions, especially in catalytic reactions.[13]

When designing a polymerization catalyst; the skeleton structure of the ligand has to be taken into account. One important variable in chelating ligand design is ring size that results upon coordination to a metal center. For example, the choice between α, β and γ complexes when using diamido ligands (see Figure 1-3) affects ring opening polymerization. This is due to the fact that the bite angle (α) between all three complexes differs, which affects how sterically protected the aluminum center is (see Figure 1-4). If a large bite angle exists, it causes the γ and β angles to be smaller. Due to these small angles, the bulky substituents tend to be closer to the methyl group, which creates more protection around the aluminum center. This can affect monomer insertion during catalysis. If the metal center is too protected, it may not allow for efficient insertion, slowing down the rate of polymerization. Therefore, we set out to develop a series of diamine complexes with varying ring size in attempts to determine the trend, if any, that the bite angle has on caprolactone polymerization.

The main focus was on the γ-diamine, versus the analogous β- or α-diamine ligand precursors. When the diamine is reacted with a metal, the metal attaches to both nitrogens in a bidentate fashion. This creates a 5, 6, or 7 membered ring with the α, β, or γ diamines, respectively. The 7 membered ring is what we are interested in; testing its stability and polymerization abilities, in comparison with the 5 and 6 membered rings. The interest in 7 membered rings comes from the fact that the bite angle is different in different sized rings, therefore, possibly having an impact on the effectiveness of polymerizations of cyclic esters. The bite angle can provide protection of the metal center, as this angle forces the R-groups on the nitrogens towards the metal center, resulting in a greater steric environment about the metal without changing the size of the R-group.

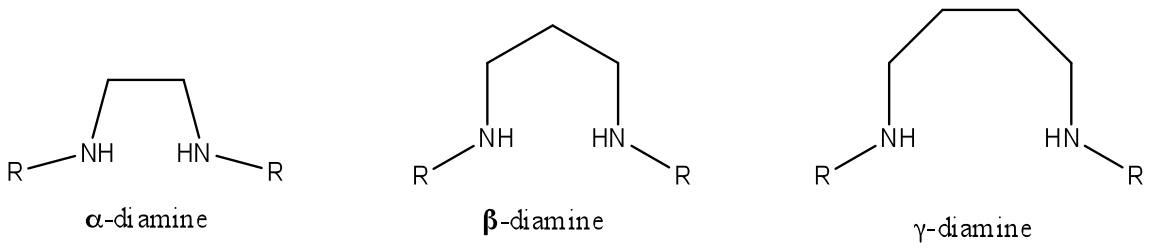
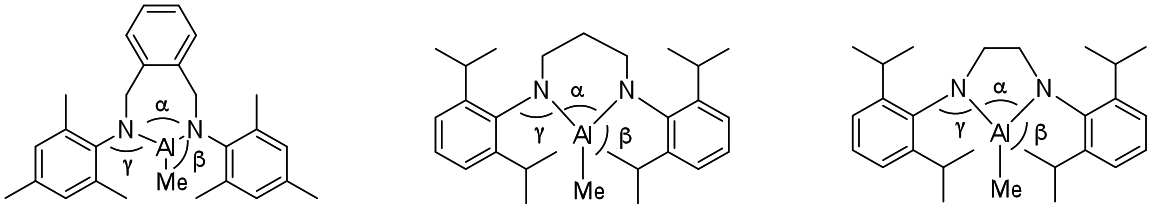


Figure 1-3: Three general classes of diamines considered in this thesis.



7 membered ring	6-membered ring	5-membered ring
$\alpha = 113.58^{o}$	$\alpha = 109.21^{o}$	$\alpha = ?$
$\beta = 123.2^{o}$	$\beta = 125.4^{o}$	$\beta = ?$
$\gamma = 122.3^{o}$	$\gamma = 127.0^{o}$	$\gamma = ?$

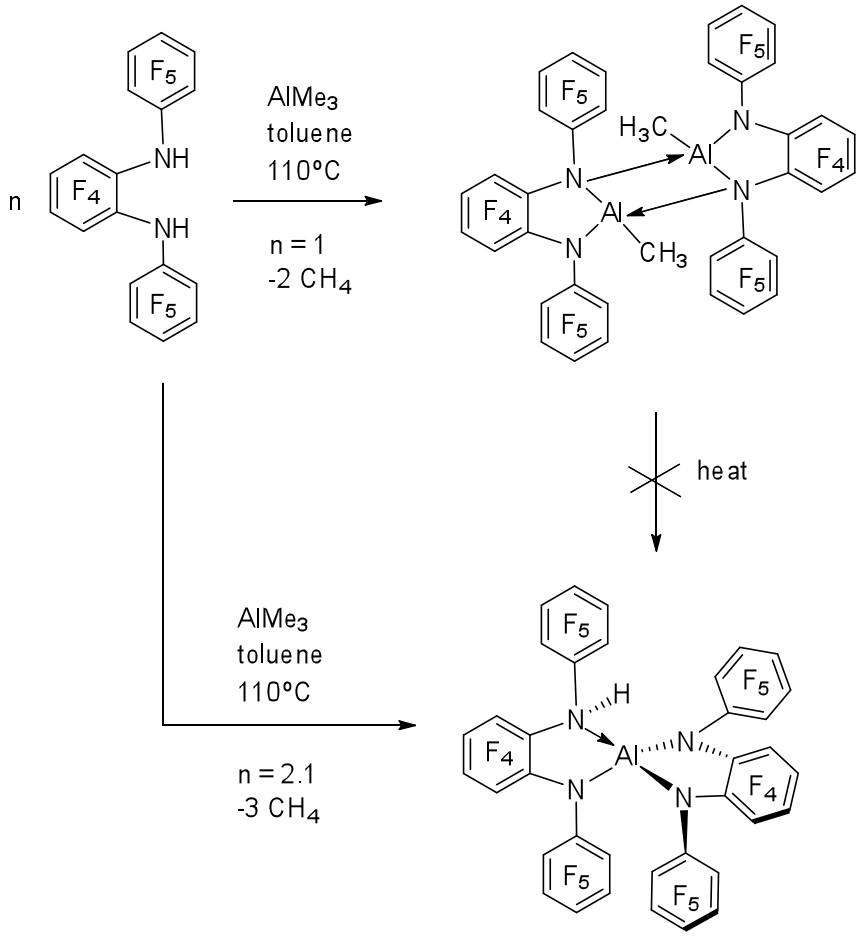
Figure 1-4: Three diamido complexes showing how the differences in ring size affects the bite angle (α).[11]

1.4 Aluminum Complexes

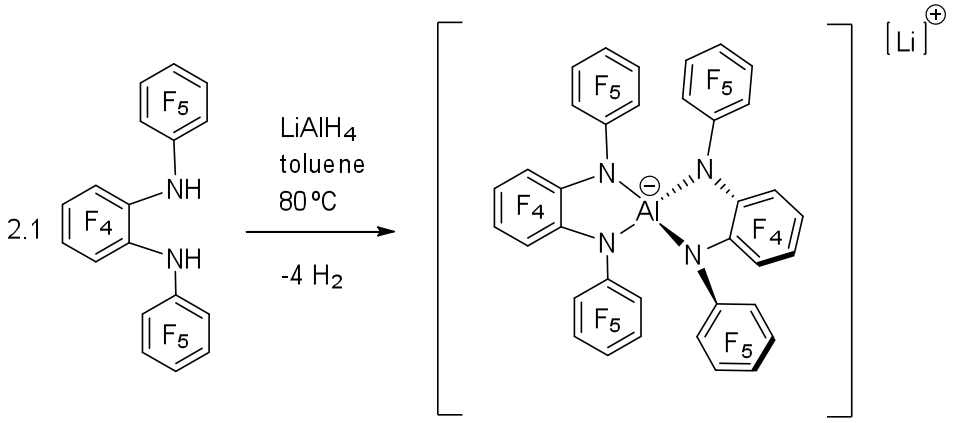
1.4.1 Structure Characteristics of Aluminum Compounds

Smith and associates were interested in studying the use of weakly coordinating anions (WCAs) to create electrophilic complexes. The perfluorated ligand N,N-diphenylphenylene-1,2-diamine, was reacted with $AlMe_3$. As seen in Scheme 1-2, when there is a 1:1 ratio (of ligand to $AlMe_3$), complex dimerization occurs. When the ratio moves to a 2:1, there is one aluminum atom found at the center of the compound. However, this compound was unsuccessful in the synthesis of olefin polymerization catalysts. Therefore, another synthetic route was explored. The aluminum source was lithium aluminum hydride instead of trimethyl aluminum, to create a four coordinate aluminun complex (see Scheme 1-3). Careful reaction temperature control was needed

with the use of lithium aluminum hydride. The reaction would not reach completion, leaving excess $LiAlH_4$ present at low temperatures, where as at high temperatures, $LiAlH_4$ would thermally decompose. This aluminate WCA has the ability to be incorporated into the synthesis of polymerization catalysts, due to its ability to stabilize electrophiles during olefin polymerization reactions.[14]



Scheme 1-2: Reaction of perfluorinated bis-aniline with $AlMe_3$ resulting in dimerization.[14]



Scheme 1-3: Formation of an aluminate WCA using $LiAlH_4$ as the aluminum source.[14]

It was reported by Cowley and colleagues that diazabutadiene (DAB) ligands show dimerization tendencies, especially when paired together with aluminum. One known such compound, a t-BuDAB Aluminum complex shows evidence of this (see Figure 1-5). The dimer species is formed through a coordination between two sets of Al-N atoms. This follow the fact that non-bulky ligands are more likely to cause dimerization.[15]

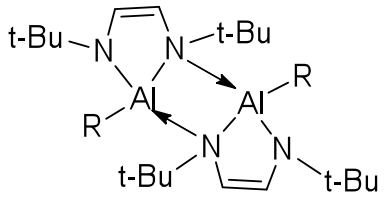
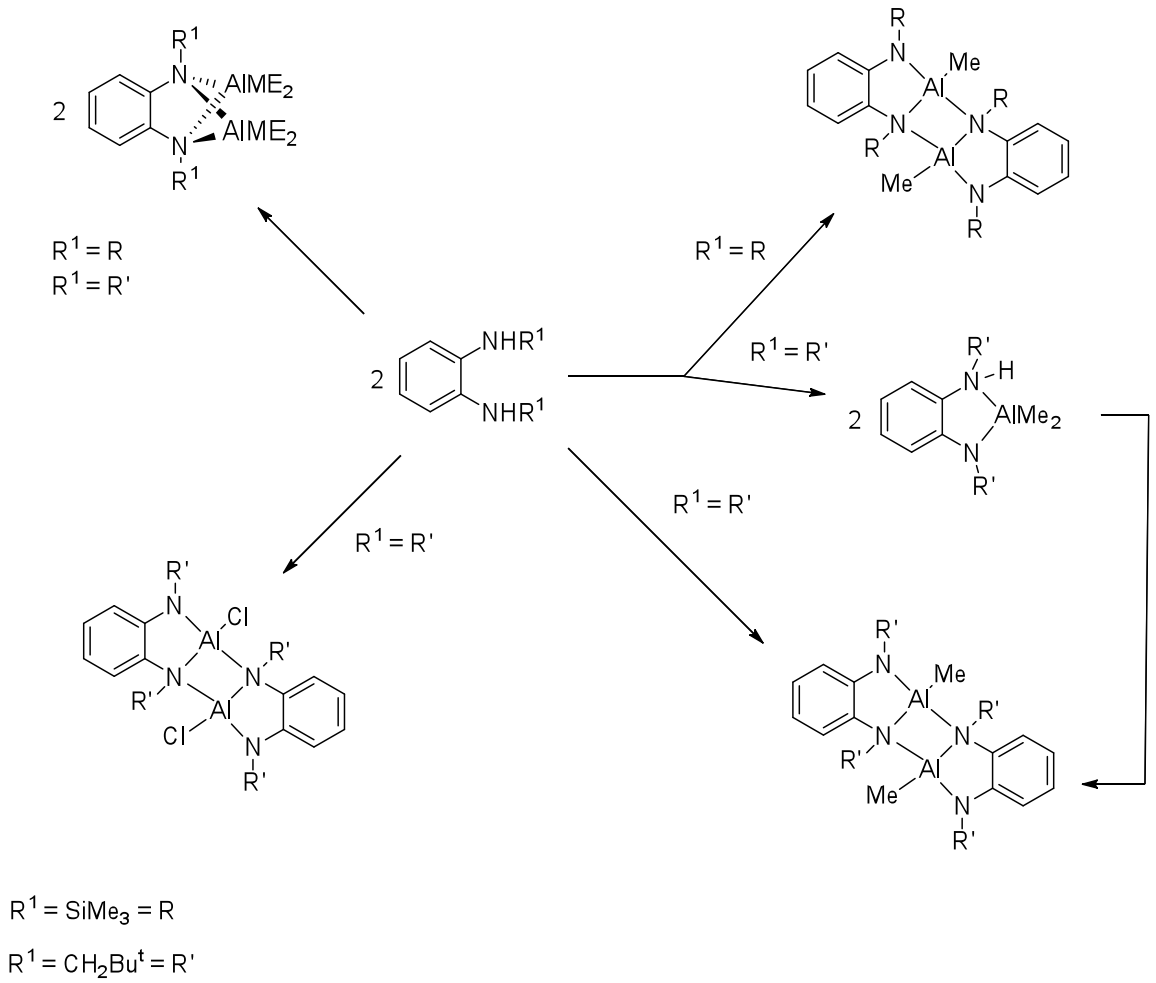


Figure 1-5: A t-BuDAB Aluminum complex featuring a dimeric structure.[15]

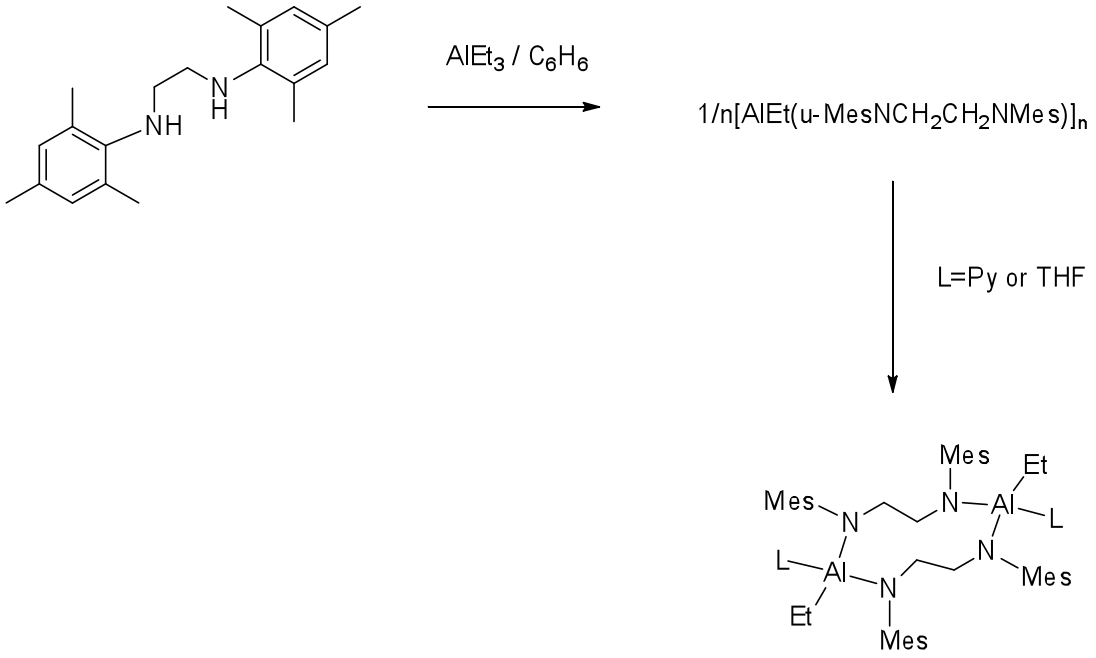
Another example of a dimeric aluminum complex was created by Lappert and colleagues. They reacted the ligand, 1,2-diamino-benzenes, with trimethyl aluminum which resulted in four coordinate aluminum complexes (see Scheme 1-4). The R groups used (-CH_2Bu^t and -$SiMe_3$) were not bulky enough to inhibit dimerization.[16]



Scheme 1-4: 1,2-diamine-benzenes reacted with $AlMe_3$ creating four coordinate aluminum complexes.[16]

Gabbai and Gardinier sought after synthesizing an organoaluminum amide complex, trying to create a catalyst with qualities that would make it an efficient catalyst for olefin polymerization. They found that reacting a diamine with triethyl aluminum resulted in the formation of a four-coordinate aluminum center within a ten membered-heterocycle

(see Scheme 1-5). This compound is not ideal for catalysis that involves interaction with incoming nucleophiles as a single-site catalyst is more desired.[17]



Scheme 1-5: Ten membered ring formation, containing aluminum, through a reaction with 1,2-diamine with $AlEt_3$.[17]

Many simple trialkylaluminum complexes exist as dimers.[18] Trimethylaluminum is such an example, where it is dimeric both in solid state and in solution.[19] The dimer structure creates a four coordinate environment around the aluminum centre. These trialkylaluminum species are not great for catalysis, as a single-site catalyst is ideal for

polymerization of cyclic esters. Thus, the synthesis of a three coordinate aluminum species is sought after to provide the most favourable catalyst structure.

1.4.2 Aluminum Complexes in Catalytic Activity for the Formation of Biodegradable Polymers

Bergman has developed an aluminum amide compound with ligands designed to faciliate polymerization of cyclic esters. As seen in Figure 1-6, the compound contains the aluminum center in a four coordinate tetrahedral environment. The neutral amine present may help to stabilize the reaction intermediates during polymerization, while the amide facilitates monomer insertion. This catalyst was found to be active for cyclic esters, such as, caprolactone, trimethylene, carbonate and lactide.[20]

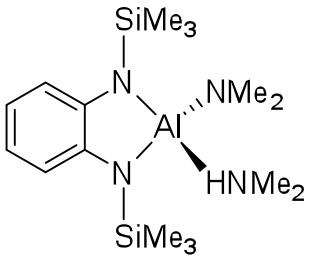


Figure 1-6: A four coordinate aluminum center containing nitrogen bearing ligands.[20]

Upon monomer insertion, the aluminum center takes on more of a trigonal-pyramidal configuration versus tetrahedral (see Figure 1-7). The amine occupies the top site of the

aluminum center, causing the bottom to be available for monomer coordination. Hydrogen bonding may also be present resulting in a net dimeric structure to be possible. This structure could cause intramolecular and intermolecular interactions during polymerizations of a cyclic ester. The alkoxide present on the polymer chain could attack the carbonyl carbon, possibly creating a cyclic polymer.[20]

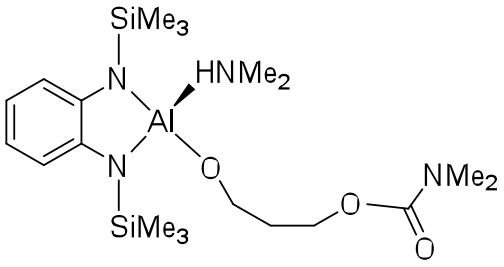
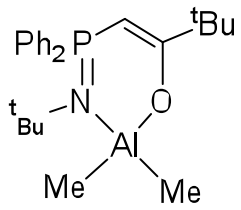


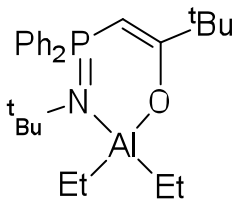
Figure 1-7: Intermediate formed during caprolactone polymerization, catalyzed by an aluminum complex.[20]

N,O-chelate aluminum complexes are already known to be great catalysts in ROP of cyclic esters. It has been shown that these N,O-chelating ligands are advantageous when combined in aluminum compounds. Two specific catalysts following this structure, seen in Figure 1-8, show catalytic activity for polymerization of cyclic esters, in the presence of an alcohol activator (BnOH). It was determined that these catalysts gave low conversions at room temperature, however, higher conversions were observed at higher temperatures; 80 ^{o}C for 280 min gave 60% conversion where as, at 100 ^{o}C for the same amount of time resulted in 100% conversion. PDI's were determined and compound **1**

had narrower PDI's than compound **2**. This may be due to the fact that transesterification poses a problem during catalysis with compound **2** and does not for compound **1**.[21]



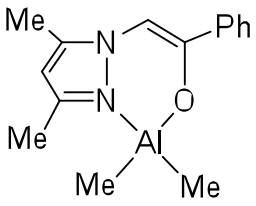
(1)



(2)

Figure 1-8: Structures of N,O-chelating aluminum complexes 1 and 2.[21]

Another class of N,O-chelate aluminum compounds (compounds **3** & **4** in Figure 1-9). showed similar catalytic activities. In the presence of an alcohol activator, at low temperatures, low conversions were found. When the reaction temperature was increased to 80 ^{o}C, 100% conversion was achieved for a reaction time of 240 min, using compound **3**; compound **4** required more time for complete conversion. However, the PDI's for both compounds are wider than those found in compound **1** & **2**. Transesterification may be present in compounds 3 and 4 during polymerization, causing high PDI's.[21]



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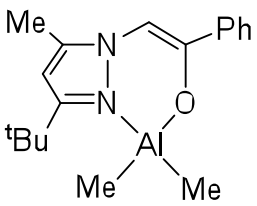

(4)

Figure 1-9: Structures of N,O-chelating aluminum complexes 3 and 4.[21]

1.5 Research Objectives

1.5.1 Synthesis of 3-coordinate Aluminum Complex

The main objective is to successfully synthesize new 3-coordinate diamido aluminum complexes with larger chelate rings to explore the effects of ring size on aluminum coordination environment and ROP of cyclic esters. The need for an activator and harsh polymerization conditions for the four coordinate species prompted us to design a different catalyst system that doesn't require harsh reaction conditions or activators. Three coordinate aluminum complexes interested us as they have many attributes that make them potentially good ROP catalysts. One main property is the lewis acidity of the aluminum center which is enhanced by the 3-coordinate environment. The 1,4-diamine, containing mesityl or diisopropylphenyl groups at the N-positions, were the main ligands studied.

1.5.2 Polymerization of Cyclic Esters

The single site aluminum catalysts contain properties that could make them efficient ROP catalysts. Since these 3-coordinate complexes are more lewis acidic than the four-coordinate aluminum analogues, an activator should not be needed during polymerization reactions. We hypothesize that our catalyst will not require an activator for cyclic ester polymerization, but in fact, be able to catalyze cyclic esters under mild reaction conditions as well.

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CHAPTER 2: ALUMINUM CHEMISTRY

2.1 Abstract

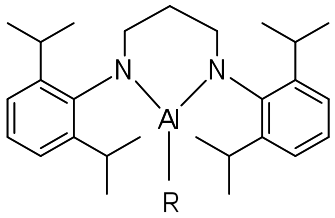
The synthesis of novel 3-coordinate aluminum alkyl species was acomplished. These aluminum complexes were made with the use of γ-diamine ligands; 1,2-[2,4,6-$(CH_3)_3$-C_6H_3NH-$CH_2]_2$-C_6H_4 and 1,2-(2,6-$^{i}Pr_2C_6H_3NHCH_2)_2$-C_6H_4. A reaction of these bulky diamines with trimethylaluminum proved favourable to the formation of γ-diamido aluminum catalysts. These catalysts were later used for cyclic ester polymerizations.

2.2 Introduction

Tin has been used as a common cataylst in the ring opening polymerization of cyclic esters. However, due to the toxicity of tin complexes, aluminum is appearing as a less toxic option for ROP catalysts.[1] Aluminum complexes have been found to be capable of ROP of cyclic esters, in the presence of alcohol. Chakraborty and Chen developed a neutral three coordinate chelating diamide aluminum complex which was active for caprolactone polymerization.[2] Apart from this example, there is still little known about aluminum catalysts that contain polydentate nitrogen-based ligands in their attempts at cyclic ester polymerization. Therefore, the main goal of our research was to utilize diamido aluminum complexes in the ROP of cyclic esters. This is of interest as polymerization of cyclic esters may provide biodegradable polyesters that have the potential for many biomedical applications.

Three coordinate aluminum complexes are relatively rare.[3,4] Although relatively rare, these aluminum complexes have some appealing qualities, making them of interest to synthesize. A three coordinate environment around the aluminum centre creates a more lewis acidic aluminum center than that found in the four coordinate aluminum analogue.[5] This greater lewis acidity plays an important role in its reactivity. Unfortunately, four coordinate aluminum species are more common than their three coordinate counterparts. To create a three coordinate aluminum species typically requires the use of bulky ligands. These bulky ligands create steric hinderance around the metal centre, which prevent dimerization or coordination of neutral molecules, allowing a three coordinate center to occur.[6,7]

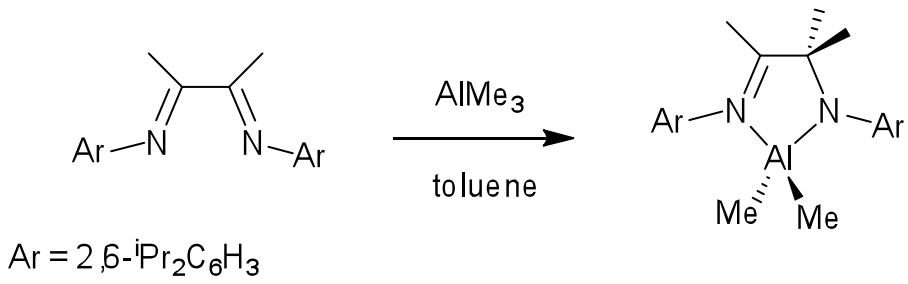
Chakraborty and Chen took advantage of the use of bulky ligands in the design of their ROP catalysts. They successfully synthesized a neutral, three coordinate diamide aluminum complex that utilized the bulky ligand ArN-$(CH_2)_3$NAr (Ar = 2,6-$^{i}Pr_2C_6H_3$) (see Figure 2-1). This 2,6-$^{i}Pr_2C_6H_3$ substituent off the nitrogens provide enough steric protection of the aluminum center to ensure a four coordinate environment does not exist. This is an essential characteristic of the catalyst, as it increases the lewis acidity of the aluminum center, aiding in monomer insertion during polymerization.[6]



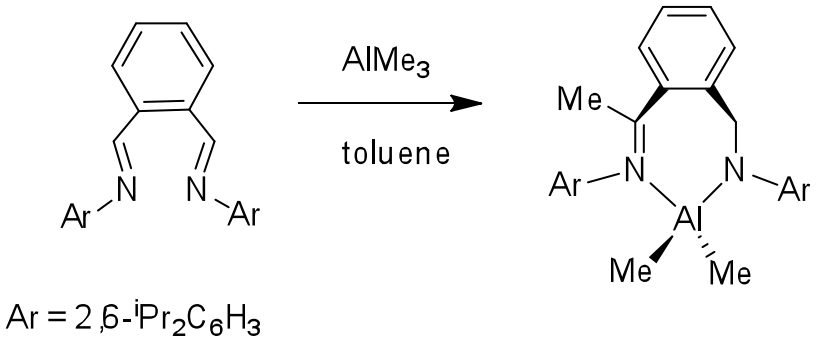
R = Me. ^{i}Bu, C_6F_5

Figure 2-1: A three coordinate diamide aluminum complex which was synthesized by Chakraborty and Chen.[6]

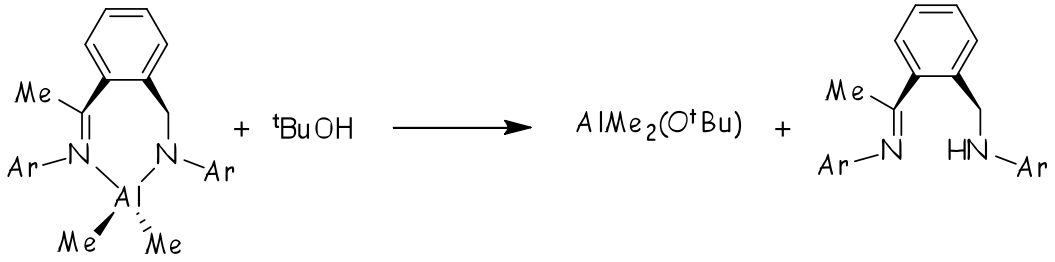
Previous aluminum work done in the Foley group involves the formation of four coordinate α-diamido aluminum complexes. $AlMe_3$ was reacted with the α-diimine ligand to produce an (iminoamido)$AlMe_2$ complex (see Scheme 2-1).[8] With this knowledge in mind, iminoamido aluminum complexes were synthesized. These complexes were created by reacting the γ-diimine ligand 1,2-(2,6-$^{i}Pr_2$-C_6H_3N=C)$_2$-C_6H_4 with $AlMe_3$, which resulted in a four coordinate (iminoamido) $AlMe_2$ complex (see Scheme 2-2). Alone, this catalyst showed no caprolactone polymerization activity. However, in the presence of an alcohol activator (in this case, ^{t}BuOH), the catalyst became active although, harsh reaction conditions were needed (60 ^{o}C for 24 hours). It was also determined that upon addition of the alcohol activator (^{t}BuOH) to the aluminum catalyst; the anticipated aluminum catalyst was no longer present and the protonated ligand and an aluminum alkoxide complex ($AlMe_2O^{t}Bu$) resulted (see Scheme 2-3). This lead us to believe that the caprolactone polymerization reaction was catalyzed by $AlMe_2O^{t}Bu$ versus the γ-diamido aluminum catalyst.



Scheme 2-1: Reaction previously done in the Foley group, showing that aluminum can coordinate to an α-diimine ligand through the use of $AlMe_3$.[8]



Scheme 2-2: Synthesis of iminoamido aluminum complex.



Scheme 2-3: The reaction scheme showing what occurs during the addition of the alcohol activator (^{t}BuOH) to the aluminum catalyst.

Our main goal was to synthesize three coordinate aluminum alkyl complexes. 1,2-diamines and 1,4-diamines were utilized to achieve this. This chapter describes the processes necessary to obtain both the ligands and the aluminum compounds. In the next chapter, it is explained how these aluminum compounds were employed for ring opening polymerization of cyclic esters.

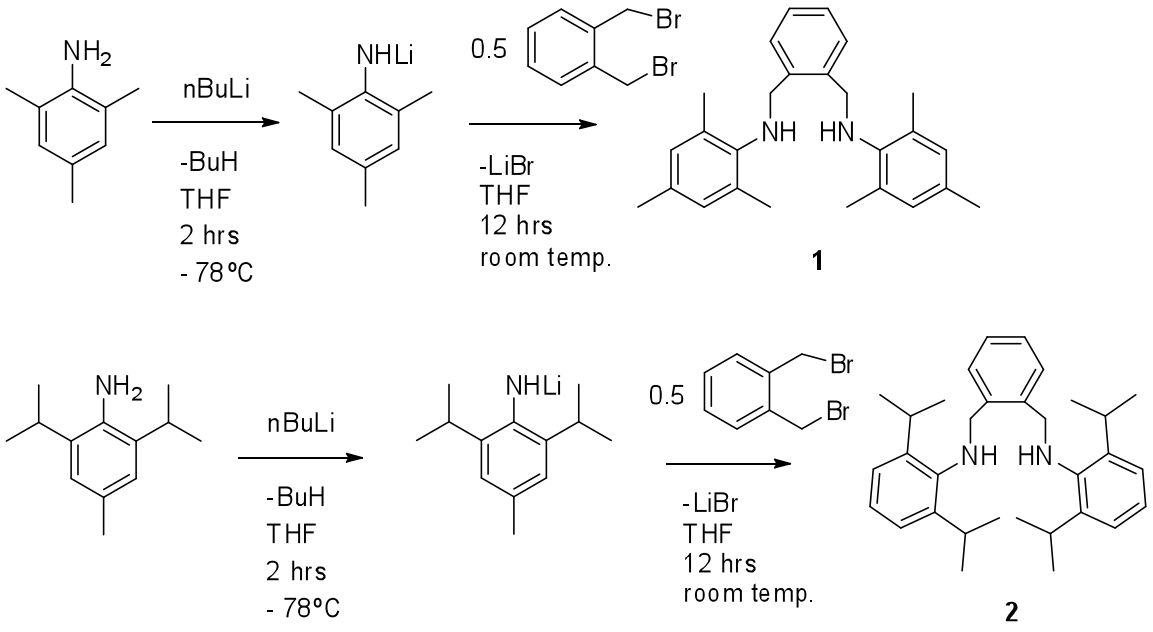
2.3 Results and Discussion

2.3.1 Ligand Synthesis

2.3.1.1 Synthesis of γ-diamine (mesityl and diisopropyl)

The mesityl and diisopropyl γ-diamine ligands (compounds **1** & **2**) were synthesized through lithiation of the appropriate aniline, followed by addition of α, α'-dibromo-o-xylene (see Scheme 2-4). The ^{1}H NMR of the mesityl ligand shows a singlet at 2.12

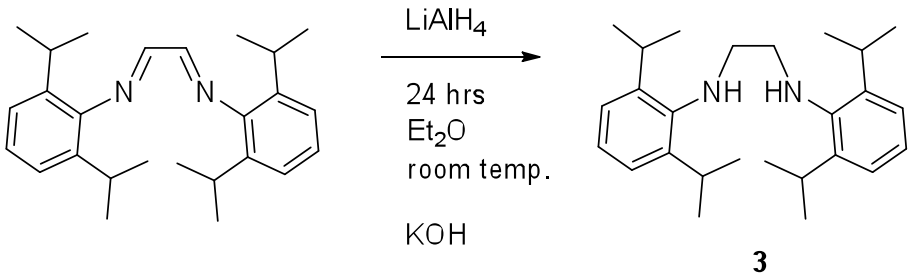
ppm, and another singlet at 2.20 ppm. These represent the ortho-methyl and para-methyl groups, respectively, signifying a C_{2v} symmetry. The ^1H NMR of the diisopropyl group of **2** contains a doublet at 1.23 ppm, which represents the methyl groups on the diisopropyl groups. Since there is only one doublet, it is consistent with a C_{2v} symmetry.



Scheme 2-4: The reaction scheme for the synthesis of the mesityl and diisopropyl γ-diamine ligands, respectively.

2.3.1.2 Synthesis of α-diamine (diisopropyl)

Reduction of a diisopropylphenyl N-substituted α-diimine led to the formation of the diisopropylphenyl N-substituted 1,2-diamine pro-ligand, through the use of lithium aluminum hydride (see Scheme 2-5), as found in literature.[5]



3

Scheme 2-5: The formation of the diisopropyl α-diamine ligand.

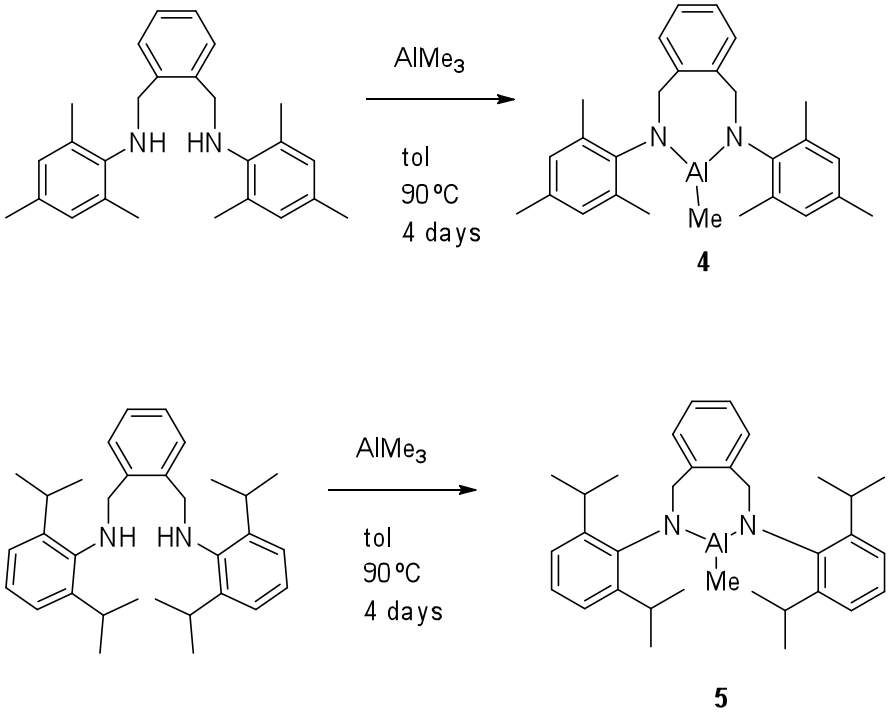
The ^{1}H NMR is also clean showing a singlet representing the four backbone protons, at 3.19 ppm, which is a characteristic shift of these protons. Again, there is a doublet found at 1.26 ppm (the methyl protons on the diisopropyl groups), consistent with C_{2v} symmetry.

2.3.2 Aluminum Chemistry

Objective: To synthesize a three-coordinate aluminum alkyl, and utilize it in ring opening polymerization of cyclic esters.

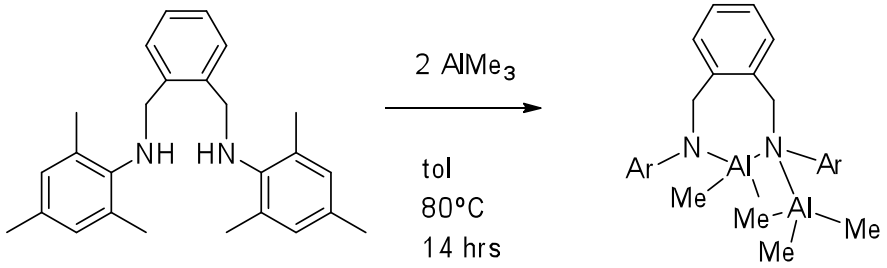
2.3.2.1 (γ-diamido)Al-Me Synthesis

Three coordinate aluminum-methyl complexes were synthesized with the γ-diamine ligands. These complexes (compounds **4** & **5**) were synthesized by heating a solution of trimethyl aluminum and the ligand at 90°C for 4 days under an atmosphere of nitrogen (see Scheme 2-6). The ^{1}H NMR of the diisopropyl aluminum-methyl complex (compound **5**) is very clean and resulted in two doublets, at 1.29 and 1.13 ppm. These doublets represent the methyl groups on the diisopropyl groups, suggesting hindered rotation about the nitrogen-carbon (on the aromatic groups) bond. The ^{1}H NMR of the mesityl aluminum-methyl complex (compound **4**), shows that not only was the desired product formed, but it also contains a second species. The second species can be seen as doublets at 3.44, 3.83, 4.87, 5.09 ppm in the ^{1}H NMR spectra which suggests that the two nitrogens are coordinating to the metal center, but that aluminum is also coordinating to two methyl groups, versus only one, consistent with the formation of compound **4a** which would result from reaction of com pound **4** with an additional equivalent of $AlMe_3$.



Scheme 2-6: The synthesis for the 3-coordinate aluminum methyl complexes.

To independently synthesize compound **4a**, two equivalents of $AlMe_3$ was reacted with the mesityl ligand (compound **1**) (see Scheme 2-7). The ^1H NMR contains doublets at 3.43, 3.82, 4.89, 5.09 ppm indicating that there are four methyl groups, all in different environments. Crystals were grown in toluene for 2 days, and a crystal structure was obtained. The crystal structure shows that the product is actually a four coordinate aluminum center (see Figure 2-2). It contains an additional $AlMe_3$ group coordinating through the lone pair on the nitrogen of the ligand and the second aluminum center, as well, there is coordination through the methyl group on the incoming $AlMe_3$ with the aluminum center of the ligand.



4a

Scheme 2-7: The reaction scheme showing the coordination of an extra $AlMe_3$.

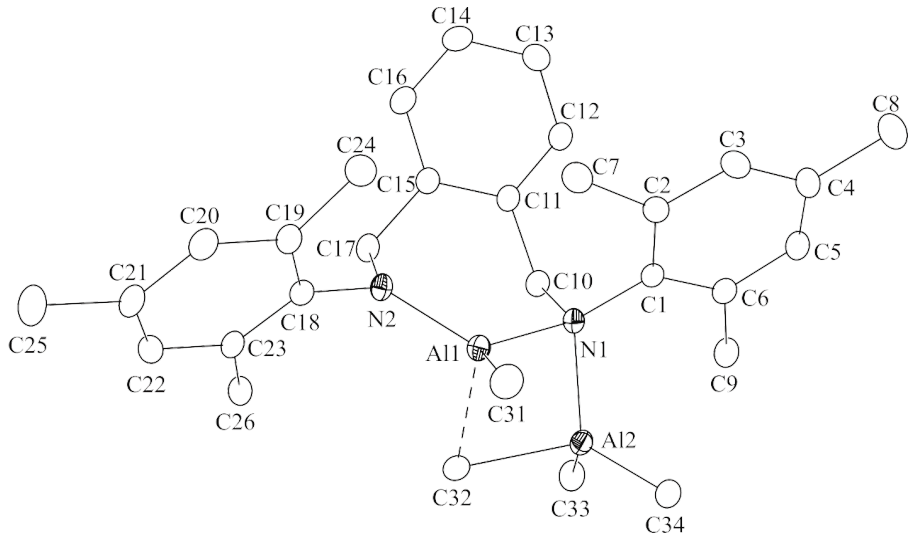
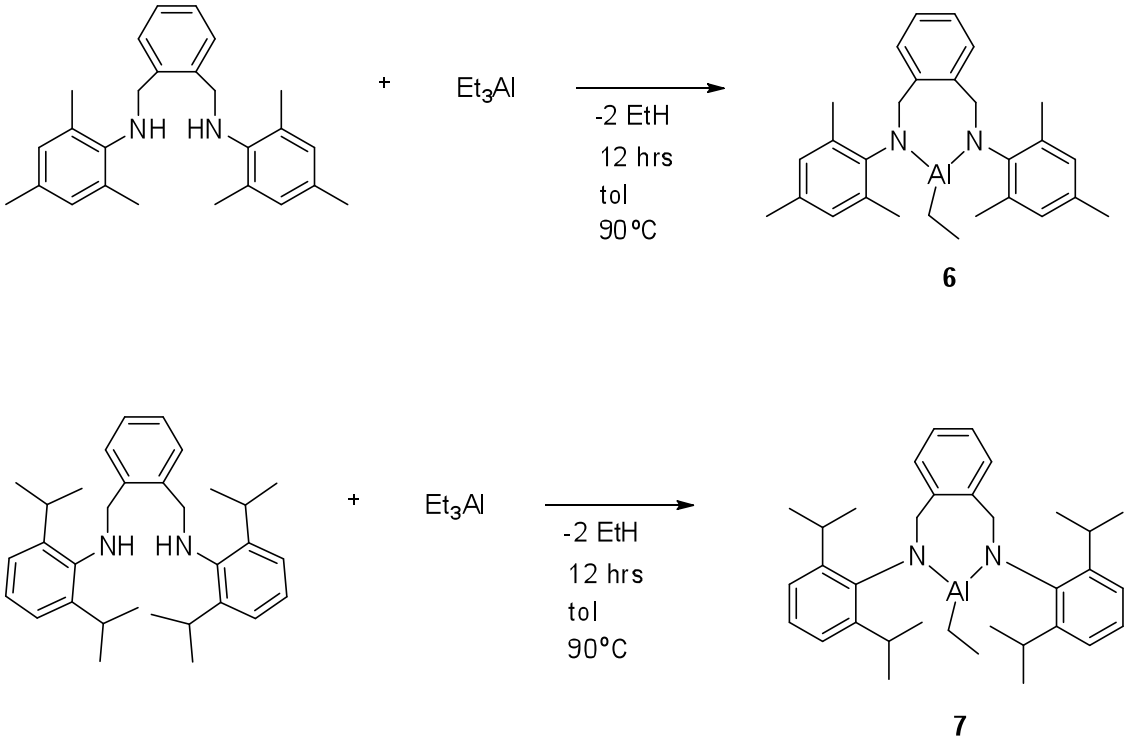


Figure 2-2: The crystal structure of compound **4a** (see Appendix A for bond distances and angles).

2.3.2.2 (γ-diamido)Al-Et Synthesis

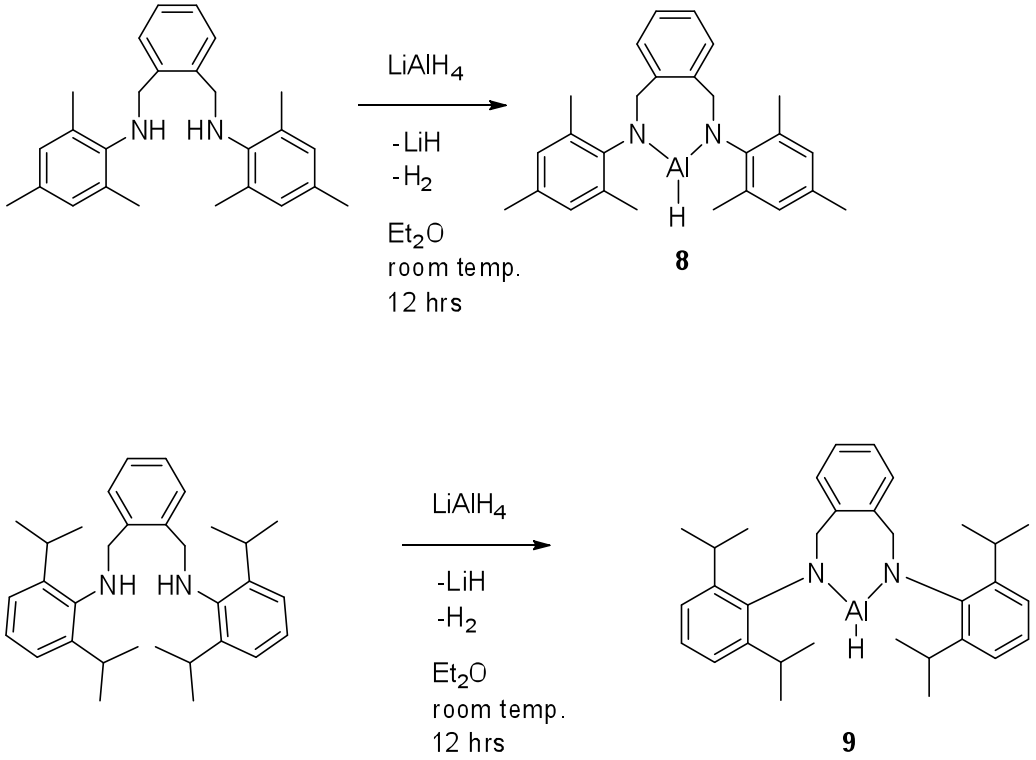
To synthesize this complex, triethyl aluminum was used in the formation of a three coordinate aluminum-ethyl complex. This reaction required heat (90 ^{o}C) under a nitrogen atmosphere (see Scheme 2-8). It produced an orange solid for both compounds (compounds **6** & **7**). The ^{1}H NMR spectra of both complexes contain characteristics signals; a quartet at -0.23 ppm, and a triplet at 0.52 ppm. The quartet is representative of the -CH_2 protons in the ethyl group, where the triplet represents the methyl group. This indicates that the ethyl group is, indeed, attached to the aluminum center. The orange solids were dissolved in a minimal amount of toluene and kept at -20 ^{o}C for 2 days, forming orange crystals. These crystals were sent for XRD. Unfortunately, these compounds are very air sensitive, and decompose with minimal air exposure, so it has been difficult to obtain a crystal structure. A preliminary structure was obtained, but better crystals need to be grown. These initial results demonstrated a three coordinate aluminum center, containing the ethyl substituent on aluminum.



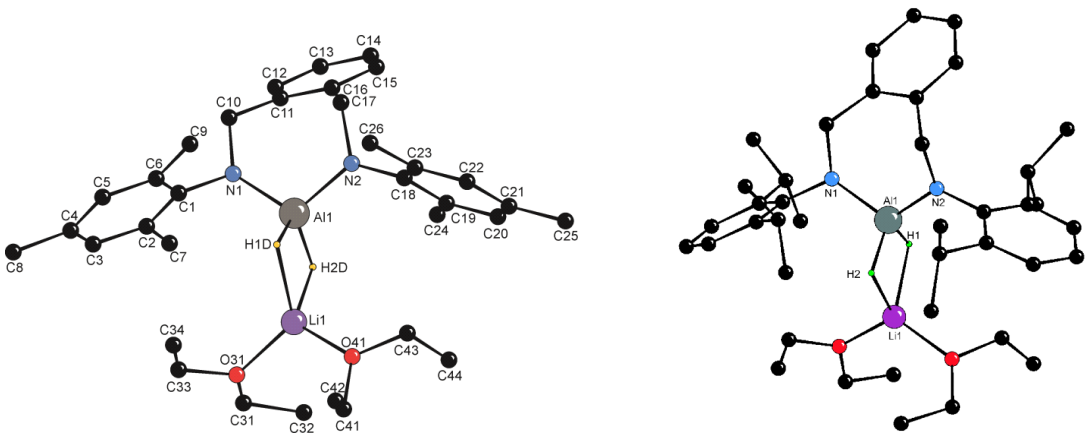
Scheme 2-8: The reaction schemes of the synthesis of the aluminum-ethyl complexes, for both the mesityl and diisopropyl ligands.

2.3.2.3 Aluminum-Hydride Synthesis

Synthesis of a three-coordinate aluminum-hydride complex was attempted, although three coordinate diamido aluminum hydrides are unknown. Lithium aluminum hydride was used, in attempts to make a three coordinate diamido aluminum complex (see Scheme 2-9). This reaction resulted in an air sensitive, light yellow solid. A crystal structure was obtained (see Figure 2-3), by dissolving the solid in a minimal amount of toluene and storing this solution at -20 ^{o}C for less than a week.



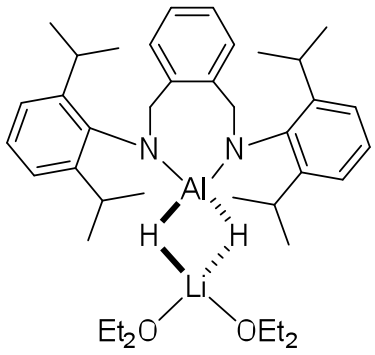
Scheme 2-9: The reaction scheme showing a possible route to aluminum-hydrides.



8a **9a**

Figure 2-3: Crystal structure of the aluminum-hydride (mesityl & diisopropyl ligand), showing coordination of diethyl ether.

The ^{1}H NMR contains a broad singlet at 4.12 ppm, indicating that the proton is bonded to the aluminum center. However, there are also signals present at 1.21 ppm and 3.48 ppm, representing diethyl ether. The integrations of these peaks suggest that the diethyl ether is coordinating to the compound. This is consistent with the crystal structure which shows that there is diethyl ether coordinating to the aluminum center through a lithium ion. Therefore, what actually is obtained is a lithium coordinated aluminum species that contains a $(Et_2O)_2LiH$ moiety bound through bridging hydrides resulting in a (γ-diamido)Al(μ-H)$_2$Li(Et$_2$O)$_2$ species (see Figure 2-4).



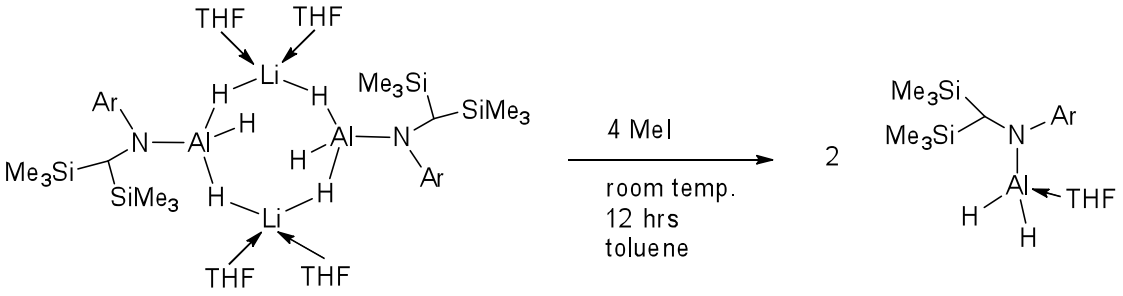
9a

Figure 2-4: Structure of the diisopropyl aluminum-hydride with coordination of diethyl ether.

In an attempt to remove the coordinated lithium ion, a crown ether was used. 12-crown-4 (12-C-4) was chosen due to its affinity for lithium cations, as 12-C-4 is often used to capture them. It was thought that the 12-C-4 would bind to the lithium ion, resulting in the aluminum hydride complex. However, the ^{1}H NMR spectra when both 1 and 2 equivalents of 12-C-4 were used, showed that the final product was the starting ligand. Therefore, 12-C-4 was unsuccessful in the removal of the lithium ion.

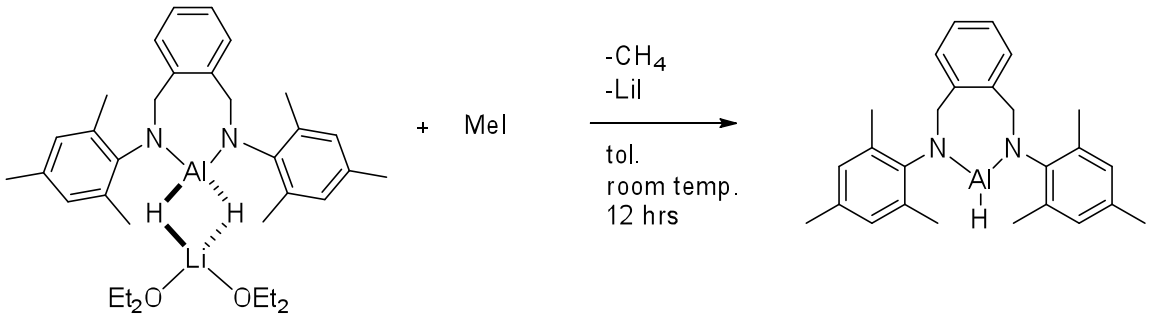
In a second attempt to remove the lithium ion, methyl iodide was used. It was found in literature that the use of methyl iodide on a dimeric hydroaluminate, was successful in the formation of a monomeric aluminum dihydride (see Scheme 2-10). Methyl iodide successfully broke the hydride-bridged compound and removed the lithium ion, which created a neutral aluminum dihydride.[9] This line of attack was applied to our (γ-diamido)Al(μ-H)$_2$Li(Et$_2$O)$_2$ species. MeI was added to the (γ-diamido)Al(μ-

$H)_2Li(Et_2O)_2$ complex (see Scheme 2-11). Following the same reaction conditions as mentioned in literature, the ^1H NMR spectra indicates formation of several species, none of which could be positively identified. Crystals suitable for x-ray could not be formed, and therefore the composition of the product could not be determined.



Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$

Scheme 2-10: The reaction scheme showing the removal of lithium from a hydride-bridged complex, through the use of MeI.[9]

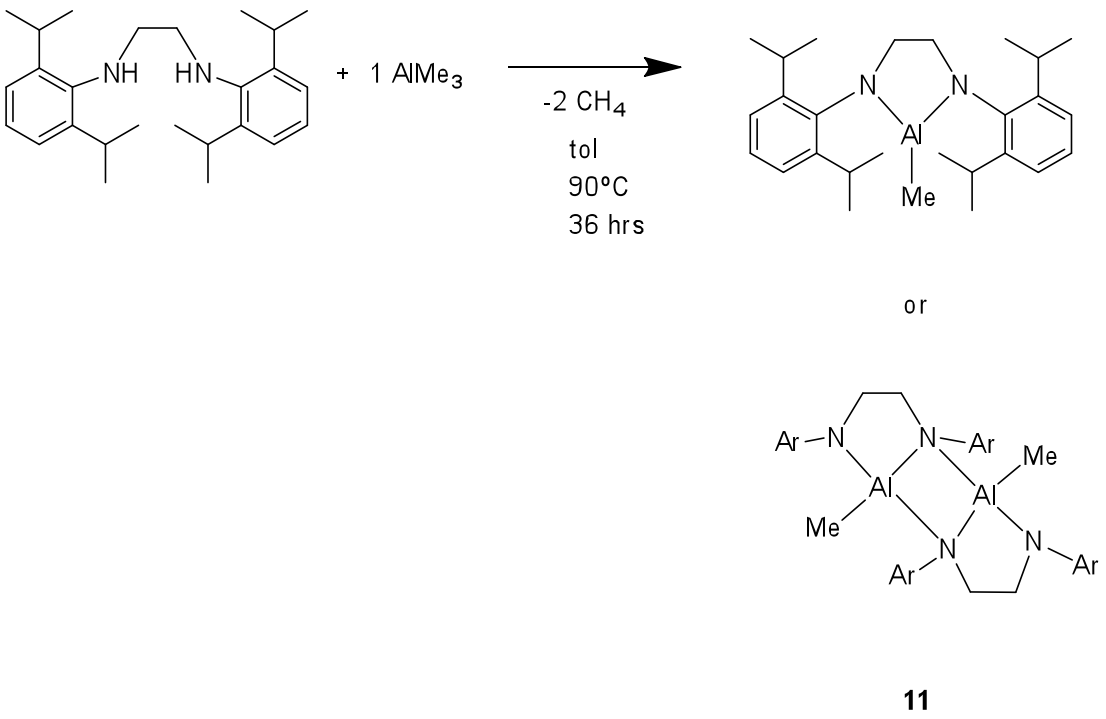


10

Scheme 2-11: The reaction followed in attempts to form a three coordinate aluminum-hydride.

2.3.2.4 (α-diamine)Al-Me Synthesis

Trimethyl aluminum was used to synthesize an (α-diamine)Al-Me complex, analogous to that of the (γ-diamine)Al-Me complexes. This reaction requires heat (90 ^{o}C) for 36 hours, under a nitrogen atmosphere (see Scheme 2-12). The ^{1}H NMR of the product contains doublets at 0.69, 0.84, 1.18, 1.23, 1.34, 1.40, 1.45, 1.47 ppm indicating that all the methyl groups are in different environments. This implies that the final product could have taken on a dimeric structure (see compound **11** below). The bite angle would be quite small for the five-membered ring, which would cause the aryl substituents on the nitrogens, to be pushed farther away from the metal centre. This lack of steric bulk surrounding the aluminum center could make dimer formation possible. A crystal structure is needed to determine the exact structure.



11

Scheme 2-12: A possible synthetic route to the (α-diamine)Al-Me complex.

2.4 Conclusion

Two 3-coordinate aluminum alkyl complexes were successfully synthesized. A γ-diamido aluminum methyl complex, and the first γ-diamido aluminum-ethyl complexes were produced, as three-coordinate aluminum-ethyl complexes are not known to exist. The crystal structures obtained of these γ-diamido aluminum-ethyl complexes prove that a three coordinate environment is present around the metal center. This three coordinate environment affords a highly lewis acidic metal center, which is a main advantage for catalysis.

A α-diamido aluminum-methyl catalyst was synthesized; however, the final product may not be three coordinate. The small bite angle, and large β and γ angles could provide an ideal spatial environment for dimer formation. A dimer, however, is not desired. A crystal structure is needed to confirm the exact structure of the α-diamido aluminum-methyl catalyst.

Unfortunately, a 3-coordinate aluminum-hydride complex was not successfully synthesized. The crystal structure revealed that there is lithium coordination to the aluminum center, forming a four coordinate environment around the metal centre. 12-C-4 and methyl iodide was ineffective in the removal of the lithium ion from the complex.

2.5 Experimental

2.5.1 General Information: All procedures involving air sensitive compounds were carried out in a nitrogen filled glove box or on a nitrogen Schlenk line. All solvents used were dry and acquired from solvent purification towers. All air sensitive compounds were run with dried deuterated solvents in air sensitive NMR tubes. The NMR solvents, deuterated benzene and deuterated chloroform, were dried through the "freeze, pump, thaw" method, and stored over molecular sieves in the glove box. The NMR data was collected with a Bruker Advance 500 MHz spectrometer at room temperature. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Trimethylaluminum (2.0M in toluene) was purchased from the Sigma-Aldrich Chemical

Company. All starting materials were checked to ensure that they contained no moisture prior to use, via ^{1}H NMR.

2.5.2 Synthesis of 1,2-[2,4,6-$(CH_3)_3$-C_6H_3NH-CH_2]$_2$-C_6H_4 (1)

n-BuLi (20.6 mL, 33.0 mmol) was added to a solution of 2,4,6-trimethylaniline (4.22 mL, 30.0 mmol) and THF at -78 ^{o}C, where it was stirred for 1 hr (at -78 ^{o}C). The cold bath was then removed, and it was further stirred for 1 hr at room temperature. α, α'-dibromo-o-xylene (3.96 g, 15.0 mmol) was then added and stirred overnight. The solution was then quenched with water (20 mL) and extracted with diethyl ether (3 x 10 mL), and dried over $MgSO_4$; the solvent was removed via vacuum. A minimal amount of diethyl ether, just enough to dissolve the solid, was added. The resulting white precipitate resulted in the desired product. ^{1}H NMR (C_6D_6): δ = 2.13 (s, 12H, *o*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 2.19 (s, 6H, *p*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 3.11 (br s, 2H, N*H*), 4.08 (s, 4H, C*H*$_2$), 6.78 (s, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.09 (m, 2H, C_6H_4), 7. 29 (m, 2H, C_6H_4). ^{13}C NMR (C_6D_6): δ = 18.4 ($ArCH_3$), 20.7 ($ArCH_3$), 51.0 ($ArCH_2NH$), 129.9, 130.5, 131.7, 139.3, 144.2 (Ar).

2.5.3 Synthesis of 1,2-(2,6-$^{i}Pr_2C_6H_3NHCH_2)_2$-C_6H_4 (2)

n-BuLi (20.6 mL, 33.0 mmol) was added to a solution of 2,6-diisopropylaniline (3.29 mL, 30.0 mmol) and THF at -78 ^{o}C, where it was stirred for 1 hr (at -78^{o}C). The cold bath was then removed, and it was further stirred for 1 hr at room temperature. α, α'-dibromo-o-xylene (3.96 g, 15.0 mmol) was then added and stirred overnight. The solution was then quenched with water and extracted with diethyl ether, and dried over

$MgSO_4$; the excess solvent was removed via vacuum. A minimal amount of hexane, just enough to dissolve the solid, was added. This solution was then put in the freezer (-25 ^oC) overnight resulting in the formation of orange crystals. The solvent was decanted off and the remaining solvent was pumped off to yield a pale orange solid. ^1H NMR (C_6D_6): δ = 1.16 (d, 24H, ^{i}Pr-C*H*$_3$), 3.22 (br s, 2H, N*H*), 3.31 (m, 4H, ^{i}Pr-C*H*), 4.21 (s, 4H, C*H*$_2$), 7.19 (s, 6H, 2,6-(^{i}Pr)$_2$-C$_6$*H*$_3$), 7.55 (m, 4H, C$_6$*H*$_4$). ^{13}C NMR (C_6D_6): δ = 24.6 (*C*H$_3$CHAr), 28.4 (ArCH), 54.2 (ArCH$_2$NH), 124.2, 124.9, 129.1, 138.8, 143.2, 144.0 (Ar).

2.5.4 Synthesis of [1,2-(2,6-^{i}Pr$_2$C$_6$H$_3$NHCH$_2$)$_2$] (3)

A solution of alpha-diimine [1,2-(2,6-^{i}Pr$_2$C$_6$H$_3$N=CH)$_2$] (300 mg, 0.805 mmol) in dry diethyl ether was cooled to -70 ^oC. Lithium aluminum hydride (2.01 mL, 2.01 mmol) was added portion wise. Once the reaction mixture was stirred for 24 hours at room temperature, it was cooled to -20 ^oC and quenched with 1% potassium hydroxide in water, producing a white precipitate. The precipitate was removed through filtration, and the filtrate was dried over $MgSO_4$, and the solvent was removed via vacuum, resulting in a white solid. ^1H NMR (C_6D_6): δ = 1.19 (d, 24H, ^{i}Pr-C*H*$_3$), 3.17 (s, 4H, C*H*$_2$), 3.35 (m, 6H, ^{i}Pr-C*H* & N*H*), 6.99 (m, 2H, 2,6-(^{i}Pr)$_2$-C$_6$*H*$_1$), 7.15 (m, 4H, C$_6$*H*$_4$).

2.5.5 Synthesis of [1,2-(2,6-^{i}Pr$_2$C$_6$H$_3$NCH$_2$)$_2$]AlMe

Compound **3** (150 mg, 0.398 mmol) was dissolved in a minimal amount of toluene (5 mL). Trimethyl aluminum (0.21 mL, 0.398 mmol) was added and the solution was allowed to stir overnight at room temperature. It was then further stirred for 24 hours at

90 °C. The solvent was removed in vacuo to yield an orange solid (93% yield). ^{1}H NMR (C_6D_6): δ = -0.61 (s, 3H, Al-CH_3), 0.69 (d, 3H, ^{i}Pr-CH_3), 0.84 (d, 3H, ^{i}Pr-CH_3), 1.18 (d, 3H, ^{i}Pr-CH_3), 1.23 (d, 3H, ^{i}Pr-CH_3), 1.37 (d, 3H, ^{i}Pr-CH_3), 1.40 (d, 3H, ^{i}Pr-CH_3), 1.45 (d, 3H, ^{i}Pr-CH_3), 1.47 (d, 3H, ^{i}Pr-CH_3), 2.70 (m, 1H, ^{i}Pr-CH), 2.99 (m, 1H, CH_2), 3.15 (m, 1H, CH_2), 3.78 (m, 1H, ^{i}Pr-CH), 3.90 (m, 1H, ^{i}Pr-CH), 4.01 (m, 1H, ^{i}Pr-CH), 5.09 (m, 1H, ^{i}Pr-CH), 6.91 (m, 1H, C_6H_3), 7.01 (m, 3H, C_6H_3), 7.18 (m, 2H, C_6H_3).

2.5.6 Attempted synthesis of [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlMe (4)

Compound **1** (1.00 g, 3.62 mmol) was dissolved in a minimal amount of toluene. Trimethyl aluminum (1.81 mL, 3.62 mmol) was added and the reaction mixture was stirred at 80 °C for 14 hours. The clear yellow solution was cooled to room temperature and the solvent was removed via vacuum. ^{1}H NMR showed the desired product along with formation of compound **4a** in a 2:1 ratio (compound **4**: compound **4a**). ^{1}H NMR (C_6D_6): δ = -0.57 (Al-CH_3), -0.10 (s, 3H, Al-CH_3), 0.57 (s, 3H, Al-CH_3), 1.72 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 1.99 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.23 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.40 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.44 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.53 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 3.46 (d, 1H, CH_2), 3.84 (d, 1H, CH_2), 4.86 (d, 1H, CH_2), 5.06 (d, 1H, CH_2), 6.68 (m, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 6.96 (m, 4H, C_6H_4).

2.5.7 Synthesis of [1,2-(2,6-^{i}Pr$_2$$C_6H_3NCH_2)_2$-$C_6H_4$]AlMe (5)

Compound **2** (500 mg, 1.10 mmol) was dissolved in a minimal amount of toluene (5 mL) in a pressure vessel. Trimethyl aluminum (0.52 mL, 1.05 mmol) was added and the reaction mixture was stirred at 90 °C for 4 days. The clear orange solution was cooled to

room temperature and the solvent was removed via vacuum, yielding an orange solid. ^{1}H NMR (C_6D_6): δ = -0.91 (q, 3H, AlCH_3), 1.19 (d,12H, ^{i}Pr-CH_3), 1.33 (d,12H, ^{i}Pr-CH_3) 3.71 (m, 4H, CH(CH_3)$_2$), 4.33 (s, 4H, N-CH_2), 7.02 (s, 4H, C_6H_4), 7.18 (s, 6H, C_6H_3). ^{13}C NMR (C_6D_6): δ = 25.2 (CH_3CHAr), 28.8 (ArCH), 59.5 (ArCH_2N), 124.1, 125.8, 130.7, 141.8, 146.5, 147.2 (Ar).

2.5.8 [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlMe[Al(μ-Me)Me_2] (4a)

Compound **1** (300 mg, 1.09 mmol) was dissolved in a minimal amount of toluene, and aluminum trimethyl (1.09 mL, 2.17 mmol) was added and the reaction mixture was stirred for 2 days at 90 ^{o}C. After the 2 days, the solution was cooled and the excess solvent was pumped off via vacuum. ^{1}H NMR (C_6D_6): δ = -0.59 (s, 6H, 2 Al-CH_3), -0.10 (s, 3H, Al-CH_3), 0.57 (s, 3H, Al-CH_3), 1.72 (s, 3H, 2,4,6-(CH_3)-C_6H_2), 1.99 (s, 3H, 2,4,6-(CH_3)-C_6H_2), 2.23 (s, 3H, 2,4,6-(CH_3)-C_6H_2), 2.45 (s, 3H, 2,4,6-(CH_3)-C_6H_2), 2.43 (s, 3H, 2,4,6-(CH_3)-C_6H_2), 2.53 (s, 3H, 2,4,6-(CH_3)-C_6H_2), 3.43 (d, 1H, CH_2), 3.82 (d, 1H, CH_2), 4.89 (d, 1H, CH_2), 5.09 (d, 1H, CH_2), 6.61 (m, 2H, C_6H_4), 6.95 (m, 2H, C_6H_4).

2.5.9 Synthesis of [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlEt (6)

Compound **1** (277 mg, 1.00 mmol) was dissolved in toluene (10 mL). Triethyl-aluminum (1.00 mL, 1.00 mmol) was added, and the solution was allowed to stir at 90 ^{o}C for 12 hours, under a nitrogen atmosphere. The solvent was removed in vacuo, producing a dark yellow solid. ^{1}H NMR (C_6D_6): δ = -0.30 (q, 2H, AlCH_2), 0.56 (t, 3H, $AlCH_2CH_3$), 2.19 (s, 6H, *p*-CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.31 (s, 12H, *o*-CH_3; 2,4, 6-$(CH_3)_3$-

C_6H_2), 4.26 (s, 2H, N-CH_2), 6.89 (s, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.08-7.17 (m, 4H, C_6H_4). Anal. Calcd. for $C_{28}H_{35}N_2Al$: C 78.82; H 8.29; N 6.57. Found: C 75.79; H 8.77; N 5.91.

2.5.10 Synthesis of [1,2-(2,6-^{i}Pr$_2$C$_6$H$_3$NCH$_2$)$_2$-C$_6$H$_4$]AlEt (7)

Compound **2** (451 mg, 1.00 mmol) was dissolved in toluene (10 mL). Triethyl-aluminum (1.00 mL, 1.00 mmol) was added, and the solution was allowed to stir at 90 ^{o}C for 12 hours, under a nitrogen atmosphere. The solution was dried via vacuum, producing an orange solid. The solid was dissolved in a minimal amount of toluene and stored at -21 ^{o}C, yielding orange crystals. ^{1}H NMR (C_6D_6): δ = -0.25 (q, 2H, AlCH_2), 0.55 (t, 3H, $AlCH_2CH_3$), 1.19 (d,12H, ^{i}Pr-CH_3), 1.33 (d,12H, ^{i}Pr-CH_3) 3.62 (m, 4H, CH(CH_3)$_2$), 4.39 (s, 4H, N-CH_2), 7.02-7.13 (m, 10H, C_6H_4 / C_6H_3)$_2$). Anal. Calcd. for $C_{34}H_{47}N_2Al$: C 79.94; H 9.29; N 5.49. Found: C 79.27; H 9.64; N 5.31.

2.5.11 Synthesis of [1,2-(2,4,6-(CH$_3$)$_3$-C$_6$H$_3$N-CH$_2$)$_2$-C$_6$H$_4$]Al(μ-H)$_2$Li(Et$_2$O)$_2$ (8a)

Compound **1** (300 mg, 1.09 mmol) was added to a solution of lithium aluminum hydride and dry diethyl ether at -60 ^{o}C. The solution was then warmed to room temperature and stirred overnight. The resulting cloudy, light yellow solution was then filtered and the solvent was removed in vacuo, to yield an air sensitive light, yellow solid. This was dissolved in a minimal amount of toluene to produce yellow crystals. ^{1}H NMR (C_6D_6): δ = 1.05 (t, 12H, Li(O(CH_2CH_3)$_2$)), 2.22 (s, 6H, *p*-CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.23 (s, 12H, *o*-CH_3; 2,4, 6-$(CH_3)_3$-C_6H_2), 3.28 (q, 8H, Li(O(CH_2CH_3)$_2$)), 4.18 (br s, 1H, AlH), 4.28 (s, 4H, CH_2), 6.78 (s, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.09-7.20 (m, 4H, C_6H_4). ^{13}C NMR (C_6D_6): δ

= 14.7 ($ArCH_3$), 20.1 ($ArCH_3$), 21.0 (CH_3CH_2O), 57.5 ($ArCH_2N$), 65.7 (CH_3CH_2O), 127.0, 129.4, 130.0, 131.3, 137.6, 142.9, 150.7 (Ar).

2.5.12 Attempted removal of co-ordinated lithium from [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]Al(μ-H)$_2$Li($Et_2O)_2$ with the use of 12-C-4

1 eq. of 12-C-4 (0.05 mL, 0.327 mmol) was added to a solution of compound **8a** (150 mg, 0.327 mmol) and tetrahydrofuran, under nitrogen, producing a clear yellow solution. This solution was stirred at room temperature, and after 4 days of stirring, precipitate appeared. The precipitate was filtered producing a light yellow solid. The filtrate was dried via vacuum to yield a light yellow solid, which ^{1}H NMR shows to be the starting ligand; compound **1**. ^{1}H NMR (C_6D_6): δ = 2.13 (s, 12H, *o*-CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.19 (s, 6H, *p*-CH_3; 2,4, 6-$(CH_3)_3$-C_6H_2), 3.11 (br s, 2H, N*H*), 4.08 (s, 4H, CH_2), 6.78 (s, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.09 (m, 2H, C_6H_4), 7. 29 (m, 2H, C_6H_4).

The same above procedure was done using 2 eq. of 12-C-4 (0.106 mL, 0.6540 mmol), under the same conditions, resulting in the same outcome

2.5.13 Attempted removal of co-ordinated Et_2O from [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]Al(μ -H)$_2$Li($Et_2O)_2$ with the use of MeI

Compound **8a** (200 mg, 0.361 mmol) was dissolved in dry toluene. Methyl iodide (0.03 mL, 0.397 mmol) was added and stirred for 12 hours at room temperature under an atmosphere of nitrogen. The solvent was removed via vacuum, yielding a white solid. ^{1}H NMR spectra indicates formation of several species, none of which could be positively identified.

2.6 References

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CHAPTER 3: POLYMERIZATION

3.1 Abstract

The three-coordinate aluminum alkyl catalysts, developed in Chapter 2, were used in ring opening polymerizations of cyclic esters. These complexes include the γ-diamido aluminum compounds as well as the aluminum-hydride compounds. Caprolactone was the main monomer studied, however, other monomers, such as lactide, butyrolactone, cis-cyclooctene and diphenylacetylene, were also employed with these catalysts.

3.2 Introduction

3.2.1 ROP of Cyclic Esters in General

Polyesters (polylactides and polylactones) have some unique properties, such as being biodegradable, that allow them to have many applications in the pharmaceutical and biomedical industries, as well as having a strong influence in plastics. They are known to be used in compost bags, food packaging and disposable tableware. More specifically, polycaprolactone is targeted towards long term drug delivery systems. Polycaprolactone can provide a protective covering of drugs allowing for controlled release. It also has applications in the dental industry, being used in night guards and root canal fillings. This is due to the fact that the degradation of polycaprolactone is slower than other

polymers.[2] This allows it to be more advantageous in the medical field over other polymers.

A catalyst is needed to control the molecular weight and polydisperisty of a polymer during ring opening polymerization. There are many known ROP catalysts, most of which contain metals, such as magnesium, iron, zinc, tin and aluminum in their structure.[3] These metals are commonly used due to their capacity to be both selective towards monomers and their ability to control molecular weight.[4]

3.2.2 Why Aluminum?

Zinc and aluminum have been widely used as common metals employed in ROP catalysts.[5] However, aluminum is looked at as the more prominent metal choice when designing a ROP catalyst. Aluminum is easy to obtain, has high reactivity,[6] relatively cheap and low metal toxicity, therefore, making it a preferred option for catalysis.[7]

3.2.3 Important Qualities of Aluminum Catalysts

The polyesters are mainly synthesized through ring opening polymerization, which is done through initiation by metal complexes.[8] These metal complexes are able to control catalytic activity due to ligands present. Ligands are able to sterically and electronically tune the catalyst, thus altering the properties of the catalyst, allowing the catalyst to be

selective towards certain polymerizations.[4] Nitrogen and oxygen bearing ligands have been known to have success with aluminum for lactide and lactone polymerization.[3]

Organoaluminum compounds are known to be initiators for ROP of lactides and lactones. These aluminum complexes require certain structural properties to make them efficient catalysts for ROP of cyclic esters. The type of ligand present and the lewis acidity of the aluminum center are two main factors in determining the efficiency of the aluminum catalyst.

Sterics and electronics of the ligand present on the aluminum center, as well as the electrophilic nature of the aluminum center are important aspects and effect catalysis. Increased polymerization activity occurs with a more lewis acidic aluminum center, which is enhanced by electron withdrawing groups.[9] Therefore, aluminum-alkyl compounds are poor initiators as they contain a lower nucleophilicity than that in the aluminum-oxide complexes.[3]

3.2.4 Comparison to Four-Coordinate Aluminum Complexes

There are many four coordinate aluminum complexes that are active for caprolactone polymerization, however, an alcohol activator is needed for many of them, along with harsh conditions (high temperatures and long reaction times). The four coordinate nature of the catalyst, along with the ligand present, effect polymerization activity.[4]

Previous aluminum catalysts used have been designed by Otero and associates, who synthesized aryloxide aluminum compounds. They found that aluminum compounds containing nitrogen and/ or oxygen ligands (see Figure 3-1) were active for caprolactone polymerization. They discovered that the polymerization with this compound was quite successful in polymerization of caprolactone, however, in order to obtain almost complete conversion, 500 eq of caprolactone was used at 70 ^{o}C for 2 hours, resulting in a molecular weight distribution (M_w/M_n = 1.38). With an increase in temperature (130 ^{o}C), complete conversion was achieved with M_w/M_n = 2.01. This same compound was analyzed for rac-lactide polymerization activity and found that it is active at 110 ^{o}C for 6 hours, resulting in 83% conversion with medium molecular weight distribution (and narrow PDI), although 90% conversion can be obtained at 130 ^{o}C for 2 hours but contains broader PDI (M_w/M_n = 1.53).[3]

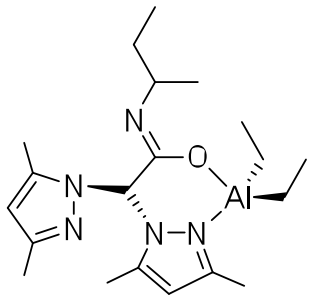
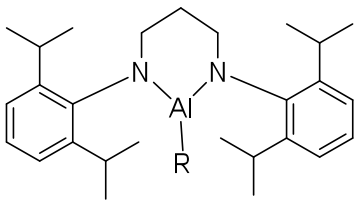


Figure 3-1: Aryloxide aluminum complex found to be active for caprolactone polymerization.[3]

3.2.5 Three-Coordinate Aluminum Catalyst Known in Literature

Chakraborty and Chen's three coordinate aluminum complex is the only three coordinate diamido aluminum speices known in literature. The catalyst was found to be successful in the ROP of ε-caprolactone (see Figure 3-2). The bulkiness of the catalyst and the three coordinate environment about the metal center contribute to an efficient catalyst system for caprolactone polymerization. Monomer insertion occurs easily due to the high lewis acidity of the aluminum center. Chakraborty and Chen noticed that the initial monomer insertion takes place into the aluminum-nitrogen bond versus the aluminum-methyl bond. They also found that subsequent insertions take place through nucleophilic attack on the monomer by the alkoxy group versus the other aluminum-nitrogen bond. This shows that there is a preference towards the alkoxy group over the aluminum-nitrogen bond.[10]



R=Me, ^{t}Bu, C_6F_5

Figure 3-2: Three coordinate aluminum catalyst designed by Chakraborty and Chen, for ROP of caprolactone.[10]

ε-caprolactone polymerization was carried out with the neutral, three coordinate aluminum catalyst that was synthesized by Chakraborty and Chen. They varied the R-group from methyl to ^{i}Bu to C_6F_5 group, and they found that the ^{i}Bu R-group produced the highest molecular weight of polycaprolactone, with 74% yield. The C_6F_5 group resulted in broad molecular weights, while the methyl group came in between the two in regards to polymerization activity.

3.2.6 Monomers (Lactide vs Caprolactone)

Structure differences in monomers effects polymerization:

Besides the steric and electronic nature of the ligand present in the catalyst, the monomer structure itself can also effect polymerization activities. When considering the two cyclic esters, caprolactone and lactide, the different ring size and positions of the ester groups play a role in polymerization. During coordination of the carbonyl oxygen to the metal center, the cyclic ester opens up and creates a chelating ring with the catalyst. In the case of lactide, a stable five-membered ring complex results, where as caprolactone produces a nine-memebered ring (see Figure 3-3). The carbonyl oxygen of caprolactone is unlikely to coordinate to the aluminum center where as the five-membered ring of lactide coordination is known to occur.[6] Also, due to the bulkiness of lactide, monomer insertion is difficult versus with caprolactone, as there is no steric bulk surrounding the ester group in caprolactone. The added combination of this bulk on lactide and the steric bulk from the ligand makes lactide polymerization more challenging than caprolactone polymerization.[6]

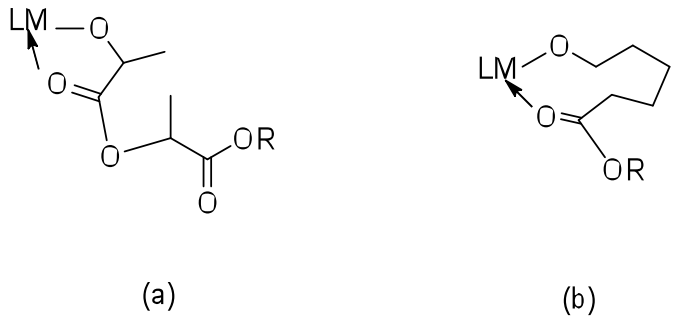


Figure 3-3: The resultant 5 & 9 membered rings that form throughout monomer insertion during polymerization with (a) lactide and (b) caprolactone.[6]

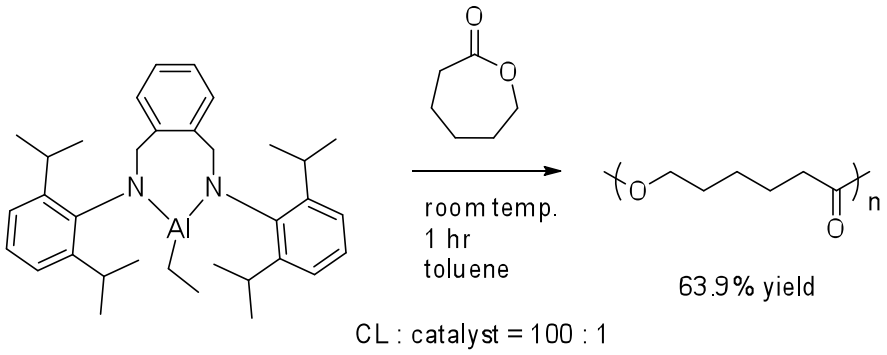
3.2.7 Research Objectives

The main objective was to create a catalyst that gave favourable conditions towards ring opening polymerizations of cyclic esters. Single site catalysts were utilized and include aluminum in a three coordinate environment. These aluminum compounds contain properties that made them viable catalysts for cyclic ester polymerization. It was of interest to explore and compare the polymerization activities of differing ring sizes and bite angles found in the 1,2-diamido ligand, 1,3-diamido ligand and the 1,4-diamido ligand. This chapter deals with mainly caprolactone polymerization, employing the three coordinate diamido aluminum catalysts that were discussed in Chapter 2.

3.3 Results and Discussion

3.3.1 Caprolactone Polymerization

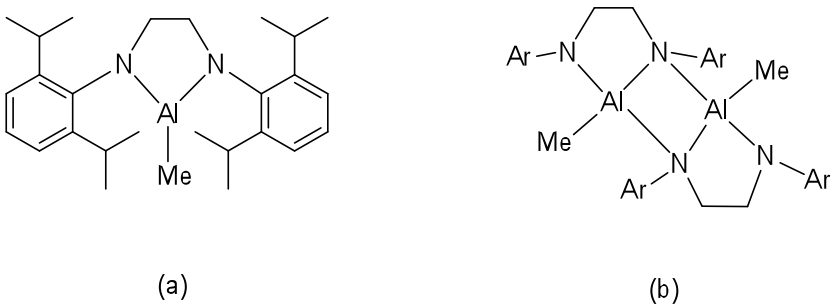
The γ-diamido aluminum-ethyl complexes (compounds **6** & **7**) and the γ-diamido aluminum-hydride complex (compounds **8a**) were investigated for caprolactone polymerization activity. The aluminum-ethyl catalyst was found to be active for caprolactone, however, the aluminum-hydride complex and lithium aluminum hydride, were not active, under conditions of one hour reaction time at room temperature. The length of time for polymerization was adjusted to 16.5 hours, and the catalyst was still inactive. Even with the addition of heat (60 ^{o}C), polycaprolactone did not result. This suggests that four-coordinate aluminum hydrides are not effective for caprolactone polymerization where as the aluminum-ethyl catalysts are.



Scheme 3-1: Caprolactone polymerization with the aluminum-ethyl diisopropyl catalyst.

The γ-diamido aluminum-methyl complexes, containing the mesityl and disopropyl subsitutents (compounds **4** & **5**), were both tested for caprolactone polymerization activity. It was found that harsh conditions were not needed for these catalysts, and reasonable yields were achieved at room temperature.

On the other hand, the α-diamido aluminum-methyl complex (compound **3**) was not active for caprolactone polymerizations under the same conditions as those described above. However, with the application of heat (90 ^{o}C) for 24 hours, with 100 equivalence of caprolactone, the catalyst became active, and polycaprolactone was produced with a 88.0% yield. The polymerizations may not have been successful at room temperature due to the fact that the exact structure of the α-diamido complex is unknown (see Figure 3-4). If this catalyst contains a dimer structure, this would inhibit polymerization, as the dimer would block an open coordination site around the metal center. With a blocked site, initial monomer insertion would be more difficult and less likely to occur.



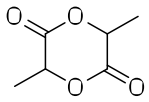
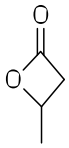
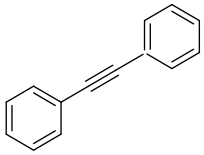
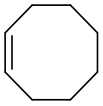
(a) (b)

Figure 3-4: The possible structures of the α-diamido aluminum-methyl complex; (a) the desired product (b) the dimer formation.

3.3.2 Other Monomer Polymerizations

Polymerizations with the γ-diamido aluminum complexes were also carried out with different monomers (see Table 3.1). Lactide, butyrolactone, diphenylacetylene and cis-cyclooctene were the monomers attempted. It was discovered that these aluminum catalysts were not active for any of the above mentioned monomers.

Table 3.1: Polymerizations utilizing [1,2-(2,6-$^{i}Pr_2C_6H_3NCH_2)_2$]AlMe

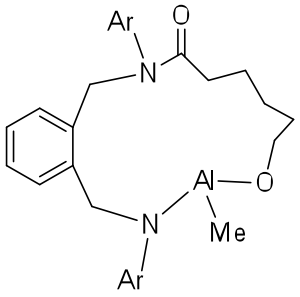
Monomer (structure)	Temperature (^{O}C)	Reaction Time (hr)	Equivalence (catalyst : monomer)
Rac-lactide 	room temp.	1	1 : 100
	80	24	1 : 50
(β)-butyrolactone 	room temp.	24	1 : 100
	90	24	1 : 100
Diphenylacetylene 	room temp.	24	1 : 10
	90	24	1 : 10
Cis-cyclooctene 	room temp.	24	1 : 10
	90	24	1 : 10

* [1,2-(2,6-$^{i}Pr_2C_6H_3NCH_2)_2$]AlMe was the catalyst employed for all the above catalytic reactions

** 0% polymerization yields were obtained for all entries

3.3.3 Polymerization Mechanism Elucidation

The mechanism of caprolactone polymerization with a diamido aluminum catalyst was investigated. It was discovered that the mechanism doesn't entail usual polymerization processes, such as cationic or radical polymerizations, but rather, it occurs through a coordination-insertion mechanism. A reaction of compound **5** with caprolactone was observed through ^{1}H NMR. The ^{1}H NMR spectra clearly show a sharp singlet at -0.88 ppm. This indicates that the methyl group is still present, signifying that initial monomer insertion does not take place between the aluminum-methyl bond, but rather between the aluminum-nitrogen bond (see Figure 3-5). This is probably due to the fact that nitrogen is more nucleophilic than the methyl group, making an attack by nitrogen more probable.



Ar = 2,6-$^{i}Pr_2C_6H_3$

Figure 3-5: A depiction of monomer insertion into the Al-N bond during caprolactone polymerization with the γ-diamido dipp, Al-Me catalyst.

3.4 Conclusion

The aluminum complexes employed for caprolactone polymerization were fairly successful. The γ-diamido aluminum catalysts (containing the ethyl and methyl R-groups) were found to be active for caprolactone polymerization, giving reasonable percent yields. Unfortunately, the aluminum-hydride complexes were not active for caprolactone polymerization. Electronics may be the reason for unsuccessful polymerization for the hydrides. Harsh conditions were needed for the α-diamido aluminum catalyst to become active for caprolactone polymerization. However, a crystal structure is still required to conclusively determine if this complex is a dimer.

The mechanism of caprolactone polymerization with a diamido aluminum catalyst was found to involve initial monomer insertion between the nitrogen-aluminum bond, versus the aluminum-methyl bond. This may indicate that electronics plays more of a role in polymerization than does sterics.

3.5 Experimental

3.5.1 General Information:

All procedures involving air sensitive compounds were carried out in a nitrogen filled glove box or on a nitrogen Schlenk line. All solvents used were dry and acquired from solvent purification towers. All air sensitive compounds were run with dried deuterated solvents in air sensitive NMR tubes. The NMR solvents, deuterated benzene and

deuterated chloroform, were dried through the "freeze, pump, thaw" method, and stored over molecular sieves in the glove box. The NMR data was collected with a Bruker Advance 500 MHz spectrometer at room temperature. GPC data was obtained from a Viscotek high-temperature GPC. ε-caprolactone and other monomers were purchased form Sigma-Aldrich Chemical Company. ε-caprolactone was distilled and stored under nitrogen over molecular sieves. All other monomers were dried via vacuum and stored under nitrogen over molecular sieves.

3.5.2 General caprolactone polymerization procedure (using [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlMe (4), and [1,2-(2,6-$^{i}Pr_2C_6H_3NCH_2)_2$]AlMe (5) as catalysts)

The catalyst (20 mg) was dissolved in dry toluene (10 mL), under nitrogen. Caprolactone (varying equivalents*) was added and the clear solution was stirred for one hour at room temperature. At higher equivalents, the solution became thick closer to the end of the hour of stirring. The solution was then quenched with methanol (~15 mL), resulting in the formation of a white precipitate. The precipitate was washed with methanol (3x 10 mL) and filtered and dried via vacuum, yielding a white solid.

*100, 200, 400 equivalents = 0.49 mL, 4.40 mmol (77.9% yield); 0.98 mL, 8.80 mmol (87.0% yield); 1.95 mL, 17.6 mmol (12.0% yield), respectively; using [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlMe **(4)**

*100, 200, 400 equivalents = 0.45 mL, 4.06 mmol (60.4% yield); 0.90 mL, 8.12 mmol (47.0% yield); 1.80 mL, 16.2 mmol (23.5% yield), respectively; using [1,2-(2,6-$^{i}Pr_2C_6H_3NCH_2)_2$]AlMe **(5)**

3.5.3 Caprolactone polymerization with [1,2-(2,6-$^{i}Pr_2C_6H_3NCH_2)_2$]AlMe (11)

Compound **11** (20 mg, 0.048 mmol) was dissolved in dry toluene (10 mL), under nitrogen. Caprolactone (0.53 mL, 4.75 mmol) was added, producing a clear solution, which was stirred for 1 hour at room temperature. The solution was then quenched with methanol (~15 mL), where it remained a clear solution.

Another attempt: The same amounts and procedure was followed as above, with the exception of the duration of stirring which was changed to 24 hours. This also resulted in no polymer. Therefore, another attempt was made following the same procedure with the exception that it was stirred for 24 hours at 90 ^{o}C. Upon quenching with methanol, a white precipitate formed, which was washed with methanol (3 x 10 mL) and filter via vacuum, producing a white solid (88.0% yield) .

3.5.4 Caprolatone polymerization with [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlMe[Al(μ-Me)Me_2] (4a)

Compound **4a** (20 mg, 0.0515 mmol) was dissolved in dry toluene (10 mL), under nitrogen. Caprolactone (0.57 mL, 5.15 mmol) was added, producing a clear solution, which was stirred for 1 hour at room temperature. The solution was then quenched with methanol (~15 mL), where it remained a clear solution. ^{1}H NMR (C_6D_6): δ = 0.57 (Al-CH_3), -0.10 (s, 3H, Al-CH_3), 0.57 (s, 3H, Al-CH_3), 1.72 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 1.99 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.23 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.40 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.44 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 2.53 (s, 3H, 2,4,6-(CH_3)$_3$-C_6H_2), 3.46 (d, 1H, CH_2), 3.84 (d, 1H, CH_2), 4.86 (d, 1H, CH_2), 5.06 (d, 1H, CH_2), 6.68 (m, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 6.96 (m, 4H, C_6H_4).

3.5.5 Caprolactone polymerization with [1,2-(2,6-$^{i}Pr_2C_6H_3NCH_2)_2$-C_6H_4]AlEt (7)

Compound **7** (20 mg, 0.0396 mmol) was dissolved in dry toluene (10 mL), under nitrogen. ε-caprolactone (0.44 mL, 20 mg) was added, producing a clear solution, which was stirred for 1 hour at room temperature. The solution was quenched with methanol (15 mL). Upon methanol addition, white precipitate appeared. The precipitate was washed with methanol (2 x 10 mL) and filtered via vacuum, yielding a white solid (50.6% yield).

^{1}H NMR (C_6D_6): δ = 1.16 (m, 2H, C*H*$_2$), 1.35 (m, 2H, C*H*$_2$), 1.55 (m, 2H, C*H*$_2$), 2.12 (m, 2H, C*H*$_2$(CO)), 3.99 (m, 2H, O-C*H*$_2$).

3.5.6 Caprolactone polymerization with [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]Al(μ-H)$_2$Li($Et_2O)_2$ (8a)

Compound **8a** (20 mg, 0.0436 mmol) was placed in a flask in toluene (20 mL). ε-caprolactone (0.48 mL, 4.36 mmol) was added and the solution was stirred for 1 hour at room temperature. This clear solution was quenched with methanol (10 mL), and then washed with methanol (2 x 10 mL). The ^{1}H NMR shows caprolactone.

3.5.7 Caprolactone polymerization with $LiAlH_4$

Same procedure followed as that done with "Caprolactone Polymerization with [[1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]Al-H_2-Li($Et_2O)_2$ (**8a**)]" (as above). The resultant product was caprolactone.

3.5.8 Butyrolactone polymerization

Compound **5** (20.0 mg, 0.0410 mmol) was dissolved in dry toluene (10 mL), under nitrogen. Butyrolactone (0.33 mL, 4.06 mmol) was added producing a translucent yellow solution. The solution was stirred for 24 hours at room temperature, after which, it was quenched with methanol. The excess methanol was then pumped off. This resulted in no polymer formation. The reaction was then attempted again with the same conditions with the exception that the solution was stirred under heat (90 ^{o}C) for 24 hours, versus room temperature. This also gave the same result of no polymer formation.

3.5.9 Lactide polymerization

Compound **5** (5.0 mg, 0.0102 mmol) was dissolved in deuterated benzene in an air sensitive NMR tube, under nitrogen. Rac-lactide (0.0366 g, 0.254 mmol) was added and a ^{1}H NMR was taken, which showed both starting material. The NMR tube was then heated at 90 ^{o}C for 1 day and another ^{1}H NMR was run, showing both catalyst and lactide; no polymer was observed.

3.5.10 Diphenylacetylene and cis-cyclooctene polymerization

Compound **5** (5.0 mg, 0.0102 mmol) was dissolved in deuterated benzene in an air sensitive NMR tube, under nitrogen. The monomer was added (10 eq.) and a ^{1}H NMR was taken, which showed the catalyst and monomer in both cases. The solution was allowed to react overnight, where another ^{1}H NMR was run. No change in the spectrum was seen so the NMR tube was heated to 90 ^{o}C overnight. A third ^{1}H NMR revealed no change in the spectrum. ^{1}H NMR [cis-cyclooctene] (C_6D_6): δ = -0.91 (q, 3H, AlCH_3),

1.18 (d,12H, ^{i}Pr-CH_3), 1.33 (d,12H, ^{i}Pr-CH_3), 1.45* (m, 8H, C_8H_8), 2.07* (m, 4H, C_8H_4), 3.70 (m, 4H, CH(CH_3)$_2$), 4.32 (s, 4H, N-CH_2), 5.65* (m, 2H, C_8H_2), 7.02 (s, 4H, C_6H_4), 7.18 (s, 6H, C_6H_3)

^{1}H NMR [diphenylacetylene] (C_6D_6): δ = -0.91 (q, 3H, AlCH_3), 1.17 (d,12H, ^{i}Pr-CH_3), 1.33 (d,12H, ^{i}Pr-CH_3) 3.69 (m, 4H, CH(CH_3)$_2$), 4.31 (s, 4H, N-CH_2), 6.98* (m, 6H, C_6H_3), 7.06 (s, 4H, C_6H_4), 7.18 (s, 6H, C_6H_3), 7.51* (m, 4H, C_6H_2).

*indicates chemical shift of monomer

3.5.11 Mechanism determination of caprolactone polymerization with [1,2-(2,6-^{i}Pr$_2$C$_6$H$_3$NCH$_2$)$_2$]AlMe (5)

Compound **5** (10 mg, 0.0203 mmol) and a minimal amount of C_6D_6 (0.5 mL) was added to an NMR tube. ε-caprolactone (varying equivalents*) was added to the NMR tube. A ^{1}H NMR was run within 15 min of the start of the reaction. The spectra clearly show a singlet peak at -0.90 ppm , representing the Al-Me protons.

*1, 4, 10 equivalents = 2.25 μL, 0.0203 mmol; 8.00 μL, 0.0812 mmol; 22.5 μL, 0.203 mmol, respectively

^{1}H NMR (C_6D_6): δ = -0.90 (s, 3H, AlCH_3), 1.15 (d, 12H, ^{i}Pr-CH_3), 1.30 (d, 12H, ^{i}Pr-CH_3), 1.35 (m, 2H, $CH_2CH_2CH_2$), 1.59 (m, 4H, $CH_2CH_2CH_2$), 2.20 (t, 2H, CH_2CO) 3.31 (s, 1H, NH), 3.73 (m, 4H, CH(CH_3)$_2$), 4.06 (t, 2H, CH_2O) 4.23 (s, 4H, N-CH_2), 7.02 (s, 4H, C_6H_4), 7.18 (s, 6H, C_6H_3).

3.6 References

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2. (a) Wen-An, B.; Zhong-Xia, W. *Organometallics,* **2011**, 30, 4364-4373. (b) Wen-An, M.; Zhong-Xia, W. *Dalton Trans.*, **2011**, 40, 1778.

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CHAPTER 4: DIAMIDO ALUMINUM COORDINATION TO OTHER ELEMENTS

4.1 Abstract

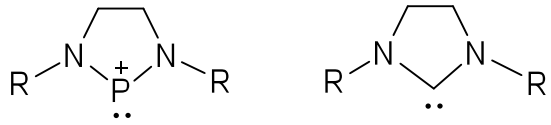
Our 1,4-diamido ligand system was explored for coordination with other metals, as well as non-metals. There showed promise, through the literature, that the ligand systems would form complexes with other metals and non-metals, such as phosphorus, boron, zinc and zirconium. This chapter provides insight into the attempted synthesis of these compounds that utilized the diamido ligands discussed in previous chapters.

4.2 Coordination of Other Elements to Diamido Ligands

4.2.1 Synthesis of (γ-diamido)PCl Complexes and Attempts to Make NHC analogues

Introduction:

N-heterocyclic carbenes (NHCs) are seen as significant ligands in coordination chemistry. The added electron density to the carbenic carbon makes NHCs more dominant in catalytic activity.[1] The reactivity of N-heterocyclic carbenes can also be seen in isoelectronic analogues; N-heterocyclic phosphenium cations (NHPs) (see Figure 4-1). NHCs and NHPs show similar characteristics structurally, but are reversed when it comes to its behaviour electronically. NHPs are relatively poor sigma donors and good pi acceptors, while NHCs are good sigma donors and poor pi acceptors.[2]



NHP NHC

Figure 4-1: General examples of NHPs as analogous to NHCs.

The NHP may cause the metal center to be more electrophilic, possibly enhancing catalysis in specific reactions. The difference in electron distribution about the metal center in both NHCs and NHPs, could change the reactivity, making them both effective catalysts for different reactions. For example, NHCs could be most effective when oxidative addition is the rate-limiting step in a catalytic reaction, while NHPs could be best when reductive elimination reactions are the rate-limiting step. Thus creating a phosphenium cation with the γ-diamine ligands, through a reaction with a phosphorous halide, was explored, in attempts to compare its reactivity with an NHC.

Phosphenium coordination to transition metals, or other atoms such as nitrogen, are not well known. One of the first compounds to exhibit this coordination feature was synthesized by Reed and co-workers (see Figure 4-2), where intermolecular coordination between the phosphorus center and nitrogen occurs. Lang and co-workers synthesized cobalt-phosphenium compounds (general formula $(R)(R')P{=}Co(CO)_3$) and Niecke

designed a nickel-phosphorus coordinate compound (Cl_2-Ga(u-$NSiMe_3$)$_2$P=Ni(CO)$_3$ while Abrams and associates developed a metallophosphenium compound utilizing rhodium (see Figure 4-3). The bulky steric environment about the phosphorus center may be the cause of the stability of these complexes, as well as the charge distribution throughout the cation.[3]

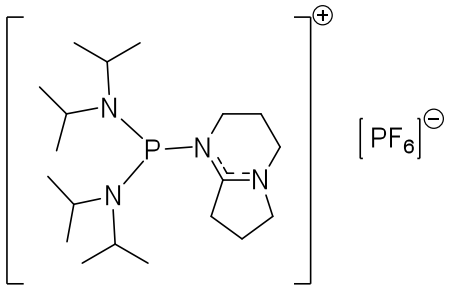
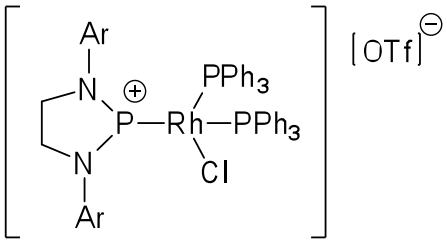


Figure 4-2: Phosphenium Complex synthesized by Reed *et al.* [3]

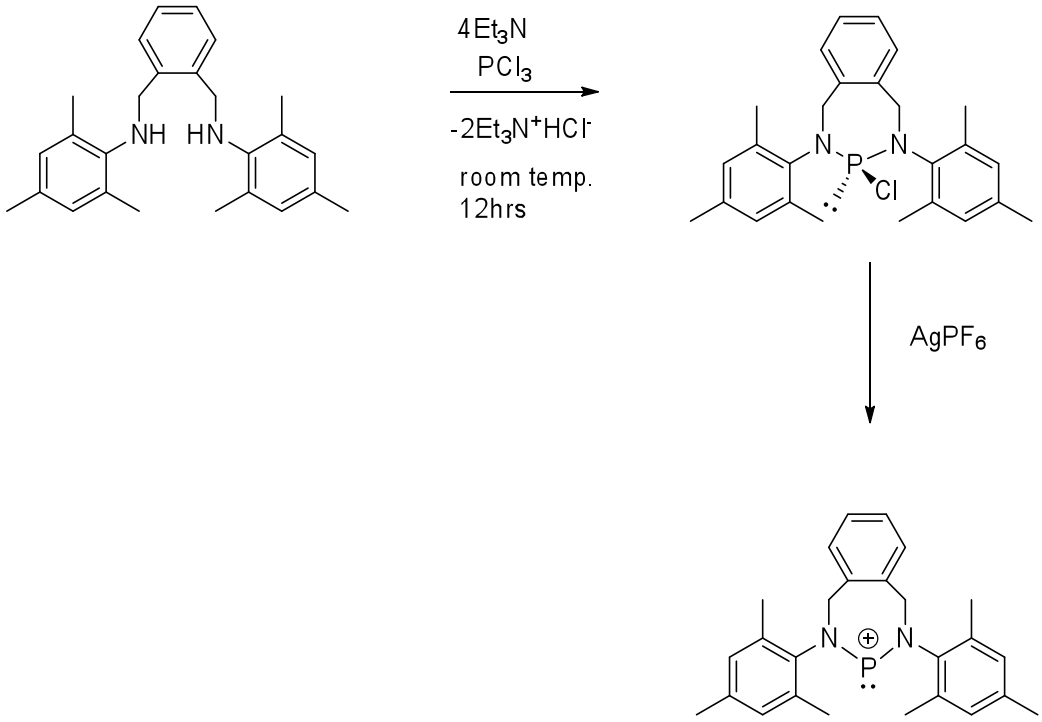


Ar = 4-MeO-C_6H_4
= 2,4,6-Me_3-C_6H_2

Figure 4-3: Rhodium Phosphenium Complexes synthesized by Abrams *et al.* [3]

Results and Discussion:

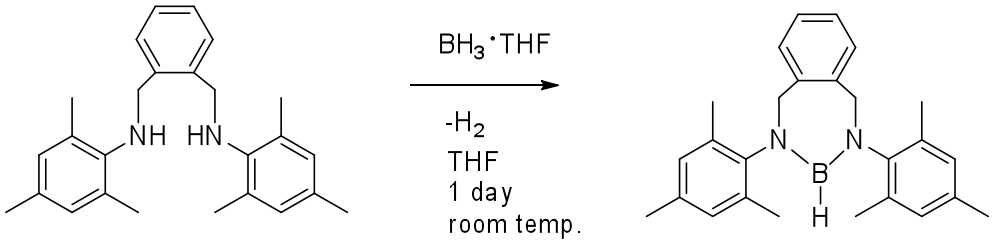
The synthesis of the phosphenium cation first involved the formation of a neutral (γ-diamido)PCl. (γ-diamido)PCl was synthesized by the addition of phosphorous trichloride to the γ-diamine ligand according to the first step found in Scheme 4-1. The successful synthesis of the (γ-diamido)PCl compound is evident through the ^{1}H NMR. There are characteristic doublet of doublets that are found at 5.80 and 3.68 ppm. These represent the two $-CH_2$ groups bound to the nitrogen atoms, wherein the $-CH_2$ protons are diastereotopic. This indicates that there is coupling between these protons and the phosphorous, signifying that the phosphorous is bonded to the two nitrogens. Also, there are two different peaks for the ortho- methyl groups; at 2.52 and 2.09 ppm. This indicates that these protons are in different environments, which suggests that there is hindered rotation about the nitrogen-carbon (of the aromatic group) bond. This limited rotation could be caused by the fact that there are interactions between the chlorine group (on phosphorous) and the ortho-groups. This confirms that the phosphorous is attached to the nitrogens. Removal of chlorine was done through the use of $AgPF_6$ (see Scheme 4-1; second step) to obtain the phosphenium cation. The ^{1}H NMR spectrum of this compound contains one singlet at 1.73 ppm, representing the mesityl methyl groups. This shows that there is now free rotation about the N-Ar group bond, signifying that the chlorine ion has been successfully removed. ^{1}H NMR spectra of the putative (diamido)P^{+} shows that there are multiple species present. Unfortunately, the product was an oil making purification by crystallization difficult.



Scheme 4-1: The synthesis of the phosphenium cation.

4.2.2 Boron-Hydride Synthesis in Comparison to Aluminum-Hydride Complexes

The synthesis of a boron hydride was done with the use of the γ-diamine ligand with BH_3·THF (see Scheme 4-2). The boron-hydride was made as an analogue to the aluminum-hydrides; to see if moving up a group in the periodic table would affect its reactivity. Unfortunately, even though the ^{1}H NMR contained characteristic peaks that would be found in the desired product, this reaction yielded a yellow oil, making crystallization difficult, and therefore, a crystal structure unobtainable.

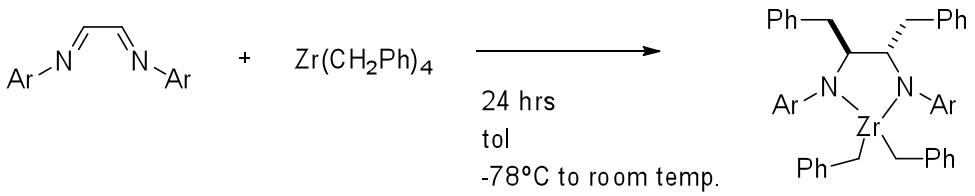


Scheme 4-2: The attempted synthesis of a boron hydride done with the γ-diamine ligand.

4.2.3 Attempt to Synthesize a Diamido Zirconium Complex

Introduction:

It was found in literature that a reaction of an α-diimine ligand with $Zr(CH_2Ph)_4$ resulted in double benzylation, with zirconium bonded to the two nitrogen atoms (see Scheme 4-3). This compound acted as a catalyst precursor with a cocatalyst, $B(C_6F_5)_3$ for α-olefin polymerization, specifically 1-hexene.[4] We wanted to extend this to the-γ-diimine ligand (compound **1**), to see if similar results could be obtained.

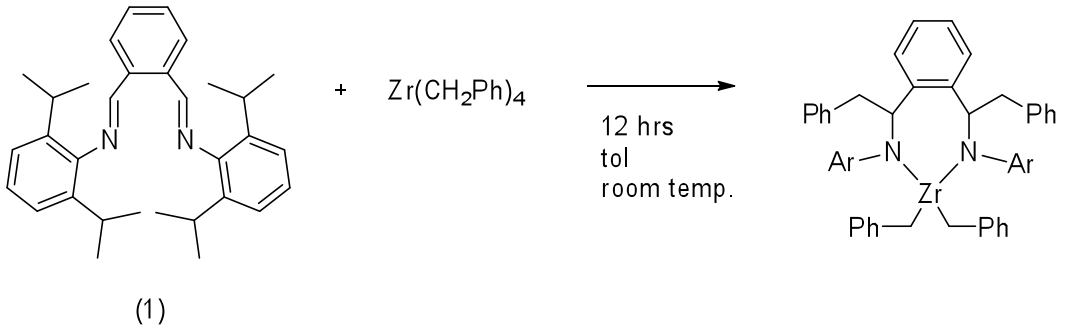


Ar = 3,5 $^{t}Bu_2C_6H_3$

Scheme 4-3: A known zirconium complex, synthesized from an α-diimine ligand and $Zr(CH_2Ph)_4$.[4]

Results and Discussion:

$Zr(CH_2Ph)_4$ was synthesized with a reaction involving slow addition of $(PhCH_2)MgCl$ to a solution of zirconium tetrachloride in diethyl ether, under nitrogen in the absence of light. This resulted in a yellow-goldish solid, and the ^1H NMR matched that of literature. This compound was then reacted with the γ-diimine ligand (compound **1**) in toluene at -20 ^oC, under nitrogen. It was then stirred for 12 hours, filtered and dried (see Scheme 4-4). The ^1H NMR showed a mixture of starting material; the γ-diimine (diisopropyl) ligand and $Zr(CH_2Ph)_4$. The reaction was then tried again, varying the conditions; to stir for 1 day at 100 ^oC. Unfortunately, the results were the same and only starting material was obtained.



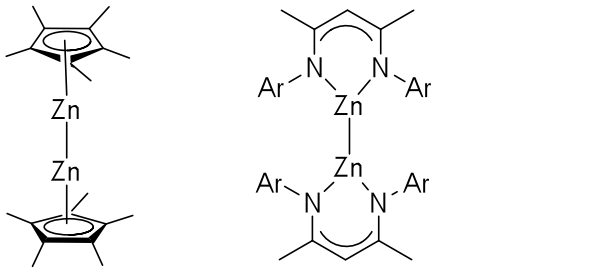
(1)

Scheme 4-4: Attempted synthetic route for the zirconium complex.

4.2.4 Attempted Formation of Zn(I) Species from a Low Coordinate Zn Complex:

Introduction:

Little is known about the reactivity and stability of Zn-Zn complexes, as this puts zinc in a very rare Zn(I) oxidation state. Although, Zn-Zn bonds have been found in a few complexes, where steric bulk was found as a contributor for the stability of the Zn-Zn bonds. Two of the first examples of Zn(I) complexes include one that was developed by Resa *et al* and contains the structure Cp*Zn-ZnCp* (Cp* = C_5Me_5),[5] while the second compound incorporated β-diketiminate ligands and was synthesized by Robinson (see Figure 4-4).[6] These complexes all contained bulky ligands and it was believed that the steric bulk affects the stability of the complex and allows the complex to remain as a dimer.[7] The bulky substituent has proven effective in the formation of Zn-Zn bonds, therefore, our fundamental goal was to attempt to produce a Zn(I) complex using our γ-diamido ligands.



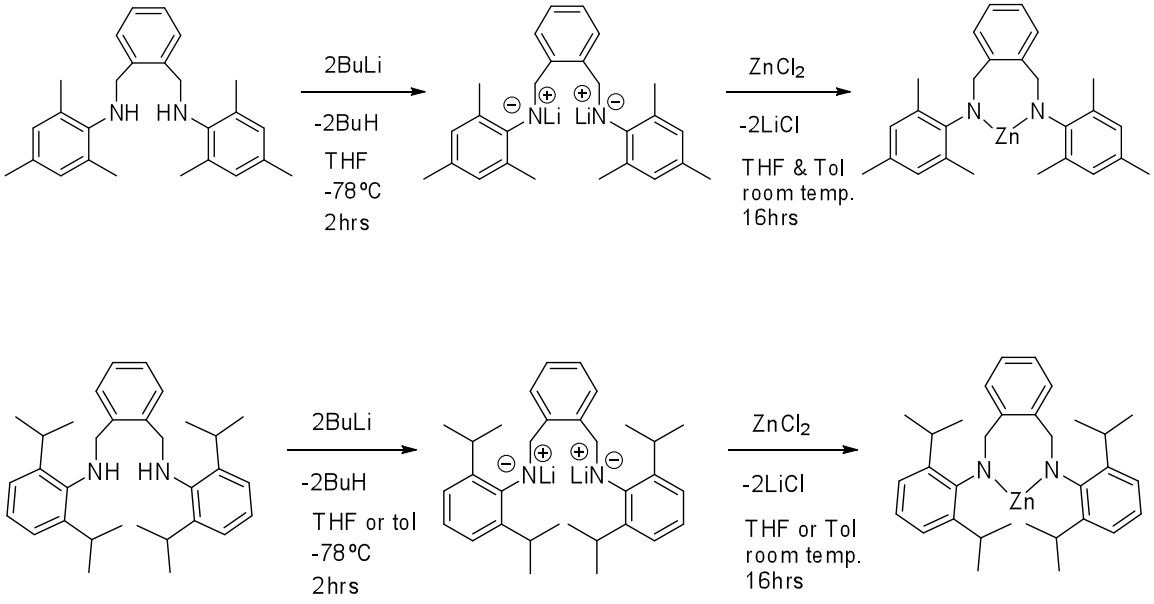
(a) (b)

Figure 4-4: First examples of Zn(I) complexes that were synthesized by (a) Resa *et al* (b) Robinson.[6]

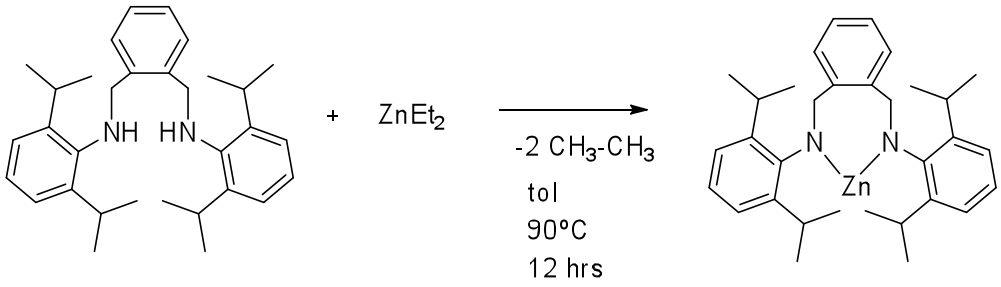
Results and Discussion:

The mesityl γ-diamine Zn complex was synthesized by lithiation and then by addition of zinc dichloride and allowed to stir for 16 hours at room temperature (see Scheme 4-5). Its interesting to note that the ^{1}H NMR for the mesityl γ-diamine Zn complex, contains four doublets, at 5.90, 5.32, 4.79, 3.61 ppm, representing the four CH_2 protons, which indicates that the CH_2 protons are diastereotopic. As well, there are six singlets present, at 2.90, 2.38, 2.29, 2.08, 1.91, 0.95 ppm for the six methyl groups. The doublets refer to each proton on the -CH_2 groups bonded to the nitrogen, where the singlets refer to the methyl groups coming off the phenyl rings. This indicates that all the protons are in different environments, causing the overall Zn compound to be C_1 symmetric. Unfortunately, the crystals grown were not appropriate for XRD, and a crystal structure is yet to be obtained to fully define the structure.

Unfortunately, the synthesis of the diisopropyl γ-diamine Zn complex, did not work using the same method that was done to produce the mesityl version. Therefore, another synthetic route was taken, that utilized diethyl zinc (see Scheme 4-6). This reaction was done by reacting the diisopropyl ligand and diethyl zinc in toluene, at 90 ^{o}C for 12 hours. ^{1}H NMR showed only the diisopropyl ligand.



Scheme 4-5: The reaction scheme for the synthesis of the Zn coordinated Complex with the mesityl and diisopropyl diamine ligands.



Scheme 4-6: Another reaction scheme showing the synthesis of the Zn coordinated Complex with the diisopropyl ligand.

4.3 Experimental

4.3.1 General Information:

All procedures involving air sensitive compounds were carried out in a nitrogen filled glove box or on a nitrogen Schlenk line. All solvents used were dry and acquired from solvent purification towers. All air sensitive compounds were run with dried deuterated solvents in air sensitive NMR tubes. The NMR solvents, deuterated benzene and deuterated chloroform, were dried through the "freeze, pump, thaw" method, and stored over molecular sieves in the glove box. The NMR data was collected with a Bruker Advance 500 MHz spectrometer at room temperature. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer.

4.3.2 Synthesis of [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]PCl (12)

A flask was charged with compound **1** (317 mg, 1.00 mmol) and distilled triethylamine (0.64 mL, 4.00 mmol) in dry dichloromethane (3 mL), under a nitrogen atmosphere.

Phosphorus trichloride (0.10 mL, 1.15 mmol) was added to the solution via syringe, and the mixture was stirred overnight at room temperature. The excess solvent (DCM) was removed via vacuum. The product was dissolved in toluene and vacuum filtered to remove $Et_3NH^+Cl^-$. The product was then dried under vacuum, yielding an orange oil. (YIELD). ^{1}H NMR ($CDCl_3$): δ = 2.17 (s, 6H, *p*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 2.18 (s, 6H, *o*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 2.60 (s, 6H, *o*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 3.68 (dd, 2H, C*H*$_2$), 5.80 (dd, 2H, C*H*$_2$), 6.71 (s, 2H, 2,4,6-$(CH_3)_3$-C_6H_2), 6.89 (m, 2H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.23 (m, 2H, C_6H_4). ^{31}P NMR ($CDCl_3$): δ = 150.5 ppm.

4.3.3 Synthesis of [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]P^+

Compound **12** (369 mg, 0.615 mmol) and $AgPF_6$ (213 mg, 0.844 mmol) were added in tetrahydrofuran (10 mL) into a round bottom schlenk flask, wrapped in foil. The reaction mixture was stirred for 19 hours, then filter through a frit, and dried via vacuum, to yield an oil. Pentane was added in attempt to produce a solid. ^{1}H NMR ($CDCl_3$): δ = 1.73 (s, 18H, *o*-C*H*$_3$, *p*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 3.33 (s, 4H, C*H*$_2$), 6.71 (s, 2H, 2,4,6-$(CH_3)_3$-C_6H_2), 6.89 (m, 2H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.23 (m, 2H, C_6H_4). ^{31}P NMR ($CDCl_3$): δ = 151.0 ppm.

4.3.4 Attempted synthesis of [1,2-(2,6-^{i}Pr$_2$$C_6H_3NHCH_2)_2$-$C_6H_4$]PCl

Compound **2** (397 mg, 0.882 mmol) and triethylamine (0.32 mL, 2.29 mmol) was placed in a reaction flask in toluene (10 mL). Phosphorous trichloride (0.10 mL, 1.15 mmol) was then added and stirred overnight at room temperature. It was then filtered (to remove

$Et_3NH^+Cl^-$) and the excess solvent was removed via vacuumed. End product was the starting ligand; compound **2**.

4.3.5 Attempted synthesis of [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]B-H

Compound **1** (300 mg, 1.09 mmol) was added to a solution of BH_3 THF and dry THF, under a nitrogen atmosphere, at -30 ^oC. This clear yellow solution was stirred at room temperature for 1 day. The excess solvent was removed via vacuum, producing a yellow oil. ^1H NMR shows starting ligand (compound **1**). ^1H NMR (C_6D_6): δ = 2.13 (s, 12H, *o*-C*H*$_3$; 2,4,6-$(CH_3)_3$-C_6H_2), 2.19 (s, 6H, *p*-C*H*$_3$; 2,4, 6-$(CH_3)_3$-C_6H_2), 3.11 (br s, 2H, N*H*), 4.08 (s, 4H, C*H*$_2$), 6.78 (s, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.09 (m, 2H, C_6H_4), 7. 29 (m, 2H, C_6H_4).

4.3.6 Synthesis of $Zr(CH_2Ph)_4$

Following the procedure in reference [8], zirconium tetrachloride (1.5339 g, 6.58 mmol) was dissolved in diethyl ether, under a nitrogen atmosphere, and in the absence of light. ($PhCH_2$)MgCl was added slowly at -15 ^oC. The solution was stirred for 15 hours, under these conditions, resulting in a cloudy brown solution. The precipitate was filtered, washed with ether (50 mL), and dried via vacuum, yielding a yellow-goldish solid. ^1H NMR (C_6D_6): δ = 1.45 (s, 8H, Zr-C*H*$_2$), 6.30 (d, 8H, C_6H_2), 6.93 (t, 4H, C_6H_1), 7.04 (t, 8H, C_6H_2).

4.3.7 [1,2-(2,6-$^{i}Pr_2C_6H_3N$-$CH_2)_2$-C_6H_4-($CH_2C_6H_5$)]Zr($CH_2C_6H_5)_2$

Compound **3** (294 mg, 0.658 mmol) and $Zr(CH_2Ph)_4$ were added together in toluene (10 mL) at -20 ^{o}C, under a nitrogen atmosphere. The solution was stirred overnight, filtered and the filtrate was then dried via vacuum. The ^{1}H NMR shows a mixture of starting material; compound **3** and $Zr(CH_2Ph)_4$. ^{1}H NMR (C_6D_6) **(compound 3)**: δ = 1.18 (d, 24H, ^{i}Pr-CH_3), 2.99 (m, 4H, ^{i}Pr-C*H*), 7.19 (m, 6H, 2,6-(^{i}Pr)$_2$-C_6H_3), 7.63 (m, 2H, C_6H_4), 8.19 (m, 2H, C_6H_4), 8.85 (s, 2H, N-C*H*). ^{1}H NMR (C_6D_6) (**Zr($CH_2Ph)_4$)**: δ = 1.45 (s, 8H, Zr-CH_2), 6.30 (d, 8H, C_6H_2), 6.93 (t, 4H, C_6H_1), 7.04 (t, 8H, C_6H_2).

Another attempt: Compound **3** (294 mg, 0.658 mmol) and $Zr(CH_2Ph)_4$ were added together in toluene (10 mL) at room temperature, under a nitrogen atmosphere. The solution was stirred for 1 day at 100 ^{o}C. The solution was filtered and the filtrate was then dried via vacuum. The same ^{1}H NMR as above results.

4.3.8 Synthesis of [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]Zn

nBuLi (1.31 mL, 2.09 mmol) was added to a solution of compound **1** (0.2884g, 1.04 mmol) in toluene at -78 ^{o}C. It was stirred at this temperature for 2 hours. The cold bath was then removed, and the $ZnCl_2$ (0.1421 g, 1.00 mmol) at room temperature where the reaction mixture stirred for 16 hours. The excess solvent was then removed via vacuum, and the solid was extracted with hexane (20 mL). The final product was an orange solid. ^{1}H NMR (C_6D_6): δ = 0.95 (s, 3H, CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 1.91 (s, 3H, CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.08 (s, 3H, CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.29 (s, 3H, CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.38 (s, 3H, CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 2.90 (s, 3H, CH_3; 2,4,6-$(CH_3)_3$-C_6H_2), 3.61

(d, 1H, N-CH_2), 4.79 (d, 1H, N-CH_2), 5.32 (d, 1H, N-CH_2), 5.90 (d, 1H, N-CH_2), 6.89 (s, 4H, 2,4,6-$(CH_3)_3$-C_6H_2), 7.01-7.21 (m, 4H, C_6H_4).

4.3.9 Attempted synthesis of [1,2-(2,6-^{i}Pr$_2$C$_6$H$_3$NCH$_2$)$_2$-C$_6$H$_4$]Zn

nBuLi (1.25 mL, 2.00 mmol) was added to a solution of compound **2** (452.7 g, 1.00 mmol) in toluene at -78 ^{o}C. It was stirred at this temperature for 2 hours. The cold bath was then removed, and the $ZnCl_2$ (0.1363 g, 1.00 mmol) at room temperature where the reaction mixture stirred for 16 hours. The excess solvent was then removed via vacuum, and the solid was extracted with hexane (20 mL). The final product turned out to be the starting ligand (compound **2**). ^{1}H NMR (C_6D_6): δ = 1.16 (s, 24H, ^{i}Pr-CH_3), 3.22 (br s, 2H, N*H*), 3.31 (m, 4H, ^{i}Pr-C*H*), 4.21 (s, 4H, CH_2), 7.19 (s, 6H, 2,6-(^{i}Pr)$_2$-C_6H_3), 7.55 (m, 4H, C_6H_4).

Another synthetic route: Compound **2** (300 mg, 0.666 mmol) was added to a solution of $ZnEt_2$ (0.67 mL, 0.666 mmol) in toluene (10 mL), under nitrogen. This solution was stirred for 12 hours at 90 ^{o}C under nitrogen, and then dried via vacuum. This gave a white solid as the end product which turned out to be compound **2**. ^{1}H NMR (C_6D_6): δ = 1.16 (s, 24H, ^{i}Pr-CH_3), 3.22 (br s, 2H, N*H*), 3.31 (m, 4H, ^{i}Pr-C*H*), 4.21 (s, 4H, CH_2), 7.19 (s, 6H, 2,6-(^{i}Pr)$_2$-C_6H_3), 7.55 (m, 4H, C_6H_4).

4.4 References

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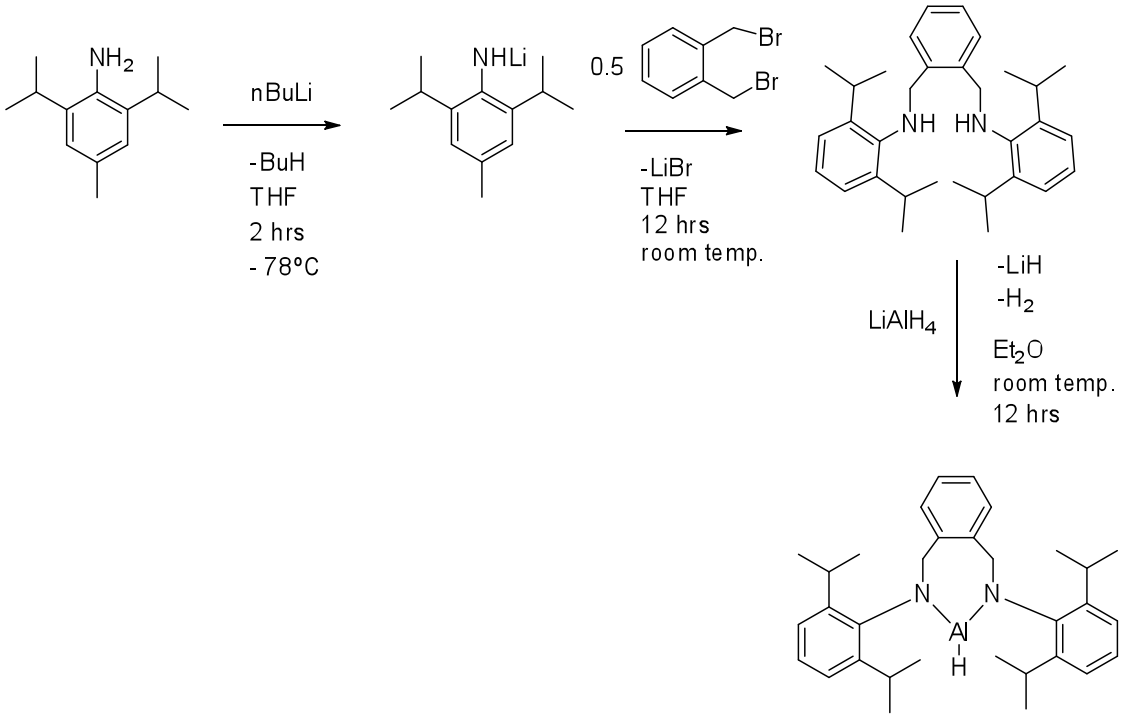
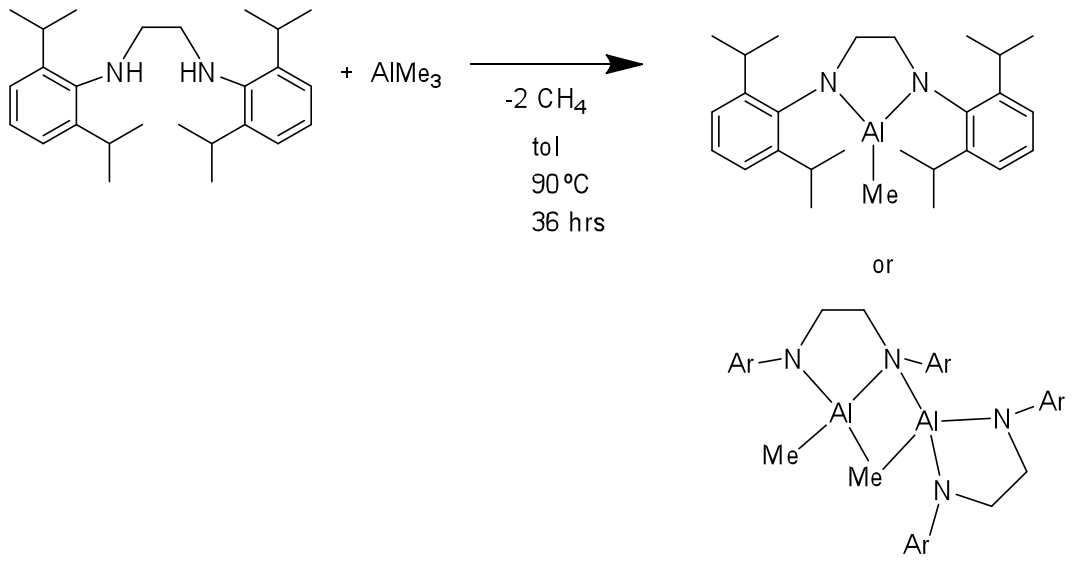
CHAPTER 5: SUMMARY AND CONCLUSIONS

Three coordinate aluminum alkyl complexes capable of ring opening polymerization (ROP) of cyclic esters were successfully synthesized. These complexes utilized the γ- and α-diamine ligands which incorporated different steric properties around the metal center (see Scheme 5-1 and Scheme 5-2).

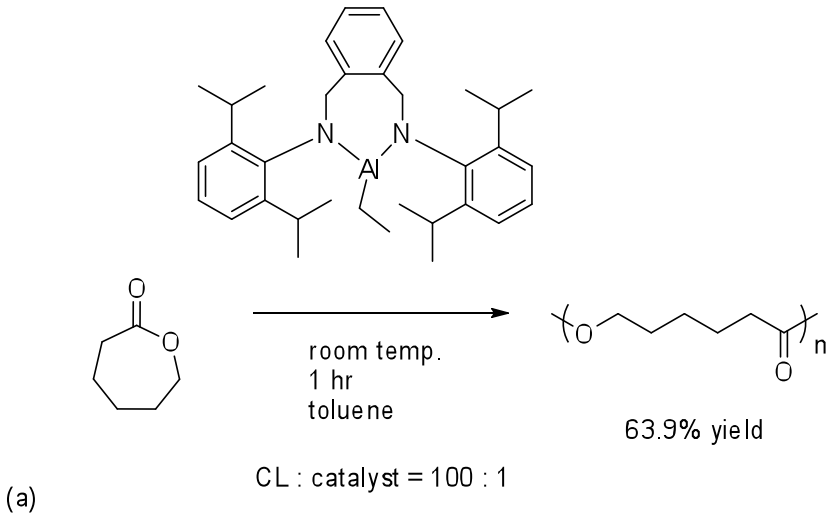


Scheme 5-1: The synthetic route for the γ aluminum catalyst (shown with the diisopropyl ligand).

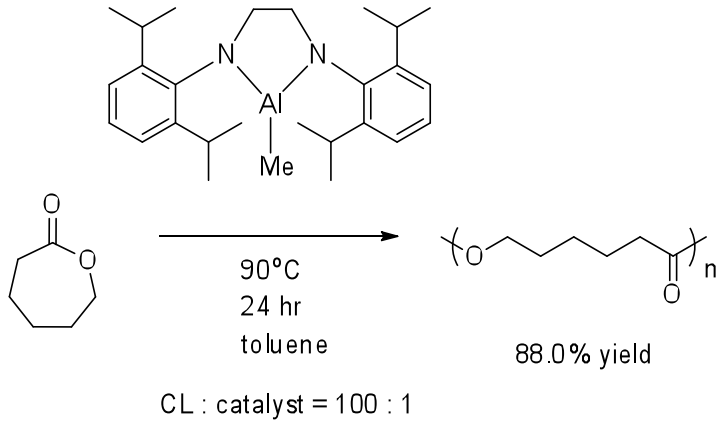


Scheme 5-2: A possible synthetic route designed for the α-diamido aluminum-methyl catalyst.

It was determined that these three coordinate aluminum alkyl complexes are active towards ε-caprolactone polymerization. The ligand attached to aluminum altered the polymerization activities, and it was found that the γ-diamido complexes were more active towards caprolactone polymerization than the α analogues (see Scheme 5-3). The α-diamido catalysts required harsh conditions, which is not ideal.



(a)

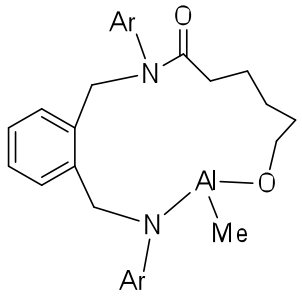


(b)

Scheme 5-3: Caprolactone polymerization reactions carried out with the (a) aluminum γ-diamido catalyst and (b) α-diamido aluminum.

The polymerization mechanism for ε-caprolactone was established and found to follow a coordination-insertion mechanism. This occurs with initial monomer insertion taking place between the Al-N bond versus the Al-Me bond (see Figure 5-1). This is due to the

fact that an attack by nitrogen is more likely than an attack by the methyl group, due to the nucleophilicity of nitrogen.



Ar = 2,6-$^{i}Pr_2C_6H_3$

Figure 5-1: A drawing depicting monomer insertion into the Al-N bond during caprolactone polymerization with the γ-diamido dipp, Al-Me catalyst.

Ultimately, the caprolactone polymerization capabilities of these three coordinate aluminum alkyl catalysts provides an efficient route for the synthesis of polyesters, making them an essential component in the production of biodegradable polymers.

APPENDIX A:

CRYSTAL STRUCTURE INFORMATION FOR COMPOUND 4a [1,2-(2,4,6-$(CH_3)_3$-C_6H_3N-$CH_2)_2$-C_6H_4]AlMe[Al(μ-Me)Me_2]

Table 1. Crystal data and structure refinement

Empirical formula	C30 H42 Al2 N2	
Formula weight	484.62	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.8691(13) Å	α= 100.251(2)°
	b = 10.2801(15) Å	β= 100.621(2)°
	c = 16.035(2) Å	γ = 95.019(2)°
Volume	1403.0(4) $Å^3$	
Z	2	
Density (calculated)	1.147 Mg/m^3	
Absorption coefficient	0.124 mm^{-1}	
F(000)	524	
Crystal size	0.11 x 0.05 x 0.04 mm^3	
Theta range for data collection	2.03 to 26.64°.	
Index ranges	-11<=h<=11, -12<=k<=12, -20<=l<=20	
Reflections collected	15767	
Independent reflections	5858 [R(int) = 0.0517]	
Completeness to theta = 26.64°	99.5 %	
Max. and min. transmission	0.9951 and 0.9865	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5858 / 0 / 316	
Goodness-of-fit on F^2	1.024	
Final R indices [I>2sigma(I)]	R1 = 0.0548, wR2 = 0.1334	
R indices (all data)	R1 = 0.0931, wR2 = 0.1560	
Largest diff. peak and hole	0.455 and -0.536 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for ao043. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Al(1)	9306(1)	5586(1)	2048(1)	25(1)
Al(2)	7377(1)	7243(1)	1428(1)	30(1)
N(1)	7572(2)	6419(2)	2474(1)	25(1)
N(2)	9164(2)	3788(2)	1991(1)	25(1)
C(1)	7717(3)	7317(2)	3325(2)	26(1)
C(2)	8780(3)	7168(3)	4054(2)	30(1)
C(3)	8857(3)	8027(3)	4848(2)	35(1)
C(4)	7892(3)	8999(3)	4960(2)	36(1)
C(5)	6806(3)	9089(3)	4240(2)	35(1)
C(6)	6694(3)	8292(3)	3429(2)	30(1)
C(7)	9833(3)	6102(3)	4056(2)	39(1)
C(8)	7992(4)	9883(3)	5832(2)	51(1)
C(9)	5468(3)	8535(3)	2704(2)	37(1)
C(10)	6211(3)	5353(3)	2353(2)	28(1)
C(11)	6430(3)	4413(2)	2982(2)	27(1)
C(12)	5948(3)	4708(3)	3761(2)	34(1)
C(13)	6153(3)	3883(3)	4357(2)	40(1)
C(14)	6824(3)	2731(3)	4167(2)	38(1)
C(15)	7300(3)	2423(3)	3386(2)	32(1)
C(16)	7133(3)	3252(2)	2791(2)	26(1)
C(17)	7726(3)	2926(2)	1965(2)	29(1)
C(18)	10381(3)	3035(2)	1761(2)	24(1)
C(19)	11695(3)	2978(2)	2400(2)	27(1)
C(20)	12853(3)	2240(3)	2164(2)	30(1)
C(21)	12756(3)	1535(2)	1335(2)	30(1)
C(22)	11425(3)	1559(3)	721(2)	29(1)
C(23)	10238(3)	2291(2)	921(2)	26(1)
C(24)	11832(3)	3626(3)	3329(2)	37(1)
C(25)	14011(3)	715(3)	1102(2)	41(1)
C(26)	8820(3)	2207(3)	227(2)	32(1)
C(31)	11353(3)	6628(3)	2341(2)	39(1)

C(32)	8462(3)	5785(3)	729(2)	32(1)
C(33)	5344(3)	6946(3)	645(2)	42(1)
C(34)	8634(4)	8994(3)	1740(2)	41(1)

Table 3. Bond lengths [Å] and angles [°] for ao043.

Al(1)-N(2)	1.826(2)
Al(1)-C(31)	1.958(3)
Al(1)-N(1)	1.993(2)
Al(1)-Al(2)	2.7031(11)
Al(2)-C(33)	1.962(3)
Al(2)-C(34)	1.964(3)
Al(2)-N(1)	1.998(2)
Al(2)-C(32)	2.116(3)
N(1)-C(1)	1.481(3)
N(1)-C(10)	1.517(3)
N(2)-C(18)	1.445(3)
N(2)-C(17)	1.478(3)
C(1)-C(2)	1.401(3)
C(1)-C(6)	1.419(3)
C(2)-C(3)	1.400(4)
C(2)-C(7)	1.502(4)
C(3)-C(4)	1.381(4)
C(4)-C(5)	1.384(4)
C(4)-C(8)	1.510(4)
C(5)-C(6)	1.389(4)
C(6)-C(9)	1.510(4)
C(10)-C(11)	1.516(4)
C(11)-C(12)	1.386(4)
C(11)-C(16)	1.406(3)
C(12)-C(13)	1.386(4)
C(13)-C(14)	1.383(4)
C(14)-C(15)	1.387(4)
C(15)-C(16)	1.386(4)
C(16)-C(17)	1.507(4)
C(18)-C(23)	1.403(3)
C(18)-C(19)	1.415(3)
C(19)-C(20)	1.396(3)
C(19)-C(24)	1.499(4)
C(20)-C(21)	1.380(4)

C(21)-C(22)	1.396(4)
C(21)-C(25)	1.514(3)
C(22)-C(23)	1.398(3)
C(23)-C(26)	1.503(3)

N(2)-Al(1)-C(31)	118.98(11)
N(2)-Al(1)-N(1)	113.68(9)
C(31)-Al(1)-N(1)	118.16(11)
N(2)-Al(1)-Al(2)	134.40(7)
C(31)-Al(1)-Al(2)	104.56(9)
N(1)-Al(1)-Al(2)	47.44(6)
C(33)-Al(2)-C(34)	121.64(13)
C(33)-Al(2)-N(1)	117.17(12)
C(34)-Al(2)-N(1)	108.72(11)
C(33)-Al(2)-C(32)	98.70(12)
C(34)-Al(2)-C(32)	112.00(12)
N(1)-Al(2)-C(32)	94.48(10)
C(33)-Al(2)-Al(1)	133.26(9)
C(34)-Al(2)-Al(1)	104.10(10)
N(1)-Al(2)-Al(1)	47.30(6)
C(32)-Al(2)-Al(1)	51.54(7)
C(1)-N(1)-C(10)	108.60(19)
C(1)-N(1)-Al(1)	124.91(16)
C(10)-N(1)-Al(1)	109.06(15)
C(1)-N(1)-Al(2)	117.59(15)
C(10)-N(1)-Al(2)	109.18(15)
Al(1)-N(1)-Al(2)	85.26(8)
C(18)-N(2)-C(17)	112.60(19)
C(18)-N(2)-Al(1)	121.27(16)
C(17)-N(2)-Al(1)	124.65(16)
C(2)-C(1)-C(6)	118.4(2)
C(2)-C(1)-N(1)	121.4(2)
C(6)-C(1)-N(1)	120.1(2)
C(3)-C(2)-C(1)	119.4(2)
C(3)-C(2)-C(7)	116.5(2)
C(1)-C(2)-C(7)	124.1(2)

C(4)-C(3)-C(2)	123.1(3)
C(3)-C(4)-C(5)	116.5(2)
C(3)-C(4)-C(8)	121.3(3)
C(5)-C(4)-C(8)	122.1(3)
C(4)-C(5)-C(6)	123.3(3)
C(5)-C(6)-C(1)	119.3(2)
C(5)-C(6)-C(9)	116.8(2)
C(1)-C(6)-C(9)	124.0(2)
C(11)-C(10)-N(1)	114.1(2)
C(12)-C(11)-C(16)	119.5(2)
C(12)-C(11)-C(10)	119.6(2)
C(16)-C(11)-C(10)	120.9(2)
C(13)-C(12)-C(11)	121.2(2)
C(14)-C(13)-C(12)	119.6(3)
C(13)-C(14)-C(15)	119.6(3)
C(16)-C(15)-C(14)	121.5(2)
C(15)-C(16)-C(11)	118.7(2)
C(15)-C(16)-C(17)	120.4(2)
C(11)-C(16)-C(17)	120.9(2)
N(2)-C(17)-C(16)	112.0(2)
C(23)-C(18)-C(19)	119.1(2)
C(23)-C(18)-N(2)	120.8(2)
C(19)-C(18)-N(2)	120.0(2)
C(20)-C(19)-C(18)	119.0(2)
C(20)-C(19)-C(24)	119.3(2)
C(18)-C(19)-C(24)	121.6(2)
C(21)-C(20)-C(19)	122.7(2)
C(20)-C(21)-C(22)	117.5(2)
C(20)-C(21)-C(25)	121.6(2)
C(22)-C(21)-C(25)	120.8(2)
C(21)-C(22)-C(23)	122.0(2)
C(22)-C(23)-C(18)	119.5(2)
C(22)-C(23)-C(26)	118.0(2)
C(18)-C(23)-C(26)	122.4(2)

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for ao043. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Al(1)	25(1)	22(1)	27(1)	3(1)	4(1)	2(1)
Al(2)	38(1)	23(1)	27(1)	5(1)	3(1)	7(1)
N(1)	26(1)	21(1)	26(1)	2(1)	6(1)	3(1)
N(2)	21(1)	21(1)	31(1)	2(1)	5(1)	3(1)
C(1)	30(1)	21(1)	26(1)	5(1)	5(1)	3(1)
C(2)	33(2)	29(1)	29(2)	6(1)	8(1)	5(1)
C(3)	39(2)	37(2)	26(2)	4(1)	4(1)	2(1)
C(4)	46(2)	28(2)	34(2)	0(1)	13(1)	4(1)
C(5)	41(2)	26(1)	39(2)	4(1)	14(1)	6(1)
C(6)	33(2)	25(1)	34(2)	7(1)	10(1)	4(1)
C(7)	42(2)	44(2)	30(2)	5(1)	0(1)	13(1)
C(8)	65(2)	45(2)	40(2)	-4(2)	13(2)	7(2)
C(9)	39(2)	32(2)	41(2)	6(1)	7(1)	14(1)
C(10)	23(1)	27(1)	33(2)	5(1)	4(1)	5(1)
C(11)	23(1)	24(1)	32(2)	3(1)	4(1)	1(1)
C(12)	38(2)	28(2)	41(2)	6(1)	14(1)	6(1)
C(13)	49(2)	37(2)	37(2)	8(1)	18(1)	4(1)
C(14)	44(2)	34(2)	37(2)	13(1)	5(1)	-1(1)
C(15)	30(2)	26(1)	39(2)	8(1)	3(1)	2(1)
C(16)	23(1)	23(1)	32(2)	3(1)	4(1)	-2(1)
C(17)	27(1)	22(1)	35(2)	1(1)	5(1)	1(1)
C(18)	24(1)	22(1)	29(1)	6(1)	6(1)	2(1)
C(19)	26(1)	24(1)	31(1)	3(1)	2(1)	3(1)
C(20)	25(1)	28(1)	35(2)	6(1)	-1(1)	4(1)
C(21)	26(1)	23(1)	44(2)	7(1)	8(1)	6(1)
C(22)	33(2)	25(1)	29(2)	2(1)	9(1)	3(1)
C(23)	25(1)	20(1)	31(1)	5(1)	4(1)	4(1)
C(24)	36(2)	42(2)	30(2)	5(1)	-2(1)	12(1)
C(25)	35(2)	35(2)	49(2)	0(1)	4(1)	12(1)
C(26)	34(2)	29(2)	29(1)	0(1)	1(1)	7(1)
C(31)	32(2)	36(2)	45(2)	6(1)	3(1)	-2(1)

C(32)	41(2)	28(1)	27(1)	8(1)	3(1)	4(1)
C(33)	49(2)	39(2)	35(2)	4(1)	-4(1)	17(2)
C(34)	62(2)	25(2)	37(2)	5(1)	15(2)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for ao043.

	x	y	z	U(eq)
H(3)	9610	7936	5332	42
H(5)	6102	9727	4302	42
H(7A)	10044	5875	4632	59
H(7B)	10807	6425	3912	59
H(7C)	9337	5308	3626	59
H(8A)	7179	10470	5791	77
H(8B)	9006	10423	6014	77
H(8C)	7854	9330	6258	77
H(9A)	5950	9050	2343	56
H(9B)	4706	9034	2949	56
H(9C)	4953	7680	2351	56
H(10A)	5278	5792	2418	34
H(10B)	6024	4826	1755	34
H(12)	5469	5491	3888	41
H(13)	5834	4107	4893	48
H(14)	6959	2154	4570	46
H(15)	7751	1625	3256	39
H(17A)	7922	1983	1869	35
H(17B)	6925	3036	1473	35
H(20)	13743	2223	2592	36
H(22)	11322	1062	150	35
H(24A)	12162	4582	3407	55
H(24B)	12596	3227	3696	55
H(24C)	10827	3493	3493	55
H(25A)	13697	-223	1100	61
H(25B)	14974	1032	1529	61
H(25C)	14174	807	526	61
H(26A)	8520	3100	220	48
H(26B)	7973	1635	345	48
H(26C)	9042	1829	-337	48

H(31A)	11748	6652	1811	58
H(31B)	12060	6216	2732	58
H(31C)	11277	7538	2628	58
H(32A)	9526	5800	1041	39
H(32B)	7890	4903	671	39
H(32C)	8474	5978	153	39
H(33A)	5472	6697	45	63
H(33B)	4852	7765	714	63
H(33C)	4694	6227	784	63
H(34A)	8080	9631	1454	61
H(34B)	9620	8920	1553	61
H(34C)	8830	9306	2369	61

Table 6. Torsion angles [°] for ao043.

N(2)-Al(1)-Al(2)-C(33)	-6.96(18)
C(31)-Al(1)-Al(2)-C(33)	155.81(16)
N(1)-Al(1)-Al(2)-C(33)	-89.14(16)
N(2)-Al(1)-Al(2)-C(34)	-175.20(13)
C(31)-Al(1)-Al(2)-C(34)	-12.43(13)
N(1)-Al(1)-Al(2)-C(34)	102.62(12)
N(2)-Al(1)-Al(2)-N(1)	82.19(13)
C(31)-Al(1)-Al(2)-N(1)	-115.05(13)
N(2)-Al(1)-Al(2)-C(32)	-68.12(14)
C(31)-Al(1)-Al(2)-C(32)	94.65(14)
N(1)-Al(1)-Al(2)-C(32)	-150.30(13)
N(2)-Al(1)-N(1)-C(1)	110.03(19)
C(31)-Al(1)-N(1)-C(1)	-36.6(2)
Al(2)-Al(1)-N(1)-C(1)	-120.6(2)
N(2)-Al(1)-N(1)-C(10)	-20.72(18)
C(31)-Al(1)-N(1)-C(10)	-167.32(16)
Al(2)-Al(1)-N(1)-C(10)	108.67(17)
N(2)-Al(1)-N(1)-Al(2)	-129.38(9)
C(31)-Al(1)-N(1)-Al(2)	84.01(13)
C(33)-Al(2)-N(1)-C(1)	-107.74(19)
C(34)-Al(2)-N(1)-C(1)	35.1(2)
C(32)-Al(2)-N(1)-C(1)	150.10(18)
Al(1)-Al(2)-N(1)-C(1)	127.20(19)
C(33)-Al(2)-N(1)-C(10)	16.5(2)
C(34)-Al(2)-N(1)-C(10)	159.31(16)
C(32)-Al(2)-N(1)-C(10)	-85.65(16)
Al(1)-Al(2)-N(1)-C(10)	-108.55(17)
C(33)-Al(2)-N(1)-Al(1)	125.06(11)
C(34)-Al(2)-N(1)-Al(1)	-92.14(12)
C(32)-Al(2)-N(1)-Al(1)	22.90(10)
C(31)-Al(1)-N(2)-C(18)	-28.8(2)
N(1)-Al(1)-N(2)-C(18)	-175.09(17)
Al(2)-Al(1)-N(2)-C(18)	132.08(16)
C(31)-Al(1)-N(2)-C(17)	166.20(19)

N(1)-Al(1)-N(2)-C(17)	19.9(2)
Al(2)-Al(1)-N(2)-C(17)	-32.9(2)
C(10)-N(1)-C(1)-C(2)	98.5(3)
Al(1)-N(1)-C(1)-C(2)	-32.4(3)
Al(2)-N(1)-C(1)-C(2)	-136.9(2)
C(10)-N(1)-C(1)-C(6)	-76.9(3)
Al(1)-N(1)-C(1)-C(6)	152.18(19)
Al(2)-N(1)-C(1)-C(6)	47.6(3)
C(6)-C(1)-C(2)-C(3)	-3.4(4)
N(1)-C(1)-C(2)-C(3)	-178.9(2)
C(6)-C(1)-C(2)-C(7)	174.4(3)
N(1)-C(1)-C(2)-C(7)	-1.1(4)
C(1)-C(2)-C(3)-C(4)	2.3(4)
C(7)-C(2)-C(3)-C(4)	-175.7(3)
C(2)-C(3)-C(4)-C(5)	0.5(4)
C(2)-C(3)-C(4)-C(8)	178.6(3)
C(3)-C(4)-C(5)-C(6)	-2.2(4)
C(8)-C(4)-C(5)-C(6)	179.7(3)
C(4)-C(5)-C(6)-C(1)	1.0(4)
C(4)-C(5)-C(6)-C(9)	-178.6(3)
C(2)-C(1)-C(6)-C(5)	1.8(4)
N(1)-C(1)-C(6)-C(5)	177.4(2)
C(2)-C(1)-C(6)-C(9)	-178.5(2)
N(1)-C(1)-C(6)-C(9)	-2.9(4)
C(1)-N(1)-C(10)-C(11)	-66.0(3)
Al(1)-N(1)-C(10)-C(11)	73.1(2)
Al(2)-N(1)-C(10)-C(11)	164.66(17)
N(1)-C(10)-C(11)-C(12)	90.8(3)
N(1)-C(10)-C(11)-C(16)	-88.4(3)
C(16)-C(11)-C(12)-C(13)	0.3(4)
C(10)-C(11)-C(12)-C(13)	-178.9(3)
C(11)-C(12)-C(13)-C(14)	-1.1(4)
C(12)-C(13)-C(14)-C(15)	0.7(4)
C(13)-C(14)-C(15)-C(16)	0.7(4)
C(14)-C(15)-C(16)-C(11)	-1.5(4)
C(14)-C(15)-C(16)-C(17)	177.2(2)

C(12)-C(11)-C(16)-C(15)	1.1(4)
C(10)-C(11)-C(16)-C(15)	-179.8(2)
C(12)-C(11)-C(16)-C(17)	-177.6(2)
C(10)-C(11)-C(16)-C(17)	1.6(4)
C(18)-N(2)-C(17)-C(16)	128.6(2)
Al(1)-N(2)-C(17)-C(16)	-65.2(3)
C(15)-C(16)-C(17)-N(2)	-105.0(3)
C(11)-C(16)-C(17)-N(2)	73.7(3)
C(17)-N(2)-C(18)-C(23)	65.9(3)
Al(1)-N(2)-C(18)-C(23)	-100.8(2)
C(17)-N(2)-C(18)-C(19)	-110.3(3)
Al(1)-N(2)-C(18)-C(19)	83.0(3)
C(23)-C(18)-C(19)-C(20)	3.4(4)
N(2)-C(18)-C(19)-C(20)	179.7(2)
C(23)-C(18)-C(19)-C(24)	-173.2(2)
N(2)-C(18)-C(19)-C(24)	3.1(4)
C(18)-C(19)-C(20)-C(21)	-1.5(4)
C(24)-C(19)-C(20)-C(21)	175.2(3)
C(19)-C(20)-C(21)-C(22)	-1.0(4)
C(19)-C(20)-C(21)-C(25)	-178.4(3)
C(20)-C(21)-C(22)-C(23)	1.6(4)
C(25)-C(21)-C(22)-C(23)	179.1(2)
C(21)-C(22)-C(23)-C(18)	0.3(4)
C(21)-C(22)-C(23)-C(26)	-177.4(2)
C(19)-C(18)-C(23)-C(22)	-2.9(4)
N(2)-C(18)-C(23)-C(22)	-179.2(2)
C(19)-C(18)-C(23)-C(26)	174.8(2)
N(2)-C(18)-C(23)-C(26)	-1.5(4)