

**THE VERSATILITY OF ALUMINUM SYSTEMS:
LIGAND TRANSFER AGENTS AND POLYMERIZATION CATALYSTS**

A Thesis Submitted to the College of
Graduate Studies and Research
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for the Degree of Masters of Science
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Saskatoon

By

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ABSTRACT

Aluminum complexes, specifically those employing bulky ligand frameworks such as sal (sal = 2-[CH=N(2,6-ⁱPr₂-C₆H₃)]-4,6-^tBu₂-phenoxide) and α -diimine (α -diimine = [(2,6-ⁱPr₂-C₆H₃)N=C(Me)]₂) derivatives are studied in various contexts. During ethylene polymerization with LCu(II) catalysts in the presence of methylaluminoxane (MAO), ligand (L) transfer is observed from the copper centre to the aluminum centre present in MAO. In the α -diimine case, an (imino-amido)AlMe₂ complex is formed by α -diimine ligand transfer to aluminum followed by alkylation of one imino moiety in the ligand backbone. These ligand transfer products are then shown to be active as ethylene polymerization catalysts, bringing into question the role of the copper species.

The (sal)AlMe₂, (sal)AlMeCl and (imino-amido)AlMe₂ complexes were also used as initiators in the ring-opening polymerization of ϵ -caprolactone. Polymerization was studied with and without addition of *tert*-butanol as a co-initiator to determine its role and necessity in the catalytic cycle.

Finally, the (imino-amido)AlMe₂ complex was also used as the starting complex in attempts at forming a mononuclear aluminum(I) target species. Reaction of (imino-amido)AlMe₂ with excess I₂ proved successful in forming the isolable precursor, (imino-amido)AlI₂. Attempts at reducing (imino-amido)AlI₂ with excess potassium were carried out in hopes of forming a very rare example of a mononuclear aluminum(I) species.

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LIST OF ABBREVIATIONS AND ACRONYMS

Abbreviation

CL.....	ε-caprolactone
Cp*.....	pentamethylcyclopentadienyl
GPC.....	gel permeation chromatography
MAO.....	methylaluminoxane
M _n	number average molecular weight
M _w	weight average molecular weight
MS.....	mass spectrometry
PCL.....	poly(caprolactone)
PDI.....	polydispersity index
PE.....	polyethylene
ROP.....	ring-opening polymerization
sal.....	salicylaldiminato, 2-[CH=N(2,6- ⁱ Pr ₂ -C ₆ H ₃)]-4,6- ^t Bu ₂ -phenoxide
salH.....	salicylaldimine, 2-[CH=N(2,6- ⁱ Pr ₂ -C ₆ H ₃)]-4,6- ^t Bu ₂ -phenol
TMA.....	trimethylaluminum

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Chapter 1: Introduction

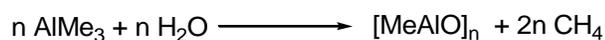
1.1 Ethylene Polymerization

1.1.1 Early Transition Metal Systems for Ethylene Polymerization

Ethylene polymerization has been an extremely important catalytic process for over 50 years. In 1954, Karl Ziegler developed and patented what is now known as the Ziegler-Natta heterogeneous process using supported Group IV metal systems, specifically TiCl_3 or $\text{TiCl}_4/\text{MgCl}_2$, coupled with an aluminum alkyl activator and this area of research has not been the same since.¹ Giulio Natta studied the polymerization activity of these complexes with triethylaluminum activators and found the presence of the aluminum species to be completely necessary for the formation of polyethylene (PE).² In 1963 the Nobel Prize in chemistry was awarded to Ziegler, along with Natta, for his work that showed a modified version of Ziegler's catalysts could be used to control the stereoregularity of polypropylene chains allowing for formation of isotactic polypropylene.³ Along with any discovery worthy of a Nobel Prize, great attention was drawn to the area and further research began in earnest worldwide; Ziegler's discovery has transformed the polyolefin market into a multibillion dollar a year industry.⁴

From the initial explosion in the 1960's chemists sought to develop new, more efficient systems that might have similar, or even higher activity for ethylene polymerization but with added control.⁵ In the mid 1970's, Walter Kaminsky was

following up on Natta's discovery using alkyl aluminum species as activators, when he serendipitously found that the introduction of water into a similar $\text{Cp}_2\text{ZrCl}_2/\text{AlMe}_3$ system tremendously increased the activity of the catalysts.⁶ This was the starting point of employing methylaluminoxane (MAO) as an activator, which is now used nearly ubiquitously in ethylene polymerizations and can be prepared by the controlled hydrolysis of trimethylaluminum (Scheme 1).⁶



Scheme 1. Synthesis of methylaluminoxane (MAO)

The ability of MAO to alkylate and activate the transition metal chloride pre-catalyst, as well as scavenge any unwanted moisture and impurities in the reaction mixture, make it an excellent activator for these metallocene catalysts as well as many other systems.

Soon after Kaminsky's discovery, homogeneous group IV metallocene systems were investigated allowing even greater control over stereospecificity due to their single-site properties and higher activities due to their homogeneous nature.⁵ Once these systems showed promise in catalyzing the formation of polyethylene, numerous variations were developed and studied (Figure 1).

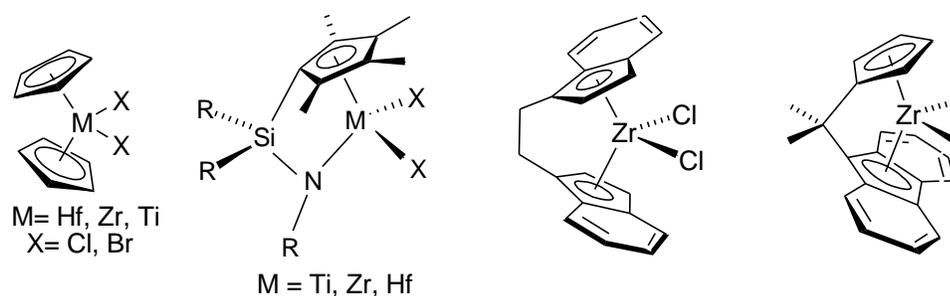
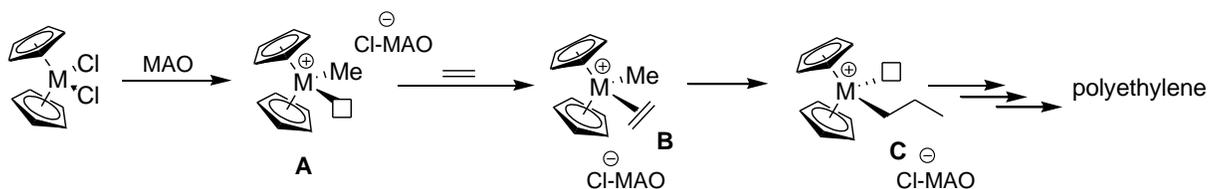


Figure 1. A sample of group IV metallocene catalysts and derivatives ⁵

These metallocene systems gave some mechanistic insight into the heterogeneous Ziegler-Natta systems that came before and showed that early transition metal systems were far better olefin polymerization catalysts than any known analogous late transition metal systems. Mechanistically these metallocene catalysts have been shown to polymerize via a coordination-insertion mechanism where the active species (**A**) is first generated by addition of an aluminum alkyl or a borane complex to a metal-chloride or metal-alkyl complex, followed by the coordination of an ethylene monomer to the vacant site (**B**), migratory insertion of ethylene into the M-C bond then occurs, followed by coordination of another monomer and subsequent insertions resulting in chain propagation (Scheme 2).⁵



Scheme 2. Metallocene polymerization mechanism

Although the activity for these complexes was extremely high, early transition metal systems struggled when used as catalysts for copolymerization with polar monomers. Polar monomers normally include acrylates, vinyl ketones and CO among others; all of which contain functional groups incorporating oxygen atoms. These functional groups have been shown to poison the early transition metal catalysts due to the high oxophilicity of the metal centre.⁴

1.1.2 Late Transition Metal Systems for Ethylene Polymerization

Until 1995, when Maurice Brookhart developed group 10 olefin polymerization catalysts using chelating α -diimine ligands (Figure 2),⁷ late metal systems had only been shown to oligomerize olefins at best, due to competing β -hydride elimination reactions.⁴ This oligomerization via β -hydride elimination was taken advantage of in the SHOP process (Shell Higher Olefin Process) in the 70's using Ni(II) systems to form low molecular weight oligomers which are used as value-added chemicals such as α -olefins and waxes.⁸ Brookhart's systems employed sterically bulky chelating α -diimine ligands, coordinated to highly electrophilic cationic metal centres, stabilized by non-coordinating counterions **1** (Figure 2).

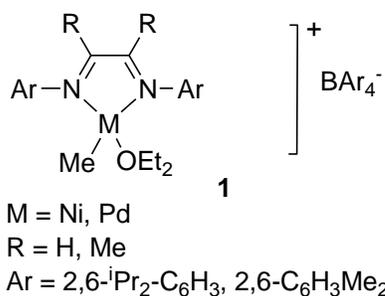


Figure 2. Active species in Brookhart's olefin polymerization systems ⁷

The combination of these three parameters overcame the problem of competing β -hydride elimination seen with previous late metal systems resulting in high molecular weight polymers. Brookhart's late metal systems were also able to catalyze olefin polymerization in the presence of ethers, esters and acids which remain a problem for the early metal systems.⁴ Brookhart showed that these systems could not only be used to form high molecular weight polyolefins, but could also incorporate polar monomers in copolymerizations with olefins, specifically methyl acrylate with ethylene.⁹ When a promising system for a catalytic process is found, the next logical step is to use the ligand on new metal centres to determine if they can mediate the catalysis with comparable results or even possibly more efficiently. Subsequently, Brookhart published a patent application using his α -diimine ligands in a poorly defined system with iron and cobalt, which showed some activity for olefin polymerization but these catalysts were less efficient than the palladium and nickel systems.¹⁰ A few years later, Brookhart¹¹ and Gibson¹² published parallel works using tridentate pyridine diimine ligands on iron and cobalt in attempts to improve on Brookhart's patent literature (Figure 3).

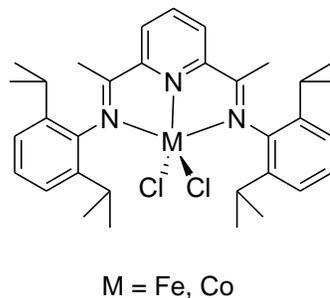
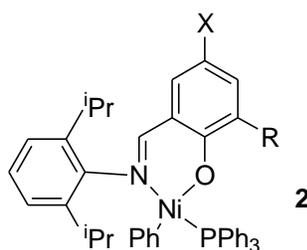


Figure 3. Pyridine diimine complexes

Both groups reported that the iron complex was more active than the corresponding cobalt complex.^{11,12} The new iron and cobalt complexes produced highly linear polyethylene as compared to Brookhart's original Ni and Pd diimine systems, which produced polyethylene with a large degree of branching.¹² A few years after Brookhart showed that late metals could polymerize olefins, Grubbs developed another nickel system employing bulky salicylaldiminato (sal) ligands of type **2** (Figure 4).¹³



R = H, ^tBu, Ph, 9-phenanthrenyl, 9-anthracenyl
X = H, OMe, NO₂

Figure 4. Grubbs' Ni(II) olefin polymerization catalyst¹³

These sal ligands are easily tunable both sterically and electronically by modifying X and/or R in Figure 4, and are synthesized without difficulty, making them ideal ligands for studying their effects in catalytic reactions. Grubbs later showed that

these systems could efficiently promote olefin polymerization under moderate conditions.¹³ A major difference between Grubbs' system and Brookhart's system is the use of a neutral nickel species, as opposed to a cationic species that Brookhart thought was an important factor. Grubbs postulated that using a neutral nickel species would give better results when incorporating polar monomers for copolymerization because a cationic metal centre is more oxophilic than its neutral counterpart.¹³

1.1.3 Copper(II) Systems for Ethylene Polymerization

Logically, other late metal centres were examined as potential catalysts and new ligand systems — containing similar properties to the Brookhart α -diimine and Grubbs sal species, such as high steric bulk — were designed and studied in the polymerization of olefins. In the late 90's, Stibrany at Exxon Mobil showed that copper(II) systems employing bis(benzimidazole) ligands **3** (Figure 5) could promote olefin polymerization in the presence of methylaluminoxane (MAO) as an activator or co-catalyst.¹⁴

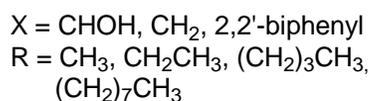
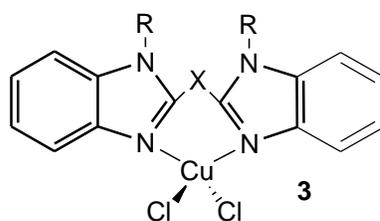


Figure 5. Stibrany's bis(benzimidazole) Cu(II) catalyst¹⁴

In an attempt to further increase the ability of late metal systems to copolymerize olefins with polar monomers, Stibrany hypothesized that copper would be even more efficient than nickel and palladium. While Brookhart and Grubbs showed that nickel and

palladium catalysts were effective in copolymerization of olefins and polar monomers, both systems left something to be desired with respect to efficiency.^{14b} The sal-Ni(II) systems copolymerize ethylene with polar monomers, but only when the functional group is separated from the reactive double bond, while the α -diimine systems only incorporate less than 20% of the polar monomer and only at the ends of the chain as opposed to being dispersed throughout the polymer backbone.^{14b,15} Stibrany's copper systems not only showed they were active for the homopolymerization of ethylene and alkyl-acrylates, they also showed copolymerization of the two co-monomers incorporating between 50 and 75% of the acrylate monomer in the polymer chain.¹⁴ Although an increase in copolymerization was seen, much lower activities were observed for ethylene homopolymerization when compared with the early transition metal systems. Other groups picked up on the reported activity of copper systems to catalyze this reaction due to the low cost of copper, relative to nickel and palladium and more systems were introduced. In 2002, Gibson further developed the area of copper(II) systems for ethylene polymerization, employing the Brookhart α -diimine system and tuning the sterics on the *ortho*-positions of the aryl-amine groups.¹⁶ These new α -diimine copper(II) systems (**4** in Figure 6) were active for the formation of high molecular weight polyethylene although the activity was relatively low and the amount of MAO activator required was between 2 and 2.5 times more than in the Stibrany systems. More recently, three other groups also reported new copper(II) systems that were active for ethylene polymerization coupled with an aluminum activator, but again with low activities relative to the early transition metal systems as well as the Brookhart and Grubbs systems previously discussed (**5**, **6**, **7** in Figure 6).^{17,18,19}

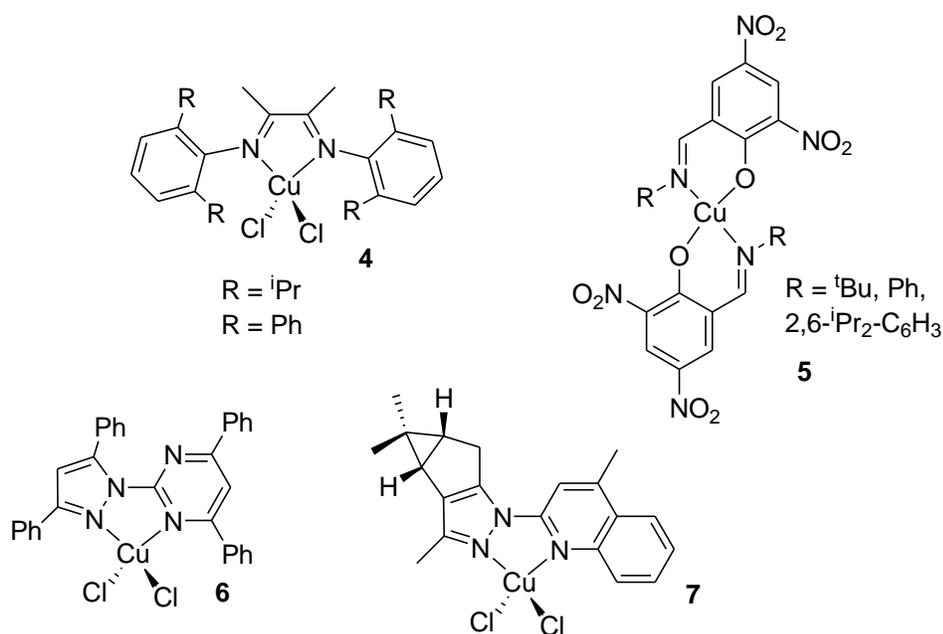
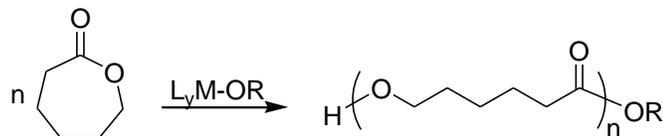


Figure 6. Copper(II) systems reported to be active for ethylene polymerization

Of all the copper(II) systems reported to date, only Stibrany suggested a mechanism based on the information he gathered from his results. He postulated that based on the polydispersity index and the high linearity of the polymers obtained that this reaction likely proceeds via a standard migratory insertion mechanism at the copper centre as shown for the metallocene systems (Scheme 2).¹⁴

1.2 ϵ -Caprolactone Polymerization

The ring-opening polymerization (ROP) of lactones and lactides has been shown to produce polyesters that have a wide variety of applications.^{20,21} Specifically, ϵ -caprolactone (CL) (Scheme 3) has been shown to undergo ring-opening to form polyesters that have found medicinal and pharmaceutical applications²⁰ as well as incorporation in biodegradable polymers.²¹



Scheme 3. Ring-opening polymerization of ϵ -caprolactone

These polymers can be broken down at the C-O bonds by hydrolysis and further decomposed by fungi, bacteria or yeast, ultimately yielding CO₂, H₂O and other naturally occurring matter.^{22,23} Poly(caprolactone) (PCL) has even been shown to break down in household compost bins over reasonable periods of time.²² Such biocompatible and biodegradable polymers have quickly become a topic of interest due to growing concerns over the state of the environment and the rapidly expanding quantity of conventional polyolefin and other polymer wastes in landfills. Not only do conventional polymers break down extremely slowly, they are also synthesized using non-renewable petrochemical precursors which are also a cause for concern as oil reserves are rapidly exhausted.²⁴

To date, metal alkoxides, such as tin and zinc alkoxides,²⁰ as well as magnesium, calcium, titanium, iron and rare earth metal complexes have been most widely used as initiators for the polymerization of CL.^{20,25} Industry currently employs a bis(2-ethylhexanoate) tin(II) system which is accepted by the U.S. Food and Drug Administration (FDA) as a food additive, but in case of leeching, tin proves to be too toxic for use in biomedical applications.²⁶ Because of the toxicity of industry used tin catalysts they have been excluded as catalysts for the formation of PCL for biomedical applications.²⁶ Less toxic aluminum systems, often combined with a primary alcohol co-

initiator, have shown promise in catalyzing this ring-opening polymerization, particularly with CL and are now widely studied.^{20,21,25,26,27,28,29,30,31}

The high Lewis acidity of these aluminum oxide complexes is the desirable property which enables them to initiate the ring-opening reaction of cyclic esters effectively by allowing the monomer to be activated by σ -bond coordination at the carbonyl moiety.^{25,26,31} In many cases, these aluminum systems have even been shown to operate in a living fashion which is in contrast to previously employed tin systems.^{28,30,32} Many attempts have been made at modifying the electronic properties of the ligands in hopes of finding a better catalyst than any previously synthesized. Changing functional groups on the ligands modifies the steric environment and often affects the electronic properties of the metal centre, in turn having an impact on the catalytic activity.^{21,25,26} Other groups have attempted the polymerization using binuclear²⁸ and even multinuclear³⁰ (Figure 7) systems to prevent catalyst aggregation and to take advantage of a possible synergistic effect that may occur between metal centres.³⁰

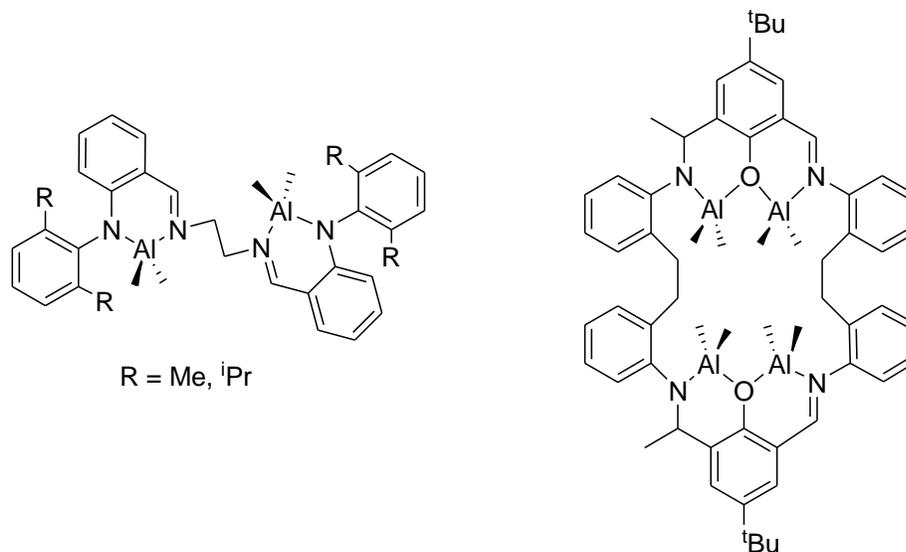
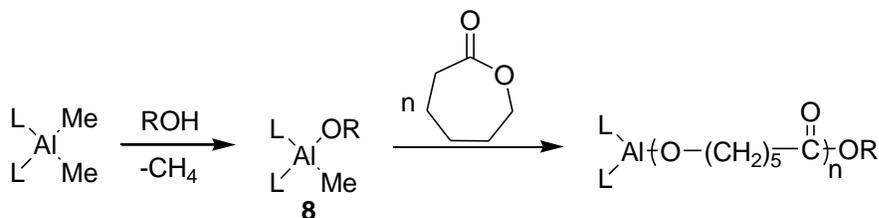


Figure 7. Multinuclear aluminum systems for ROP of CL^{28,30}

Mechanistically, the reaction has been thought to proceed through an alkoxy-aluminum active species which is formed upon addition of a primary alcohol to the aluminum precatalyst (Scheme 4).^{24,25}



Scheme 4. Proposed general mechanism for CL^{24,25}

Evidence for the alkoxy-aluminum active species **8** has been shown through ¹H NMR spectroscopy upon 1:1 addition of the precatalyst to the primary alcohol and isolation of the product (Figure 8).²⁵ The fate of the methyl group on the aluminum centre in the active species is poorly understood and has yet to be ascertained.

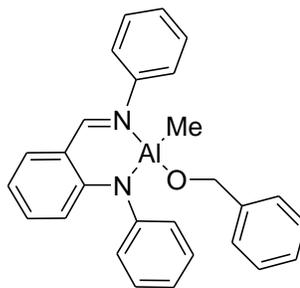
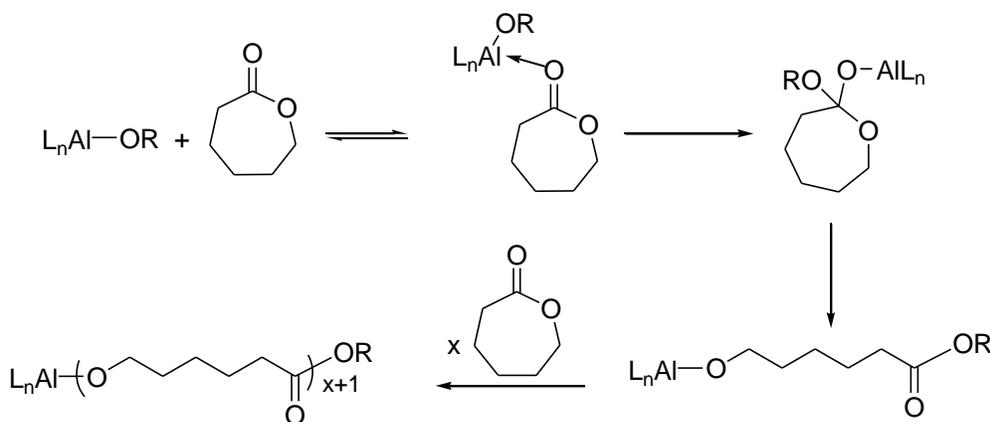


Figure 8. Example of a proposed active species in CL polymerization ²⁵

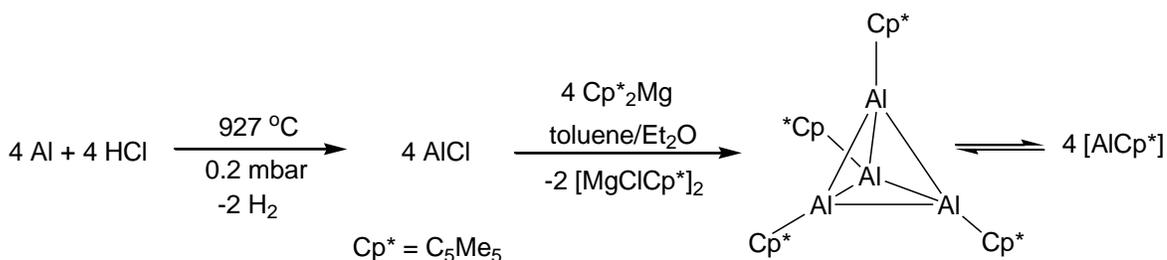
Following this step, the active species then coordinates to a CL monomer via electron pair donation by the carbonyl oxygen to the Lewis acidic aluminum where ring-opening and insertion occurs.²⁵ From here, chain propagation can occur in the same manner as the next monomer coordinates to the aluminum centre (Scheme 5). As the reported aluminum species have been shown to be living systems, high control over polymer molecular weights with low polydispersity indices (PDIs) can be obtained.²⁹ This control is desirable in any polymerization reaction, especially as applications of the polymer can change with its properties which are often dictated by molecular weight (MW) and PDI.



Scheme 5. Proposed mechanism for the ROP of CL ^{25b}

1.3 Aluminum(I) Species

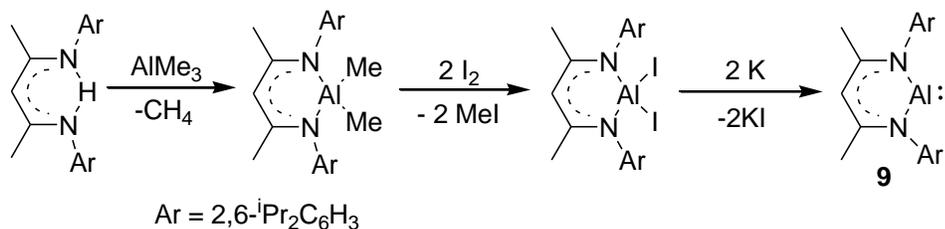
Aluminum is most frequently found in the +3 oxidation state. This is the most stable state both thermodynamically and kinetically and therefore the majority of known aluminum complexes are in this oxidation state.³³ There has also been reports of aluminum in a +2 oxidation state, however these species are not as common and not nearly as stable as their +3 counterparts.³⁴ Aluminum(I) compounds are even more rare, as this oxidation state is not thermodynamically stable,³³ and synthesis of these species has proved quite challenging, especially compared with other carbene analogues such as Si and Ge, which have been known for some time.³³ Some simple inorganic Al(I) species are known, however, they exist only in the gas phase at high temperature and low pressure as mononuclear species, for example AlX (X =H, halide),³⁵ and until recently, only isolable in the solid state, as tetramers in organometallic compounds (Scheme 6).³⁶



Scheme 6. Formation of tetrameric aluminum(I) by Schnöckel's method³⁶

Schnöckel showed that AlX compounds could be prepared by combining elemental aluminum and HCl in the gas phase at 927 °C and 0.2 mbar and further reacted with pentamethylcyclopentadienyl (Cp*) magnesium to form the tetrameric (AlCp*)₄ (Scheme 6).³⁶ Schnöckel's tetrameric aluminum species represent the first known and

structurally characterized example of Al(I) organometallic compounds. After the discovery and characterization of this complex, Herbert Roesky began to search for easier ways to synthesize the same $(\text{AlCp}^*)_4$ complex and published results showing it was not necessary to go through the extremely high temperature AlX route. Roesky found that after a simple preparation of Cp^*AlCl_2 , the same product could be obtained on reaction with 2 equivalents of potassium metal.³⁷ Although these tetrameric Al(I) compounds are thermally stable up to 200 °C,³⁷ they do have a tendency to disproportionate to elemental aluminum and AlCp_3^* , keeping the number of examples relatively low.³³ The few examples known, synthesized by Schnöckel³⁸ and Roesky³⁹ are generally stabilized by employing bulky substituents on aluminum in order to protect against this disproportionation. Roesky then began to employ even bulkier substituents on the aluminum centre in order to give even more steric protection to the metal in hopes of isolating a mononuclear aluminum(I) species. These attempts proved successful on utilization of a bidentate β -diketiminato (nacnac) ligand followed by reduction of aluminum(III), similar to the procedure he had shown to work in synthesizing $(\text{AlCp}^*)_4$ (Scheme 7) using potassium metal.⁴⁰



Scheme 7. Synthesis of mononuclear aluminum(I) complex

The 2,6-ⁱPr₂C₆H₃ substituents on the nitrogen are very bulky and afford steric protection of the otherwise unstable aluminum(I) centre. To date, there is only one other

example of mononuclear aluminum(I) species (**10** in Figure 9) that is stable at room temperature with only a slight variation on the ligand backbone with *tert*-butyl groups in place of the methyl substituents.⁴¹ Not only is **9** the first example of an isolable mononuclear aluminum(I) species, it is also the first example of a two-fold coordinate aluminum species.⁴⁰

Roesky likens his aluminum(I) species to the N-heterocyclic carbenes (NHCs) that Arduengo made famous in the 1990's which are now employed ubiquitously as excellent σ -donating ligands in organometallic complexes used for catalysis (Figure 9).⁴²

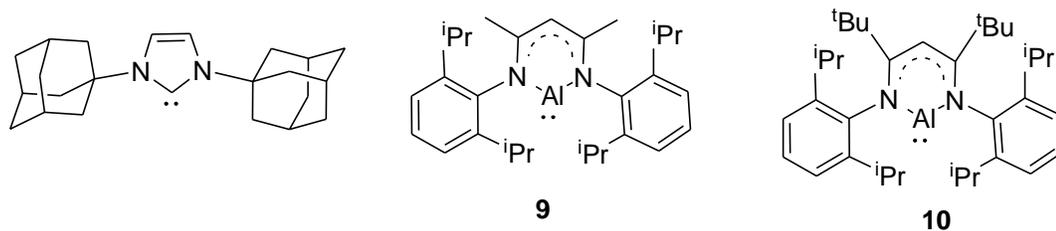
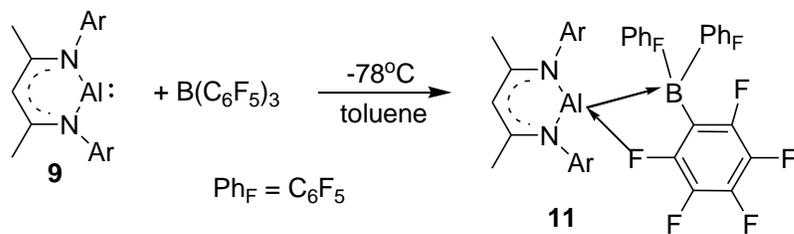


Figure 9. Arduengo's carbene⁴² and Roesky's⁴⁰ and Cui's⁴¹ aluminum analogues

As Figure 9 shows, both the carbenic carbon and the aluminum centre are sufficiently protected by steric bulk on the nitrogen substituents allowing both complexes to be stable at room temperature in the absence of air and moisture. As Arduengo's carbene has been known for almost ten years longer than Roesky's analogue, the applications are also much more developed. Synthesis of Roesky's aluminum complex is less than trivial, making the study of its properties and applications much more challenging. However, theoretical studies on **9** show that it has both Lewis acid and Lewis base attributes, and can act as a reducing agent;⁴⁰ these properties alone make the potential list of applications rather interesting. This theoretical data was also consolidated experimentally by reaction of **9** with an equivalent of $B(C_6F_5)_3$ (Scheme 8) to isolate **11**

showing the ability of the aluminum centre to accept and donate electron density concurrently.⁴³



Scheme 8. Simultaneous Lewis acid and Lewis base properties of aluminum(I) species

To date, Roesky has shown a number of applications including the formation of the first aluminacyclopropene,⁴⁴ via reaction of **9** with acetylene at -78°C and insertions of numerous molecules into these strained three-membered rings including CO_2 and nitriles to afford the corresponding five-membered ring. Mononuclear aluminum(I) species are also good reducing agents, shown to reduce white phosphorous to $[\text{P}_4]^{4-}$ at room temperature in toluene.⁴⁵ Further reducing ability is still being investigated but potential applications are exciting.

Mononuclear aluminum(I) species are only beginning to be explored and developed, as new examples are discovered, their applications will also increase.

1.4 Research Objectives

I. Illuminating the mechanisms by which Cu(II) / methylaluminoxane systems polymerize ethylene

The objectives of this M.Sc. research project initially began as an exploration into the generality of Cu(II) systems for homogeneous ethylene polymerization. Work was to be done to deduce a mechanism for ethylene polymerization by the reported copper(II) systems discussed in 1.1.3. When results began to show ligand transfer from copper to aluminum was occurring at stoichiometric ratios, the focus shifted to determining the interaction between the copper precatalyst and the aluminum activator in ethylene polymerization reactions. Copper and analogous aluminum systems were synthesized and their activity in ethylene polymerization was studied.

II. Application of (imino-amido)aluminum(III) complexes for the ring-opening polymerization of ϵ -caprolactone

As an extension of the work on the formation of polyethylene, the current literature showed that similar aluminum complexes to the ones we had synthesized were also active for the ring-opening polymerization of ϵ -caprolactone (see 1.3). With this in mind, a new objective presented itself as we also set out to study the activity of our aluminum systems for the formation of poly(caprolactone).

III. Synthesis of aluminum(I) complexes

Finally, we also observed that the only two mononuclear aluminum(I) species known, both employed a bidentate N,N' coordinated ligand system that was also similar to (imino-amido) complexes we had used in both ethylene and ϵ -caprolactone polymerization. Using our imino-amido system, we set out to synthesize and structurally characterize the third example of a mononuclear aluminum(I) system.

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Chapter 2: Copper(II) Catalysts for Ethylene Polymerization: Do They Really Exist?

2.1 Abstract

Large portions of this chapter are taken verbatim from an article published in *Organometallics** in August 2008† wherein the reactions of two types of copper(II) ethylene polymerization catalysts, [(sal)CuCl]₂ (sal = 2-[CH=N(2,6-ⁱPr₂-C₆H₃)]-4,6-^tBu₂-phenoxide) and (α-diimine)CuCl₂ (α-diimine = [(2,6-ⁱPr₂-C₆H₃)N=CMe]₂), with methylaluminoxane (MAO) and trimethylaluminum (TMA) have been investigated. In both examples, facile and irreversible ligand (L) transfer from copper to TMA present in MAO was observed resulting in formation of the corresponding (sal)AlMe₂ and (imino-amido)AlMe₂ complexes. The (imino-amido)AlMe₂ complex is formed by α-diimine ligand transfer to aluminum followed by alkylation of one imino moiety in the ligand backbone. Both aluminum complexes were active catalysts for ethylene polymerization with activities similar to their Cu(II) precursors. Simple addition of a neutral salicylaldimine or α-diimine ligand to MAO in the absence of any copper species resulted in the formation of the corresponding LAlMe₂ complexes which are again active for ethylene polymerization. These results indicate that ethylene polymerization does not occur by a migratory insertion mechanism at the copper center, but is the result of ligand

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† Olson, J.A.; Boyd, R.; Quail, J.W.; Foley, S.R. *Organometallics*, **2008**, *27*, 5333-5338.

transfer to aluminum, and it is the resulting $\text{LAlMe}_2/\text{LAlMe}^+$ complexes which are likely the active species.

2.2 Introduction

In Chapter 1, it was shown that early transition metal complexes have long dominated the field of homogeneous ethylene polymerization and have been the subject of numerous reviews.¹ Research into late transition metal systems began in earnest when Brookhart discovered that α -diimine ligated nickel and palladium systems produced high molecular weight polyethylene with an activity comparable to early transition metal systems (Figure 1).²

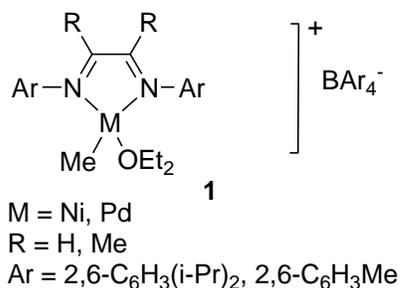


Figure 1. Active species in Brookhart's olefin polymerization systems²

Since this discovery, there has been tremendous research into a variety of late transition metal systems and this has been the subject of several recent reviews.³ One general trend that has emerged is to explore the reactivity of transition metals not previously known to polymerize ethylene via a migratory insertion mechanism. Late transition metal species

have been especially targeted for the development of catalysts for the co-polymerization of ethylene with polar monomers due to their greater functional group tolerance (Chapter 1, Figure 6).⁴ Direct copolymerization of ethylene with polar monomers remains one of the most sought after goals in the design of new olefin polymerization catalysts. Copper has become an attractive candidate for the homo- and co-polymerization of ethylene with functionalized monomers. It was only recently that the first reports of copper complexes being active for the polymerization of ethylene to high molecular weight polyethylene were reported by the groups of Stibrany and Gibson employing either (bisbenzimidazole)CuCl₂ systems⁵ (**1**) or (α -diimine)CuCl₂ (**2**).⁶ Since then, several other reports have emerged of LCuCl₂ or L₂Cu complexes employing salicylaldiminato⁷ (**3**), pyrazolylpyrimidine⁸ (**4**) and chiral pyrazolylquinoline⁹ (**5**) ligands that were also active for ethylene polymerization (Figure 2). Apart from complex **3**, all the reported copper precatalysts maintain a very similar coordination environment about the metal center. In all cases, methylaluminoxane (MAO) was used as a co-catalyst with moderate to very low activities and high polymer molecular weights reported (Table 1). No mechanism for polymerization was deduced although a coordination/insertion mechanism was postulated in some cases.⁵

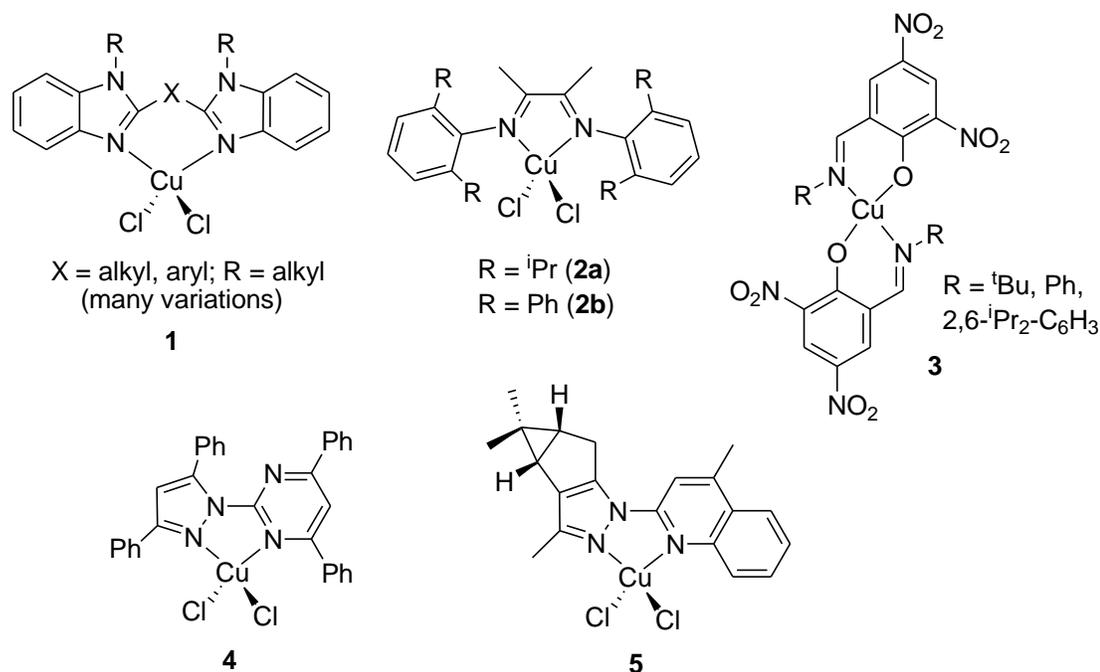


Figure 2. Reported Cu(II) ethylene polymerization precatalysts

We initially intended to investigate the generality of homogeneous Cu(II) systems for ethylene polymerization and the factors that influence both catalyst activity and polymer molecular weight. However, given that no Cu(II) alkyl species has ever been isolated due to rapid reduction at the metal center,¹⁰ it appeared unlikely that ethylene polymerization could occur by a migratory insertion mechanism at the Cu(II) center. While many Cu(I) alkyl species exist, they are usually unstable at ambient temperatures unless supported by bulky electron-rich phosphine or N-heterocyclic carbene ligands.¹¹

We now propose that ethylene polymerization does not occur by a migratory insertion mechanism at the copper center but in fact ligand transfer occurs from copper to trimethylaluminum (TMA) present in MAO and it is the resulting aluminum alkyl complexes ($\text{LAiMe}_2/\text{LAiMe}^+$) that are likely the active species for ethylene

polymerization. Commercial MAO solutions contain large amounts of trimethylaluminum (30-35%)¹² and aluminum complexes are well known to polymerize ethylene,¹³ although the polymerization mechanism in these systems is poorly understood.¹⁴ Facile ligand transfer from nickel to aluminum has been previously reported by Collins *et al.* employing electron rich Ni(II) iminophosphonamide complexes in the presence of TMA (Figure 3).¹⁵

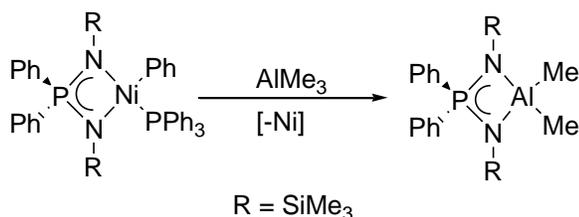


Figure 3. Ligand transfer from Ni to Al¹⁵

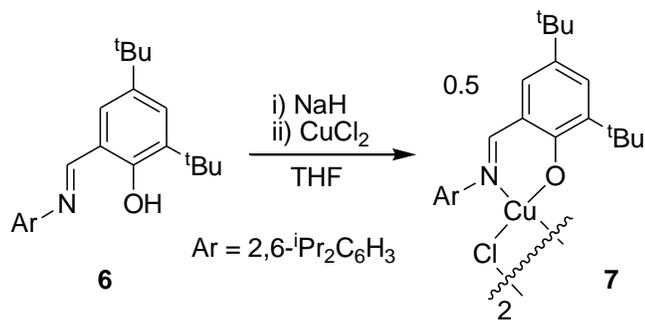
Herein we detail ligand transfer studies between copper and aluminum and ethylene polymerization activities of the resulting complexes.

2.3 Results and Discussion

2.3.1 Synthesis of [(sal)CuCl]₂

To investigate the reactivity of copper(II) complexes with aluminum alkyl species, we first synthesized a (sal)Cu(II) complex (sal = salicylaldiminato). The particular interest in bulky sal ligands stems from neutral nickel ethylene polymerization catalysts, (sal)Ni(Ph)PPh₃, developed by Grubbs.¹⁶ Reaction of the sodium salt of bulky salicylaldimine **6** with CuCl₂ resulted in formation of [(sal)CuCl]₂ (**7**) as a paramagnetic dark green solid in 74% yield (Scheme 1). In the IR spectra of **7**, the azomethine band

($\nu_{\text{CN}} = 1612 \text{ cm}^{-1}$) is shifted to lower wavenumber compared to that of the free ligand ($\nu_{\text{CN}} = 1622 \text{ cm}^{-1}$) consistent with coordination through the azomethine nitrogen. Elemental analysis is consistent with the proposed structure for **7** and a crystal structure determination clearly showed that **7** is a dinuclear chloride-bridged dimer in the solid state consistent with previously proposed structures for a $[(\text{sal})\text{CuCl}]_2$ -type complex (Figure 2).^{17,†} Somewhat surprisingly, given the near ubiquitous employment of sal ligands across the periodic table, dinuclear 4-coordinate chloride-bridged $[(\text{sal})\text{CuCl}]_2$ complexes are rare species with no previous characterization by crystallography. Upon activation with MAO, copper complex **7** was active for ethylene polymerization albeit with low activity (Table 1).



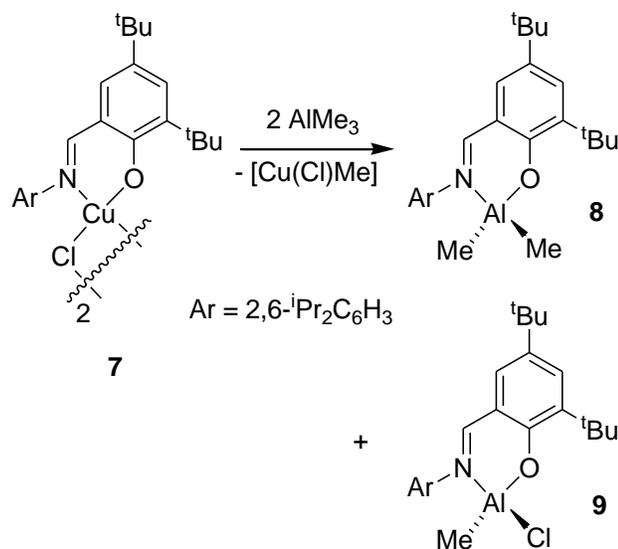
Scheme 1. Formation of $[(\text{sal})\text{CuCl}]_2$

2.3.2 Reaction of $[(\text{sal})\text{CuCl}]_2$ with AlMe_3

Addition of the neutral salH ligand **6** to MAO *in the absence* of any copper complex resulted in the formation of species that were also active for ethylene polymerization with similar activity to that of **7** (Table 1). Thus, it appeared that copper was not required to initiate ethylene polymerization. To investigate if ligand transfer was

occurring from copper to aluminum, stoichiometric reactions of **7** with trimethylaluminum (TMA) were carried out. Commercial MAO solutions contain high amounts of TMA (30 -35%)¹² with a significant percentage remaining present in MAO even after distillation.¹⁸ This is due to the fact that TMA in MAO solutions can exist in two distinct forms: first as “free” TMA in its dimeric form, Al₂Me₆, and secondly as complexed TMA, associated with the various MAO chains.¹² Upon addition of 2 equiv TMA to **7** in toluene, the dark green solution immediately became pale yellow. After filtration and removal of solvent, a yellow powder was isolated. Analysis by ¹H NMR revealed that the reaction of **7** with TMA resulted in ligand transfer to aluminum yielding two products, (sal)AlMe₂ (**8**) and (sal)Al(Cl)Me (**9**), in a 1:1 ratio in 85% isolated yield (Scheme 2). The resulting products showed that not only does sal ligand transfer occur from copper to aluminum, but chloride/methyl metathesis also occurs between the two metal centers. The final fate of the copper species was not ascertained.

2.3.3 Confirming the Identity of products from 2.3.2

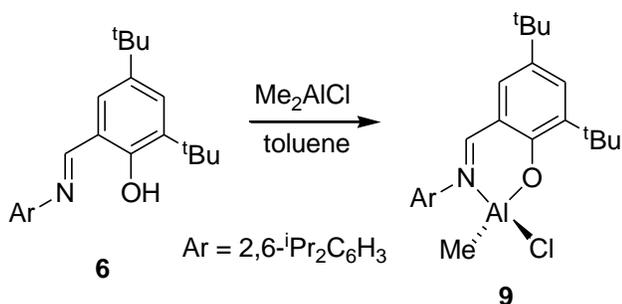


Scheme 2. Ligand transfer from Cu to Al

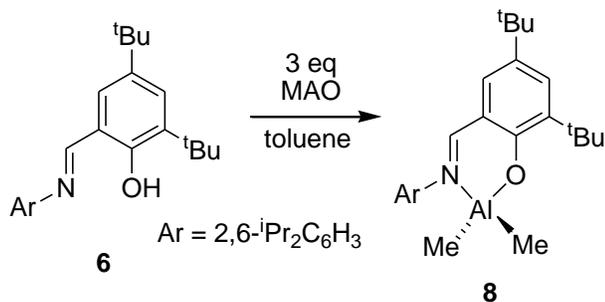
No attempt to separate **8** from **9** was made, however, the identity of both species was further confirmed by comparison to independently synthesized samples of **8** and **9**. The (sal)AlMe₂ complex, **8**, has been previously reported by Gibson and is active for ethylene polymerization when activated with B(C₆F₅)₃.^{13c,d} (Sal)Al(Cl)Me (**9**) is readily synthesized by reaction of the neutral salH ligand **6** with Me₂AlCl in 96% yield (Scheme 3). Both **8** and **9** were active for ethylene polymerization in the presence of MAO and have similar activities (Table 1).

2.3.4 Reaction of salH with MAO and Determination of AlMe₃ content in MAO

SalH ligand **6** was also reacted with 3 equiv MAO in place of TMA which resulted in formation of (sal)AlMe₂ complex **8** in 95% yield (Scheme 4). Using the phosphine method developed by Andrew Barron,¹⁹ the percentage of the total aluminum content existing as TMA in the commercially obtained MAO solution was determined to be 35%. Therefore, three equivalents of MAO were employed resulting in approximately one equivalent of TMA per salH ligand. Control polymerization experiments where MAO was used in the absence of any complex or ligand did not yield any solid polyethylene (Table 1).



Scheme 3. Independent synthesis of **9**



Scheme 4. Synthesis of (sal)AlMe₂ **8** using MAO

2.3.5 Ethylene Polymerization Results

Table 1. Results of ethylene polymerization studies. ^a

Entry	Precat.	MAO (eq)	P (atm)	T (°C)	Yield (g)	Activity (g PE/mmol)	M_w	M_w/M_n
1	6	200	4.7	70	0.028	1.4	7.2×10^5	3.6
2	7	200	4.7	70	0.034	1.7	1.0×10^5	1.5
3	8	200	4.7	70	0.046	2.3	1.1×10^6	3.3
4	9	200	4.7	70	0.031	1.6	6.7×10^5	2.0
5	10	200	4.7	70	0.007	0.35	1.4×10^6	5.5
6	11	200	4.7	70	0.030	1.5	4.1×10^5	1.1
7	2a	200	4.7	70	0.010	0.5	4.2×10^5	1.1
8 ^b	---	3 mL	4.7	70	0	0	---	---
9 ⁵	1	> 200	50	80	---	---	“high”	---
10 ⁶	2a	500	5.0	70	trace	---	$> 5 \times 10^6$	---
11 ⁶	2b	500	4.5	20	0.4	23	$> 5 \times 10^6$	---
12 ⁷	3	200	80	80	0.11	5.5	---	---
13 ⁸	4	500	10	35	0.7	350	---	---
14 ⁹	5	500	10	35	1.3	650	---	---

^a Reaction conditions: Fischer-Porter glass reactor, toluene (20 mL), precatalyst (20 μ mol), reaction time: 24 h. Average of 2 experiments. Molecular weights determined by GPC at 140 °C. ^b Control experiment performed in absence of any complex or ligand (3 mL = 200 eq for entries 1-7). For entries 9-14, results taken from literature.⁵⁻⁹

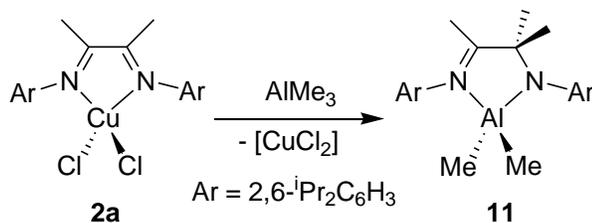
Having demonstrated that a copper(II) precatalyst of our own design, upon reaction with TMA or MAO, resulted in facile ligand transfer to aluminum and that these species were active for ethylene polymerization in the absence of copper species, we set about investigating if the same results would be observed with Gibson's (α -diimine) CuCl_2 complex, **2a**.

2.3.6 (α -diimine)CuCl₂ and ligand transfer with AlMe₃

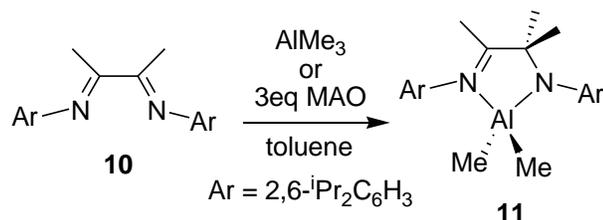
In our hands, precatalyst **2a** was indeed active for ethylene polymerization in the presence of MAO, again with very low activity (Table 1). Addition of the neutral α -diimine ligand **10** to MAO *in the absence* of any copper species resulted in the formation of species that were also active for ethylene polymerization with similar activity to that of **2a** (Table 1). Reaction of (α -diimine)CuCl₂ **2a** with TMA resulted in formation of aluminum complex **11**, however, rather than having a neutral diimine coordinated to the aluminum center, alkylation of one of the imino moieties of the ligand backbone occurred, resulting in formation of (imino-amido)AlMe₂ complex **11** as the major product (Scheme 5). This reaction did not proceed as cleanly as the analogous reaction for [(sal)CuCl]₂ (**7**). One other species was present in the reaction mixture that has not yet been identified. (Formation of the analogous (imino-amido)Al(Cl)Me has been ruled out, as it was independently synthesized and spectral data compared.) To further confirm the identity of the major product from Scheme 5, α -diimine **10** (the neutral ligand from **2a**) was reacted with 1 equiv of TMA in toluene resulting unequivocally in the formation of **11** in 71% yield (Scheme 6). The alkylation of an imino moiety of a diimine ligand, upon reaction with TMA, has previously been observed for both α -diimine and pyridine-diimine ligands.^{13f,h,i,20} The ¹H NMR spectra for **11** indicated a loss of symmetry in the ligand and formation of a C_s symmetric species with one singlet for the imino-methyl group at 1.42 ppm integrating for three protons and another singlet for the two amino-methyl groups at 1.15 ppm integrating for six protons. Characteristic high field resonances for the aluminum methyl groups are observed at -0.40 ppm (s, 6H). Single

crystals of **11** were obtained from a concentrated toluene solution at $-25\text{ }^{\circ}\text{C}$, thus allowing for an X-ray structure determination (Figure 3).²¹ The X-ray data showed that the N1-C1-C2-N2 portion of the imino-amido ligand is almost planar with a torsional angle of 3.9° . The aluminum atom lies within this plane and adopts a distorted tetrahedral geometry. The Al-Me distances are identical at $1.961(3)\text{ \AA}$. As expected, the Al-N bond with the formally negatively charged amido nitrogen N1 is significantly shorter at $1.845(2)\text{ \AA}$ than the neutral imino nitrogen Al-N2 at $1.980(2)\text{ \AA}$.

α -Diimine **10** was also reacted with 3 equiv MAO in place of TMA which again resulted in formation of (imino-amido)AlMe₂ complex **11** in 78% isolated yield (Scheme 6).



Scheme 5. Ligand transfer with α -diimine species



Scheme 6. Two routes into formation of **11**

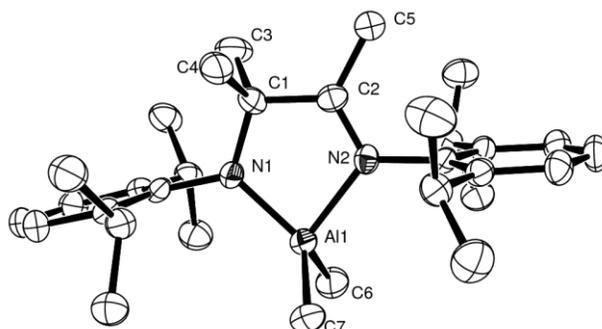


Figure 3. ORTEP ²² plot of **11** at the 50% probability level. The hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) = 1.845(2), Al(1)-C(7) = 1.961(3), Al(1)-C(6) = 1.961(3), Al(1)-N(2) = 1.980(2), N(1)-C(1) = 1.477(3), N(2)-C(2) = 1.303(4), C(7)-Al(1)-C(6) = 108.21(15), N(1)-Al(1)-N(2) = 84.59(10).

2.4 Conclusions

In conclusion, we have shown in two separate examples of copper(II) complexes active for ethylene polymerization in the presence of MAO, that the copper itself was not required to initiate polymerization. In both cases, facile ligand transfer takes place from the LCu(II) complexes to trimethylaluminum resulting in formation of the corresponding LAIME₂ complexes. The same aluminum species can be generated by simple ligand addition to MAO in the absence of any copper species and the resulting aluminum complexes are all active catalysts for ethylene polymerization, albeit with low activity.

For over a decade now, well-defined aluminum alkyl complexes have been reported to produce polyethylene.¹³ However, theoretical studies on cationic aluminum centres have offered some insight, suggesting that β-H transfer competes with chain

propagation, therefore questioning the ability of an aluminum catalytic centre to produce high molecular weight polymers.¹⁴ Other reports mention that transition metal impurities, even at ppb levels, could have a significant influence on the activity of the reported aluminum complexes.²³ While it now appears unlikely that a copper species can be an active catalyst for ethylene polymerization under mild conditions due to ligand transfer to aluminum, it remains unclear what the mechanism for polymerization is for aluminum or even if the aluminum complexes are directly responsible for the observed catalytic activity.^{14,23}

2.5 Experimental

2.5.1 General Information. Unless otherwise stated, all reactions were performed under N₂ or vacuum using standard Schlenk techniques or in a N₂-filled drybox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated oil baths. All melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. ¹H and ¹³C {¹H} NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ¹H and ¹³C NMR are reported in ppm in reference to the residual ¹H and ¹³C resonances of CDCl₃ (¹H: δ 7.24; ¹³C: δ 77.24) and C₆D₆ (¹H: δ 7.16). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Elemental analyses for the air-sensitive alkylaluminum complexes **9** and **11** were performed by Midwest Microlabs. IR data was collected by Diffuse Reflectance Spectroscopy. GPC data was obtained from a Viscotek high-temperature GPC. Methylaluminoxane (10 wt. % in toluene), Dimethylaluminum

chloride (1.0 M in hexanes) and trimethylaluminum (2.0 M in toluene) were purchased from the Sigma-Aldrich Chemical Company. The percentage of the total aluminum content existing as TMA in the MAO solution was determined to be 35%.¹⁹ Salicylaldimine (**6**),^{13d} (sal)AlMe₂ (**8**),^{13d} α -diimine (**10**)² and (α -diimine)CuCl₂ (**2a**)⁶ were all synthesized according to literature procedures.

2.5.2 Synthesis of [(sal)CuCl]₂ (7). A 100 mL round bottom flask was charged with salicylaldimine **6** (0.500 g, 1.27 mmol) and THF (20 mL). 2 equiv of NaH (0.062 g, 2.56 mmol) were slowly added and the suspension was stirred for 1 h, filtered to remove excess NaH, and the filtrate then added to a second round bottom flask containing 1.5 equiv CuCl₂ (0.255 g, 1.89 mmol). The yellow filtrate immediately turned dark brown. The reaction mixture was allowed to stir 24 h, whereupon it was filtered and the solvent removed under vacuum resulting in a dark green solid. The product was crystallized from a concentrated 1:1 solution of hexane and toluene at -25 °C (0.462 g, 74%). $\mu_{\text{eff}} = 2.23 \mu_{\text{B}}$. IR (KBr, cm⁻¹): 2960 (s), 2906 (s), 2868 (s), 1612 v(C=N), 1599 (s), 1585 (s), 1551 (s), 1530 (s), 1462 (s), 1442 (s), 1426 (s), 1384 (s), 1362 (s), 1326 (s), 1272 (s), 1255 (s), 1168 (s), 800 (s), 786 (s), 765 (s). Anal. calcd for C₅₄H₇₆Cl₂Cu₂N₂O₂: C 65.97, H 7.79, N 2.85; found: C 65.63, H 8.01, N 2.71. Mp: 176-178 °C (dec).

2.5.3 Synthesis of (sal)Al(Cl)Me (9). A 100 mL round bottom flask was charged with salicylaldimine **6** (0.158 g, 0.402 mmol) and toluene (20 mL). Dimethylaluminum chloride (0.40 mL, 1.0 M in hexanes, 0.40 mmol) was added drop wise via syringe and the solution stirred for 24 h at ambient temperatures. The solution was filtered and

excess solvent was removed under vacuum resulting in a yellow solid (0.180 g, 96%). ^1H NMR (C_6D_6): δ 7.90 (s, 1H, Ar-N=CH-Ar), 7.77 (d, $J = 2.6$, 1H, NCAr-H), 7.12-7.08 (m, 3H, NAr-H), 6.92 (d, $J = 2.6$, 1H, NCAr-H), 3.53 (sept, $J = 6.7$, 1H, $\text{CH}(\text{CH}_3)_2$), 2.97 (sept, $J = 6.7$, 1H, $\text{CH}(\text{CH}_3)_2$), 1.58 (s, 9H, ^tBu), 1.35 (d, $J = 6.7$, 3H, $\text{CH}(\text{CH}_3)_2$), 1.22 (s, 9H, ^tBu), 1.12 (d, $J = 6.7$, 3H, $\text{CH}(\text{CH}_3)_2$), 0.87 (d, $J = 6.7$, 3H, $\text{CH}(\text{CH}_3)_2$), 0.70 (d, $J = 6.7$, 3H, $\text{CH}(\text{CH}_3)_2$), -0.11 (s, 3H, AlCH_3). ^{13}C NMR (CDCl_3): δ 175.49 (C=N), 161.92, 143.61, 142.60, 141.36, 141.10, 134.36, 129.12, 128.78, 125.24, 124.07, 118.21, 35.64, 34.39, 31.39, 29.63, 28.84, 28.39, 26.43, 26.40, 23.54, 22.35. Anal. calcd for $\text{C}_{28}\text{H}_{41}\text{AlClNO}$: C 71.54, H 8.79, N 2.98; found: C 71.33, H 8.69, N 2.94. EI-MS (m/z): calcd for $\text{C}_{27}\text{H}_{38}\text{AlClNO} [\text{M}-\text{CH}_3]^+$: 454.2, found: 454.3.

2.5.4 Ligand transfer between [(sal)CuCl]₂ (7) and AlMe₃. A 100 mL round bottom flask was charged with [(sal)CuCl]₂ (7) (0.201 g, 0.205 mmol) and toluene (20 mL). Two equiv of trimethylaluminum (0.23 mL, 2.0 M in toluene, 0.46 mmol) were added drop wise via syringe and the solution stirred for 24 h. Upon addition of trimethylaluminum, the dark green solution immediately turned bright yellow. The resulting reaction mixture was filtered and solvent removed under vacuum resulting in formation of a yellow solid (0.179 g, 85% yield based on 1:1 ratio of **8** and **9**). Only two products were observed by ^1H NMR consisting of a 1:1 mix of (sal)AlMe₂ (**8**) and (sal)Al(Cl)Me (**9**). Identity of products was confirmed by comparison to independently synthesized samples of **8** and **9**.

2.5.5 Synthesis of (sal)AlMe₂ (8) from Salicylaldimine (6) and MAO. A 100 mL round bottom flask was charged with salicylaldimine **6** (0.104 g, 0.265 mmol) and toluene (20 mL). 3 equiv methylaluminoxane (0.51 mL, 10 wt% in toluene, 0.76 mmol) was added drop wise via syringe and the solution stirred for 24 h. After stirring, the solution was filtered and the solvent was removed under vacuum resulting in a yellow solid. ¹H NMR showed formation of **8** as the only observed species along with residual MAO (0.113 g, 95%). ¹H NMR (C₆D₆): δ 7.86 (s, 1H, Ar-N=CH-Ar), 7.74 (d, ⁴J = 2.4, 1H, NCAr-H), 7.15-7.0 (m, 2H, NAr-H), 7.05 (s, 1H, NAr-H), 6.91 (d, ⁴J = 2.4, 1H, p-NCAr-H), 3.17 (sept, J = 6.7, 2H, CH(CH₃)₂), 1.60 (s, 9H, ^tBu), 1.25 (s, 9H, ^tBu), 1.19 (d, J = 6.7, 6H, CH(CH₃)₂), 0.81 (d, J = 6.7, 6H, CH(CH₃)₂), -0.24 (s, 6H, Al(CH₃)₂).

2.5.6 Synthesis of (imino-amido)AlMe₂ (11). A round bottom flask was charged with toluene (20 mL) and α-diimine ligand **10** (0.170 g, 0.421 mmol). Trimethylaluminum (0.22 mL, 2.0 M in toluene, 0.44 mmol) was added drop wise via syringe and the solution stirred for 24 h. The initial bright yellow solution of **10** changed to a pale yellow upon addition of trimethylaluminum. The solution was filtered and solvent removed under vacuum resulting in formation of a white solid. The product was crystallized from a concentrated toluene solution at -25 °C (0.141 g, 71 %). ¹H NMR (C₆D₆): δ 7.25 (m, 3H, Ar-H), 7.10 (m, 3H, Ar-H), 3.93 (sept, J = 6.7, 2H, CH(CH₃)₂), 3.11 (sept, J = 6.7, 2H, CH(CH₃)₂), 1.42 (s, 3H, H₃C-C=N), 1.39 (d, J = 6.7, 6H, CH(CH₃)₂), 1.31 (d, J = 6.7, 6H, CH(CH₃)₂), 1.28 (d, J = 6.7, 6H, CH(CH₃)₂), 1.15 (s, 6H, (CH₃)₂C-N), 0.96 (d, J = 6.7, 6H, CH(CH₃)₂), -0.40 (s, 6H, Al(CH₃)₂). ¹³C NMR (C₆D₆): δ 199.09, 151.54, 147.53, 143.03, 141.61, 138.74, 125.19, 124.31, 67.84, 28.58, 28.23, 27.99, 25.13, 24.84,

24.63, 24.54, 18.43, -6.53. Anal. calcd for C₃₁H₄₉AlN₂: C 78.10, H 10.36, N 5.88; found: C 77.82, H 10.05, N 5.57. EI-MS (*m/z*): calcd for C₃₀H₄₆AlN₂ [M-CH₃]⁺: 461.3, found: 461.4.

2.5.7 Ligand transfer between (α -diimine)CuCl₂ (2a**) and AlMe₃.** A round bottom flask was charged with toluene (20 mL) and (α -diimine)CuCl₂ **2a** (0.157 g, 0.291 mmol). Trimethylaluminum (0.201 mL, 2.0 M in toluene, 0.402 mmol) was added drop wise via syringe and the solution stirred for 24 h. The initial dark brown solution changed to a pale orange color upon addition of trimethylaluminum. After stirring, the solution was filtered and the solvent removed resulting in formation of an orange solid. The ¹H NMR showed the presence of (imino-amido)AlMe₂ (**11**) as the dominant species, however one other species was also observed by ¹H NMR which has not been identified.

2.5.8 Ligand transfer between (α -diimine)CuCl₂ (2a**) and MAO.** A 100 mL round bottom flask was charged with diimine ligand **10** (0.107 g, 0.265 mmol) and toluene (40 mL). 3 equiv of methylaluminoxane (0.58 mL, 10 wt% in toluene, 0.86 mmol) was added drop wise via syringe and the solution stirred for 24 h. After stirring, the solution was filtered and the solvent was removed under vacuum resulting in a yellow solid. ¹H NMR showed formation of **11** as the only observed species along with residual MAO (0.098 g, 78%).

2.5.9 General Ethylene Polymerization Procedure. In a glovebox, the precatalyst (20 μmol) was dissolved in toluene (20 mL) in a Fischer-Porter bottle. The bottle was connected to a valve-polymerization system, sealed, and taken out of the glove box. The system was connected to a Schlenk line, purged three times with N_2 and filled with 10 psi ethylene. 200 equivalents of MAO (10 wt. % in toluene) were added via syringe, and the ethylene pressure increased to 70 psi. The reaction mixture stirred for 24 h while heating at 70 $^\circ\text{C}$. After stirring, the reaction was quenched with 1M acidified methanol, filtered and the resulting polymer washed with 1M acidified methanol, followed by methanol. The polymer was dried under vacuum. Molecular weights and M_w/M_n were determined using a Viscotek High Temperature GPC at 140 $^\circ\text{C}$.

2.6 References

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21. X-ray structure determination of **11**: C₃₁H₄₉AlN₂, M_w 476.70, colorless, crystal size (0.12 x 0.12 x 0.03 mm³), triclinic, space group P-1, a = 8.4373(5) Å, b = 9.7007(5) Å, c = 19.3460(11) Å, α = 82.033(4)°, β = 80.769(3)°, γ = 69.565(3)°, V = 1458.71(14) Å³, Z = 2, D_{calc}: 1.085 Mg/m³, F(000): 524, T = 173(2) K, MoKα radiation (0.71073 Å; μ 0.090mm⁻¹). 9900 collected reflections, 5436 unique (R_{int} = 0.0631); Final R indices [I > 2σ (I)] were R1 = 0.0679, wR2 = 0.1354, R indices (all data): R1 = 0.1129, wR2 = 0.1551; data/restraints/parameters 5436 / 0 / 321; GoF = 1.033. Largest peak and hole 0.613 and -0.266 e.Å⁻³.
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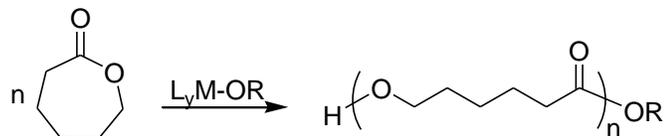
Chapter 3: ϵ -Caprolactone Polymerization Using Aluminum Catalysts

3.1 Abstract

Aluminum complexes from chapter 2 including (sal)AlMe₂, (sal)AlMeCl, and (imino-amido)AlMe₂ were used as initiators in the ring-opening polymerization of ϵ -caprolactone. A similar γ -diimine aluminum complex prepared by Jackson M. Chitanda was also employed as an initiator. Polymerization was studied with and without addition of *tert*-butanol as a co-initiator to determine its role and necessity in the catalytic cycle.

3.2 Introduction

Conventional polymers, such as polyethylene and polypropylene, are synthesized using petrochemical precursors and degrade extremely slowly under natural conditions, resulting in the buildup of such polymers in urban landfills.^{1,2} In more recent years, catalyst development for the synthesis of “environmentally friendly” polymers has become an area of interest both academically and industrially.¹ Lactic acid and ϵ -caprolactone (CL) have emerged as monomers that are capable of forming biodegradable, biocompatible polymers with a variety of applications, including packaging as well as incorporation in medical devices.^{3,4} The C-O linkage in the polymer chain (Scheme 1) allows the material to be broken down by hydrolysis and further reduced to CO₂, H₂O and other naturally occurring material by bacteria and other microorganisms.^{2,5}



Scheme 1. Ring opening polymerization of CL

Industrial systems currently employ a tin(II) bis(2-ethylhexanoate) ($\text{Sn}(\text{Oct})_2$) (Figure 1) catalytic system to initiate ring opening due to its good solubility in the CL monomer and other lactones,⁶ however, toxicity of most tin compounds are pushing researchers to find new initiators with lower toxicity.³

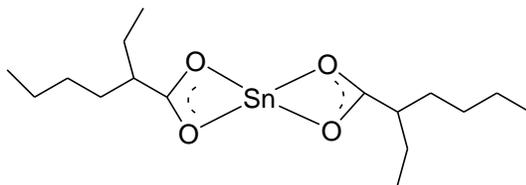


Figure 1. tin(II) bis(2-ethylhexanoate)

The mechanism by which $\text{Sn}(\text{Oct})_2$ polymerizes lactones is complicated with several possible active species being argued throughout the years, however, the generation of a tin-alkoxide species in the presence of an alcohol has been suggested as the most likely after many years of speculation.⁷

A variety of aluminum complexes have emerged as promising catalysts for the ring opening polymerization (ROP) of cyclic esters and are currently being explored with a wide range of ligand systems (Figure 2).^{3,4,8,9}

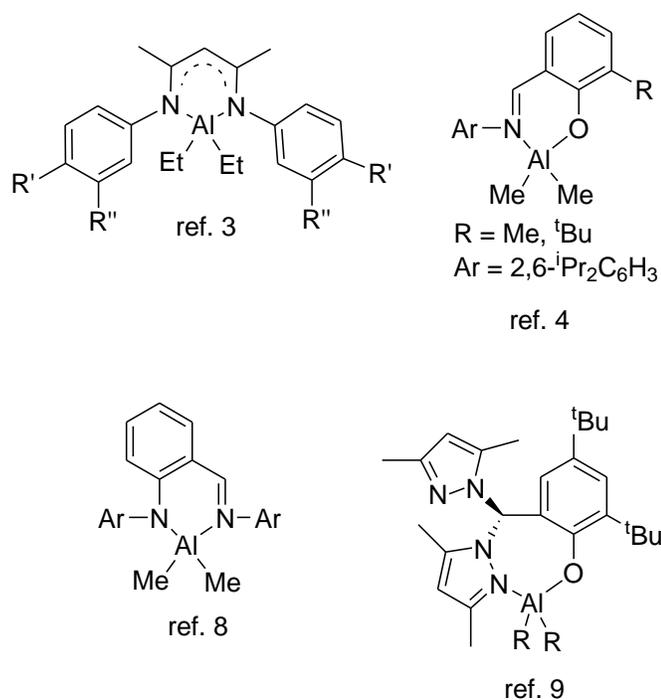
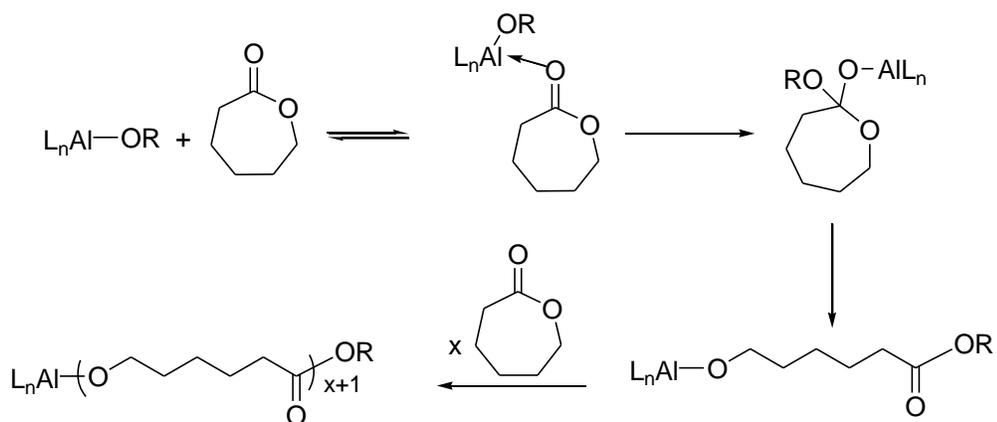


Figure 2. Examples of a few aluminum systems employed in ROP of ϵ -CL

Along with lower reported toxicity compared to tin, Al(III) systems are also strong Lewis acids which allows the monomer to coordinate via a σ -bond interaction and consequently be activated (Scheme 2).^{8,10}



Scheme 2. Proposed mechanism for the ROP of CL¹⁰

Many of the known aluminum systems have also been shown to behave in a living fashion which was not observed with the previously known tin compounds.^{11,12} The “living” properties of these aluminum catalysts stem from their single-site nature and are attractive systems due to the tunability of their ligands. Ideally with such systems, the relationship between catalyst structure and polymerization activity can be more easily studied by changing electronic and steric properties of the ancillary ligands. Single-site catalysts of the general formula LM-OR (L = bulky, inert ligand) currently represent the best strategy to obtain good control of polymerization activity of CL often resulting in polymers with low poly-dispersity index (PDI) and high molecular weights. Herein we report the findings for the activity of the aluminum systems prepared in Chapter 2 for the polymerization of ϵ -caprolactone.

3.3 Results and Discussion

All the syntheses of the aluminum complexes used are reported in detail in chapter 2 of this thesis with the exception of complex **4** (Figure 3).¹³

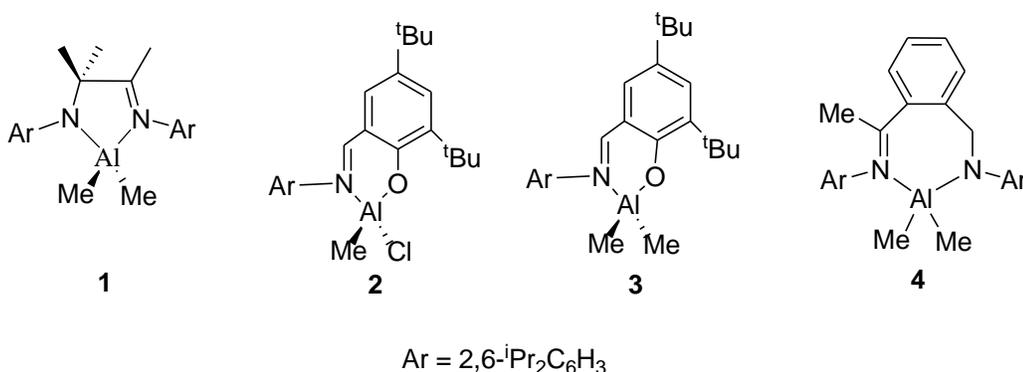
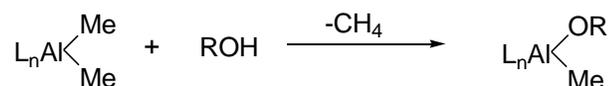


Figure 3. Al complexes used in this chapter

The preliminary results for the polymerization reactions are reported in Table 1. Test reactions were performed with **1**, in the absence of ^tBuOH to determine its role in polymerization experiments. It has been suggested that the alcohol co-initiator is required to remove a methyl group from the aluminum precatalyst,⁸ in order to form the speculated active species (Scheme 3). In some cases, the aluminum systems reported are completely inactive in the absence of an alcohol co-initiator.^{4,8,14}



Scheme 3. Example of the speculated Al active species in the formation of PCL

Further test reactions were carried out using AlMe₃ as the aluminum system in the absence of any ligand framework (Table 1, entries 6 and 7). Surprisingly, AlMe₃ showed activity for the ROP of CL with and without ^tBuOH present. Further investigations into the role of the ligand and its influence on M_w and PDI will be important in determining the necessity of a ligand framework at all. As well, polymerization was attempted in the absence of any catalyst -- aluminum or ^tBuOH -- to ensure that ROP does not occur from heating alone (Table 1, entry 8). As expected, this reaction yielded no PCL and shows that the monomer must be activated by an outside source.

Table 1. Results of ϵ -caprolactone polymerization

Entry	Precat.	^t BuOH (equiv)	CL (equiv)	Temperature (°C)	Yield ^a %	M_w ^b	M_w/M_n
1	1	1	100	60	78.0	67532	2.06
2	1	0	100	60	43.7	288326	1.48
3	2	1	100	25	69.8	142085	1.63
4	3	1	100	60	60.0	56359	1.59
5	3	1	100	25	63.2	52783	1.41
5	4	1	100	60	78.2	65005	2.09
6	AlMe₃	1	100	60	61	124496	3.25
7	AlMe₃	0	100	60	50	38524	1.81
8**	none	0	0.600 mL	60	-	-	-
9	1	0	100*	60	28.5	228454	2.33
10	1	1	100*	60	54.6	46834	2.00
11	1	2	100*	60	58.7	44928	1.16
12	1	4	100*	60	88.3	38828	2.67
13	1	1	200*	60	90.0	71266	1.68
14	1	1	400*	60	95.3	138467	2.39
15	1	1	1000*	60	94.7	235747	1.74

* CL for these reactions was distilled and dried over CaH₂. **, ** Control experiment performed in absence of any complex or ligand (0.600mL ~ 100 eq for other entries). ^a Isolated yield. ^b Determined by GPC at 40°C in THF.

Entries 1-8 in Table 1 employed 99% CL from Aldrich without any treatment, while entries 9-15 employed the monomer after it had been distilled and dried over CaH₂. The untreated monomer has potential moisture content which could poison the aluminum catalyst rendering it inactive. If some of the aluminum species present are deactivated by moisture, this effectively increases the CL:Al ratio and hence the M_w will also rise. This could explain some of the high numbers for M_w observed when using the untreated monomer. As the ratio of CL:Al increased in entries 10 to 13, 14 and 15, M_w increased

accordingly while PDI remained relatively constant, consistent with a living polymerization mechanism.

The ^1H NMR for PCL (Figure 4) shows the expected splitting pattern for the repeating CL units. The protons in the ^tBuO end group can be observed at 1.41 ppm, which is also consistent with the chemical shift of an ^iPrO end group of the same material reported in 2000.^{15a} The methylene protons nearest the OH group at the opposite end of the chain (e in Figure 4) are observed at 3.64 ppm which also coincides with previously reported data.^{8,15a} The integral for the ^tBuO protons can be used to get a rough estimate of the M_n of the polymer chain. The shown integral, 0.047 can be divided by 9 to get $n = 190$, which shows that there are roughly 190 repeating units in the polymer, consistent with the NMR in Figure 4 which is the spectra for the reaction of a 200:1 CL:Al ratio.

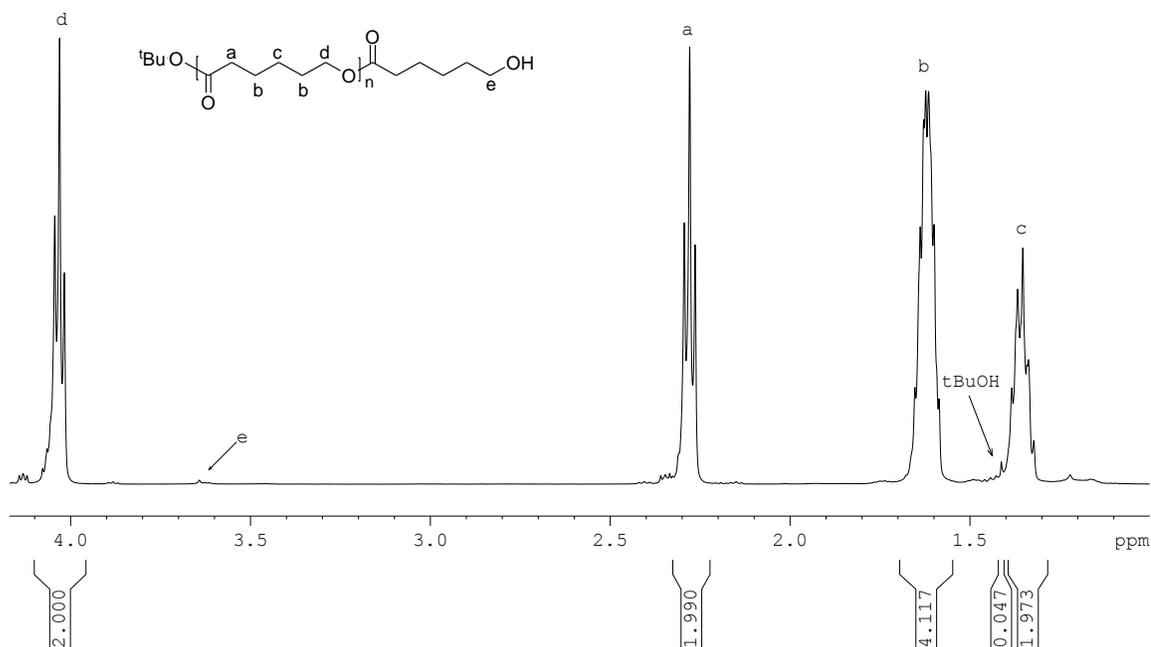


Figure 4. ^1H NMR of a typical polymer sample

Similar aluminum systems reported in literature vary in reaction conditions as well as results. The four examples of aluminum systems from literature, shown in Figure 2, display activities that change based on the ancillary ligands that are employed. Complex **A** and its derivatives show that the electronic nature of the substituents plays a very important role in the ability of the aluminum complexes to initiate polymerization.³ As the substituents become more electron donating in the *para*-position, from H, to Me, to OMe (R' in **A**, Figure 2), the activity decreases due to a proposed increase in electron density at the aluminum centre.³ Complex **C** shows a decrease in activity as the sterics of the aryl groups increase which one would expect when employing a large monomer such as CL.⁸ These reported trends show that both electronics and sterics are important properties to consider when designing ligand systems for aluminum mediated ROP of CL.

In general, systems **1-4**, show lower yields than were expected as compared with literature results, which often show isolated yields around 90% over the course of much shorter reaction times.^{3,4,8,9,12,14,15} These somewhat surprising results led us to examine the effects of using distilled CL in order to eliminate potential poisoning of the catalyst. Further work must also be done to optimize the reactions performed in Table 1 in order to obtain a more direct comparison with systems **1-4** and literature results. Other possible future work could include tuning the ligand systems to find the right combination of sterics and electronics to enhance the ability of the aluminum centre to initiate the reaction.

3.4 Conclusions

The four aluminum systems studied for the polymerization of ϵ -caprolactone were all active with varying degrees of success. To this point, the general polymerization procedure has not been optimized to any extent. Further work is required in order to optimize this reaction now that these systems have been shown to be active for the ROP of CL. Studies to further understand the mechanism by which these systems initiate polymerization will also be beneficial. Test reactions using **1** in the absence of ^tBuOH showed surprising results as compared with previously reported systems that showed no activity in the absence of the primary alcohol co-initiator.^{4,8}

3.5 Experimental

3.5.1 General Information. Unless otherwise stated, all reactions were performed under N₂ or vacuum using standard Schlenk techniques or in a N₂-filled drybox. All reaction temperatures for catalytic reactions refer to the temperature of pre-equilibrated oil baths. All melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. ¹H and ¹³C {¹H} NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical shifts for ¹H and ¹³C NMR are reported in ppm in reference to the residual ¹H and ¹³C resonances of CDCl₃ (¹H: δ 7.24; ¹³C: δ 77.24) and C₆D₆ (¹H: δ 7.16). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. GPC data was obtained from a Viscotek high-temperature GPC at 40°C in THF. ϵ -caprolactone (99%), and ^tBuOH, anhydrous (\geq 99.5) were purchased from the Sigma-Aldrich Chemical Company. ϵ -caprolactone was distilled and dried over CaH₂.

3.5.2 General ϵ -Caprolactone Polymerization Procedure. In a glovebox, the precatalyst (20 mg) was dissolved in toluene (20 mL) and 1 equiv of ^tBuOH was added via microsyringe and the mixture was allowed to stir. After 5 minutes, 100 equiv of ϵ -caprolactone were added and the flask was sealed and taken out of the glovebox and immersed in a 60°C pre-equilibrated oil bath. Polymerization was allowed to continue for 24 hours, at which point the reaction mixture was quenched by addition to 150 mL of methanol. The resulting precipitated poly(caprolactone) was filtered and washed with methanol and dried under vacuum to a constant weight. ¹H NMR (CDCl₃): δ 4.03 (t, 2H), 2.28 (t, 2H), 1.62 (m, 4H), 1.36 (m, 2H).

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Chapter 4: Attempts into the Synthesis of Mononuclear (imino-amido)Aluminum(I) Complexes

4.1 Abstract

The (imino-amido)AlMe₂ complex synthesized in chapter 2 was used as the starting complex in attempts at forming a mononuclear aluminum(I) target species. Reaction of (imino-amido)AlMe₂ with excess I₂ proved successful in forming the isolable precursor, (imino-amido)AlI₂. Attempts at reducing (imino-amido)AlI₂ with excess potassium were attempted in hopes of forming a very rare example of a mononuclear aluminum(I) species.

4.2 Introduction

Aluminum is well known to exist as Al(III) in the majority of its inorganic and organometallic complexes due to the inherent stability of this oxidation state.¹ Although not as common, nor as stable as Al(III) complexes, aluminum has also been shown to exist in a +2 oxidation state involving formation of an Al-Al bond (Figure 1).²

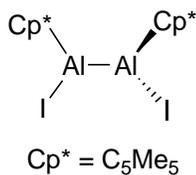
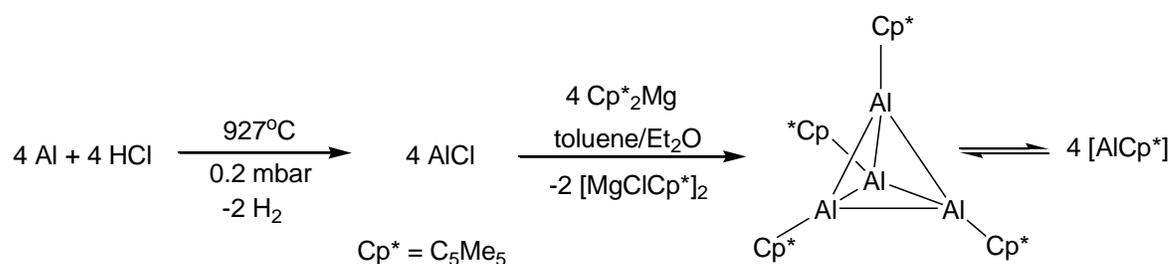


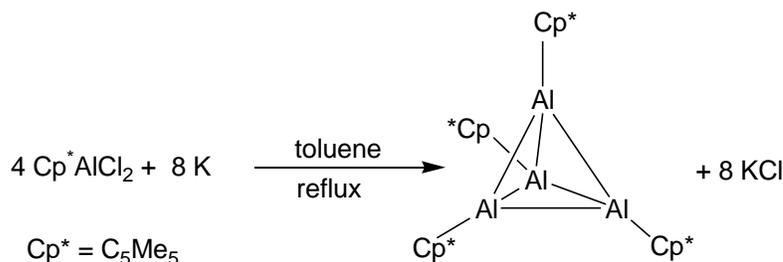
Figure 1. Example of an Al(II) species. ^{2b}

Considerably more rare, are aluminum complexes containing Al(I), as this oxidation state is not thermodynamically stable.¹ Schnöckel showed routes into a variety of AlX (X = H, halides) species but these were only obtainable at extremely high temperatures and low pressures (Step 1 in Scheme 1).³ Employing a similar synthesis, the first example of an organometallic Al(I) species was discovered by Schnöckel (Scheme 1), however, this was only stable as a tetramer in the solid and liquid phases at temperatures below 30°C.⁴ Above 30°C these complexes begin to develop an equilibrium between the tetramer and the gas-phase favored monomer, which can be detected by gas-phase electron diffraction.¹



Scheme 1. Schnöckel's synthetic method for the first solid state Al(I) species⁴

A few years later, Roesky developed a new route into the same tetrameric aluminum(I) species employing less forcing conditions (Scheme 2).⁵



Scheme 2. Roesky's synthesis of (AlCp*)₄

Both Schnöckel and Roesky's discoveries were very important in aluminum chemistry and laid the groundwork for the first mononuclear Al(I) species to be isolated in the solid state. In 2000, Roesky used the knowledge he gained during preparation of $(AlCp^*)_4$ and isolated the first example of a mononuclear organometallic complex (**1** in Figure 2) with aluminum in the +1 oxidation state (Figure 2).⁶ Eight years later, it remains only one of two very similar, structurally characterized aluminum carbene analogues.^{6,7}

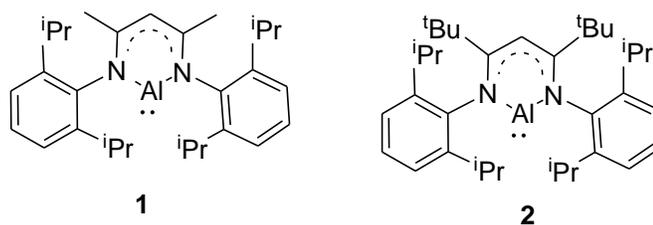


Figure 2. Roesky's⁶ mononuclear Al(I) species **1** and Cui's⁷ more recent version **2**

The steric bulk of the β -diketiminato ligand is crucial in protecting the extremely sensitive Al(I) centre and preventing it from tetramerizing.⁶ This example of a mononuclear aluminum(I) species displays interesting properties including the ability to act as a Lewis acid and Lewis base simultaneously,⁶ as well as the ability to act as a reducing agent.¹

With only two examples of such a system known, the applications are relatively undeveloped as compared with the analogous and ubiquitous N-heterocyclic carbene system.⁸ Roesky, however, has shown an increasing number of applications including formation of aluminacyclopentane and subsequent insertions of small molecules into the

corresponding three membered ring.¹ He has also explored the reducing ability of these complexes, via the reaction with white phosphorous (P₄) and its reduction to [P₄]⁴⁻ at room temperature in toluene.⁹

4.3 Results and Discussion

Beginning with the (imino-amido)AlMe₂ complex synthesized in Chapter 2 and used in Chapter 3 of this thesis, we noticed similarity between our ligand system and the one Roesky used to isolate his mononuclear aluminum(I) species **1**.⁶ Our imino-amido ligand system similarly contains bulky substituents, bidentate coordination to the aluminum centre and is also a mono-anionic 4 electron donor. With this knowledge in mind, we set out to synthesize an analogous mononuclear Al(I) complex **3** employing our ligand system (Figure 3).

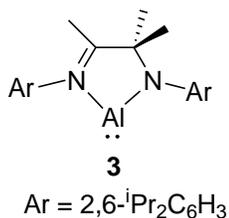
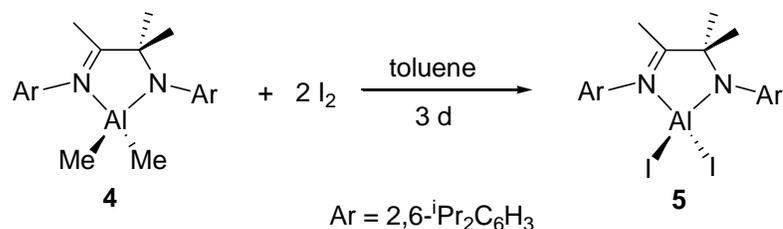


Figure 3. Target aluminum(I) species

Initially, (imino-amido)AlMe₂ **4** was allowed to react with 2 equivalents of I₂ in toluene for 3 days according to Scheme 3.



Scheme 3. Initial attempt at formation of (imino-amido)AlI₂

Upon workup, it was noticed that only partial exchange between the AlMe₂ and I₂ occurred resulting in a mixture of products which have yet to be verified. Two of these products are postulated to be (imino-amido)AlMeI and (imino-amido)AlI₂ from the ¹H NMR spectrum. Further reaction with excess I₂ resulted in the product (imino-amido)AlI₂ **5** and one other product which has yet to be determined. Any excess I₂ was removed under vacuum and X-ray quality crystals of **5** were grown from a concentrated solution in toluene at -27 °C in 62% yield (Figure 4).¹⁰

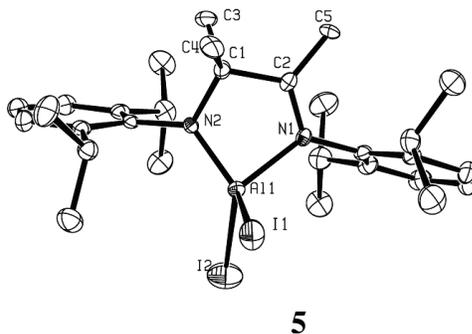
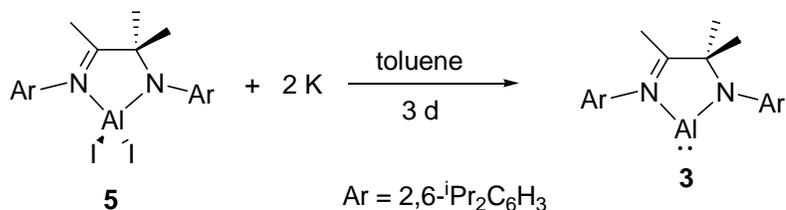


Figure 4. A general ORTEP¹¹ view of **5** with non-hydrogen displacement ellipsoids drawn at the 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Al(1)-N(1) = 1.950(6), Al(1)-I(1) = 2.564(2), Al(1)-I(2) = 2.458(2), Al(1)-N(2) = 1.801(6), N(1)-C(2) = 1.309(9), N(2)-C(1) = 1.478(9), I(1)-Al(1)-I(2) = 103.25(8), N(1)-Al(1)-N(2) = 86.8(3).

The X-ray data showed that the N1-C2-C1-N2 portion of the imino-amido ligand

bends out of the plane with a torsional angle of 13.2° which is large compared with 3.9° for the corresponding atoms in the (imino-amido)AlMe₂ **4** prepared in chapter 2. The aluminum centre adopts a distorted tetrahedral geometry. The Al-I distances are relatively similar at 2.564(2) and 2.458(2) Å respectively. As expected, the Al-N bond with the formally negatively charged amido nitrogen N2 is significantly shorter at 1.801(6) Å than the neutral imino nitrogen Al-N1 at 1.950(6) Å.

Upon isolation of **5**, it was further reacted with 2 equiv of potassium in toluene at room temperature for 3 days (Scheme 4).



Scheme 4. Initial attempt at formation of target species **3**.

Over the course of the reaction, the mixture changed from an orange solution to a pale yellow solution containing a grey precipitate, leading us to believe some transformation had taken place. The suspension was filtered and washed with toluene and the filtrate was concentrated and put in the freezer at -27°C to crystallize. The ^1H NMR and the crystal structure data however only confirmed the presence of the starting material, (imino-amido)AlI₂ **5**. It was then noticed in literature, a similar reduction of an LMgI₂ system (L= [{(Ar)NC(Me)}₂CH]) also employed potassium as a reducing agent, but required 10 equiv.¹² With this knowledge in mind, potassium in large excess was

used hereafter in attempts at reducing **5**. At the time of writing, the three day reactions in the presence of a large excess of potassium yielded an almost black reaction mixture. This mixture was filtered and the light yellow filtrate collected and concentrated in toluene and stored at -27 °C to crystallize. The reaction shown in Scheme 4 still requires optimization in order to form and isolate **3**. The presence of a color change and the formation of a precipitate indicate that some reaction is occurring. Further attempts at optimizing this reaction need to be carried out in order to find reaction conditions that generate reproducible results.

4.4 Conclusions

In conclusion, attempts at synthesis of a mononuclear aluminum(I) system employing an imino-amido ligand backbone have so far been unsuccessful. Steps in the right direction, however, have been taken, as preparation of the imino-amidoAlI₂ has been completed. Reduction of aluminum(III) to aluminum(I) remains a difficult task due to the high instability of aluminum(I) species. Further work needs to be done to optimize the clean formation of **5** and subsequently generate the target species **3**.

4.5 Experimental

4.5.1 General Information. Unless otherwise stated, all reactions were performed under N₂ or vacuum using standard Schlenk techniques or in a N₂-filled drybox. ¹H and ¹³C {¹H} NMR spectra were recorded on a Bruker 500 MHz Avance spectrometer. Chemical

shifts for ^1H and ^{13}C NMR are reported in ppm in reference to the residual ^1H and ^{13}C resonances of CDCl_3 (^1H : δ 7.24; ^{13}C : δ 77.24) and C_6D_6 (^1H : δ 7.16). Coupling constants are given in Hz. Elemental analyses were performed on a Perkin-Elmer 2400 CHN elemental analyzer. Iodine (99.99% metals basis) was purchased from the Sigma-Aldrich Chemical Company and used as is.

4.5.2 Synthesis of (imino-amido)AlI₂ (5). In the glove box, a round bottom flask was charged with toluene and (imino-amido)AlMe₂ (0.1994g, 0.419 mmol). Upon dissolution, excess I₂ (0.3955g, 1.56 mmol) was added leaving the solution a dark red color. After stirring for 3 days at room temperature, the solvent was removed under vacuum along with unreacted I₂ leaving an orange solid of the target complex. The product was crystallized from a concentrated toluene solution at -25 °C (0.1819 g, 62 %). ^1H NMR (C_6D_6): δ 7.07 (m, 3H, Ar-H), 7.05 (m, 3H, Ar-H), 3.86 (sept, 2H, CH(CH₃)₂), 3.34 (sept, 2H, CH(CH₃)₂), 1.42 (d, 6H, 2H, CH(CH₃)₂), 1.39 (s, 3H, H₃C-C=N), 1.34 (d, 6H, 2H, CH(CH₃)₂), 1.28 (d, 6H, 2H, CH(CH₃)₂), 1.13 (s, 6H, (H₃C)₂-CN), 0.91 (d, 6H, 2H, CH(CH₃)₂).

4.5.3 Attempts at (imino-amido)Al(I). In the glove box, a round bottom flask was charged with toluene and (imino-amido)AlI₂ **5**, initially 2 equiv of finely divided potassium were added and stirring at room temperature was carried on for 3 days. When this yielded no positive results, reactions were then carried out using large excess of potassium as per Stasch et. al.¹²

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10. X-ray structure determination of **5**: C₂₉H₄₃AlI₂N₂, M_w 700.43, colorless, crystal size (0.15 x 0.10 x 0.06 mm³), triclinic, space group P-1, a = 9.0800(3) Å, b = 9.3462(4) Å, c = 19.9846(7) Å, α = 77.783(2)°, β = 79.345(2)°, γ = 67.922(2)°, V = 1525.58(10) Å³, Z = 2, D_{calc}: 1.525 Mg/m³, F(000): 700, T = 173(2) K, MoKα radiation (0.71073 Å; μ 0.090mm⁻¹). 18698 collected reflections, 5789 unique (R_{int} = 0.0562); Final R indices

[$I > 2\sigma(I)$] were $R1 = 0.0686$, $wR2 = 0.1833$, R indices (all data): $R1 = 0.0821$, $wR2 = 0.1934$; data/restraints/parameters 5789 / 0 / 322; GoF = 1.059. Largest peak and hole 3.625 and -2.751 e.Å⁻³.

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Chapter 5: Summary and Conclusions

The initial direction of exploring the generality of Cu(II)/MAO systems for ethylene polymerization quickly shifted upon the examination of preliminary results. It was soon discovered that ligand transfer was occurring from the proposed active copper centre to the co-catalyst/activator aluminum centre in MAO at stoichiometric ratios. During standard literature ethylene polymerization reactions, 200-500 eq of MAO were being added allowing ligand transfer to occur even more readily than in our stoichiometric test reactions. For all the copper complexes reported as active ethylene polymerization catalysts,^{1,2,3,4,5} activities were low in comparison with other late transition metal systems such as Brookhart's Ni and Pd α -diimine complexes.⁶

Low activities, no proposed mechanism, and the lack of evidence for Cu(I) alkyls unless supported by bulky N-heterocyclic carbenes,⁷ and the ease with which Cu(II) alkyls undergo rapid reduction at the metal centre⁸ are all evidence for the discovery we later made showing that copper is not the active species as previously reported.⁹

Not only did we observe ligand transfer from the copper to aluminum species, the corresponding aluminum species were also active for ethylene polymerization with similar activities to those obtained for the copper species. This indicated that, in fact, copper is not required to mediate the formation of polyethylene and is therefore not the active species. All aluminum species that were obtained as ligand transfer products were also independently synthesized in order to confirm the products of the transfer reactions.

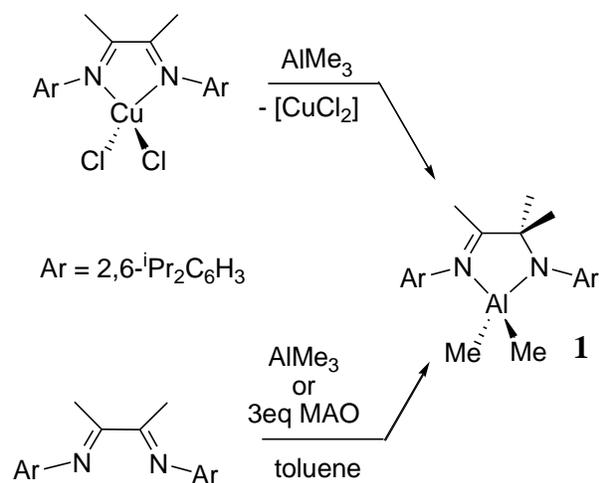
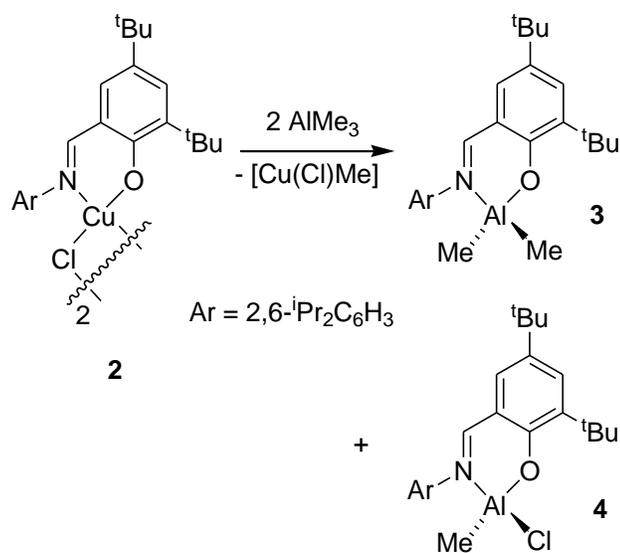


Figure 1. Synthetic routes into (imino-amido)AlMe₂ **1**

A novel (imino-amido)AlMe₂ **1** was synthesized using three different routes (Figure 1) and fully characterized, including by X-ray crystallography. Ligand transfer was also observed when reacting the [(sal)CuCl]₂ **2** with 1 eq TMA per copper centre yielding a 1:1 ratio of (sal)AlMe₂ **3** and (sal)Al(Cl)Me **4** (Scheme 1).



Scheme 1. Ligand transfer from [(sal)CuCl]₂ to Al

Complexes **1-4** along with (α -diimine)CuCl₂,² the free α -diimine ligand, and salH were used as pre-catalysts in the presence of MAO, in attempts to polymerize ethylene. All systems mediated the formation of polyethylene, albeit with low activity. More importantly, this work shows convincing evidence for the occurrence of ligand transfer from copper to aluminum in “copper-mediated” ethylene polymerization reactions. The mechanism by which aluminum polymerizes ethylene is up to this point unknown. It has even been speculated that up to ppb levels of transition metal impurities present in the reaction mixture may actually be the active species.¹⁰ Further investigations into the mechanism by which aluminum polymerizes ethylene could be undertaken and would be beneficial in determining the actual active species in these reactions.

The aluminum complexes, **1**, **3** and **4**, discussed above, as well as **5**¹¹ (Figure 2) were also used as co-initiators, with ^tBuOH, in the ROP of CL.

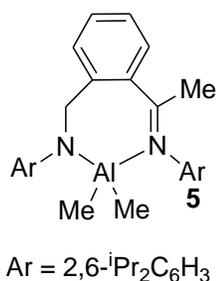


Figure 2. γ -(imino-amido)AlMe₂¹¹

As a number of papers reported that their systems were inactive for the ROP of CL in the absence of any primary alcohol initiator,^{12,13} test reactions were performed in

order to aid in understanding the role of the aluminum centre as well as the ^tBuOH in the reaction mechanism. Results showed that even in the absence of ^tBuOH, complex **1** was active for initiating the ROP of CL.

All systems employed, **1**, **3**, **4**, and **5**, were indeed active for the ROP of CL as expected. Isolated yields, however, were lower than anticipated, as compared with published results for other aluminum complexes. Optimization of the performed reactions is necessary in order to achieve a more direct comparison between our results and literature values.

Complex **1** was also employed as starting material in attempted synthesis of a mononuclear aluminum(I) species **6** (Figure 3).

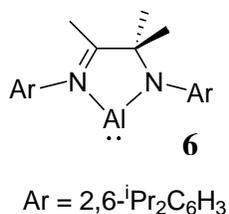


Figure 3. Target mononuclear aluminum(I) species

Attempts began by synthesis and isolation of a precursor, (imino-amido)AlI₂, via a ligand substitution reaction with **1** and excess of I₂ (Scheme 2). Crystals of (imino-amido)AlI₂ **7**, suitable for X-ray diffraction, were grown from a concentrated solution in toluene at -27 °C.

5.1 References

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