

**NEW CATALYSTS FOR OLEFIN POLYMERIZATION**

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by

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## Abstract

Aluminum- and gallium-bridged *ansa*-zirconocene compounds (Pytsi)Al[1]ZCP (**31a**) and (Pytsi)Ga[1]ZCP (**31b**) containing a bulky trisyl-based ligand with a pyridyl donor group [Pytsi = -C(SiMe<sub>3</sub>)<sub>2</sub>SiMe<sub>2</sub>(2-C<sub>5</sub>H<sub>4</sub>N)] were synthesized in 31% and 40% yield, respectively, by the reaction of (Pytsi)ECp<sub>2</sub> [E = Al (**29a**), Ga (**29b**)] with Zr(NMe<sub>2</sub>)<sub>4</sub> followed by reaction with Me<sub>3</sub>SiCl. Compounds **29a** and **29b** were prepared by the reaction of (Pytsi)ECl<sub>2</sub> [E = Al (**28a**), E = Ga (**28b**)] with two equivalents of NaCp. The molecular structures of **29a** and **29b** were elucidated in solution by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Species **31a** was characterized by multinuclear NMR spectroscopy while **31b** was characterized by CHN elemental analysis, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and mass spectrometry. Both species are the only known examples of aluminum- and gallium-bridged *ansa*-zirconocenes. Compound **31b** in combination with MAO was applied and shown to be highly active for ethylene polymerization at room temperature. The activity of **31b** was compared to that obtained for Cp<sub>2</sub>ZrCl<sub>2</sub> using a glass reactor system and was found to be comparable. The influence of precatalyst concentration and ethylene pressure on activity of **31b** was studied.

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## **Dedication**

To God Almighty,

And

To My Parents

Mr. Sunday Hanson of Blessed Memory and Mrs. Edemanwan Sunday.

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## List of Abbreviations

### Abbreviation

Atm.....	atmosphere
BHT.....	2,6-di- <i>tert</i> -butyl-4-methylphenol
CGC.....	constrained geometry complex
Cp.....	cyclopentadienyl
EPDM.....	ethylene-propylene-ethylidene norbornene
EPR.....	ethylene-propylene elastomers
Et.....	ethyl
Flu.....	fluorenyl
HDPE.....	high density polyethylene
HMWPE.....	high molecular weight polyethylene
Ind.....	indenyl
<i>i</i> Pr.....	isopropyl
LCB.....	long chain branching
LDPE.....	linear density polyethylene
LLDPE.....	linear low density polyethylene
MAO.....	methylaluminoxane
MDPE.....	medium density polyethylene
mPE.....	metallocene polyethylene
MS.....	mass spectrometry
MWD.....	molecular weight distribution
NMR.....	nuclear magnetic resonance
PE.....	polyethylene
Ph.....	phenyl
PP.....	polypropylene
Pytsi.....	-C(SiMe <sub>3</sub> ) <sub>2</sub> SiMe <sub>2</sub> (2-C <sub>5</sub> H <sub>4</sub> N)
ROP.....	ring-opening polymerization
SCB.....	short chain branching
<i>t</i> Bu.....	<i>tert</i> -butyl
TM.....	trade mark
TMA.....	trimethylaluminum
UHMWPE.....	ultra high molecular weight polyethylene
VLDPE.....	very low density polyethylene
ZCPs.....	zirconocenophanes ( <i>ansa</i> -zirconocenes)
Z-N catalysts.....	Ziegler-Natta catalysts

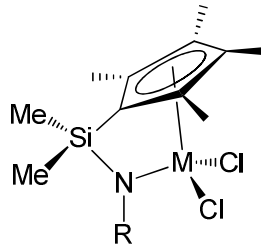
# 1 Introduction

## 1.1 Polyolefin Production

Polyolefins have been widely acclaimed as the largest volume polymers in the plastic industry today with consumption reaching 117 million tons in 2007.<sup>1,2,3</sup> Polyolefin comprises polyethylenes (PE), polypropylenes (PP), and other specialty materials such as ethylene-propylene elastomers (EPR) and ethylene-propylene-ethylidene norbornene (EPDM). Polyethylene consumption in 2007 was about 71 million tons and is expected to grow to 88 million tons by the year 2012<sup>1</sup> making it the most widely used polymer in the world today.<sup>4</sup> To meet this growing demand, more versatile catalyst systems are needed. From the 1930s to date, several generations of catalysts have been employed in polymerizing olefins: from the high-pressure free radical process of the 1930s,<sup>3</sup> the Phillips and Ziegler-Natta catalysts (Z-N catalysts) of the 1950s to the metallocene and post-metallocenes era of the last three decades. All of these catalysts have continued to make huge impacts in the polyolefin industry.

Metallocene and non-metallocene catalysts which were hitherto unexplored in the industry have gained wide usage today with the commercialization of metallocene and non-metallocene catalysed polymers.<sup>3</sup> Exxon (now ExxonMobil) first launched its EXXPOL<sup>TM</sup> technology, a metallocene based technology in 1991 using conventional Kaminsky-typed unbridged bis(cyclopentadienyl) catalysts system while in 1992, Dow launched its INSITE technology based on constrained geometry catalyst (CGC) systems (Figure 1.1).<sup>3</sup> Both catalyst systems produce polymers with improved properties and processability.<sup>3,4,5</sup> Exxon's EXACT<sup>TM</sup> plastomers, EXCEED<sup>TM</sup> and ENABLE<sup>TM</sup> metallocene polyethylene (mPE), and Dow's

AFFINITY polyolefin plastomers POPs (CGCs), ENGAGE (ethylene–octene copolymer) and ELITE polyethylene are all made through metallocene technology.<sup>3,4</sup>

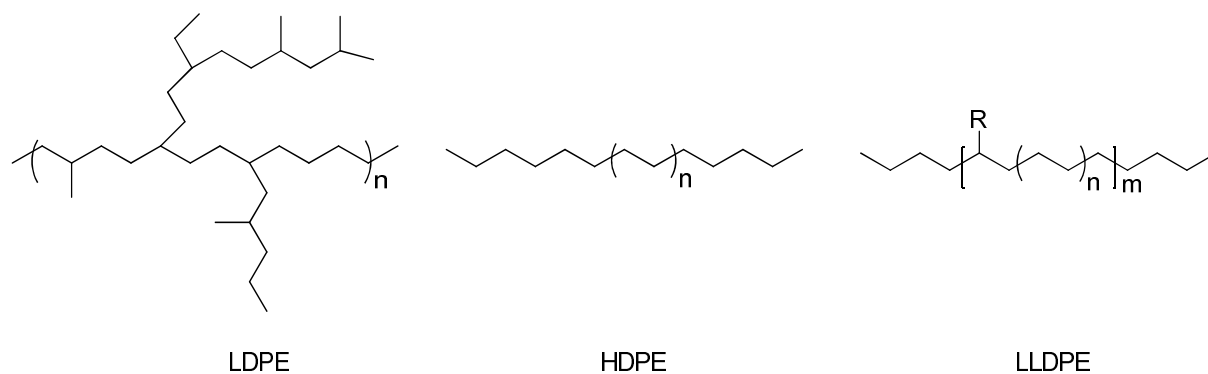


**Figure 1.1.** Constrained geometry complex.

Though the commercialization of metallocene catalysts in the polyolefin industry is still in its infant stage, it is believed that metallocene catalysts will replace the known traditional catalyst families in the near future.<sup>6</sup>

## 1.2 Classification of Polyethylene and their Applications

PE can be classified into several different categories based on density, branching and molecular weight. The classes are low density polyethylene (LDPE), high density polyethylene (HDPE), linear low density polyethylene (LLDPE), very low density polyethylene (VLDPE), high molecular weight polyethylene (HMWPE), ultrahigh molecular weight polyethylene (UHMWPE), amongst others.<sup>3,4</sup> Three classes of polyethylene are shown in Figure 1.2.<sup>4</sup>



**Figure 1.2.** Types of polyethylene.

### 1.2.1 Low Density Polyethylene (LDPE)

This is the first type of PE to be produced. Discovered in the 1930s by The Imperial Chemical Industry, LDPE is produced by free radical initiated polymerization process.<sup>3</sup> LDPE contains many long chain branches of undetermined length and short branches of mostly two to four carbons along the polymer backbone. The long branches have a significant effect on the melt properties, while the short branches affect the crystallinity. LDPE has a density range of 0.915-0.93 g cm<sup>-3</sup> with a melting point range of 106-120 °C and a percentage crystallinity of 40-60%.<sup>3</sup> These polymeric materials are held together by weak intermolecular forces resulting in their low tensile strength and increased ductility.

### 1.2.2 High Density Polyethylene (HDPE)

HDPE is PE with fewer or no measurable chain branching (linear backbone)<sup>3,4</sup> and was first developed in the 1950s. The molecular weight of HDPE is about 200,000 g mol<sup>-1</sup> with a density range of 0.94-0.965 g cm<sup>-3</sup> or greater.<sup>3,4</sup> Due to this high density, these materials possess a higher melting point (125-135 °C) and a higher percentage crystallinity (65-80%) than those of LDPE.<sup>3,4</sup> HDPE can be produced using Phillips catalysts, Z-N catalysts or metallocene catalysts.



These polymeric materials are held together by stronger intermolecular force resulting in high tensile strength, high melt-fracture resistance and poor toughness.

### **1.2.3 Linear Low Density Polyethylene (LLDPE)**

LLDPE is PE formed from copolymerization of ethylene with  $\alpha$ -olefins.<sup>3,4</sup> The density ranges from 0.91-0.94 g cm<sup>-3</sup> with melting points of approximately 120-125 °C.<sup>3</sup> LLDPEs are polymers with linear backbones and a significant number of short chain branches. These polymers can be made using metallocene catalysts. LLDPE possesses higher tensile strength and exhibits higher impact, stress and puncture resistance than LDPE.

### **1.2.4 Ultra High Molecular Weight Polyethylene (UHMWPE)**

UHMWPE is PE with very high molecular weight, usually between 3-6 x 10<sup>6</sup> g mol<sup>-1</sup> and density range of 0.930-0.935 g cm<sup>-3</sup>.<sup>3,4</sup> The polymer molecular weight is so high that it can only be measured by its intrinsic viscosity and not by conventional means.<sup>4</sup> UHMWPE can be made using any catalyst, but Z-N catalysts are the most common. UHMWPE have outstanding toughness, excellent wear or abrasion resistance and very good chemical resistance (chemical inertness).<sup>4</sup> More than 90% of the UHMWPE produced in the world is used industrially.<sup>4</sup>

### **1.2.5 Other Classes of Polyethylene**

Other classes of polyethylene include medium density polyethylene (MDPE) with a density range of 0.926-0.940 g cm<sup>-3</sup> and can be produced using Philips catalysts, Z-N catalysts or metallocene catalysts. MDPE possesses better stress cracking resistance than HDPE. Very low density polyethylene (VLDPE) has a density range of 0.880-0.915 g cm<sup>-3</sup>. VLDPE, just like LLDPE, is a linear polymer with a high level of short chain branches and can be produced by

copolymerization of ethylene with  $\alpha$ -alkenes. They are commonly produced using metallocene catalysts.

### **1.2.6 Applications of Polyethylene**

Polyethylene and ethylene-based copolymers find major applications in packaging, consumer and industrial products which include garbage bags, plastic bags, industrial packaging films, food packaging films, rigid food containers, hose and tubing, ice and frozen food bags, plastics, pipes, wire and cable coatings and coverings, storage containers and other products that must withstand a relatively long service life.<sup>3</sup> LLDPE is predominantly used in film applications due to its toughness, flexibility and relatively high transparency. UHMWPE is used for applications that require toughness. It is used in making machine parts, moving parts, bearings, artificial joints, such as those used for hip and knee replacements (implants),<sup>4</sup> among others.

### **1.3 Catalysts for Polyethylene Production**

Several catalysts are being used for the production of polyethylene. They are however classified into homogenous and heterogeneous catalysts. Heterogeneous catalytic systems are those systems in which the catalysts are being dispersed on solid surface or supports, while in homogeneous catalytic systems, the catalysts are dissolved in the reaction medium.<sup>7</sup> Phillips and Z-N catalysts are the known examples of heterogeneous catalysts, while metallocene and post metallocene catalysts are examples of homogeneous catalysts.

### 1.3.1 Heterogeneous Catalysts

#### 1.3.1.1 Phillips Catalysts

Phillips catalyst, developed simultaneously as the Z-N catalysts in 1955, is made of chromium oxide ( $\text{CrO}_3$ ) on silica ( $\text{SiO}_2$ ) or alumina ( $\text{Al}_2\text{O}_3$ ) support. It is one of the main industrial catalysts for ethylene polymerization.<sup>7-12</sup> It is responsible for the production of about one third of the world's HDPE, with abilities to copolymerize ethylene with  $\alpha$ -olefins (1-butene, 1-hexene).<sup>8,9,12-14</sup> About 7 million tons of commercial polyethylene (nearly 40% of all PE produced worldwide) is produced commercially using these catalysts.<sup>7a,14</sup> Phillips catalysts can produce HDPE with abilities to copolymerize ethylene with some  $\alpha$ -olefins<sup>12</sup> but the active sites are unknown. More so, only a small fraction of the chromium centers are known to be active.<sup>12,13</sup>

The Cr catalysts, as they are sometimes called, produce polymers with a broad molecular weight distribution typical for multiple site catalysts. The polydispersity index (PDI) of Cr catalysts is within the range of 10-30.<sup>9</sup> The catalysts are activated thermally, by ethylene monomer, and by CO.<sup>7,14</sup> During activation, Cr catalysts are reduced from Cr(IV) to Cr(II) with the formation of formaldehyde as a byproduct, as detailed in the mechanistic study recently reported by Fang *et al.*<sup>7</sup> To be able to access the oxidized surface, CO (or  $\text{H}_2$ ) is used as a reducing agent resulting in the formation of  $\text{CO}_2$  (or  $\text{H}_2\text{O}$ ) and the presumed active Cr(II) species.<sup>14</sup> Characterization of the active surface sites, however, remain a complex problem.<sup>12</sup>

Though with a relatively low activity, Cr catalysts polymerize ethylene under comparatively mild conditions (65-180 °C; 25-40 bar)<sup>9</sup> thereby reducing industrial production cost, hence its wide usage in industry. Their low activity and poor selectivity however, limit their use for the production of crystalline polypropylene or any other polyolefin.<sup>9,12</sup> The use of Higher

ethylene pressure, lower polymerization temperature and addition of hydrogen favors the production of HMWPE.<sup>9,12</sup>

### 1.3.1.2 Ziegler-Natta Catalysts (Z-N catalysts)

With an annual PP production exceeding 30 million metric tons for various applications, Z-N catalysts, developed in the 1950s, are known to be very efficient for ethylene and propylene homo- and co-polymerizations.<sup>9</sup> These systems are widely used in the polyolefin industry for the production of PE (LLDPE and HDPE) and isotactic PP at fairly low temperature and pressure (70-105 °C and 25-40 bar).<sup>9,15</sup> Though Z-N catalysts have been used to copolymerize ethylene with other  $\alpha$ -olefins to form LLDPE, they become grossly inefficient when the  $\alpha$ -olefins contains more than eight carbon atoms.<sup>16</sup> Z-N catalysts are catalysts made up of titanium chloride (TiCl<sub>4</sub>) on MgCl<sub>2</sub> support with aluminum alkyls as activator. The activator serves as an alkylating and reducing agent.<sup>9,15</sup> It reduces Ti(IV) ions to Ti(III) via a bimolecular reductive elimination.<sup>9</sup> Though Ti ions of various oxidation states (+2, +3, +4) are presumed to be the active oxidation states for olefin polymerization,<sup>9,17-18</sup> the active sites are however not precisely known.

Several generations of Z-N catalysts are known.<sup>19</sup> Every new generation is equipped with more capabilities. Initially a combination of AlR<sub>3</sub>/TiCl<sub>3</sub> was used. Currently, MgCl<sub>2</sub>/TiCl<sub>4</sub>/AlR<sub>3</sub> are used with some internal and external electron donors (modifiers) such as ethylbenzoate, aromatic esters phthalates, diethers, alkoxy silanes as tacticity promoters for the production of isotactic propylene.<sup>9,19</sup> The internal donors (additives added to the solid catalysts) and the external donors (additives added to the polymerization system) interact with the catalysts and prevent the formation of the non-stereospecific sites or convert them (the non-stereospecific sites) to more isospecific sites while at the same time help in the formation of highly isospecific

sites.<sup>19</sup> The mechanism of how such isospecific sites are formed is however unclear.<sup>19</sup> The inability to tune heterogeneous catalysts to obtain different types of polyolefin limits their use.

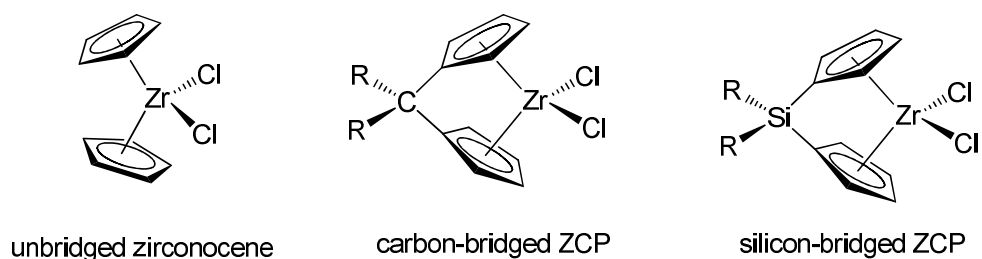
Despite its versatility in the production of PE and highly crystalline isotactic PP with high activity,<sup>7</sup> Z-N catalysts are known to produce polymers with broad molecular weight distributions (PDI: 4-8) and has poor comonomer incorporation capabilities.<sup>9</sup> More so, the active sites of Z-N catalysts are not precisely known. However, recent generations have been shown to copolymerize ethylene with 1-butene, 4-methylpentene or 1-hexene with the formation of short chain branches on the linear polymer chain.<sup>9,16</sup> Beside isotactic PP, no other type of crystalline PP, syndiotactic, stereoblock or other poly( $\alpha$ -olefin) can be produced with these catalysts. Though a combination of isotactic and syndiotactic and stereoblock chains in the same polymer framework have been reported using this catalyst.<sup>19</sup>

### **1.3.2 Homogenous Catalysts**

Homogenous catalysts for olefin polymerization are basically classified into two categories; metallocene and non-metallocene catalysts (also referred to as post-metallocene catalysts).

#### **1.3.2.1 Metallocene Catalysts**

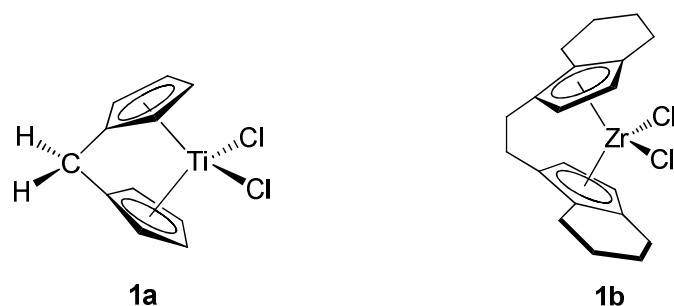
These are catalysts that contain a transition metal sandwiched between two cyclopentadienyl (substituted or unsubstituted) ligand systems. Unbridged and bridged metallocene complexes are the two main types known (Figure 1.3).



**Figure 1.3.** Unbridged and bridged zirconocene catalysts.

Metallocene catalysts based on group-4 metals form the bulk of catalysts widely studied till date, with zirconium-based catalysts dominating. Sinn *et al.* and Kaminsky *et al.* in the late 1970s and early 1980s, respectively, became the first researchers to report on the polymerization of ethylene with high activity using  $\text{Cp}_2\text{TiMe}_2$ ,  $\text{Cp}_2\text{ZrMe}_2$  and  $\text{Cp}_2\text{ZrCl}_2$  with MAO as a cocatalyst.<sup>20,21,22</sup> Since then, many other metallocene catalysts have been synthesized and used for the polymerization of ethylene, propylene and other  $\alpha$ -olefins.<sup>23</sup>

Although unbridged metallocene complexes that possess high activity exist, the bridged counterparts (also called *ansa*-metallocene) have continued to dominate the area of olefin polymerization.<sup>24</sup> The study of *ansa*-metallocene catalysts started in 1970 with the synthesis of the first group-4 *ansa*-metallocene complex  $\text{H}_2\text{C}(\eta^5\text{-C}_5\text{H}_4)_2\text{TiCl}_2$  (**1a**) by Katz and Acton,<sup>25</sup> but not much attention was drawn to it until 1985, when Kaminsky and coworkers<sup>26</sup> reported the polymerization of propene and 1-butene employing Brintzinger's chiral ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (**1b**)<sup>27</sup> using MAO as a cocatalyst (Figure 1.4).



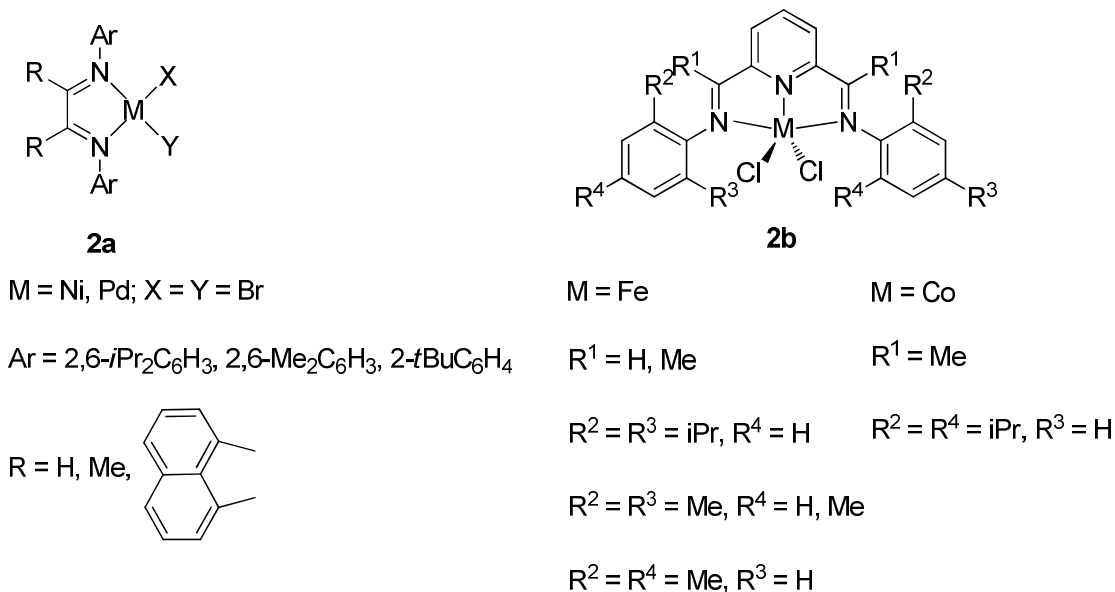
**Figure 1.4.** First group-4 *ansa*-metallocene complex and Brintzinger's ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride.

The activity, stereoselectivity and crystallinity of this catalyst were remarkable. Several other *ansa*-zirconocene catalysts have been reported with abilities to produce polymers with different activity, degree of branching and tacticity. These catalysts have continued to make huge impacts in the polyolefin industry with the commercialization of metallocene-catalyzed polyolefins in 1991 by ExxonMobil.<sup>3a,28</sup>

Polymers obtained using a metallocene catalyst possess fascinating properties such as high impact strength, improved clarity, high flexibility, narrow molecular weight distribution (MWD) and uniform comonomer distribution (CD) which makes them suitable for a wide variety of applications which were hitherto unattainable with earlier versions of olefin polymerization catalysts.<sup>28</sup> MWD, CD and chain branching control the rheological and processing behaviors of PE.<sup>28</sup> The ability to tune the catalyst based on the understanding of the influence of the catalyst structure on the activity, MWD, stereoselectivities and properties of the resulting polymer is behind the tremendous advances already made in this area of research in academic laboratories and in industry.<sup>3-5</sup>

### 1.3.2.2 Non-Metallocene Catalysts

Non-metallocene catalysts also known as post-metallocene catalysts represent the newest family of catalysts to be developed for the polymerization of ethylene,<sup>29</sup>  $\alpha$ -olefins,<sup>30</sup> cyclic olefins,<sup>31</sup> *cis*- and *trans*-2-butene,<sup>32</sup> and copolymerization of ethylene/propylene with functionalized vinyl monomers.<sup>33,34</sup> Brookhart and co workers first reported an example of this type of catalysts in the 1990s when they used  $\alpha$ -diimine ligands to synthesize what is known today as one of the most active catalysts for olefin polymerization.<sup>35-37</sup> Several other non-metallocene catalysts have appeared in the literature.<sup>35,36</sup> They can be used for the copolymerization of ethylene with polar monomers such as acrylates and acetates due to their low propensity to bind with oxygen.<sup>37</sup>



**Figure 1.5.** Bidentate and tridentate nitrogen-based non-metallocene catalysts.

The catalysts are based on main group and late transition metals equipped with bidentate or tridentate (pincer) nitrogen-based ligands containing bulky aryl substituents (Figure 1.5).



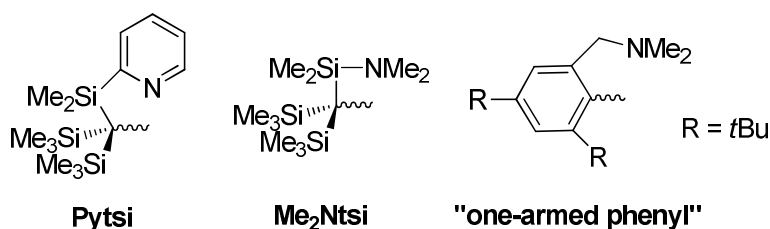
$\alpha$ -Diimine complexes of Ni and Pd (**2a**)<sup>30,33,37</sup> and tridentate bis(imino)pyridine complexes of Fe and Co (**2b**)<sup>38,39</sup> polymerize ethylene and other  $\alpha$ -olefin with high activities,<sup>36</sup> degree of branching and stereoselectivity.<sup>30,36,37</sup> Complexes of rhodium,<sup>40,41</sup> platinum,<sup>41</sup> and other main group and early transition metals have also been reported as olefin polymerization catalysts.<sup>36</sup> Non-metallocene catalysts can produce HMWPE with narrow PDIs, moderate to high activity and some degree of branching.<sup>30,37</sup> Though some non-metallocene catalysts show higher activity for polymerizing ethylene and other higher  $\alpha$ -olefins, the majority of them generally show lower activity than that of metallocene catalysts.<sup>35</sup>

The bulkiness of the aryl substituents, monomer concentration, and temperature are known to influence the activity of this new family of catalysts. The bulky aryl substituents on the nitrogen donors are believed to provide steric protection to the amide functionality from attack by cocatalysts which may lead to catalysts deactivation,<sup>42</sup> prevent the formation of bis-chelate complexes, prevent dimerization of  $\alpha$ -olefins or formation of oligomers due to increase rate of chain transfer<sup>29,31</sup> by blocking associative olefin exchange and thus retard chain termination or transfer, thereby leading to the production of high molecular weight polymer.<sup>32-33,35,37</sup> Brookhart *et al.* reported the dimerization of  $\alpha$ -olefins when the steric bulk on the aryl imino substituents on the bis(imino)pyridine complexes was reduced.<sup>43</sup>

Industrially, these catalysts have been used by ExxonMobil in 2003 for the production of VISTAMAXX (propylene-ethylene copolymers) and the Dow Company in 2006 for the production of ethylene-octene block copolymers (INFUSE<sup>TM</sup>OBCs), VERSIFY<sup>TM</sup> plastomers and elastomers (propylene-ethylene copolymers) with uniform copolymer distribution.<sup>3a,44-46</sup>

## 1.4 Strained and Unstrained Sandwich Compounds

Metallocene compounds have been known for decades; the earliest example being ferrocene and ferrocene derivatives.<sup>47,48</sup> Attempts to modify this compound and explore its properties led to the inclusion of different bridging moieties in between the two cyclopentadienyl rings giving rise to what is known today as ferrocenophanes.<sup>48</sup> Compounds of this nature are found to possess ring strain due to the inclusion of the bridging moieties. The ring strain is subsequently used as a driving force towards obtaining metal-containing polymers via ring opening polymerization (ROP).<sup>48,49</sup> Polyferrocenylsilanes, polymers obtained from sila[1]ferrocenophanes, are well studied examples of such metal-containing polymers.<sup>48</sup> Several ferrocenophanes and other metallocenophanes bearing different bridging units have been reported in the literature.<sup>48</sup> Ferrocenophanes containing heavier group-13 elements (Al, Ga) in the bridge have been synthesized and applied for ROP by the Müller group.<sup>49</sup> Intramolecularly coordinating ligands of the type  $-\text{C}(\text{SiMe}_3)_2(\text{SiMe}_2\text{R})$  with R being  $\text{NMe}_2$  ( $\text{Me}_2\text{Ntsi}$  ligand) and  $2\text{-C}_5\text{H}_4\text{N}$  (Pytsi ligand; to be discussed later), first synthesized by Eaborn and coworkers,<sup>50</sup> and other coordinating ligands such as the recently synthesized “one armed phenyl” ligand (Figure 1.6) were employed in the syntheses of these heavier group-13-bridged [1]ferrocenophanes.<sup>49</sup>



**Figure 1.6** Intramolecularly coordinating ligands.

Metallocenophanes of the group-4 elements (commonly called *ansa*-metallocenes), on the other hand, have attracted much interest due to their importance as precatalysts for olefin

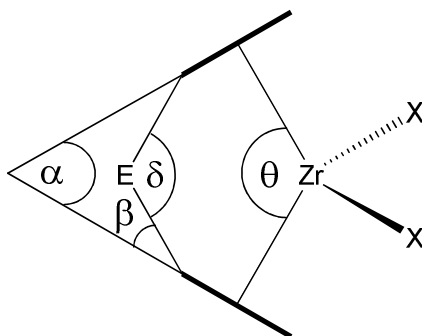
polymerization.<sup>51a-g</sup> Notable in this class of compounds is [1]zirconocenophanes, otherwise called *ansa*-zirconocene. They are inherently tilted (bent metallocene) and do not possess any ring strain hence do not undergo ring-opening polymerization.<sup>51g</sup>

## 1.5 General Structure and Synthetic Routes to *ansa*-Zirconocene Compounds

### 1.5.1 General Structure of *ansa*-Zirconocene Compounds

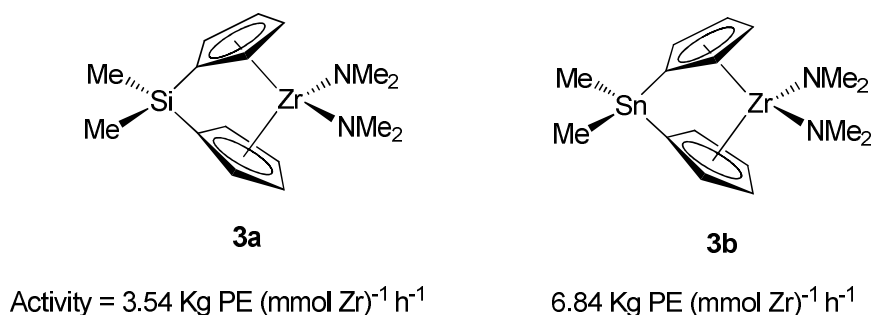
*ansa*-Zirconocene complexes are zirconocene complexes consisting of two cyclopentadienyl-type ligands such as cyclopentadienyl, indenyl and fluorenyl (substituted or unsubstituted), either the same or different, tethered by a bridging unit or interannular bridge.<sup>51a</sup> The *ansa* bridge or interannular bridge is the element or bridging unit between the two cyclopentadienyl-type ligands. Examples of unbridged and bridged ZCP are shown in Figure 1.3. Several *ansa*-zirconocene compounds with different *ansa* bridges are known in literature.<sup>51a-g</sup> It has been widely accepted that introducing substituents at different positions on the two aromatic rings and/or the bridge modifies not only the steric and electronic environment in the molecule but also the symmetry<sup>51e-f</sup> which automatically affects the activity and stereoselectivity of the catalysts. The bridging atoms not only restricts free rotation of the aromatic rings, which gives the catalyst a particular orientation, but also affect the dihedral angle and increase the rigidity of the molecular framework.<sup>51b</sup>

The defining angles of ZCPs are as shown in Figure 1.7.<sup>51d</sup> The degree of ring tilt or tilt angle,  $\alpha$  is the angle between the planes of the two Cp rings. The value of  $\alpha$  largely depends on the size of the bridging element. As the size of the bridging element becomes smaller, the value of the tilt angle  $\alpha$  gets larger and vice versa. The angle,  $\beta$  measures the  $\text{Cp}_{\text{centroid}}\text{-C}_{\text{ipso}}\text{-E}$  angle and signifies the amount of ring strain caused by the bridge while the angle  $\delta$  symbolizes the  $\text{C}_{\text{ipso}}\text{-E-C}_{\text{ipso}}$  angle. The angle  $\theta$  defines the  $\text{Cp}_{\text{centroid}}\text{-Zr-Cp}_{\text{centroid}}$ .



**Figure 1.7.** Component angles  $\alpha$ ,  $\beta$ ,  $\delta$ , and  $\theta$  of ZCPs.

Reducing the size of the bridge increases the reaction space around the group-4-metal center which subsequently improves the catalytic activity. For example, replacing  $[-CH_2CH_2-]$  with  $[-SiMe_2-]$  increases the tilt angle,  $\alpha$ , with a corresponding increase in the degree of polymerization and isotacticity.<sup>51c</sup> However, generally, the effect of ring tilt on the olefin polymerization activity of metallocene catalysts is unpredictable.<sup>48a</sup> The effect of bridging elements has been widely studied by Herrmann *et al.*<sup>52a</sup> and others.<sup>52b-c,53</sup> Herrmann *et al.* observed that by replacing the silicon in **3a** with tin (**3b**), the activity increase by approximately two fold (Figure 1.8).<sup>52a</sup>

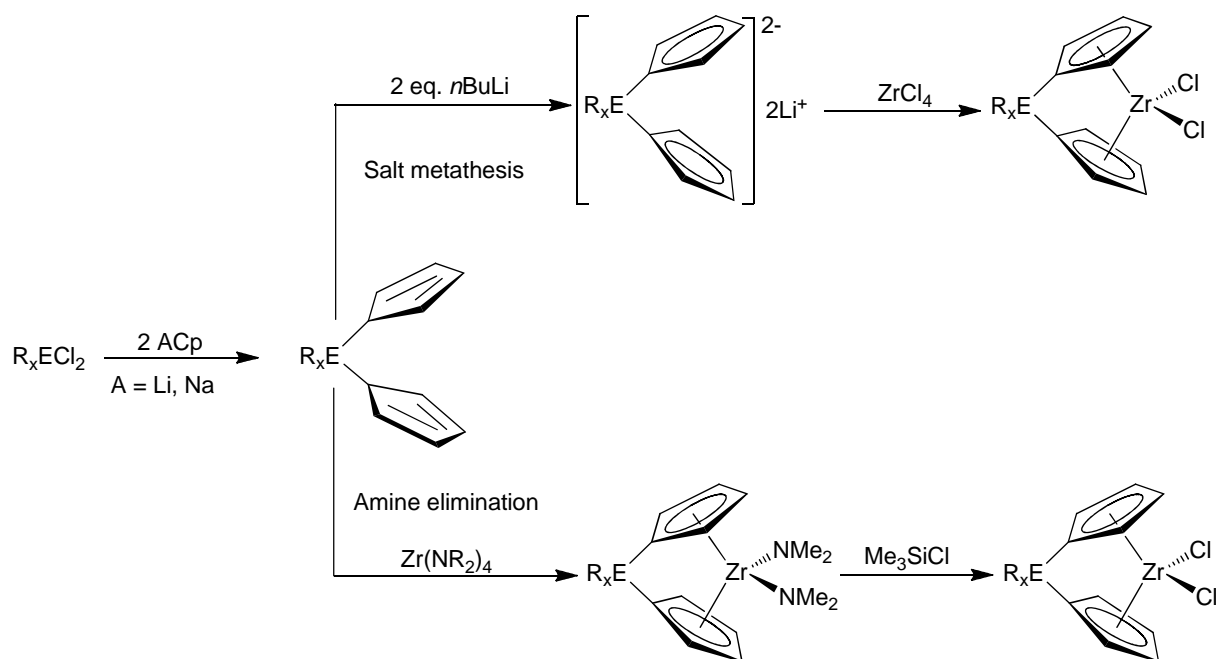


**Figure 1.8.** Effect of bridging elements on catalytic activities.

### 1.5.2 Synthetic Routes to *ansa*-Zirconocene Compounds

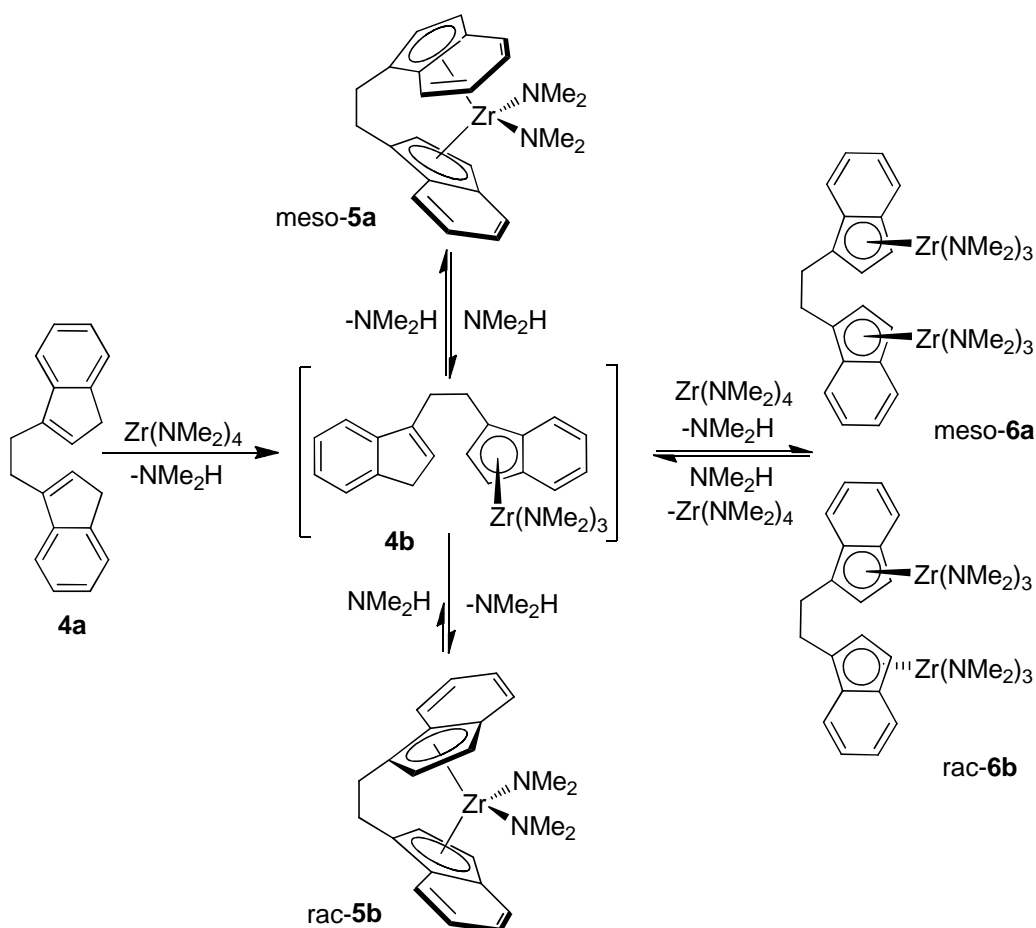
Several routes to synthesize group-4 *ansa*-zirconocene complexes are known. The widely employed route is, however, the flytrap route which comprises of the salt metathesis and the amine elimination (Scheme 1.1). The salt metathesis method involves the reaction of a dilithio salt of ligand precursors with a group-4-metal tetrahalide ( $MCl_4$ ) while the amine elimination involves the reaction of an element cyclopentadienide compound with a group-4-metal tetraamide [ $M(NR_2)_4$ ]. Although the former is more often applied than the latter, the latter has proven to be a more promising route. Salt metathesis route often results in low yield and poses difficulty in isolation and purification.<sup>54</sup> They are also not favorable in cases where the ligand precursors are resistant to alkylation or are susceptible to cleavage of the metal-Cp bonds.<sup>52a</sup>

**Scheme 1.1.** Synthetic routes to group-4 *ansa*-zirconocene compounds.



Herrmann and coworkers,<sup>52a,54</sup> Ashe *et al.*<sup>55</sup> and Jordan's group<sup>56</sup> have synthesized various ZCPs including the only reported Sn-bridged ZCP<sup>52a</sup> using the amine elimination route in moderate to high yield. Although the amine elimination method has been embraced, the control of the amine produced in such reactions remains a challenge as the presence or absence of the amine may be the determining factor in obtaining the desired *ansa*-zirconocene compound. The effect of the presence or absence of dimethylamine produced in the reaction vessel as reported by Jordan *et al.*<sup>56</sup> is shown in Scheme 1.2.

**Scheme 1.2.** Effects of dimethylamine in amine elimination reactions.



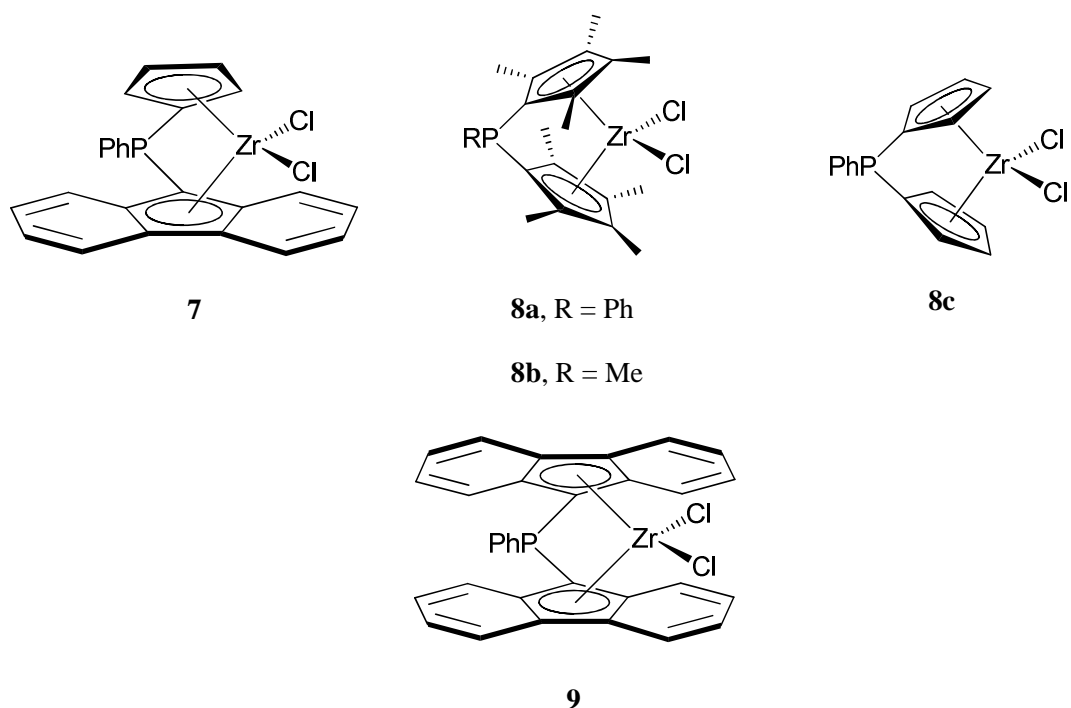
In the presence of  $\text{NMe}_2\text{H}$ , a mixture of products **4a**, **4b**, **5** and **6** were obtained, while the absence of it, led to the formation of the bridged species **5a** and **5b** in the ratio 1:1 (Scheme 1.2). However, dimethylamine was needed for the conversion of **6** to **5**.<sup>56</sup>

### 1.5.3 Known *ansa*-Zirconocene Compounds

Several ZCPs bearing different bridging groups have been reported in literature using the various synthetic routes. Group 15, 14 and 13-bridged ZCPs are known.<sup>51</sup> Some of these compounds have been shown to be highly active for olefin polymerization.

#### 1.5.3.1 Group-15-Bridged Zirconocenophanes

ZCPs bearing group-15 elements in the bridge are rare in the literature. So far, only phosphorus-bridged ZCPs are reported. Schaverien *et al.* reported the synthesis and propylene polymerization activity of  $\text{PhP}(\text{Flu})(\text{Cp})\text{ZrCl}_2$  (**7**) and some phosphorus-bridged ZCPs. The catalytic activities of these compounds were however low.<sup>57</sup> Parkin *et al.*<sup>53</sup> showed that, when activated with MAO,  $\text{PhP}(\text{C}_5\text{Me}_4)_2\text{ZrCl}_2$  (**8a**) is active for ethylene polymerization at room temperature with activity comparable to that of  $\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)_2\text{ZrCl}_2$  (**11b**). Surprisingly, no polymerization data was reported for  $\text{MeP}(\text{C}_5\text{Me}_4)_2\text{ZrCl}_2$  (**8b**)<sup>53</sup> and  $\text{PhP}(\text{C}_5\text{H}_4)_2\text{ZrCl}_2$  (**8c**).<sup>58</sup> Alt and Jung reported low activities for ethylene polymerization with  $\text{PhP}(\text{Flu})_2\text{ZrCl}_2$  (**9**) and attributed the low activity to increased electron density around the metal centre (due to the presence of the  $-\text{PR}$  moiety) which hindered olefin insertion.<sup>59</sup> Examples of some of the group-15-bridged ZCPs reported in the literature are shown in Figure 1.9.



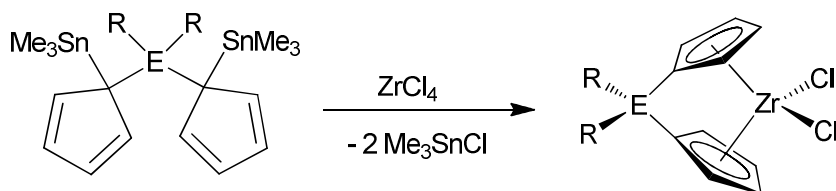
**Figure 1.9.** Examples of group-15-bridged ZCPs.

### 1.5.3.2 Group-14-Bridged Zirconocenophanes

Several ZCPs bearing group-14 elements as bridges are known.<sup>51,60</sup> They form the bulk of ZCPs reported in the literature. The reason for this is attributed to the fact that the precursors are either easily prepared or are commercially available.<sup>61,62</sup> Common bridges found in literature are  $R_2C-$ ,  $R_4C_2-$ ,  $R_2Si-$  and  $R_4Si_2$ . Many of the ZCPs with these bridging units have been found to be active for olefin polymerization.<sup>51,60</sup> They are prepared via the salt metathesis route using dilithio salt precursor or alternatively by transmetallation of distannylated bis(cyclopentadienyl) ligand with metal tetrachloride (Scheme 1.3).<sup>63</sup> The amine elimination route can also be used.<sup>52a,56</sup>

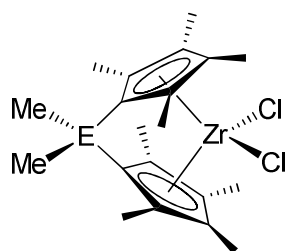


**Scheme 1.3.** Reaction of distannylated complexes with zirconium tetrachloride.

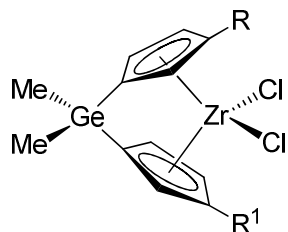


Carbon-bridged ligands are often prepared by reduction of fulvene. Silicon-bridged compounds are prepared by the reaction of a dichlorosilane (relatively inexpensive or easy to prepare) with metal cyclopentadienide reagents. Germanium-bridged ligands are prepared in a similar way as their silicon analogues. Although similar methods are used in the preparation of group-14-bridged ZCPs, very few germylene- and stannylene-bridged ZCPs have so far been reported.<sup>51e-f,52a</sup> Examples of group-14-bridged ZCPs are shown in Figure 1.10.

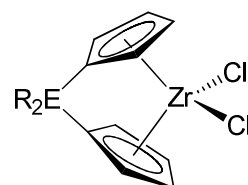
Herrmann's group<sup>52a</sup> synthesized the only tin bridged *ansa*-zirconocene complex, Me<sub>2</sub>Sn(C<sub>5</sub>H<sub>4</sub>)<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (**3b**) (Figure 1.7) by reacting (CH<sub>3</sub>)<sub>2</sub>Sn(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> with Zr(NMe<sub>2</sub>)<sub>4</sub>. When activated with MAO, the complex was found to be as active in ethylene polymerization as the silicon analogue but produced PE with higher MW. Kaminsky *et al.*<sup>64</sup> studied the polymerization of ethylene and propylene using different group-14-bridged ZCPs under the same conditions. A summary of the various group-14-bridged ZCP active for ethylene polymerization are shown in Table 1.1. It is asserted that silicon-bridged metallocenes are more active than their carbon-bridged counterparts.<sup>65</sup> Some of the group-14-bridged ZCPs have been shown to be active for both ethylene and propylene polymerization.<sup>66</sup> Compound **10c** and **11a-d** have been shown to be active for ethylene polymerization even at high temperatures. Employing **11d** as a precatalysts, activity as high as 10.3 x 10<sup>6</sup> g PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> was achieved.<sup>67</sup> **10c** showed the highest activity at 80 °C while **11b**, **11d**, and **11e** showed the highest activity at 60 °C.



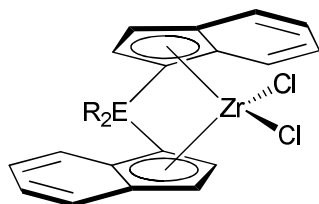
**10a** E = C  
**10b** E = Si  
**10c** E = Ge



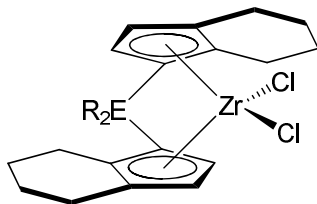
**11a** R = R<sup>1</sup> = H  
**11b** R = R<sup>1</sup> = *t*Bu  
**11c** R = R<sup>1</sup> = Me  
**11d** R = *t*Bu, R<sup>1</sup> = H  
**11e** R = Me, R<sup>1</sup> = H



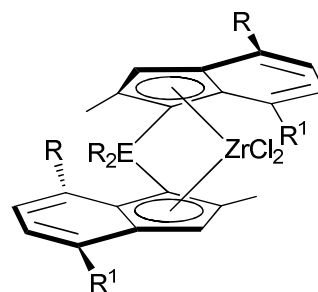
**12a** ER<sub>2</sub> = CMe<sub>2</sub>  
**12b** ER<sub>2</sub> = SiMe<sub>2</sub>  
**12c** ER<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>



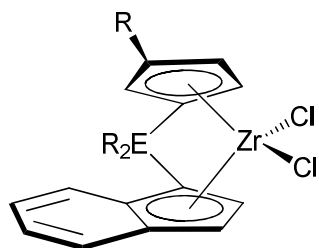
**13a** ER<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>  
**13b** ER<sub>2</sub> = SiMe<sub>2</sub>  
**13c** ER<sub>2</sub> = SiPh<sub>2</sub>



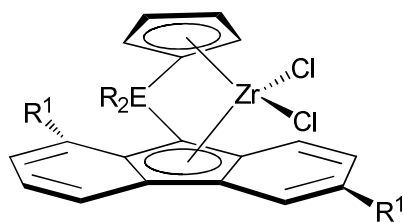
**14** ER<sub>2</sub> = SiMe<sub>2</sub>



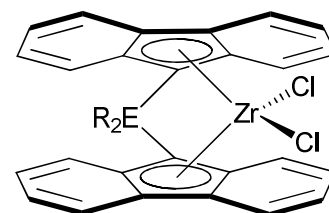
**15a** ER<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>, R = R<sup>1</sup> = Me  
**15b** ER<sub>2</sub> = SiMe<sub>2</sub>, R = R<sup>1</sup> = Me  
**15c** ER<sub>2</sub> = SiMe<sub>2</sub>, R = H, R<sup>1</sup> = Ph



**16a** ER<sub>2</sub> = CPh<sub>2</sub>, R = H  
**16b** ER<sub>2</sub> = CMe<sub>2</sub>, R = H  
**16c** ER<sub>2</sub> = CMe<sub>2</sub>, R = Me



**17a** ER<sub>2</sub> = CPh<sub>2</sub>, R<sup>1</sup> = H  
**17b** ER<sub>2</sub> = CPh<sub>2</sub>, R<sup>1</sup> = *t*Bu  
**17c** ER<sub>2</sub> = CMe<sub>2</sub>, R<sup>1</sup> = H  
**17d** ER<sub>2</sub> = SiMe<sub>2</sub>, R<sup>1</sup> = H  
**17e** ER<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>, R<sup>1</sup> = H



**18a** ER<sub>2</sub> = CMe<sub>2</sub>  
**18b** ER<sub>2</sub> = SiMe<sub>2</sub>  
**18c** ER<sub>2</sub> = C<sub>2</sub>H<sub>4</sub>

**Figure 1.10.** Examples of group-14-bridged ZCPs.

**Table 1.1.** Results of homopolymerization of ethylene<sup>a</sup> at 30°C using *ansa*-zirconocene catalysts

Catalyst	Activity <sup>b</sup>	Molar mass, M <sub>n</sub> (g mol <sup>-1</sup> )
Cp <sub>2</sub> ZrCl <sub>2</sub>	60900	620 000
[(C <sub>5</sub> Me <sub>5</sub> ) <sub>2</sub> ]ZrCl <sub>2</sub>	1300	1500 000
<i>rac</i> -[Et(IndH <sub>4</sub> ) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>1b</b> )	22200	1000 000
<i>rac</i> -[Et(Ind) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>13a</b> )	41100	140 000
<i>rac</i> -[Me <sub>2</sub> Si(Ind) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>13b</b> )	36900	260 000
[Ph <sub>2</sub> Si(Ind) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>13c</b> )	20200	320 000
<i>rac</i> -[Me <sub>2</sub> Si(IndH <sub>4</sub> ) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>14</b> )	30200	900 000
<i>rac</i> -[Et(2,4,7-Me <sub>3</sub> Ind) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>15a</b> )	78000	190 000
<i>rac</i> -[Me <sub>2</sub> Si(2,4,7-Me <sub>3</sub> Ind) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>15b</b> )	111900	250 000
[Me <sub>2</sub> Si(2-Me-4-Ph-Ind) <sub>2</sub> ]ZrCl <sub>2</sub> ( <b>15c</b> )	16600	730 000
[Ph <sub>2</sub> C(Ind)(Cp)]ZrCl <sub>2</sub> ( <b>16a</b> )	3330	18 000
[Me <sub>2</sub> C(Ind)(Cp)]ZrCl <sub>2</sub> ( <b>16b</b> )	1550	25 000
[Me <sub>2</sub> C(Ind)(3MeCp)]ZrCl <sub>2</sub> ( <b>16c</b> )	2700	30 000
[Ph <sub>2</sub> C(Flu)(Cp)]ZrCl <sub>2</sub> ( <b>17a</b> )	2890	630 000
[Me <sub>2</sub> C(Flu)(Cp)]ZrCl <sub>2</sub> ( <b>17c</b> )	2000	500 000

<sup>a</sup> Polymerization conditions: 2.5 bar ethylene, metallocene concentration = 6.25 μmol L<sup>-1</sup>, molar ratio MAO/ metallocene = 250/1

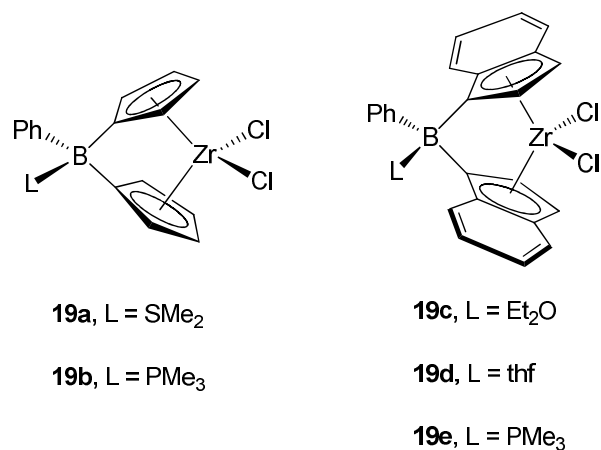
<sup>b</sup> kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>

In a comparative study of the activity of some zirconocene catalysts in ethylene polymerization performed under similar conditions, Quijada *et al.*<sup>65</sup> reported an activity of 30 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> for **12a** [70 °C for 2 h using 1750 equivalents of MAO, 2.0 bar of ethylene pressure and 0.37 mmol L<sup>-1</sup> of catalyst concentration]. They reported an activity of 18400 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> and 20500 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> for **12b** and **13a**, respectively. The polymerization was performed at 60 °C for 30 min using 1750 equivalents of MAO, 1.6 bar of ethylene pressure and 6.7 μmol L<sup>-1</sup> of catalysts concentration.

### 1.5.3.3 Group-13-Bridged Zirconocenophanes

Boron-bridged ZCPs have been extensively studied by Shapiro<sup>48a</sup> and Braunschweig *et al.*<sup>68</sup> However, till date, there is no report in the literature on any other group-13-bridged ZCP. Reetz *et al.*<sup>69</sup> and Shapiro *et al.*<sup>70</sup> synthesized the first examples of boron-bridged (based stabilized) *ansa*-zirconocene complexes (Figure 1.11) using the salt metathesis route. When

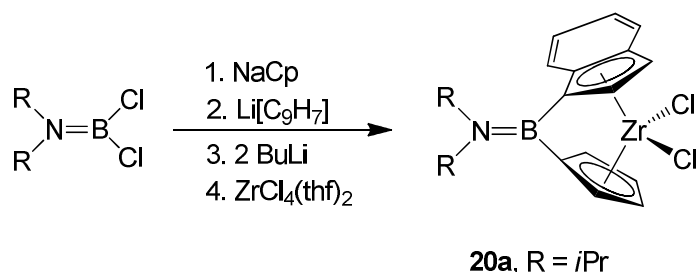
activated with MAO, **19a** was inactive for ethylene polymerization while **19b** produced polyethylene with low activity and low MW.<sup>70</sup> The Lewis acidity of bridging units is believed to enhance catalytic activity,<sup>71</sup> however, the presence of the base is believed to nullify the Lewis acid character of the boron atom.<sup>71</sup>

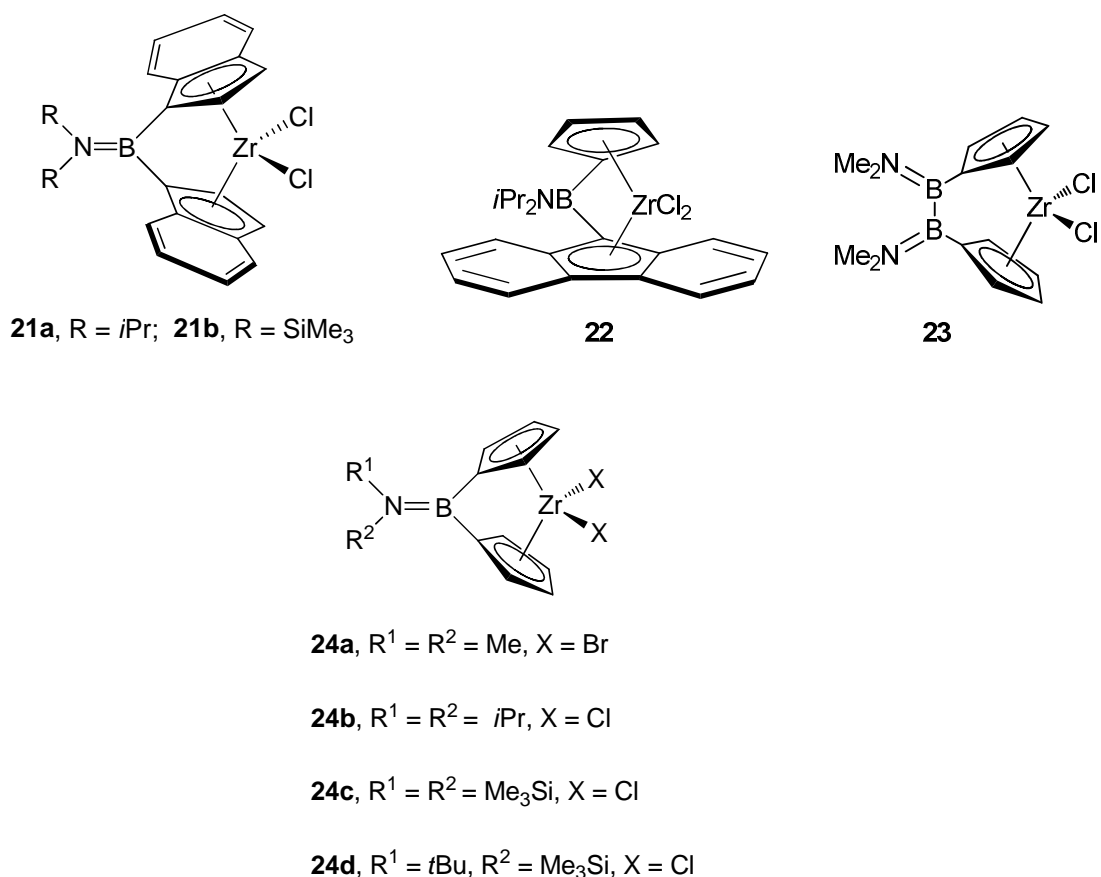


**Figure 1.11.** Examples of base-stabilized, boron-bridged ZCPs.

Base-free boron bridged *ansa*-zirconocene was first reported by Braunschweig and co workers.<sup>72</sup> Since then, several other homoleptic and heteroleptic boron-bridged ZCPs have been reported in the literature.<sup>55,72-73</sup> The synthetic route to heteroleptic B[1]ZCPs is shown in scheme 1.4. Some examples of boron-bridged ZCPs are shown in Figure 1.12.

**Scheme 1.4.** Synthesis of heteroleptic boron-bridged ZCP.





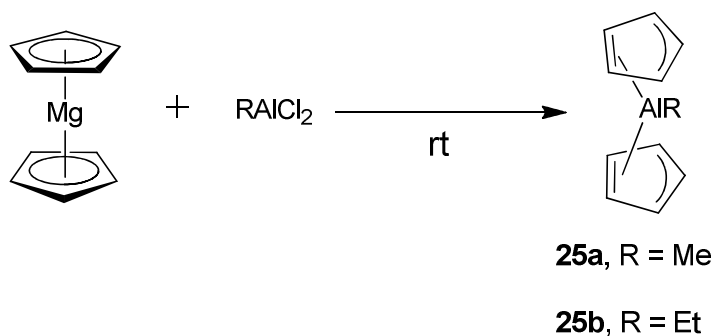
**Figure 1.12.** Examples of base-free, boron-bridged ZCPs.

Ashe *et al.*<sup>73</sup> used **21a** and **22** to copolymerize ethylene with 1-octene in the presence of MAO as a cocatalyst. So far, only very few reports for B[2]ZCPs have so far appeared in the literature. Preliminary for ethylene polymerization show that **23** is active for ethylene polymerization.<sup>74</sup>

In ethylene polymerization, the boron bridging atom being small in size and more Lewis acidic is believed to reduce the electron density around the group-4-metal center, thereby improving the catalytic activity of boron-bridged ZCPs.<sup>68</sup> This has however not been the case as most of the known boron-bridged *ansa*-zirconocenes either show low activity or are inactive for olefin polymerization.<sup>70</sup>

Despite the volumes of reports in the literature for boron-bridged ZCPs, none have been reported for aluminum and gallium. The lack of aluminum and gallium-bridged *ansa*-zirconocene complexes may be attributed to the difficulty involved in synthesizing the monomeric bis(cyclopentadienyl) ligand precursor. Attempts by many researchers to synthesize these compounds have either produced monosubstituted cyclopentadienyl derivatives, dimers, polymers or a mixture of non-isolable or separable products. To date,  $\text{Cp}_2\text{AlR}$  [ $\text{R} = \text{Me}$  (**25a**),  $\text{Et}$  (**25b**)]<sup>75</sup> are the only monomeric alkyl bis(cyclopentadienyl)aluminum compounds that have been isolated and structurally characterized. They were synthesized by reacting magnesocene with the corresponding alkyl aluminum dichloride (Scheme 1.5). The aluminum is bonded to the Cp rings in an  $\eta^2$ -fashion.

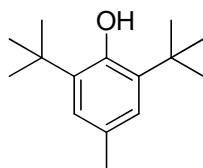
**Scheme 1.5.** Preparation of the first monomeric bis(cyclopentadienyl)aluminum compounds.



Attempts by Beachley and co workers to synthesize the gallium analogue  $\text{RGaCp}_2$  ( $\text{R} = \text{Me}, \text{Et}$ ) were unsuccessful.<sup>76a</sup> Whereas  $\text{MeGa}(\text{C}_5\text{H}_5)_2$ <sup>76a</sup> cannot be isolated as a pure compound from mixtures of several products, X-ray studies identified  $\text{EtGa}(\text{C}_5\text{H}_5)_2$  as a polymer.<sup>76b</sup> By reacting  $\text{GaCl}_3$  with three equivalents of  $\text{LiCp}$  in  $\text{Et}_2\text{O}$ /hexane at ambient temperature, Cowley's group<sup>77</sup> was only able to isolate the ethoxy-bridged dimer  $[(\eta^1\text{-C}_5\text{H}_5)_2\text{GaOEt}]_2$ .

Kunicki *et al.*<sup>78</sup> attempted to synthesize bis(cyclopentadienyl)aluminum isopropoxide by reacting NaCp with Cl<sub>2</sub>Al(OiPr) in toluene. The resulting compound was found to be an oxygen-bridged dimer [(η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>AlOiPr]<sub>2</sub>, both in the solid state and in solution, with the Cp ligands coordinated to the Al in an η<sup>1</sup> fashion.

Knowing that the structure and reactivity of cyclopentadienylaluminum and gallium compounds are sensitive to the nature of the other ligands on the aluminum and gallium centers<sup>79-81</sup> and that the use of bulky groups may help prevent dimer formation, Shapiro *et al.*<sup>82</sup> reacted AlCp<sub>3</sub> with 2,6-di-*tert*-butyl-4-methylphenol (Figure 1.13), which is sufficiently bulky to prevent dimer formation. This attempt was met with some challenges as the products of the reaction were unreacted AlCp<sub>3</sub>, [Cp<sub>2</sub>Al(BHT)]<sub>x</sub> and CpAl(BHT)<sub>2</sub>. Whereas CpAl(BHT)<sub>2</sub> was isolated and structurally characterized, the [Cp<sub>2</sub>Al(BHT)]<sub>x</sub> could not be structurally characterized, hence, its structure remains unknown. Synthesizing monomeric alkyl bis(cyclopentadienyl)aluminum- and gallium compounds have so far remained a challenge. The successful syntheses of monomeric alkyl bis(cyclopentadienyl)aluminum- and -gallium compounds and the corresponding bridged-species (this work) is therefore a major scientific breakthrough.



**Figure 1.13.** Bulky 2, 6-di-*tert*-butyl-4-methylphenol (BHT) ligand.

## 1.6 Polymerization of Olefin using *ansa*-Zirconocene Catalysts

### 1.6.1 Cocatalyst

*ansa*-Zirconocenes, just like any other metallocene, polymerizes ethylene and other  $\alpha$ -olefins only when activated. Several ways to activate *ansa*-metallocenes exists in the literature. They include methylalumoxane (MAO), which is known to be the most commonly used and most effective cocatalyst,<sup>51d,51f</sup> tris(pentafluorophenyl)borane  $[\text{B}(\text{C}_6\text{F}_5)_3]$ , tetrakis(pentafluorophenyl)borate  $[\text{B}(\text{C}_6\text{F}_5)_4]$ , triphenylmethylcarbenium tetrakis(pentafluorophenyl)borate  $[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  and N,N-dimethylphenylamine tetrakis(pentafluorophenyl)borate  $[\text{Me}_2\text{HNPh}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ . These cocatalysts abstract methyl anion from catalyst precursors.<sup>51f</sup> During precatalysts activation, MAO is used in excess, while borates and boranes are used in stoichiometric amounts. The large excess of MAO is necessary to ensure better ionic separation.<sup>51e-f</sup> However, both cocatalysts yield active catalysts but the high price, fluorine incorporation in the polymer and susceptibility to poisons (impurities) and decomposition limits the use of boron-based cocatalysts.<sup>51f</sup> Borates and boranes are specifically used to activate metallocene dialkyl complexes. They require aluminum alkyls to scavenge for impurities and to effect the alkylation of metallocene dichlorides before activation.<sup>83-85</sup> The disadvantage of using MAO is its high cost and possible  $\text{Al}_2\text{O}_3$  residuals in the polymer.<sup>51d</sup>

### 1.6.2 Mechanism

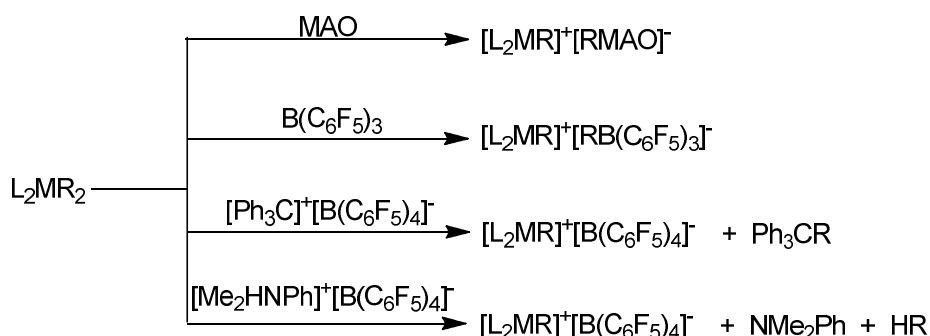
The basic polymerization mechanism involves the activation of the catalysts precursors, chain propagation and chain termination.



### 1.6.2.1 Activation

The activation of the precatalysts (Scheme 1.6) by MAO involves the methylation of the *ansa*-metallocene dichloride (or dialkyl) complexes followed by methyl (or alkyl) abstraction forming metallocene monomethyl cation  $[\text{Cp}_2\text{MMe}]^+$ , which is the active catalytic species together with a weakly coordinating counterion  $[\text{MeMAO}]^-$ .<sup>51f</sup> For boron-based cocatalysts, metallocene dichloride precatalysts are first alkylated using aluminum alkyls ( $\text{AlR}_3$ ) before the alkyl abstraction to generate the active species takes place.<sup>83-85</sup> The common cocatalysts used for the activation of metallocene catalysts and the resulting active species and counterions generated are shown in scheme 1.6.

**Scheme 1.6.** Activation of metallocene catalysts.

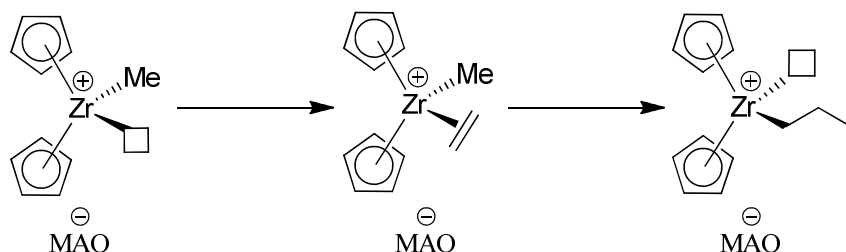


### 1.6.2.2 Chain Propagation

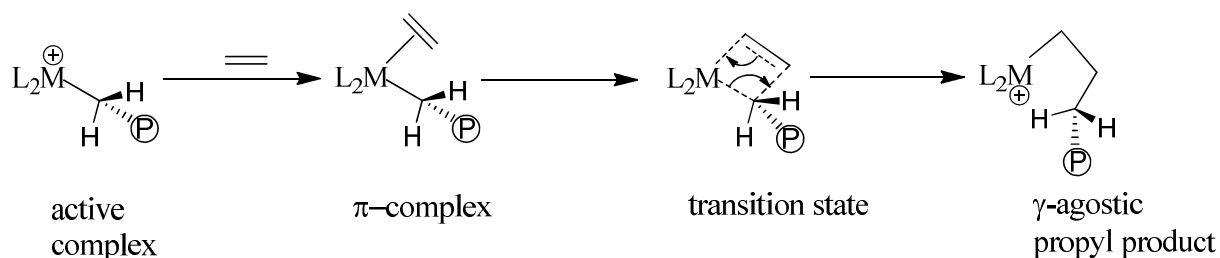
After activation, the olefin coordinates to the vacant site on the group-4-metal center. The chain propagation starts with the insertion of ethylene into the zirconium-carbon bond and then coordination of the next olefin molecule begins.<sup>51f</sup> During insertion, alkyl (chain) migration to the olefin ligand occurs, generating a new, free coordination site, previously occupied by the alkyl group (Scheme 1.7).<sup>51f</sup> Although there are other proposed mechanisms,<sup>51d,86</sup> Cossee-

Arlman mechanism (Scheme 1.8)<sup>87</sup> is the widely acceptable mechanism for polymerization of olefin with metallocene and non-metallocene catalysts.

**Scheme 1.7.** Propagation step in the polymerization of ethylene.



**Scheme 1.8.** Representation of Cossee-Arlman type reaction mechanism for homogenous polymerization with metallocene-based catalysts.

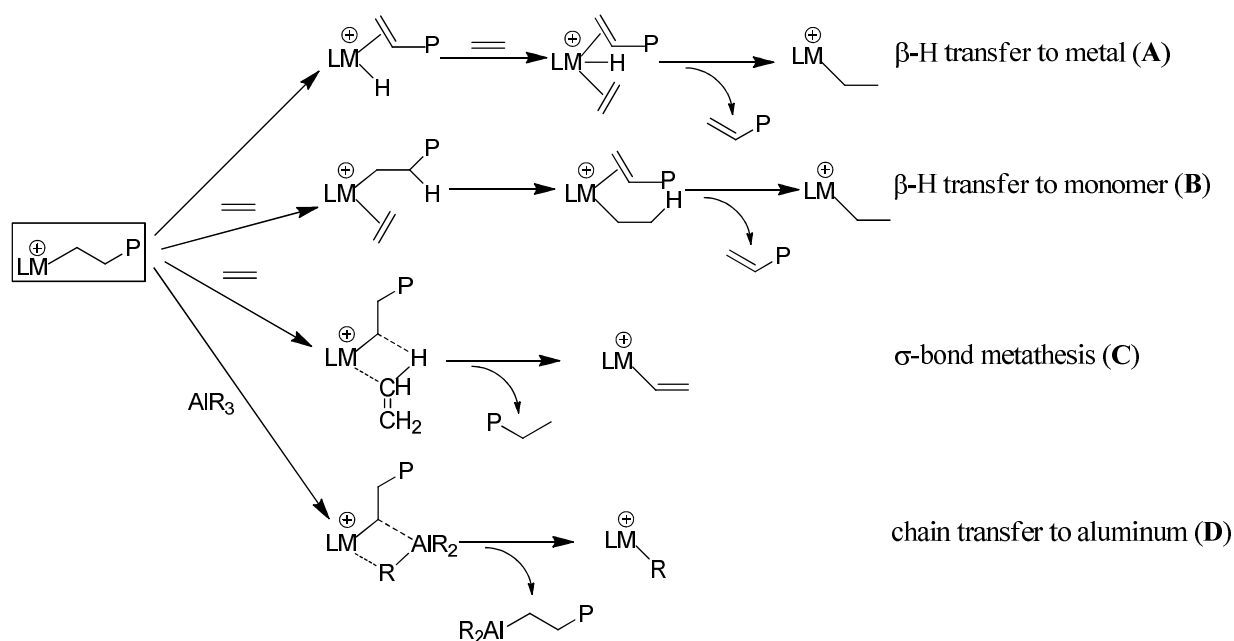


### 1.6.2.3 Chain Termination

The termination pathways in olefin polymerization are  $\beta$ -hydride transfer to the metal (**A**) ( $\beta$ -H elimination),  $\beta$ -hydride transfer to monomer (**B**), chain transfer to aluminum (**C**) and  $\sigma$ -bond metathesis (**D**) (Scheme 1.9).<sup>86,88</sup>  $\sigma$ -bond metathesis (**D**) results in the cleavage of Zr-C bond. However, in ethylene polymerization,  $\beta$ -H transfer to the metal centre,<sup>24,89-91</sup>  $\beta$ -H transfer to the monomer and chain transfer to aluminum<sup>89,92-93</sup> predominate over other methods of chain termination.  $\beta$ -H transfer to the metal is independent on olefin concentration while  $\beta$ -H transfer to monomer is linearly dependent on olefin concentration.<sup>86,90</sup> Chain-transfer processes depend

on the reaction conditions and the nature and relative concentrations of the precatalysts. Ultimately, all the chain transfer processes, which invariably lead to chain termination, result in the production of oligomers or polymers with low molecular weights.<sup>88</sup>

**Scheme 1.9.** Chain termination pathways in ethylene polymerization.



## 1.7 Branching in Ethylene Polymerization

Branching can simply be defined as side chains in polyolefins and are classified as either short or long chains. Short chain branching refers to branching with only a few carbon atoms and are much shorter than the linear polymer backbone to which they are attached, while long-chain branching (LCB) consists of branches with more carbon atoms.<sup>94</sup> Branched PE such as LLDPE is widely attractive to industry and researchers due to the ease at which they can be processed and their improved properties.<sup>4,95</sup> Branching decreases the melt temperature and also affects the rheological properties of polymers which in turn improve the processability of these polymers.<sup>96</sup>

The combination of soft, branched segment with the hard, linear segment give rise to polymers with suitable properties for use as thermoplastic elastomers and high-impact plastics.<sup>97</sup>

Long and short chain branching of PE is achieved by copolymerization of ethylene with 1-alkenes where the vinyl end of the  $\alpha$ -olefin is reincorporated into the growing polymer chain.<sup>98</sup> The ability to produce branched PE by a single metallocene catalyst precursor without resorting to copolymerization has so far remained a challenge.<sup>96</sup> Although the constrained geometry complex (CGCs) catalysts are known to form some significant amount of branched chains,<sup>99</sup> metallocene catalysts<sup>96</sup> have been found to produce only methyl and ethyl-branched polyethylene (HDPE). Metallocene catalysts such as Et[Ind]<sub>2</sub>ZrCl<sub>2</sub> (**13a**)/MAO,<sup>100,102</sup> Me<sub>2</sub>Si[Ind]<sub>2</sub>ZrCl<sub>2</sub> (**13b**)/MAO,<sup>101</sup> Ph<sub>2</sub>C(2,7-di*t*BuFlu)(Cp)ZrCl<sub>2</sub> (**17b**)/MAO (Figure 1.9),<sup>100</sup> are amongst the few that are known to produce different degrees of short chain branched PE due to reincorporation of  $\alpha$ -olefins produced as a result of high rate of chain termination<sup>101-102</sup> via  $\beta$ -H transfer to the monomer,  $\beta$ -hydrogen transfer to the metal ( $\beta$ -H elimination) or monomer C-H  $\sigma$ -bond metathesis.<sup>83,100,103</sup> These catalysts produce carbon chain (C1-C5) branching at the given polymer conditions.

It was shown by Kaminsky *et al.*<sup>100</sup> and Malmberg *et al.*<sup>102</sup> that high polymer concentration, low ethylene concentration, addition of hydrogen and optimum polymerization temperature favor the production of branched PE when **13b**/MAO is used. High ethylene concentration is said to favor the production of linear PE due to the high tendency for ethylene insertion into the growing polymer chain.<sup>102</sup> **17b**/MAO produced long branched PE only in the presence of hydrogen.<sup>100</sup>

Recently, using binary catalyst systems, many authors have developed a new way of obtaining branched PE in a one step process (tandem catalysis) from a single monomer of

ethylene and a combination of two or more catalysts precursors. The catalysts precursors are usually an oligomerization and a copolymerization catalysts, together with one or two cocatalysts in a single reactor.<sup>104</sup> The oligomerization catalysts produce long chain  $\alpha$ -olefins while the other polymerizes ethylene and also incorporates the  $\alpha$ -olefins produced by the oligomerization catalysts into the growing polymer chain thereby producing branched PE.<sup>99</sup> Appropriate choice of catalysts is however important. By using a combination of an  $\alpha$ -diimine nickel(II)bromide complex which produces the branched segment and **13b**, which produces the linear chain segment, Wang *et al.*<sup>97</sup> obtained a linear-hyperbranched multiblock PE at 20 °C with narrow MWD using ethylene as the monomer. Diethyl Zinc ( $\text{ZnEt}_2$ ) was used as the chain transfer agent, while MAO was the cocatalyst.

The branching, though sometimes complicated, is usually monitored and detected using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Other methods are also used in more complicated cases. The mechanism for the formation of ethyl-branched PE is presumed to involve isomerization, involving  $\beta$ -H transfer from the growing polymer chain to the incoming monomer followed by insertion of the vinyl end into the formed ethyl-zirconium bond.<sup>96</sup> However, the exact isomerization mechanism is not known.<sup>102</sup>

### **1.8 Activity of *ansa*-Zirconocene Catalysts in Ethylene Polymerization**

The activity of catalysts is dependent on various factors which include type of catalysts and polymerization conditions such as type of reactor used, temperature, solvent, nature and amount of cocatalysts, monomer pressure and polymerization time.<sup>94-95</sup> Researchers have always reported different experimentally determined values for different catalysts. However, in order to compare the activity of one catalyst to another, the polymerization must be carried out under the same conditions<sup>95</sup> so that useful comparison can be made.<sup>73</sup> A summary of catalyst effectiveness

in olefin polymerization, based on the activity which was reported by Gibson and co workers (Gibson Scale),<sup>36,105</sup> is shown in table 1.2.

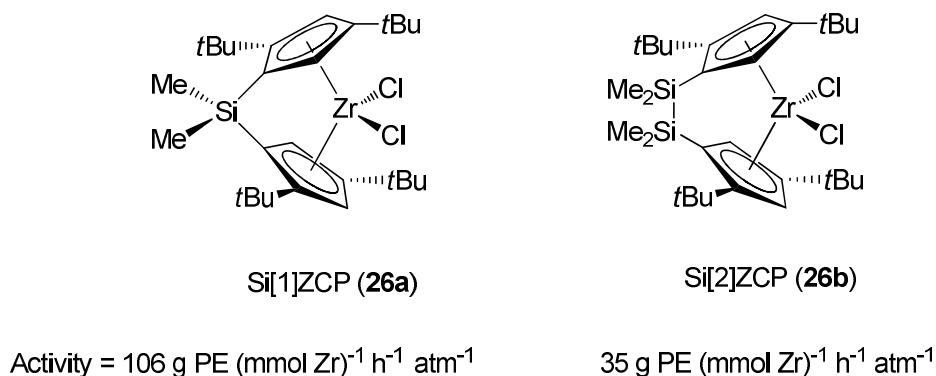
**Table 1.2.** Catalysts effectiveness in olefin polymerization.

rating	activity [g (mmol cat) <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> ]
very low	< 1
low	1-10
moderate	10-100
high	100-1000
very high	> 1000

### 1.8.1 Influence of Catalysts Structure

The bridging element, ligands and substituents on the cyclopentadienyl rings system and the concentration of the precatalysts have been found to affect the catalytic activities of *ansa*-zirconocene complexes. Generally, increase in catalyst concentration decreases activity<sup>85</sup> for some catalysts and increases activity in others.<sup>72</sup> The activity of the Cp<sub>2</sub>ZrCl<sub>2</sub>/MAO catalyst has been found to be inversely proportional to the zirconocene concentration.<sup>93</sup> The bridging element has some substantial effect on the activity of *ansa*-zirconocene catalysts.<sup>52-53</sup> Although in most cases the effect of the interannular bridge in ethylene polymerization remains largely unsubstantiated, it is assumed that the use of electron withdrawing bridging unit will lead to increased activity<sup>68</sup> due to its ability to render the group-4-metal center more electrophilic, thereby increasing the rate of olefin insertion. However, this has not been the case as most catalysts bearing other bridging units other than have so far produced PE with lower activity when compared to C- and Si-bridged *ansa*-zirconocene complexes. Schaverien and coworkers

attributed the low activity of phosphorus-bridged *ansa*-zirconocene to the coordination of MAO to the lone pair of electrons on phosphorus.<sup>57</sup>



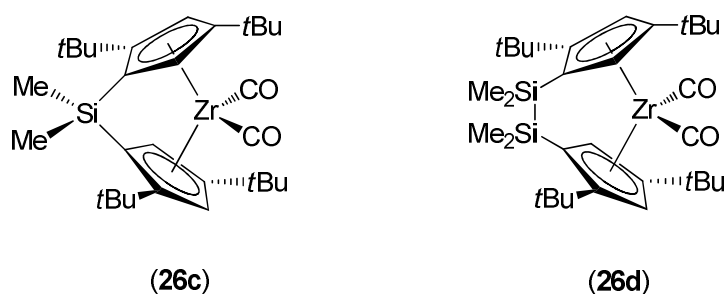
**Figure 1.14.** Activities of Si[1]ZCP and Si[2]ZCP.

Generally, single atom bridge ([1]ZCPs) are more active in olefin polymerization than their two-atom-bridged ([2]ZCP) counterparts (Figure 1.14). This is due to the ability of the former to widen the coordination space which enhances olefin insertion.<sup>24,106b</sup> Three- or four-atom-bridged *ansa*-zirconocene have been shown to be inactive for PP polymerization in the presence of MAO.<sup>24</sup>

Bulky ligands such as fluorenyl ligands at the transition metal<sup>51f</sup> are believed to play an important role in keeping the MAO anion at certain distance, thereby providing space for alkene insertion which in turn results in increased activity of the catalysts. However, the bulky ligands also have the potential of reducing the activity of some catalysts due to their ability to block olefin coordination sites.<sup>64</sup> There have been contrary views regarding steric and electronic effects on catalytic activity. Reddy and Sivaram opined that both effects can increase or decrease the activity of metallocene catalysts.<sup>107</sup> According to Alt and Jung, the presence of electron-donating groups will decrease the activity by making the metal centre electron rich and the carbon-metal

bond stronger<sup>59</sup> thus reducing the rate of olefin insertion, while Rausch and co workers<sup>106a</sup> believed that an electron-donating group or ligand could help stabilize the cationic active species leading to increased activity.

In an effort to establish the electronic effect of [Me<sub>2</sub>Si] and [Me<sub>4</sub>Si<sub>2</sub>] in *rac*-(Me<sub>2</sub>Si)(2,4-di-*t*BuCp)<sub>2</sub>ZrCl<sub>2</sub> (**26a**) and *rac*-(Me<sub>4</sub>Si<sub>2</sub>)(2,4-di-*t*BuCp)<sub>2</sub>ZrCl<sub>2</sub> (**26b**), respectively, Parkin *et al.*<sup>107b</sup> carried out IR studies of the corresponding dicarbonyl derivatives, *rac*-(Me<sub>2</sub>Si)(2,4-di-*t*BuCp)<sub>2</sub>Zr(CO)<sub>2</sub> (**26c**) and *rac*-(Me<sub>4</sub>Si<sub>2</sub>)(2,4-di-*t*BuCp)<sub>2</sub>Zr(CO)<sub>2</sub> (**26d**) (Figure 1.15) and concluded that the [Me<sub>2</sub>Si] bridge exerts an electron-withdrawing effect while the [Me<sub>4</sub>Si<sub>2</sub>] exerts an electron-donating effect.



**Figure 1.15.** Some *ansa*-zirconocene carbonyls used for IR studies

Based on this rationalization and the results of the activity of the compounds (Figure 1.14), it can be said that electron withdrawing groups increase activity.<sup>106a</sup> However, this should be considered with care, as electronic influence alone may not be sufficient to draw conclusions on catalytic activity.<sup>106b</sup>

### 1.8.2 Influence of Polymerization Conditions

Polymerization conditions have been shown to exert a strong influence on catalytic activities of *ansa*-zirconocene precatalysts. It has been shown that increase in temperature, ethylene pressure and the amount of cocatalysts (MAO) lead to an increase in activity.<sup>24,51,108</sup>



The strong dependence of activity on temperature is within a range of 30-80 °C<sup>93</sup> but above optimum temperature, which Kaminsky *et al.*<sup>109</sup> puts at 50 °C, the catalysts become unstable;<sup>110</sup> a fact that potentially leads to a decrease in catalyst activity. Brauschweig and coworkers<sup>111</sup> found that high catalyst concentration, high ethylene pressure and increased temperature lead to an increase in catalytic activity. They also noted that activity decreases sharply with increasing polymerization time due to deactivation of catalysts.

The concentration of MAO used during polymerization has a significant effect on catalytic activity. Increased activity is observed when a large excess of MAO is used. This is due to an increase in the rate of polymerization caused by an increase in the concentration of activated complex.<sup>108,112</sup> With a large excess of MAO (Al/Zr = 20,000), a high activity was reported for Et(Flu)<sub>2</sub>ZrCl<sub>2</sub> (**18c**)(Figure 1.9) , but when the amount of MAO was reduced (Al/Zr = 2500), the activity decreased substantially.<sup>51f</sup> It is asserted that the high excess of MAO is needed (to provide sufficient MAO cages) for better separation which reduces the ionic interaction, thereby leading to increased activity.<sup>51f</sup>

The use of MAO, in most cases, gives rise to higher activity than when other cocatalysts such as trialkylaluminum, borates or boranes, are used. Fairly strong ionic interactions of borates with the cationic zirconocene species (the active species) have been suggested as the obvious reason for their lower activity.<sup>24</sup>

Using Et(Ind)<sub>2</sub>ZrCl<sub>2</sub> (**13a**) and Ind<sub>2</sub>ZrCl<sub>2</sub>, Quijada and coworkers<sup>113</sup> showed that an increase in stirring rate resulted in a corresponding increase in catalytic activity for ethylene polymerization. Maximum activity was observed at stirring speed of 1000 rpm and lowest at 500 rpm. Higher activity was observed for polymerization carried out in glass reactors than those carried out in autoclave. Although the activity of **13a** in ethylene polymerization initially

increased with decreasing catalyst concentration, lower activity was observed below the optimum catalysts concentration.<sup>113</sup>

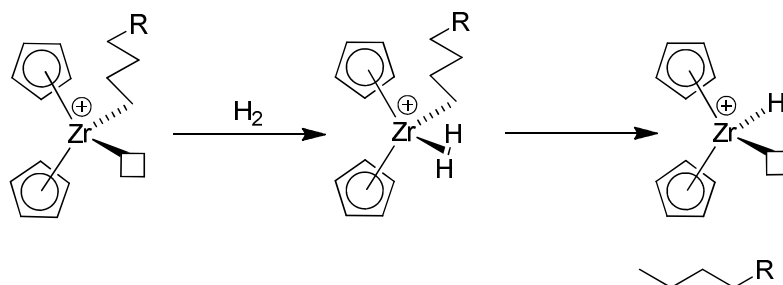
### 1.9 Factors Affecting the Molecular Weight of Polyethylene

Generally, *ansa*-zirconocene complexes are known to produce low MW PE due to their kinetically labile zirconium-carbon bond, which enhances chain transfer via  $\beta$ -H elimination.<sup>51f</sup> However, other factors also contribute to the MW of PE obtained using *ansa*-zirconocene catalysts. They include polymerization temperature, ethylene pressure and addition of hydrogen.

Higher polymerization temperature, higher precatalyst concentration, lower monomer concentration and addition of hydrogen lead to a decrease in the MW of the polymer due to increased rate of chain termination relative to chain propagation.<sup>19,95,114</sup> Addition of hydrogen facilitates chain termination leading to the production of low MW PE. The proposed mechanism for the reaction of propagating polymer chain with hydrogen is shown in Scheme 1.10. Rytter *et al.*<sup>91</sup> reported that the MW of PE is independent of ethylene pressure while the addition of hydrogen<sup>51f</sup> is known to decrease MW. Increase in polymerization temperature leads to a decrease in MW with oligomers and  $\alpha$ -olefins predominantly formed when polymerization temperature exceeds 100 °C.<sup>95</sup>

Transfer to monomer is known to be the main chain transfer mechanism for ethylene polymerization using zirconocene catalysts (Scheme 1.9).<sup>115</sup> However, residual (free) trimethylaluminum (TMA) present in commercial MAO solution can act as a chain transfer agent, suggesting that increasing the amount of MAO could also lead to a decrease in polymer MW due to increase rate of chain transfer to TMA (Scheme 1.9).<sup>110,115</sup>

**Scheme 1.10.** Proposed reaction of propagating chain with hydrogen.<sup>51f</sup>



Catalysts containing substituents at the Cp rings, in the 2-position of the indenyl rings<sup>91</sup> and those containing bulky ligands such as fluorenyl ligands (substituted and unsubstituted) lead to increased catalytic activity and higher MW PE. The bulky ligands not only prevent  $\beta$ -H elimination resulting in HMWPE<sup>51f</sup> but also provide better separation of the active catalytic species from the counterion thereby, providing enough space for ethylene insertion. This often results in increased catalytic activity.<sup>51f</sup>

## 1.10 Research Objectives

Several *ansa*-zirconocene compounds have been synthesized and applied as precatalysts for olefin polymerization. However, despite the large number of *ansa*-zirconocene compounds known in the literature, not a single example of aluminum- or gallium-bridged *ansa*-zirconocene compound is known. As stated earlier, the absence in the literature of any Al- or Ga-bridged *ansa*-zirconocene may not be unconnected to the difficulty in synthesizing the monomeric alkylbis(cyclopentadienyl)aluminum and gallium precursors, which have so far been found to exist as dimers or oligomers.<sup>76-78</sup>

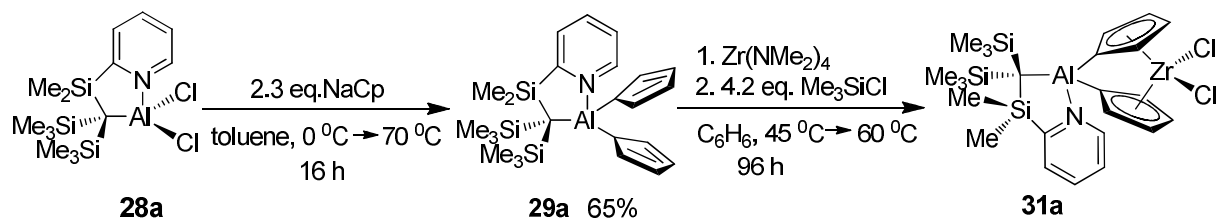
By employing trisyl-based ligands (Pytsi and Me<sub>2</sub>Ntsi) (Figure 1.6),<sup>50,116</sup> several intramolecularly stabilized compounds containing heavier group 13 (Al, Ga, In) elements have been synthesized by Müller's group.<sup>49,117</sup> One of the ligands used by the Müller group that has been shown to be effective in synthesizing strained [1]metallocenophanes is the Pytsi ligand (to be discussed in section 2.1).

Based on the successes achieved in the syntheses of [1]metallocenophanes using the Pytsi ligand, it was believed that by using the same ligand, monomeric bis(cyclopentadienyl)aluminum and gallium compounds, may be successfully synthesized as precursors for the syntheses of Al- and Ga[1]ZCPs. The later compounds can then be applied as catalysts for ethylene polymerization.

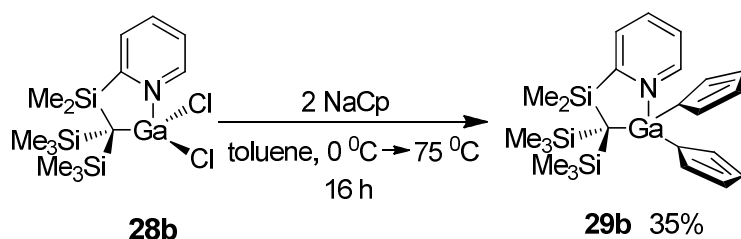
Clinton Lund (a former PhD student in Müller's group) successfully synthesized (Pytsi)AlCp<sub>2</sub> (**29a**)<sup>118</sup> in 65% yield by reacting (Pytsi)AlCl<sub>2</sub> (**28a**)<sup>116</sup> with two equivalents of NaCp. Subsequently, he synthesized the first aluminum-bridged ZCP (**31a**) by reacting **29a** with Zr(NMe<sub>2</sub>)<sub>4</sub> and Me<sub>3</sub>SiCl to effect the chloride/amide exchange (Scheme 1.11).<sup>118</sup> He also

synthesized **29b** in a yield of 35% by reacting (Pytsi)GaCl<sub>2</sub> (**28b**)<sup>117a</sup> with two equivalents of NaCp (Scheme 1.12).

**Scheme 1.11.** Reaction scheme for the syntheses of (Pytsi)AlCp<sub>2</sub> (**29a**) and (Pytsi)Al[1]ZCP (**31a**).<sup>118</sup>



**Scheme 1.12.** Reaction scheme for the synthesis of (Pytsi)GaCp<sub>2</sub> (**29b**).<sup>118</sup>



Based on the above, the objectives of my thesis were to:

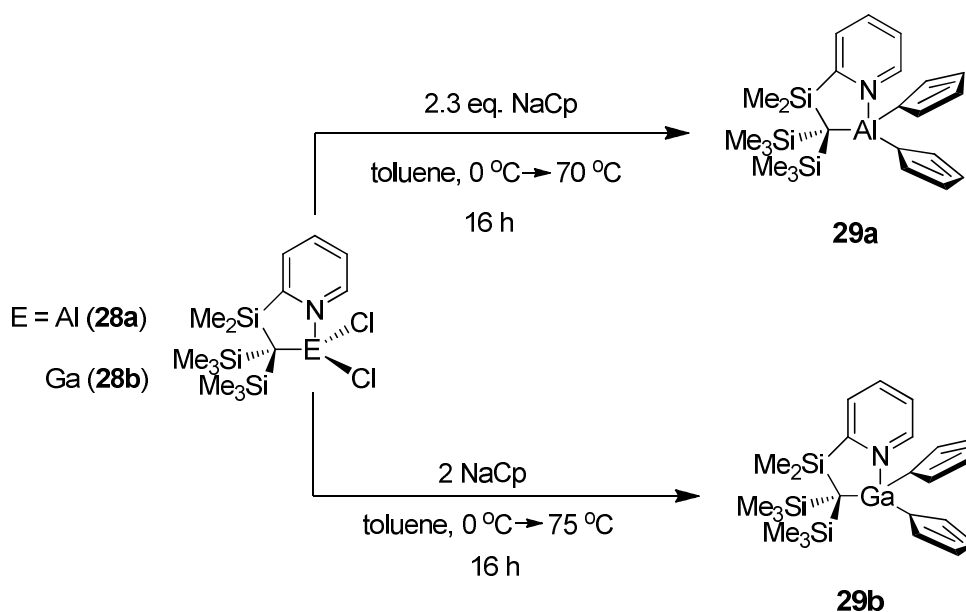
- (1) repeat and optimize the synthesis of the Al[1]ZCP (**31a**),
- (2) expand the reaction to obtain the Ga-bridged analogue (**31b**), and
- (3) test for the catalytic activities of the new compounds towards olefin polymerization and compare them with other benchmark catalysts.

## 2 Results and Discussion

### 2.1 Synthesis and Characterization of (Pytsi)AlCp<sub>2</sub> (**29a**) and (Pytsi)GaCp<sub>2</sub> (**29b**).

As mentioned earlier, Clinton Lund<sup>118</sup> synthesized the monomeric bis(cyclopentadienyl)aluminum and gallium compounds (Pytsi)AlCp<sub>2</sub> (**29a**) and (Pytsi)GaCp<sub>2</sub> (**29b**) containing the bulky Pytsi ligand, by reacting (Pytsi)AlCl<sub>2</sub> (**28a**)<sup>116</sup> and (Pytsi)GaCl<sub>2</sub> (**28b**), respectively,<sup>117a</sup> with two equivalents of NaCp in toluene (Scheme 2.1).

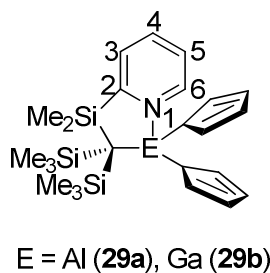
**Scheme 2.1.** Syntheses of (Pytsi)AlCp<sub>2</sub> (**29a**) and (Pytsi)GaCp<sub>2</sub> (**29b**).



Compounds **29a** and **29b** were isolated as yellow crystals from diethyl ether in 65% and 35% yield, respectively. The molecular structures of **29a** and **29b** were elucidated in solution by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy and in the solid state by X-ray diffraction studies, showing that both are monomeric in solution and in the solid state.<sup>118</sup> The Pytsi ligand, which is used to obtain the monomeric compounds, provides steric shielding through the bulky trimethylsilyl groups and

intramolecular stabilization through the nitrogen of the pyridyl moiety.<sup>49-50,116</sup> The trisyl-based ligands are formed by a formal replacement of one of the methyl group of the trisyl ligand [-C(SiMe<sub>3</sub>)<sub>3</sub>] with a substituent with  $\sigma$  donor abilities. Ligands with donor groups are known to form Lewis acid-base adduct intramolecularly, thereby preventing the formation of oligomers.<sup>117b</sup>

By following the same procedure described above, **29a** was synthesized in a yield of 58% while **29b** was synthesized in a yield of 83%. The significant improvement in the yield of **29b** may be attributed to the use of an excess of NaCp.<sup>119</sup> Compound **29a** is the first example of a monomeric bis(cyclopentadienyl)aluminum compound with a bulky ligand and the second monomeric bis(cyclopentadienyl)aluminum compound to be synthesized, while **29b** is the only isolated and structurally characterized example of a monomeric bis(cyclopentadienyl) compound of gallium. The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of compound **29a** and **29b** each show only one singlet for the SiMe<sub>2</sub> and one singlet for the SiMe<sub>3</sub> groups while the 10 protons of the Cp rings of **29a** and **29b** each appear in the <sup>1</sup>H NMR spectra as a singlet at  $\delta$  6.20 and 6.16, respectively. The crystal structure for the compounds show that the cyclopentadienyl rings are coordinated to the aluminum and gallium centre in an  $\eta^1$ -manner.<sup>118</sup> The single resonance for the Cp rings can be explained by a rapid migration of the aluminum and the gallium about the cyclopentadienyl rings.<sup>75</sup> The aluminum compound **29a** exhibits three signals in the <sup>1</sup>H NMR spectrum for the protons of the pyridine ring: a pseudotriplet at  $\delta$  6.28 (5-H), a multiplet at  $\delta$  6.76 (3-H and 4-H) and a doublet at  $\delta$  8.05 (6-H). The gallium analogue **29b**, on the other hand, exhibits four signals in the <sup>1</sup>H NMR spectrum for the protons of the pyridine ring: two pseudotriplets at  $\delta$  6.33 (5-H) and 6.78 (4-H), and two doublets at  $\delta$  6.82 (3-H) and at 8.05 (6-H). This shows that all the protons of the pyridine ring are chemically non-equivalent.

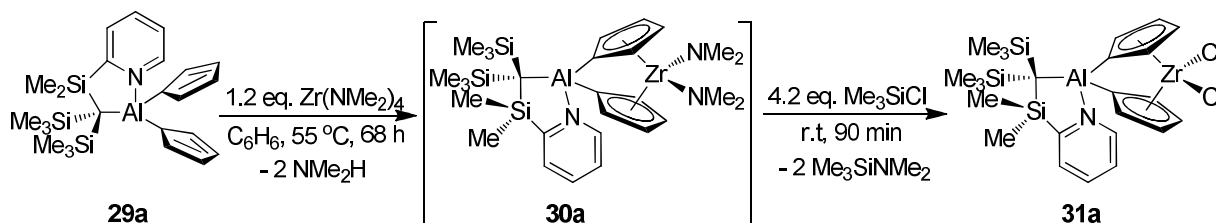


**Figure 2.1.** (Pytsi)AlCp<sub>2</sub> (**29a**) and (Pytsi)GaCp<sub>2</sub> (**29b**) showing numbering of the pyridine ring.

## 2.2 Synthesis and Characterization of (Pytsi)Al[1]ZCP (**31a**).<sup>118</sup>

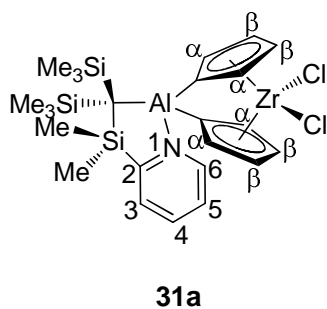
Having overcome the challenge of synthesizing the monomeric bis(cyclopentadienyl) precursor, Clinton Lund synthesized the first aluminum-bridged *ansa*-zirconocene **31a** by reacting **29a** with Zr(NMe<sub>2</sub>)<sub>4</sub> in benzene at 45 °C for 72 h. After this time, about 15-20% of the starting material was still present, so the temperature was increased to 60 °C and the reaction continued for another 24 h (Scheme 1.11).<sup>118</sup> The reaction proceeded with the formation of (Pytsi)Al[1]Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (**30a**), after which chlorination was effected with the addition of an excess of Me<sub>3</sub>SiCl resulting in the formation of (Pytsi)Al[1]ZCP (**31a**). Clinton obtained compound **31a** as colorless crystals from diethyl ether. However, a yield was not reported and he could not reproduce the result. The compound was characterized by multinuclear NMR spectroscopy and its molecular structure was solved by single-crystal X-ray analysis.<sup>118</sup>

**Scheme 2.2.** Synthesis of (Pytsi)Al[1]ZCP (**31a**).

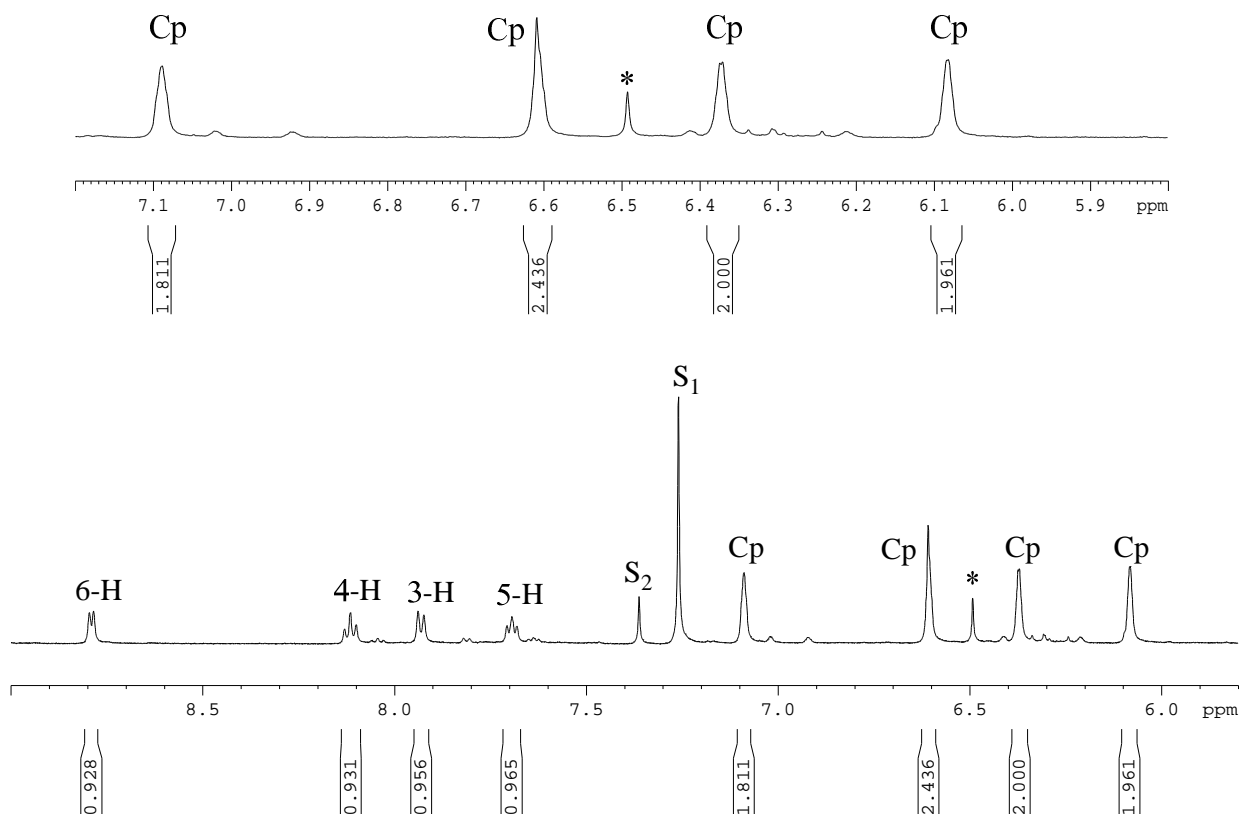




Following Clinton's procedure (Scheme 1.11) with minor modifications, **31a** was synthesized and isolated as colorless crystals (analytically impure) from diethyl ether in a crude yield of 52%. The isolated crystals contained some amount of  $\text{Cp}_2\text{ZrCl}_2$  (**27**) as impurities. As evident from the  $^1\text{H}$  NMR spectrum,  $(\text{Pytsi})\text{AlCl}_2$  (**28a**) which is another byproduct of the reaction, remained in solution. The reaction was carried out at  $55\text{ }^\circ\text{C}$  for 68 h (Scheme 2.2). The  $^1\text{H}$  NMR (in  $\text{CDCl}_3$ ) spectrum of **31a** shows that the 6 protons of  $\text{SiMe}_2$  and the 18 protons of  $\text{SiMe}_3$  moieties each give rise to one singlet, similar to what was observed in the  $^1\text{H}$  NMR spectrum of **29a**. The singlet for the 10 protons of the Cp rings in **29a** split into four pseudoquartets of equal intensity in the  $^1\text{H}$  NMR spectrum of **31a**. The four signals appear at  $\delta$  6.08, 6.37, 6.61 and 7.09 in the Cp region,<sup>118</sup> with each integrating to two protons (Figure 2.3). Four signals were observed for the protons of the pyridine ring. They appear as two doublets at  $\delta$  7.93 (3-H) and 8.79 (6-H) and two triplets at  $\delta$  7.69 (5-H) and 8.12 (4-H).<sup>118</sup> The NMR data obtained is consistent with a time-averaged  $C_s$  symmetry of the compound. The numbering system of compound **31a** is shown in Figure 2.2.



**Figure 2.2.**  $(\text{Pytsi})\text{Al}[1]\text{ZCP}$  showing  $\alpha$  and  $\beta$  positions on the Cp rings and numbering of the pyridine ring.



**Figure 2.3.**  $^1\text{H}$  NMR spectrum in the region of the Cp protons (above) and a combination of the Cp and arene regions (below) of (Pytsi)Al[1]ZCP (**31a**) at 25 °C ( $\text{CDCl}_3$ ). Impurity is marked with asterisk (\*). Solvents:  $\text{S}_1 = \text{CDCl}_3$ ,  $\text{S}_2 = \text{C}_6\text{H}_6$ .

The  $^{13}\text{C}$  NMR spectrum (in  $\text{CDCl}_3$ ) of **31a**<sup>118</sup> shows singlets at  $\delta$  114.1, 117.6, 127.8 and 134.1 and also at  $\delta$  116.7 (*ipso*-C) representing the carbon atoms of the Cp rings. Five singlets were observed in the  $^{13}\text{C}$  NMR spectrum for the carbon atoms of the pyridine ring with the *ipso*-C of the pyridine appearing downfield at  $\delta$  175.1.

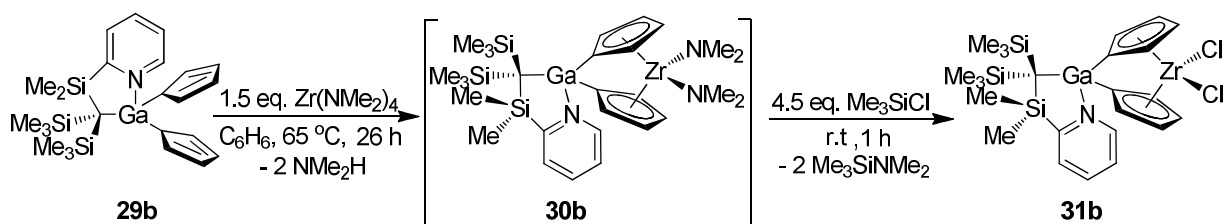
Although crystals of **31a** were initially obtained, subsequent attempts to synthesize and isolate pure samples of **31a** were unsuccessful. The  $^1\text{H}$  NMR spectra revealed the formation of the desired **31a** together with some amounts of the byproducts, **28a** and **27** (Scheme 2.5) which could not be separated from the desired product. Several attempts to obtain crystals of **31a** from the mixture of products from diethyl ether or other solvents failed. One can assume that these

byproducts are formed as a result of the reaction of the dimethylamine, produced during the course of the reaction, with the reactant **29a** or the aluminum-containing product **30a**. The challenge of this synthesis is how to deal with the dimethylamine that is produced in the reaction. This will be discussed in detail in section 2.4.

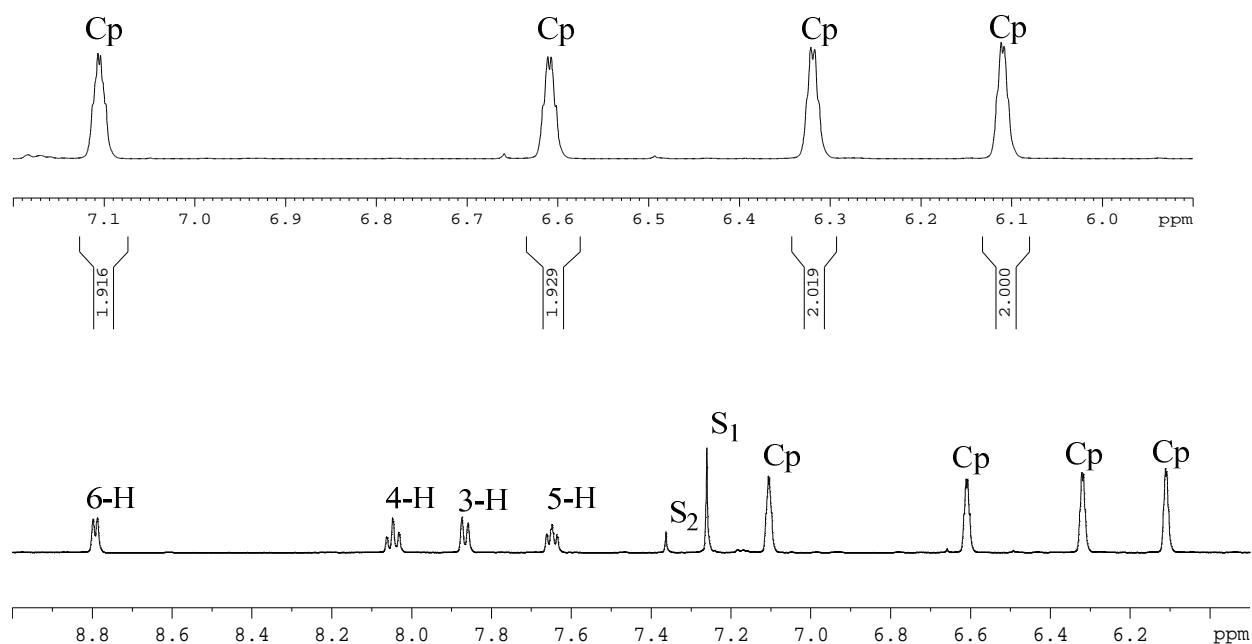
### 2.3 Synthesis and Characterization of PytsiGa[1]ZCP (**31b**).

The first gallium-bridged *ansa*-zirconocene **31b** was synthesized by reacting **29b** with  $\text{Zr}(\text{NMe}_2)_4$  in benzene at 65 °C in 26 h, following a similar procedure as described for **31a** above (Scheme 2.3). Compound **31b** was obtained as colorless crystals from benzene in 40% yield. Similar to the reaction pathway observed for **31a**,  $(\text{Pytsi})\text{Ga}[1]\text{Cp}_2\text{Zr}(\text{NMe}_2)_2$  (**30b**) (not isolated) was first formed with the liberation of two equivalents of dimethylamine, after which an excess of  $\text{Me}_3\text{SiCl}$  was added at room temperature to obtain the chlorinated species  $(\text{Pytsi})\text{Ga}[1]\text{ZCP}$  (**31b**).

**Scheme 2.3.** Synthesis of  $(\text{Pytsi})\text{Ga}[1]\text{ZCP}$  (**31b**).



The  $^1\text{H}$  NMR spectrum of **31b** shows that the 6 protons of  $\text{SiMe}_2$  and the 18 protons of the  $\text{SiMe}_3$  moieties of **31b** appear as singlets at  $\delta$  0.51 and 0.19, respectively. The singlet observed in the  $^1\text{H}$  NMR spectrum for the 10 protons of the Cp rings in **29b** is split into four pseudoquartets of equal intensity in the  $^1\text{H}$  NMR spectrum of **31b** (Figure 2.4).



**Figure 2.4.**  $^1\text{H}$  NMR spectrum in the region of the Cp protons (above) and a combination of the Cp and arene regions (below) of (Pytsi)Ga[1]ZCP (**31b**) at 25 °C ( $\text{CDCl}_3$ ). Solvents:  $S_1 = \text{CDCl}_3$ ,  $S_2 = \text{C}_6\text{H}_6$ .

The four signals, each integrating to two protons, appear at  $\delta$  6.11, 6.32, 6.61 and 7.11 in the Cp region of the  $^1\text{H}$  NMR spectrum (Figure 2.4). The assignments of these peaks were made in reference to assignments made for compound **31a**.<sup>118</sup> Similar to what was observed in the  $^1\text{H}$  NMR spectrum of **31a**, four signals was observed for the protons of the pyridine ring. They appear as two doublets at  $\delta$  7.87 (3-H) and 8.79 (6-H) and two multiplets at  $\delta$  7.65 (5-H) and 8.05 (4-H). The  $^{13}\text{C}$  NMR spectrum (in  $\text{CDCl}_3$ ) of **31b** exhibits singlets at  $\delta$  112.5, 117.5, 125.7 133.5 and also at  $\delta$  121.4 (*ipso*-C) representing the carbon atoms of the Cp rings. Just like that of the aluminum analogue (**31a**), the  $^{13}\text{C}$  NMR pattern for **31b** displays five singlets for the carbon atoms of the pyridine ring with the *ipso*-C appearing at  $\delta$  173.0. The NMR data obtained is consistent with a time-averaged  $C_s$  symmetry of the compound.

Expectedly, the positions and pattern of the signals for compound **31b** are however not significantly different from that of **31a**. Whereas the Cp protons appear almost at the same chemical shift for both **31a** and **31b**, the protons of the pyridyl moiety in the  $^1\text{H}$  NMR spectrum of **31b** appear more downfield than those observed in the  $^1\text{H}$  NMR spectrum of **31a**. Coincidentally, the proton in the 6 position of the pyridine ring in both **31a** and **31b** appears at the same chemical shifts ( $\delta$  8.79), just as it appears at the same chemical shift ( $\delta$  8.05) in **29a** and **29b**. Similar to the observation made for the synthesis of compound **31a**, the ability of isolate this compound depends on the controlled removal of the dimethylamine produced during the reaction.

#### 2.4. Influence of Dimethylamine on the Syntheses of **31a** and **31b**.

The reaction of **29a** and **29b** with  $\text{Zr}(\text{NMe}_2)_4$  to obtain **30a** and **30b**, respectively, proceeds with the elimination of two equivalents of dimethylamine. The dimethylamine is acidic enough to react with the reactants (**29a** and **29b**) and the intermediate products (**30a** and **30b**) (Scheme 2.5); hence, there is need for its controlled elimination from the reaction vessel. Clinton synthesized **31a** and asserted that turning off the  $\text{N}_2$  gas flow after the addition of  $\text{Zr}(\text{NMe}_2)_4$  and opening the oil bubbler for the amine to escape was a key strategy in obtaining the target compound.<sup>118</sup> With nitrogen gas flowing during the course of the reaction, he noted that the major product formed contained two zirconium atoms for one aluminum. Although a small amount of the amine produced may be required for the reaction,<sup>56c</sup> the presence of an excess of it will lead to the formation of unwanted byproducts (Scheme 2.5).

Unlike previously reported,<sup>118</sup> **31a** and **31b** were synthesized under a low flow of N<sub>2</sub> to sweep away the dimethylamine formed.<sup>\*1</sup> This strategy was found to be an efficient way to reduce the reaction time and also to prevent the formation of byproducts, when the reaction was carried out with no N<sub>2</sub> flow. However, this strategy did not completely prevent the formation of the byproducts. <sup>1</sup>H NMR spectra taken from the reaction mixtures during the syntheses of **31a** and **31b** revealed that the byproducts were (Pytsi)ECl<sub>2</sub> [E = Al (**28a**), Ga (**28b**)] and Cp<sub>2</sub>ZrCl<sub>2</sub> (**27**). The appearance of peaks in the <sup>1</sup>H NMR spectra (in C<sub>6</sub>D<sub>6</sub>) at δ 6.40 for Cp<sub>2</sub>ZrCl<sub>2</sub> and at δ 8.30 (**28a**) and 8.42 (**28b**) for the 6-H proton of the pyridine rings and other peaks known for compounds **28a** and **28b**, upon addition of Me<sub>3</sub>SiCl to the reaction mixture, attest to the presence of these byproducts. Separating these undesired products from the desired product is a difficult task due to the solubility of all the three compounds in benzene and other organic solvents. It is likely that the yield of the reaction is dependent on the ability to prevent the dimethylamine from reacting with the reactants (**29a** and **29b**) and/or the products (**30a** and **30b**). Its controlled exclusion from the reaction is therefore crucial.

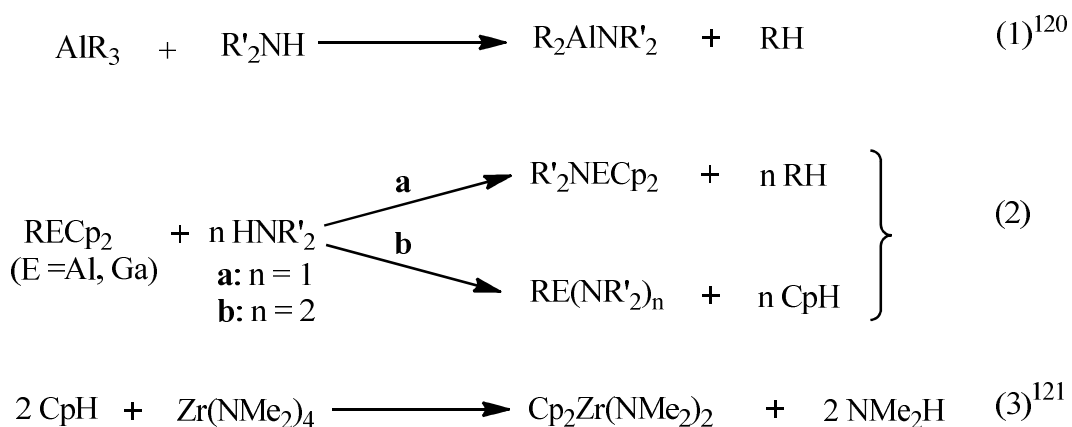
Whereas the controlled exclusion of dimethylamine was more effective in obtaining **31b** without the formation of byproducts, it was less effective in obtaining **31a** without byproducts. Attempts to obtain **31a** always lead to the formation of the desired **31a** together with some amount of the side products **28a** and **27** (Scheme 2.5). The two compounds are difficult to separate from **31a**. The result of the synthesis showed that the Al-Cp bond is more susceptible to cleavage in the presence of even traces of dimethylamine than its gallium analogue.

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<sup>\*1</sup> The setup was connected such that a N<sub>2</sub> gas inlet was fitted to a condenser tube already connected to the reaction vessel and opened to an oil bubbler. N<sub>2</sub> gas flow was passed slowly by the top of the condenser tube.

The possible route to the formation of the side products in the reaction is explained using Scheme 2.4. The scheme shows the general reaction pathways, reported decades ago for the reaction of alkylaluminum and gallium compounds with alkylamines.<sup>120</sup>

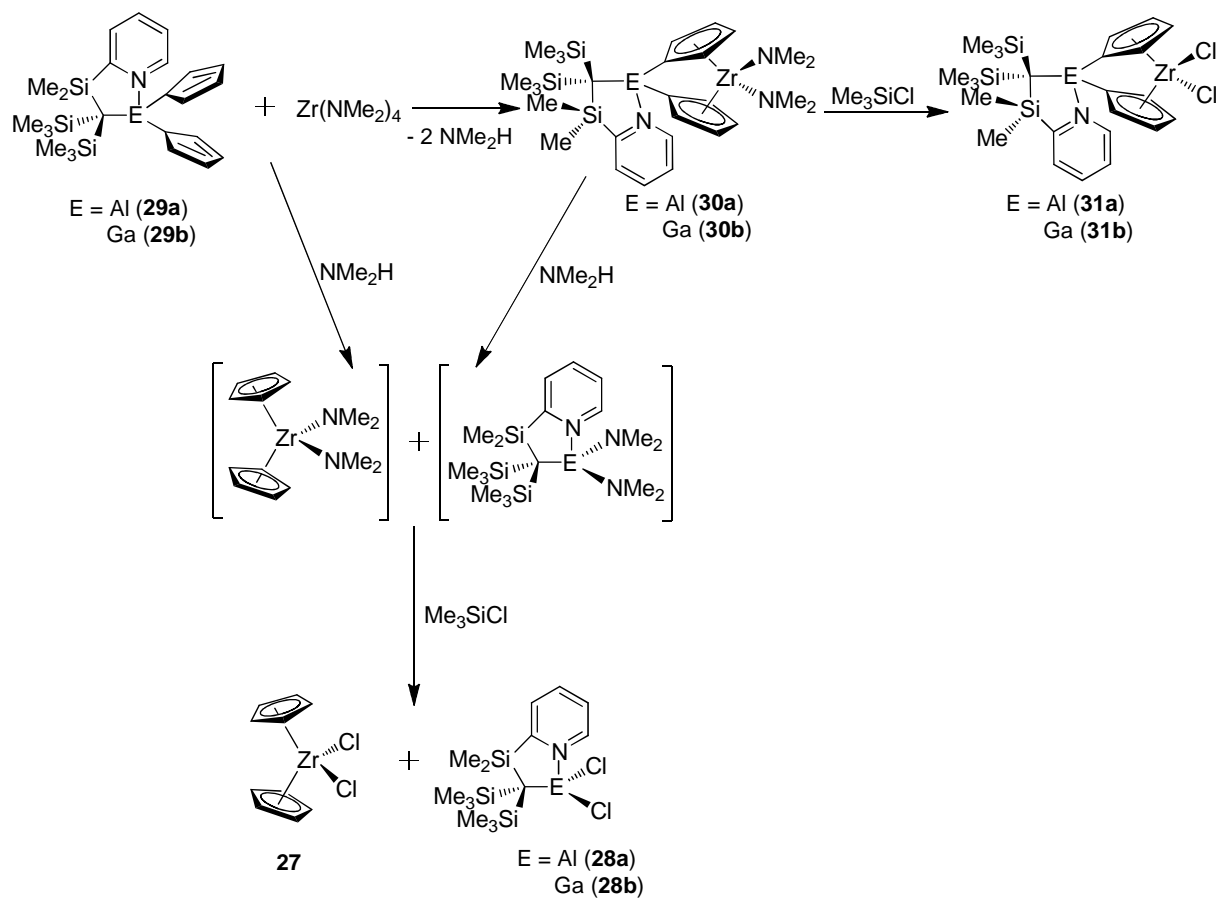
**Scheme 2.4.** General scheme for the reactions of alkylaluminum compounds with amines.



In the presence of dialkylamine, alkylaluminum compounds react with the cleavage of Al-R bonds (eq 1), forming alkyl amido compounds of aluminum and an alkane.<sup>120</sup> In the presence of dimethylamine ( $\text{R}' = \text{Me}$ ), it can be speculated that bis(cyclopentadienyl) compounds of aluminum and gallium may react according to equation 2. In the presence of an amine, path **a** involves the cleavage of E-R bonds ( $\text{E} = \text{Al, Ga}$ ), while path **b** involves the cleavage of E-Cp bonds ( $\text{E} = \text{Al, Ga}$ ). Any of the above paths (**a** and **b**) in equation 2 are feasible. Based on the above information on the feasibility of pathways **a** and **b**, in the presence of dimethylamine, PytsiH [ $\text{HC}(\text{SiMe}_3)_2\text{SiMe}_2(2\text{-C}_5\text{H}_4\text{N})$ ] and  $\text{Cp}_2\text{E}(\text{NMe}_2)_2$  ( $\text{E} = \text{Al, Ga}$ ) will be the products if the reaction according to path **a** occurs while  $(\text{Pytsi})\text{E}(\text{NMe}_2)_2$  ( $\text{E} = \text{Al, Ga}$ ) and CpH ( $\text{C}_5\text{H}_6$ ) will be the products if the reaction according to path **b** occurs. However, the  $^1\text{H}$  NMR spectrum obtained from the reaction mixtures revealed the presence of  $(\text{Pytsi})\text{ECl}_2$  [ $\text{E} = \text{Al}$  (**28a**) Ga (**28b**)] and  $\text{Cp}_2\text{ZrCl}_2$  (**27**) upon chlorination using  $\text{Me}_3\text{SiCl}$ . Hence, the most probable intermediates are

(Pytsi)E(NMe<sub>2</sub>)<sub>2</sub> (E = Al, Ga) and Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> (path **b**). The Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> is formed as a result of the reaction of CpH with Zr(NMe<sub>2</sub>)<sub>4</sub> (eq 3).<sup>121</sup> In the presence of an excess of Me<sub>3</sub>SiCl, the Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> is converted to Cp<sub>2</sub>ZrCl<sub>2</sub>.

**Scheme 2.5.** Proposed reaction pathways in the presence of dimethylamine.



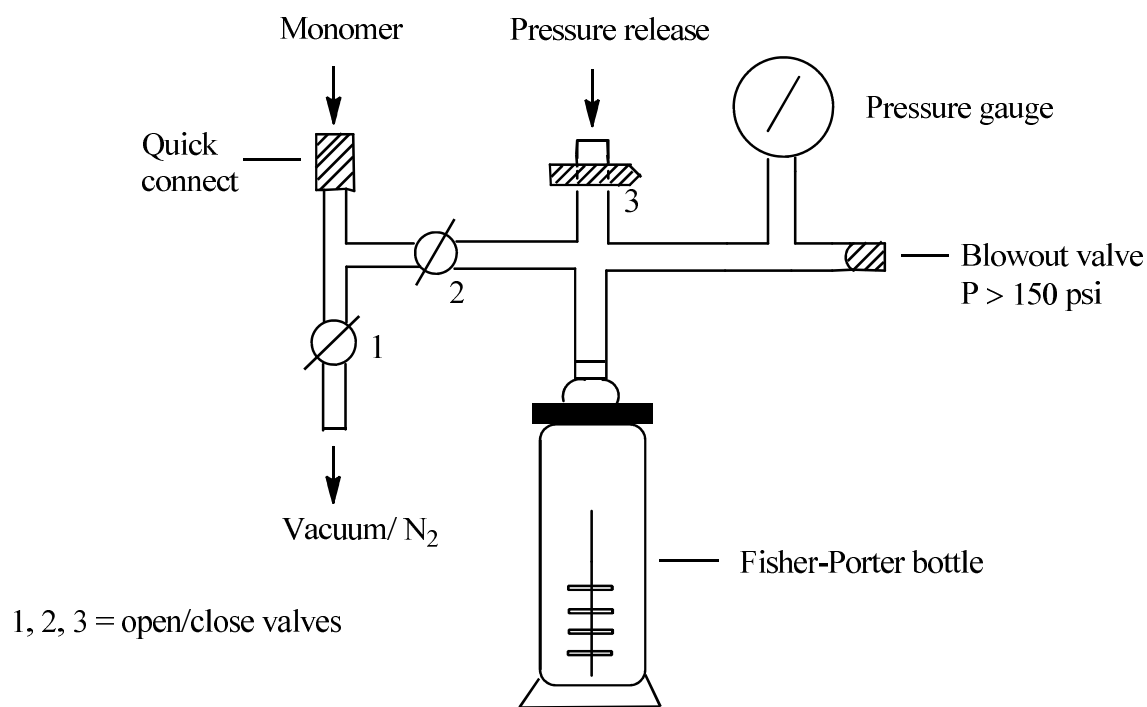
The plausible reaction scheme for the formation of the byproducts in the presence of dimethylamine is shown in scheme 2.5. Based on the result of these reactions (Scheme 2.2 and 2.3), it could be said that the reactants **29** and the aluminum and gallium-bridged *ansa*-zircononcene intermediates (**30**) may have reacted with dimethylamine to produce the side products **27** and **28**. Reactions involving path **b** was confirmed by Grundke and Paetzold,<sup>122</sup> who



reported that boron-cyclopentadienyl linkage is susceptible to cleavage by strong nucleophiles (amongst which are amines).

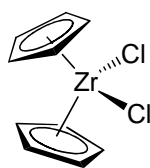
## 2.5 Polymerization Results and Discussion

The results of ethylene polymerization using (Pytsi)Ga[1]ZCP (**31b**) and the unbridged analogue  $\text{Cp}_2\text{ZrCl}_2$  (**27**) activated by MAO is summarized in Table 2.1. The polymerization was performed using a Fisher-Porter bottle glass polymerization reactor system (Figure 2.5).

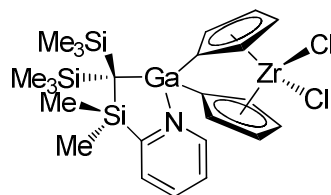


**Figure 2.5.** Fisher-Porter bottle glass polymerization reactor system.

Compound **27** was chosen as a standard to compare the catalytic activity of **31b** because it has been widely accepted by researchers that the conventional  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  system is the most widely studied with known catalytic behavior in ethylene polymerization.<sup>65b,93,105,123</sup>



**27**



**31b**

**Table 2.1.** Results of Ethylene Polymerization<sup>a</sup>

Entry	Precat.	Amount of precat. ( $\mu\text{mol}$ )	P (atm)	MAO (equiv.)	Yield (g)	Activity kg PE (mol Zr) <sup>-1</sup> h <sup>-1</sup> atm <sup>-1</sup>
1	<b>27</b>	10	4.8	300	7.681	640
2	<b>27</b>	5	4.8	300	3.989	665
3	<b>27</b>	5	1.0	300	3.251	2601
4	<b>31b</b>	10	4.8	300	7.648	637
5	<b>31b</b>	5	4.8	300	2.300	383
6	<b>31b</b>	5	1.0	300	1.354	1083

<sup>a</sup>Reaction conditions: Fisher-Porter glass reactor; toluene (15 mL); reaction time: 15 min; average of 2 experiments conducted at ambient temperature.

The isolated yield of polyethylene was used to determine the activity of the catalysts. These results (Table 2.1) show that when the catalyst concentration is 10  $\mu\text{mol}$ , the activity for catalyst **31b** was 637 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup>. This result compares favorably to 640 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> obtained for **27** at the same polymerization conditions using our reactor system. When the concentration of our precatalysts were reduced to 5  $\mu\text{mol}$ , the activity of **31b** decreased substantially from 637 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> to 383 kg PE (mol Zr)<sup>-1</sup> h<sup>-1</sup> atm<sup>-1</sup> (entry 5), unlike **27**, which showed an increase in activity (entry 2). The increase in activity for **27** at low precatalyst concentration is however not surprising as the activity of the precatalyst is known to increase with decrease in catalyst concentration.<sup>93</sup> The reason behind this difference in activity trend at 5  $\mu\text{mol}$  with precatalyst **31b** remains unknown.

It is worthy of note that several experimental values for activity of **27** have been cited in the literature.<sup>65b,93,105,123</sup>

Janiak *et al.* reported an activity of  $11.0 \times 10^3 \text{ kg PE (mol Zr)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$  for  $\text{Cp}_2\text{ZrCl}_2$  [70 °C; 5 bar (4.9 atm) ethylene pressure; 30 min; 4000 equivalents of MAO;  $1 \times 10^{-5} \text{ mol/L}$  of precatalyst; 300 mL toluene]. The activity was however increased to  $29.2 \times 10^3 \text{ kg PE (mol Zr)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$  when the precatalyst concentration was decreased to  $5.0 \mu\text{mol/L}$  and MAO equivalents was increased to 8000. A further increase in the activity was reported when the concentration of  $\text{Cp}_2\text{ZrCl}_2$  was decreased to  $2.5 \times 10^{-7} \text{ mol/L}$  and MAO equivalent increased to 160,000.<sup>93b</sup> However, due to difference in polymerization conditions, it is difficult to use the cited values to make useful comparison with the values obtained for **27** using our glass reactor polymerization system.

Decreasing the monomer concentration (ethylene pressure) from 4.8 to 1.0 atm led to a significant increase in the catalytic activity for both precatalysts **27** and **31b** (entry 3 and 6). This observed increase in activity at low ethylene pressure is however surprising since it is widely believed that a decrease in pressure should lead to a decrease in catalytic activity.<sup>24,51,108,111</sup> According to Gibson's rating, precatalysts with catalytic activities greater than  $1000 \text{ kg PE (mol Zr)}^{-1} \text{ h}^{-1} \text{ bar}^{-1}$  [ $1012 \text{ kg PE (mol Zr)}^{-1} \text{ h}^{-1} \text{ atm}^{-1}$ ] are considered very active for olefin polymerization.<sup>36,105</sup> The effect of the Ga-bridging unit for ethylene polymerization is only pronounced at low catalyst concentration since the activity of **31b** compares favorably with that of the unbridged analogue (**27**) at higher precatalysts concentration.

The results generally show that the gallium-bridged *ansa*-zirconocene complex **31b**, according to Gibson's catalyst rating,<sup>105</sup> is highly active for ethylene polymerization. Also, it can be concluded that the activity of the catalysts is dependent on several reaction conditions such as ethylene pressure (monomer concentration) and catalysts concentration and also catalysts structure (bridging effect and/or ligands). Although the MW of the PE produced with **31b** and

the resultant PDIs are yet to be determined, it will however be interesting to see how the MW changes with changes in precatalyst and monomer concentrations and also to explore the effect of the bridging unit in the polymerization of propylene.

### 3 Summary and Conclusion

Two new aluminum- and gallium-bridged *ansa*-zirconocene compounds, (Pytsi)Al[1]ZCP (**31a**) and (Pytsi)Ga[1]ZCP (**32a**) (Figure 3.1), containing a bulky ligand with a pyridyl donor group, have been synthesized in moderate yields. The aluminum-bridged zirconocene was characterized using multinuclear NMR spectroscopy while the gallium-bridged analogue was characterized using mass spectrometry, multinuclear NMR spectroscopy and elemental analysis.



**Figure 3.1.** The new aluminum- and gallium-bridged *ansa*-zirconocene compounds equipped with intramolecularly coordinated Pytsi ligand.

The compounds were synthesized using the known amine elimination method. The key to obtaining these compounds is found to be the controlled removal of the produced dimethylamine formed during the course of the reaction. The produced amine, when present in the reaction vessel, is acidic enough to react with starting materials (Pytsi)ECp<sub>2</sub> [E = Al (**29a**), Ga (**29b**)] and also with (Pytsi)E[1]Cp<sub>2</sub>Zr(NMe<sub>2</sub>)<sub>2</sub> [E = Al (**30a**), Ga (**30b**)] to produce (Pytsi)ECl<sub>2</sub> [E = Al (**28a**), Ga (**28b**)] and Cp<sub>2</sub>ZrCl<sub>2</sub> (**27**) as the byproducts. The presence of these byproducts made isolation of pure (Pytsi)Al[1]ZCP (**31a**) impossible as both the desired **31a** and the side products (**27** and **28a**) are soluble in most of the solvents used for crystallization. A plausible reaction

scheme for the syntheses of **31a** and **31b** in the presence of dimethylamine has been proposed. The outcome of these syntheses suggests that, although the amine elimination has been widely embraced, the results can be challenging if the amine produced is not controlled appropriately.

The Ga-bridged compound (Pytsi)Ga[1]ZCP (**31b**) was employed as a precatalyst for ethylene polymerization using MAO as the cocatalyst and was found to be highly active with activity rivaling that of  $\text{Cp}_2\text{ZrCl}_2$  obtained using our system. A decrease in ethylene pressure and precatalysts concentration was found to decrease the activity of **31b** significantly. The result of the polymerization shows that the incorporation of the Ga-bridge does not enhance the activity of **31b** in any significant way when compared to  $\text{Cp}_2\text{ZrCl}_2$ . However, this compound when applied for propylene polymerization may be very effective in obtaining polypropylene with interesting tacticity since *ansa*-zirconocene compounds are known to be more stereoselective than their unbridged analogues.

## 4. Experimental Section

### 4.1 General Procedures.

All manipulations were done using standard Schlenk and glovebox techniques ( $N_2$  atmosphere) except where otherwise stated. Solvents were dried using a MBraun solvent purification system and stored under nitrogen over activated 4-Å molecular sieves prior to use.  $C_6D_6$  and  $CDCl_3$  were degassed and stored under nitrogen over 4-Å molecular sieves prior to use.  $^1H$  and  $^{13}C$  NMR spectra were recorded at 25 °C on a Bruker 500 MHz Avance Spectrometer.  $^1H$  NMR chemical shifts were referenced to the residual protons of the deuterated solvent ( $C_6D_6$ :  $\delta$  7.15;  $CDCl_3$ : 7.26);  $^{13}C$  chemical shifts were referenced to:  $\delta$  128.00 ( $C_6D_6$ ) or 77.00 ( $CDCl_3$ ). The chemical shifts were reported in ppm. Mass spectra were measured on a VG 70SE and were reported in the form  $M$  (%I) [F], where  $M$  is the mass observed,  $I$  (%) is the intensity of the peak relative to the most intense peak in the spectrum, and  $F$  is the molecular ion or fragment; only partial data are reported. Elemental analyses were performed on a Perkin Elmer 2400 CHN Elemental Analyzer using  $V_2O_5$  to promote combustion. The Fisher-Porter glass polymerization reactor system was obtained from the laboratory of Dr. Stephen Foley of the Department of Chemistry, University of Saskatchewan. Methylalumoxane (10 wt % in toluene),  $Me_3SiCl$ , and  $Cp_2ZrCl_2$  were purchased from Sigma-Aldrich Chemical Co. and used without further purification.  $Zr(NMe_2)_4$ ,<sup>124a,124b</sup>  $(Pytsi)AlCl_2$ ,<sup>116</sup>  $(Pytsi)GaCl_2$ <sup>117a</sup> and  $NaCp$ <sup>125</sup> were synthesized according to literature procedure.

### Synthesis of $(Pytsi)AlCp_2$ (29a).

$(Pytsi)AlCl_2$ <sup>116</sup> (0.668 g, 1.70 mmol) in toluene (10 mL, 0 °C) was added to  $NaCp$  (0.378 g, 4.29 mmol) in toluene (15 mL, 0°C) and stirred for 10 min before being warmed to

room temperature. The reaction mixture was stirred for an additional 16 h at 70 °C to give a yellow solution. All volatiles were removed in vacuum to give a yellow residue which was extracted with diethyl ether (4 x 10 mL), filtered and the solvent reduced to 6 mL and kept at -25 °C to yield light yellow crystals (0.445 g, 58% ). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.31 (s, 18H, SiMe<sub>3</sub>), 0.39 (s, 6H, SiMe<sub>2</sub>), 6.20 (s, 10H, Cp), 6.28 (pst, 1H, CH-5), 6.76 (m, 2H, CH-3, CH-4), 8.05 (d, 1H, CH-6). <sup>13</sup>C NMR: 5.5 (SiMe<sub>2</sub>), 7.3 (SiMe<sub>3</sub>), 115.5 (CH, Cp), 122.8 (CH-5), 128.7 (CH-3), 139.1 (CH-4), 147.6 (CH-6), 172.1 (C-*ipso*, Cp). <sup>27</sup>Al NMR: 146 (w<sub>1/2</sub> = 1400 Hz). MS: m/z 386 (100) [C<sub>19</sub>H<sub>33</sub>AlNSi<sub>3</sub><sup>+</sup>], 294 (27) [C<sub>14</sub>H<sub>28</sub>NSi<sub>3</sub><sup>+</sup>], 264 (53) [C<sub>12</sub>H<sub>22</sub>NSi<sub>3</sub><sup>+</sup>], 73 (13). Anal. Calcd for C<sub>24</sub>H<sub>38</sub>AlNSi<sub>3</sub> (451.21): C, 63.80; H, 8.48; N, 3.10; Found: C, 62.83; H, 9.05; N, 2.90.

#### Synthesis of (Pytsi)GaCp<sub>2</sub> (29b).

(Pytsi)GaCl<sub>2</sub><sup>117a</sup> (0.927 g, 2.14 mmol) in toluene (15 mL, 0 °C) was added to NaCp (0.466 g, 5.29 mmol) in toluene (10 mL, 0 °C) and stirred for 30 min before being warmed to room temperature. The reaction mixture was stirred for an additional 16 h at 75 °C to give a yellow solution. All volatiles were removed in vacuum to give a yellow residue which was extracted with diethyl ether (3 x 15 mL), filtered and the solvent reduced to 6 mL and kept at -25 °C to yield light yellow crystals (0.877 g, 83% ). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 0.24 (s, 18H, SiMe<sub>3</sub>), 0.37 (s, 6H, SiMe<sub>2</sub>), 6.16 (s, 10H, Cp), 6.33 (pst, 1H, CH-5), 6.78 (pst, 1H, CH-4), 6.82 (d, 1H, CH-3), 8.05 (d, 1H, 6-H). <sup>13</sup>C NMR: 4.9 (SiMe<sub>2</sub>), 6.88 (SiMe<sub>3</sub>), 115.9 (CH, Cp), 123.6 (CH-5), 129.0 (CH-3), 138.4 (CH-4), 147.6 (CH-6), 170.6 (C-*ipso*, Cp). MS: m/z 428 (62) [C<sub>19</sub>H<sub>33</sub>GaNSi<sub>3</sub><sup>+</sup>], 314 (17), 264 (100) [C<sub>12</sub>H<sub>22</sub>NSi<sub>3</sub><sup>+</sup>]. Anal. Calcd for C<sub>24</sub>H<sub>38</sub>GaNSi<sub>3</sub> (494.54): C, 58.29; H, 7.74; N, 2.83; Found: C, 58.27; H, 7.59; N, 2.84.



### Synthesis of (Pytsi)Al[1]ZCP (31a).

A solution of **29a** (0.370 g, 0.82 mmol) in benzene (10 mL) was added to a solution of Zr(NMe<sub>2</sub>)<sub>4</sub> (0.269 g, 1.00 mmol) in benzene (10 mL) at room temperature. The yellow solution was stirred for 10 minutes before being heated to 55 °C for 68 h with a reflux condenser connected to a N<sub>2</sub> inlet and opened to an oil bubbler. N<sub>2</sub> gas was passed by the reflux condenser slowly. Me<sub>3</sub>SiCl (0.374 g, 3.44 mmol) was added dropwise to the solution at room temperature and stirred for 90 min. Volatiles were removed at reduced pressure to give a solid (foam). The product was extracted with 20 mL of diethyl ether, filtered and concentrated to a volume of 5 mL and kept at -25 °C to give analytically impure colorless crystals containing **31a** (0.150 g, 31%) and **27** (0.009 g, 2%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.21 (s, 18H, SiMe<sub>3</sub>), 0.53 (s, 6H, SiMe<sub>2</sub>), 6.08 (pq, 2H, Cp), 6.37 (pq, 2H, Cp), 6.61 (pq, 2H, Cp), 7.09 (pq, 2H, Cp), 7.69 (t, 1H, CH-5), 7.93 (d, 1H, CH-3), 8.12 (t, 1H, CH-4), 8.79 (d, 1H, CH-6). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 3.3 (SiMe<sub>2</sub>), 6.0 (SiMe<sub>3</sub>), 114.1 (CH, Cp), 116.7 (C-*ipso*, Cp), 117.6 (CH, Cp), 125.2 (C5), 127.8 (CH, Cp), 130.2 (CH-3), 134.1 (CH, Cp), 140.4 (CH-4), 147.7 (CH-6), 175.12 (C-2).

### Synthesis of (Pytsi)Ga[1]ZCP (31b).

A solution of **29b** (0.356 g, 0.72 mmol) in benzene (15 mL) was added to a solution of Zr(NMe<sub>2</sub>)<sub>4</sub> (0.289 g, 1.08 mmol) in benzene (10 mL) at room temperature. The yellow solution was heated to 65 °C for 26 h with a reflux condenser connected to a N<sub>2</sub> inlet and opened to an oil bubbler. N<sub>2</sub> gas was passed by the reflux condenser slowly. Me<sub>3</sub>SiCl (0.361 g, 3.30 mmol) was added dropwise to the solution at room temperature and stirred for 1 h. Volatiles were removed at reduced pressure to give a solid. The product was extracted with 20 mL of benzene, filtered and concentrated to a volume of 5 mL and kept at 6 °C to give colorless crystals (0.190 g, 40%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.19 (s, 18H, SiMe<sub>3</sub>), 0.51 (s, 6H, SiMe<sub>2</sub>), 6.11 (pq, 2H, Cp), 6.32 (pq, 2H,

Cp), 6.61 (pq, 2H, Cp), 7.11 (pq, 2H, Cp), 7.65 (m, 1H, CH-5), 7.87 (d, 1H, CH-3), 8.05 (m, 1H, CH-4), 8.79 (d, 1H, CH-6).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ): 2.9 ( $\text{SiMe}_2$ ), 5.5 ( $\text{SiMe}_3$ ), 112.5 (CH, Cp), 117.5 (CH, Cp), 121.4 (C-*ipso*, Cp), 125.1 (CH-5), 125.7 (CH, Cp), 130.1 (CH-3), 133.5 (CH, Cp), 139.5 (CH-4), 148.2 (CH-6), 173.0 (C-2). MS (70 eV, EI+): m/z (%) 653 (18) [ $\text{M}^+$ ], 427 (17) [ $\text{PytsiGaCp}^+$ ], 348 (17) [ $\text{PytsiGa}^+-\text{Me}$ ], 294 (24) [ $\text{PytsiH}^+$ ], 293 (77) [ $\text{Pytsi}^+-\text{H}$ ], 278 (26) [ $\text{Pytsi}^+-\text{H-Me}$ ], 264 (100) [ $\text{Pytsi}^+-2\text{Me}$ ]. Anal. Calcd for  $\text{C}_{24}\text{H}_{36}\text{Cl}_2\text{GaNSi}_3\text{Zr}$  (654.659): C, 44.03; H, 5.54; N, 2.14; Found: C, 43.82; H, 5.71; N, 2.19.

### General Ethylene Polymerization Procedure

A 250 mL Fisher-Bottle supplied by Andrews Glass Company, was oven-dried, charged with a stir bar, connected to a valve polymerization system and sealed (Figure 3.2). The system was connected to a Schlenk line and purged with  $\text{N}_2$  three times. Toluene (15 mL) was added into the bottle (through a septum) using a syringe. The system was evacuated again and filled with  $\text{N}_2$ . 2.8 mL (10  $\mu\text{mol}$ ) or 1.4 mL (5  $\mu\text{mol}$ ) of a solution of  $(\text{Pytsi})\text{Ga}[1]\text{ZCP}$  (**31b**) in toluene ( $3.6 \times 10^{-3}$  M) was added as required using a syringe. The system was evacuated and filled with vacuum after which the reactor was then filled with 10 psi (0.68 atm) of ethylene. MAO solution in toluene (300 equiv; 2.0 mL for 10  $\mu\text{mol}$  of precatalyst or 1.0 mL for 5  $\mu\text{mol}$  of precatalyst) was added to the stirring solution using a syringe. Ethylene pressure was increased to 70 psi (4.7 atm) or 15 psi (1 atm) as applicable. The mixture was then stirred vigorously (1200 rpm) at room temperature. After 15 min, ethylene flow was turned off and the reactor depressurized. Acidified methanol (60 mL of 1M HCl/  $\text{CH}_3\text{OH}$ ) was added using a syringe to quench the polymerization reaction. The mixture was then filtered (gravity filtration) under normal atmosphere and washed with acidified methanol (60 mL), followed by methanol (60 mL). The resulting polymer was dried under high vacuum at 70  $^\circ\text{C}$  overnight, giving polyethylene as a white powder. The yield

(g) of PE reported in each entry (Table 2.1) is the average obtained from two runs. For each of entries 1-6, the yields of PE obtained are 7.728 and 7.633, 4.121 and 3.856, 3.117 and 3.386, 7.367 and 7.929, 2.315 and 2.284, and 1.362 and 1.339, respectively.

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