

**Substituted nickel pyrazole and palladium pyrazolyl  
complexes as catalyst precursors for ethylene  
polymerization**

**By**

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**A thesis submitted in partial fulfilment for the degree of  
Master of Science in the Department of Chemistry at the  
University of the Western Cape.**

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Date: May 2003**

## Declaration

I declare that **Substituted pyrazole nickel and pyrazolyl palladium complexes as catalyst precursors for ethylene polymerization** is my own work, that it has not been submitted before for any degree or examination in any other university and that all the sources I have used or quoted have been indicated and acknowledged by complete references.

SIMPHIWE MAURICE NELANA

DATE

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*22-05-2003*  
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## ACKNOWLEDGEMENTS

First of all I would like to thank God for protecting me all these years. Secondly I am grateful to my supervisor Prof. J. Darkwa for the support and encouragement. My sincere gratitude goes out to my co-supervisor Prof. S. F. Mapolie for guidance and for performing the high temperature NMR spectroscopy of the polymers. I would also like to thank my colleagues Mr. R. M. Moutloali, Ms. M. S. Mohlala, Mr. T. V. Segapelo and Mr. W. P. Swiggelaar. To the entire staff and postgraduate students of the Department of Chemistry at the University of the Western Cape thank you for everything.

Financial support from NRF and ESKOM is gratefully acknowledged. Thanks to Dr I.A. Guzei (University of Wisconsin, Madison, USA) for all the X-ray crystallography analyses. Thanks to Dr Ddamba (University of Botswana) and Mr W. Mhlongo (University of Cape Town) for thermal analyses. I would like to thank Mr S. de Goude (SASOL Technologies) and Dr V. Grumel (Institute for Polymer Science, University of Stellenbosch) for high temperature GPC analyses. I would like to thank my family especially my dad Mr. Buyekile Geza for believing in me. To my close friends Mr M.M. Ganto and Mr T. Ngenelwa thank you very much for encouraging me.

**ABSTRACT**

This study concerns the synthesis of pyrazole and substituted pyrazole nickel complexes of the type  $[(3,5-R,R'pz)_2NiBr_2]$  (pz = pyrazole; R = R' = CH<sub>3</sub> (**1**), <sup>t</sup>Bu (**4**)) and of the type  $[(3,5-R,R'pz)_4NiBr_2]$  (R = H, R' = CH<sub>3</sub>, (**2**); R = R' = H (**3**)). These complexes were synthesized by reacting (DME)NiBr<sub>2</sub> and the appropriate pyrazole or substituted pyrazole in dichloromethane. The products were obtained in moderate to good yields. All the complexes isolated were characterized by a combination of IR spectroscopy, <sup>1</sup>H NMR spectroscopy and elemental analysis. Complexes **1** and **2** were further characterized by single crystal X-ray crystallography. Complex **1** was found to have a tetrahedral geometry and complex **2** has an octahedral geometry. In addition to the pyrazole nickel complexes, new pyrazolyl ligands with alkane- $\alpha,\omega$ -dione linkers  $[RpzC(O)(CH_2)_nC(O)pzR]$ ; R = CH<sub>3</sub>, n = 0 (**A1**), n = 2 (**A2**), n = 3 (**A3**) and R = <sup>t</sup>Bu, n = 3 (**A4**) were synthesized. These new ligands were characterized by IR spectroscopy, <sup>1</sup>H NMR, <sup>13</sup>C NMR spectroscopy and elemental analysis. They were further reacted with (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> in attempts to obtain  $\alpha,\omega$ -bis(3,5-R<sub>2</sub>pyrazolyl)alkane- $\alpha,\omega$ -dione palladium chloride complexes. These ligands tend to undergo hydrolysis when they are reacted with (CH<sub>3</sub>CN)<sub>2</sub>PdCl<sub>2</sub> as confirmed by <sup>1</sup>H NMR spectral analysis. One complex, 1,5-bis(3,5-Me<sub>2</sub>pz)pentane-1,5-dione palladium chloride was successfully prepared under very dry solvent conditions. The 1,5-bis(3,5-Me<sub>2</sub>pz)pentane-1,5-dione palladium chloride complex was characterized by <sup>1</sup>H NMR spectroscopy.

The pyrazole nickel complexes **1** and **3** were used as catalysts for ethylene polymerization after activation with methylaluminoxane (MAO) to give high-density polyethylene (HDPE). Complex **3** was found to have a higher activity than complex **1**, since the metal centre is more accessible in **3** than **1**. In these polymerization reactions temperature, pressure and MAO concentration were varied. Activities ranging from 40 kg PE/mol Ni h to 3000 kg PE/mol Ni h were obtained with these catalysts depending on the conditions used. Polymers obtained were characterized by high temperature  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, high temperature gel permeation chromatography (GPC) and thermal analysis. Molecular weights between  $0.84 \times 10^6$  –  $3.86 \times 10^6$  g/mol and melting point range of 130 – 137 °C were observed for these polymers. All this data suggests that the polyethylene produced in this study is linear. Molecular weight of the polymers produced tends to decrease with increasing temperature and increasing pressure. This is due to the high rate of  $\beta$ -hydride elimination over chain propagation.

Another ethylene polymerization catalyst used in this study was 1,3,5-benzenetricarbonylpyrazolyl palladium complex (**4**). Activities ranging from 440 kg PE/mol Pd h to 2497 kg PE/mol Pd h were observed for this catalyst. The effect of MAO concentration and temperature on the catalyst activity was investigated. At co-catalyst to catalyst ratio (Al: Pd) above 3000:1 catalyst activity decreases and at high temperatures (50-70 °C) low molecular polyethylene is produced. The polymers produced using **4** have melting points between 136 and 138 °C, which is indicative of linear polyethylene.

**List of abbreviations**

DFT	Density Functional Theory
DSC	Differential Scanning Calorimetry
Et <sub>3</sub> N	Triethylamine
DME	1,2-dimethoxyethane
GPC	Gel Permeation Chromatography
HDPE	High Density Polyethylene
IR	Infrared
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
M	Transition metal
MAO	Methylaluminoxane
MeCN	Acetonitrile
M <sub>n</sub>	Number-average molecular weight
M <sub>w</sub>	Weight-average molecular weight
NMR	Nuclear magnetic resonance
PD	Polydispersity
PE	Polyethylene
R	Alkyl
TON	Turnover numbers
T <sub>m</sub>	Melting point
X	Halogen

**TABLE OF CONTENTS**

<b>Content</b>	<b>Page</b>
DECLARATION	ii
ACKNOWLEDGEMENTS	iii
ABSTRACT	iv
LIST OF ABBREVIATIONS	vi
LIST OF SCHEMES	x
LIST OF FIGURES	xi
LIST OF TABLES	xiii
<b>CHAPTER 1: Overview of olefin polymerization catalysis and coordination chemistry of pyrazole based ligands</b>	<b>1</b>
1.1 General background	1
1.1.1 Polyethylene structural details	2
1.2 Early work in olefin polymerization catalysis	6
1.3 Metallocenes as olefin polymerization catalysts	8
1.3.1 Co-catalysts for single site catalysts	11
1.4 Late transition metal complexes as olefin polymerization catalysts	12
1.4.1 Nickel complexes as olefin oligomerization and oligomerization catalysts	12
1.4.2 Nitrogen based late transition metal complexes as olefin polymerization catalysts	15
1.4.3 Synthesis of nitrogen based nickel and palladium complexes	19
1.5 Pyrazole based ligands and complexes	24

1.5.1 Synthesis of substituted pyrazole ligands	24
1.5.2 The coordination chemistry of pyrazole ligands	25
1.5.3 The coordination chemistry of pyrazolyl ligands	29
1.5.3.1 Poly(1-pyrazolyl)borates or scorpionates	30
1.5.3.2 Poly(1-pyrazolyl) alkanes	32
1.6 Objectives of the study	36
References	37
<b>Chapter 2: Synthesis of substituted pyrazole nickel complexes and pyrazolyl ligands and their palladium complexes</b>	<b>45</b>
2.1 Introduction	45
2.1.1 Synthesis of substituted pyrazole nickel complexes and linked pyrazolyl ligands	45
2.2 Experimental section	46
2.2.1 Materials and instrumentation	46
2.2.2 Preparation of nickel complexes	47
2.2.2.1 Preparation of (3,5-Me <sub>2</sub> pz) <sub>2</sub> NiBr <sub>2</sub>	47
2.2.2.2 Preparation of (5-Mepz) <sub>4</sub> NiBr <sub>2</sub>	47
2.2.2.3 Preparation of (pz) <sub>4</sub> NiBr <sub>2</sub>	48
2.2.2.4 Preparation of (3,5- <sup>t</sup> Bu <sub>2</sub> pz) <sub>2</sub> NiBr <sub>2</sub>	48
2.2.3 Preparation of $\alpha,\omega$ -bis(3,5-R <sub>2</sub> pyrazolyl)alkane - $\alpha,\omega$ -dione ligands	48
2.2.3.1 Preparation of 1,2-bis(3,5-Me <sub>2</sub> pz)ethane-1,2-dione	48
2.2.3.2 Preparation of 1,4-bis(3,5-Me <sub>2</sub> pz)butane-1,4-dione	49
2.2.3.3 Preparation of 1,5-bis(3,5-Me <sub>2</sub> pz)pentane-1,5-dione	49
2.2.3.4 Preparation of 1,5-bis(3,5- <sup>t</sup> Bu <sub>2</sub> pz)pentane-1,5-dione	50



2.3 Synthesis of pyrazolyl palladium complexes	50
2.3.1 Reaction of 1,5-bis(3,5-dimethylpyrazolyl)pentane-1,5-dione ( <b>A3</b> ) and $(\text{CH}_3\text{CN})_2\text{PdCl}_2$	50
2.4 X-ray crystal structure determination of $(3,5\text{-dimethylpyrazole})_2\text{NiBr}_2$ and $(5\text{-methylpyrazole})_4\text{NiBr}_2$	51
2.5 Results and discussions	53
2.5.1 Synthesis of substituted pyrazole nickel complexes	53
2.5.2 Molecular structure of <b>1</b>	60
2.5.3 Molecular structure of <b>2</b>	64
2.5.4 Synthesis of $\alpha,\omega$ -bis(3,5- $\text{R}_2$ pyrazolyl)alkane - $\alpha,\omega$ -dione ligands	69
2.5.5 Synthesis of $\alpha,\omega$ -bis(3,5- $\text{R}_2$ pyrazolyl)alkane - $\alpha,\omega$ -dione palladium complexes	75
2.6 Summary	81
References	82
<b>CHAPTER 3: Ethylene polymerization catalyzed by nickel and palladium pyrazolyl complexes</b>	84
3.1 Introduction	84
3.1.1 Nitrogen based late transition metal complexes as olefin polymerization catalysts	84
3.2 General procedure for ethylene polymerization	85
3.3 Results and discussions	86
3.3.1 Polymerization results using nickel catalysts	86
3.3.1.1 Comparison between catalyst <b>1</b> and <b>2</b> in ethylene polymerization	87
3.3.1.2 The effect of temperature on ethylene polymerization by catalyst <b>1</b>	89
3.3.1.3 The effect of pressure on ethylene polymerization by catalyst <b>1</b>	98

3.3.2 Polymerization results for the pyrazolyl palladium catalyst	103
3.4 Summary	107
References	108
<b>CHAPTER 4: Conclusions</b>	111

### List of Schemes

Scheme 1.1: Cossee-Arlman mechanism for olefin polymerization	7
Scheme 1.2: Synthesis of P,O chelated nickel complexes	13
Scheme 1.3: Synthesis of Grubbs catalysts	14
Scheme 1.4: General mechanism for ethylene polymerization by Brookhart catalysts	23
Scheme 1.5: Synthesis of substituted pyrazole palladium complexes	29
Scheme 1.6: Activation pathway of bis(pyrazolyl)methane palladium complexes	34
Scheme 1.7: Synthesis of 1,3-benzenedicarbonylpyrazolyl palladium chloride complexes	35
Scheme 1.8: Synthesis of 1,3,5-benzenetricarbonylpyrazolyl palladium chloride complexes	35
Scheme 2.1: Synthetic route to substituted pyrazole nickel complexes	54
Scheme 2.2: Synthesis of substituted $\alpha,\omega$ -bis(3,5-R <sub>2</sub> pyrazolyl)alkane- $\alpha,\omega$ -dione ligands	69
Scheme 2.3: Synthesis of substituted $\alpha,\omega$ - bis(3,5-R <sub>2</sub> pyrazolyl)alkane- $\alpha,\omega$ -dione palladium complexes	75

**List of Figures**

Figure 1.1: Schematic representation of various types of polyethylene	4
Figure 1.2: $^{13}\text{C}$ NMR spectrum of linear polyethylene	5
Figure 1.3: $^{13}\text{C}$ NMR spectrum of branched polyethylene	5
Figure 1.4: General structure of a pyrazole compound	24
Figure 1.5: Mesogenic pyrazole palladium complex	27
Figure 2.1: $^1\text{H}$ NMR spectrum (in $\text{CDCl}_3$ ) of complex <b>1</b>	57
Figure 2.2: $^1\text{H}$ NMR spectrum (in $\text{D}_2\text{O}$ ) of complex <b>3</b>	58
Figure 2.3: IR spectrum of complex <b>3</b>	59
Figure 2.4: ORTEP diagram of complex <b>1</b>	61
Figure 2.5: ORTEP diagram of complex <b>2</b>	66
Figure 2.6: IR spectrum of ligand <b>A3</b>	72
Figure 2.7: $^1\text{H}$ NMR spectrum (in $\text{CDCl}_3$ ) of ligand <b>A3</b>	73
Figure 2.8: $^{13}\text{C}$ NMR spectrum (in $\text{CDCl}_3$ ) of ligand <b>A3</b>	74
Figure 2.9: $^1\text{H}$ NMR spectrum (in $\text{CDCl}_3$ ) of the mixture of <b>A2</b> ligand complex $(3,5\text{-Me}_2\text{pz})_2\text{PdCl}_2$	76
Figure 2.10: $^1\text{H}$ NMR spectrum (in $\text{CDCl}_3$ ) of $(3,5\text{-Me}_2\text{pz})_2\text{PdCl}_2$	76
Figure 2.11: $^1\text{H}$ NMR spectrum (in $\text{CDCl}_3$ ) of <b>A3</b> ligand complex	80
Figure 2.12: $^1\text{H}$ NMR spectrum (in $\text{CDCl}_3$ ) of <b>A3</b> ligand	80
Figure 3.1: Nickel catalysts used in this study	86
Figure 3.2: A graph showing the effect of temperature on ethylene polymerization using <b>1</b>	92
Figure 3.3: A GPC trace of polyethylene produced at 25 °C using <b>1</b>	93
Figure 3.4: A GPC trace of polyethylene produced at 70 °C using <b>1</b>	94

Figure 3.5: $^1\text{H}$ NMR spectrum of polyethylene produced at 25 °C using <b>1</b>	95
Figure 3.6: TGA-DTA thermogram of polyethylene produced at 25 °C using <b>1</b>	97
Figure 3.7: A graph showing the effect of pressure on ethylene polymerization using <b>1</b>	100
Figure 3.8: TGA-DTA thermogram of polyethylene produced at 1 atm using <b>1</b>	102
Figure 3.9: Palladium pyrazolyl catalysts ( <b>3</b> and <b>4</b> )	104
Figure 3.10: A graph showing the effect of MAO concentration on the catalyst activity of <b>4</b>	106

**List of Tables**

Table 1.1: The melting point ranges characteristic of each type of polyethylene	5
Table 2.1: Crystal data and structure refinement for <b>1</b>	62
Table 2.2: Bond lengths and angles for <b>1</b>	63
Table 2.3: Crystal data and structure refinement for <b>2</b>	67
Table 2.4: Bond lengths and angles for <b>2</b>	68
Table 2.5: Hydrogen bonds for <b>2</b>	68
Table 3.1: Ethylene polymerization data and conditions for catalyst <b>1</b> and <b>2</b>	89
Table 3.2: Effect of temperature on ethylene polymerization by catalyst <b>1</b>	90
Table 3.3: Effect of pressure on ethylene polymerization by catalyst <b>1</b>	99
Table 3.4: Ethylene polymerization data and conditions for catalyst <b>4</b>	104

## CHAPTER 1

### Overview of olefin polymerization catalysis and coordination chemistry of pyrazole based ligands

#### 1.1 General background

Catalysis has made a huge contribution to the chemical, petrochemical and oil refining industry. Catalysis is divided into three subdivisions namely: heterogeneous, homogeneous and bio-catalysis. Homogeneous catalysis is used in a number of industrial processes, such as hydrogenation, oxidation, oligomerization, polymerization and hydrocyanation and many more. For most industrial reactions, highly effective catalysts are required to accelerate these processes. For a catalyst to be effective, it has to combine high efficiency, high selectivity and total turnover with high durability.

Polymerization is a process whereby a monomer such as ethylene or propylene is converted to a large molecule called a polymer or a macromolecule. Polymer molecules consist of a restricted number of chemically different organic monomer residues: one for homopolymers, two in copolymers and three in terpolymers. The term polydispersity is used as a measure of polymer molecular weight distribution. In most cases polydispersity (PD) is measured as the weight average-molecular weight ( $M_w$ ) divided by the number average molecular weight ( $M_n$ ) (i.e.  $PD = M_w/M_n$ ). Polydispersity imparts certain properties to the polymer like toughness, rigidity and

strength. The bulk of polyolefin (i.e. a product from the polymerization of olefins) production involves catalysis, either homogeneous or heterogeneous. Polyolefins are interesting polymers because they have diverse applications and are non toxic. For years, polyethylene (PE) has been used in food packaging, coatings, countless molded toys, and other household items, and it is now finding its way into the market to replace common materials such as glass, metal, paper and concrete.<sup>1</sup> Compared to other conventional materials, polyolefins require low energy in their production. Different transition metals are involved as catalysts in olefin polymerization. It is now possible to tailor the coordination environment of a metal centre in a catalyst to control molecular weight, molecular weight distribution, co-monomer incorporation, end groups and absolute stereochemistry of a polymer. Catalysts development has thus been and continues to be important to the polyolefin industry. This thesis combines the synthesis and testing of catalysts for polyethylene production. The following sections will focus on the structural details and catalysts development in this area of research.

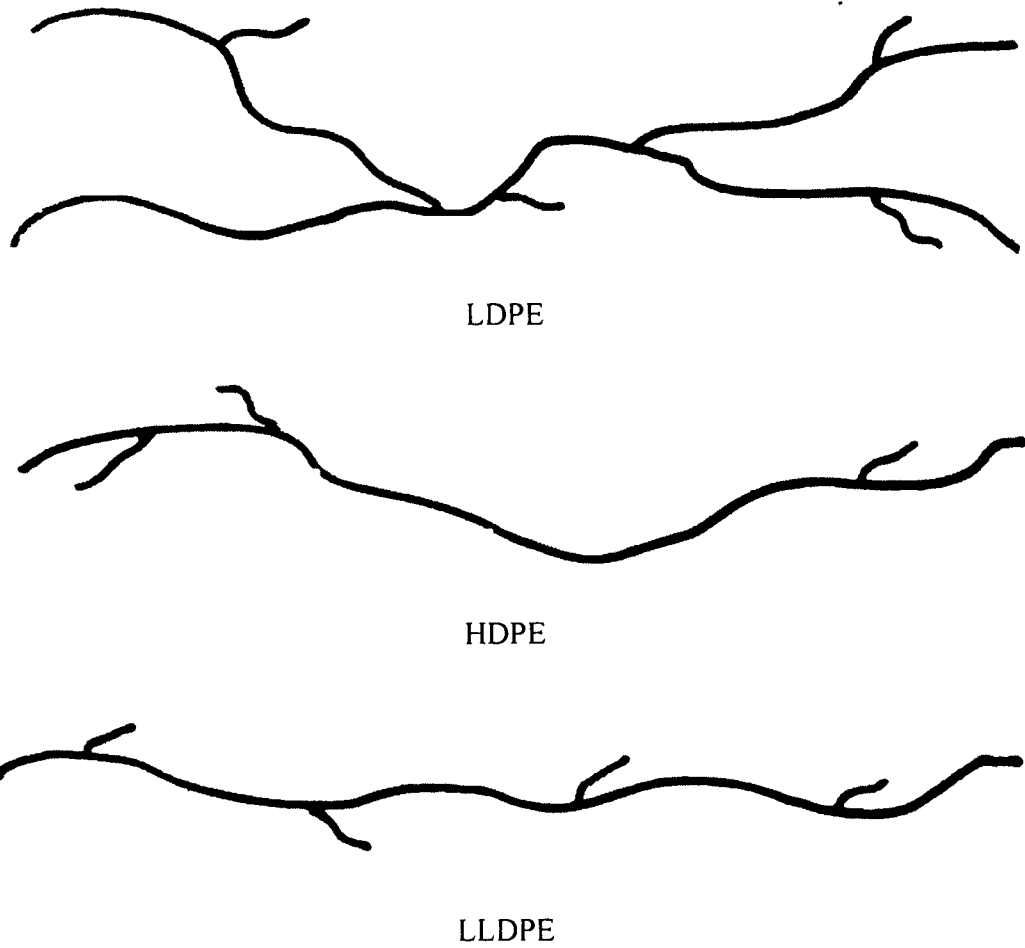
### ***1.1.1 Polyethylene structural details***

Polyethylenes are olefinic polymers manufactured in the largest tonnage of all the thermoplastic materials.<sup>1</sup> They are produced by addition polymerization of ethylene to give the basic structure  $-(CH_2-CH_2)_n-$ . Polyethylene is classified according to density and the density of the polymer dictates its application. The first type of polyethylene is called low-density polyethylene (LDPE), which is a polymer with a density of 0.915-0.935 g/cm<sup>3</sup>. It is a highly branched material. This polymer is

prepared by a free radical polymerization process at high temperatures (300-400 °C) and extremely high pressures (3000 atm). The second type is high-density polyethylene (HDPE), which has a density between 0.941-0.967 g/cm<sup>3</sup>. This form of polyethylene contains moderate branches and is prepared using both conventional Ziegler-Natta and metallocene catalysts. Another form of HDPE, is called ultrahigh molecular weight polyethylene (UHMWPE), has a molecular weight ( $M_w$ ) in the range 3-6 million, while the normal HDPE has molecular weight less than 3 million. The third type of polyethylene is linear low-density polyethylene (LLDPE), with density of 0.910-0.925 g/cm<sup>3</sup>. Here the word 'linear' refers to the absence of long branches in the polymer chain. LLDPE is formed from the co-polymerization of ethylene with other olefins, such as 1-butylene and 1-hexene. The different types of polyethylene are shown schematically in Figure 1.1.

To identify the above types of polyethylene, certain properties are investigated. One of these properties is melting point, which is measured using differential scanning calorimetry (DSC). Each type of polyethylene has a characteristic melting point range as shown in Table 1.1. Another analytical technique that is used to characterize polyethylene is NMR spectroscopy. NMR spectroscopy can be used to distinguish between branched and linear polymers. Typical <sup>13</sup>C NMR spectra for linear and branched polyethylene are shown in Figure 1.2 and Figure 1.3 respectively.





**Figure 1.1:** Schematic representation of the various types of polyethylene

**Table 1.1:** The melting point ranges characteristic of each type of polyethylene.

Type of polyethylene	Melting point range (°C)
LDPE	106-112
LLDPE	120-25
HDPE	130-133
UHMWPE	130-132

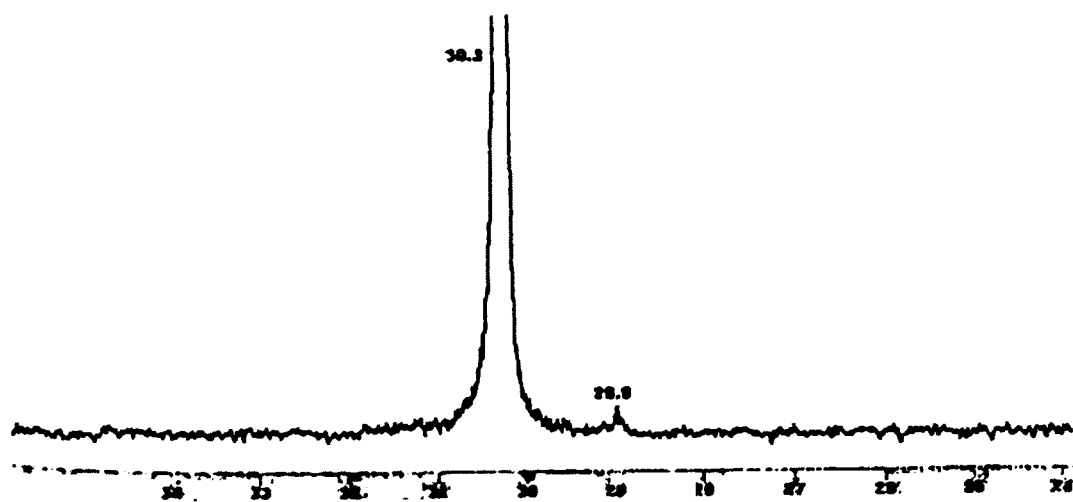


Figure 1.2:  $^{13}\text{C}$  NMR spectrum of a linear polyethylene

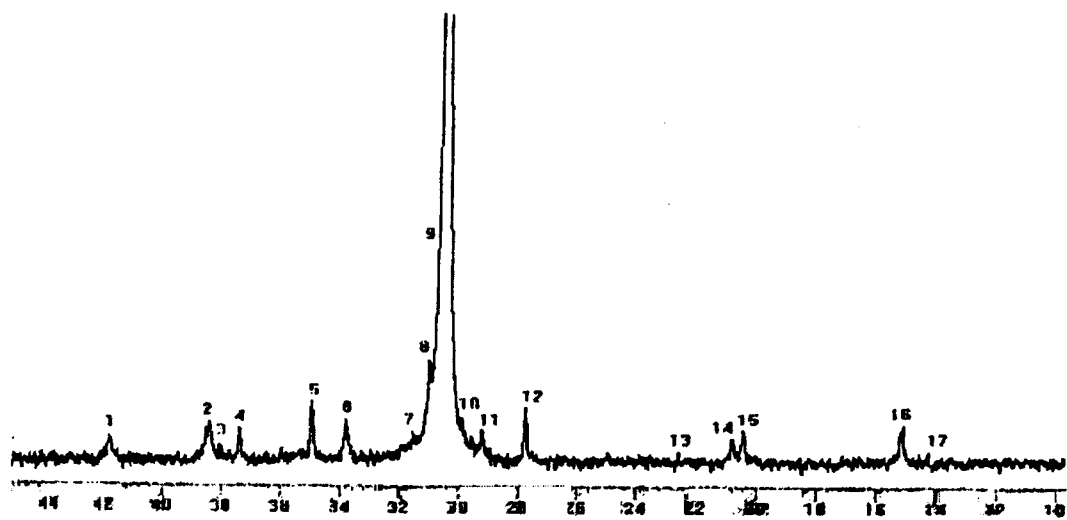


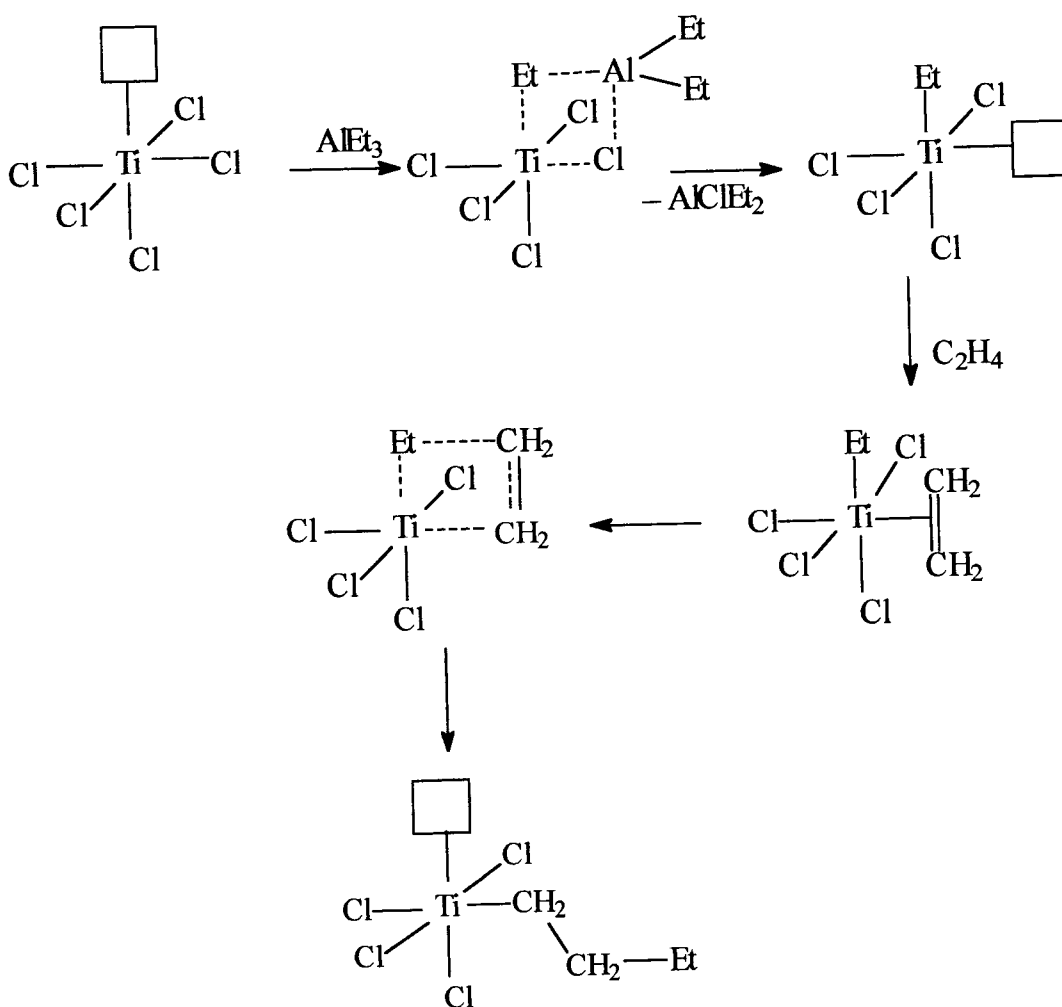
Figure 1.3:  $^{13}\text{C}$  NMR spectrum of branched polyethylene

## 1.2 Early work on olefin polymerization catalysis

The discovery by Ziegler and Natta that transition metal complexes can catalyze polymerization of ethylene and other olefins is one of the great discoveries in the history of chemistry.<sup>2</sup> Prior to that free radical polymerization was the only process used for olefin polymerization reactions. The shortcoming of free radical polymerization is that harsh conditions that are needed for this process to take place, with pressures as high as 3000 atm and temperatures of 300 to 400 °C. Another shortcoming of free radical polymerization is that the process only gives low-density polyethylene. In 1955 Ziegler found that a  $\text{TiCl}_4\text{-Et}_3\text{AlCl}$  catalyst system could polymerize ethylene to high molecular weight polyethylene under mild conditions.<sup>2</sup> About the same time Natta independently showed that propylene can be stereoselectively polymerized to stereo-regular polypropylene, using a catalyst system closely related to that of Ziegler.<sup>3</sup>

A few years after the findings by Ziegler and Natta, Hogan<sup>4</sup> at Philips Petroleum Co., reported that a mixture of oxides of chromium, supported on silica polymerizes ethylene to high-density polyethylene. The advantage of this catalyst over the Ziegler-Natta catalysts is that no co-catalyst is needed in the polymerization reaction. All the olefin polymerization catalysts described above are heterogeneous, they require a solid support for them to function effectively. The support system that makes  $\text{TiCl}_4\text{-AlEt}_3$  catalysts highly active in olefin polymerization is  $\text{MgCl}_2$ . The catalyst is prepared by co-milling  $\text{TiCl}_3$  and  $\text{TiCl}_4$  with  $\text{MgCl}_2$ . Another widely used support for these catalysts is silica.<sup>5</sup> The mechanism by which olefins polymerize via

the Ziegler-Natta process was first proposed by Cossee.<sup>5</sup> After various modifications olefin polymerization is now generally accepted to proceed via what is known as the Cossee and Arlman mechanism (Scheme 1.1).<sup>5</sup> The mechanism involves chain growth by *cis*-insertion of the olefin into a Ti-C bond.



**Scheme 1.1:** Cossee-Arlman mechanism for olefin polymerization

### 1.3 Metallocenes as olefin polymerization catalysts

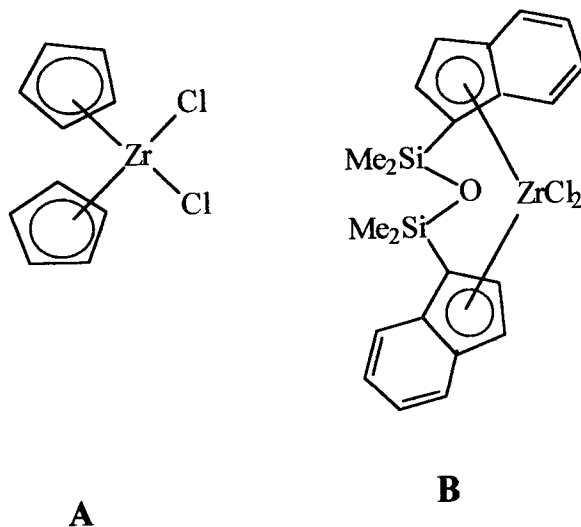
The active sites in heterogeneous catalyst systems are non-uniform. The non-uniformity of the active sites at times results in the formation of different products. It is thus difficult to have concrete evidence of the reaction mechanism in heterogeneous catalysis. It is believed that homogeneous catalyst systems can provide clues on the reaction mechanisms involved in catalytic processes in general and olefin polymerization in particular. In 1957 Breslow<sup>7a</sup> and Natta<sup>7b</sup> independently reported that homogeneous reaction mixtures of dicyclopentadienyltitanium dichloride ( $\text{Cp}_2\text{TiCl}_2$ ) and diethylaluminium chloride ( $\text{Et}_2\text{AlCl}$ ) polymerize ethylene with moderate activity, under conditions similar to those used for Ziegler-Natta catalysts.<sup>2,3</sup> These homogeneous catalyst systems could not polymerize propylene and other higher  $\alpha$ -olefins. Mechanistic studies by Breslow<sup>8</sup> and Chien<sup>9</sup> led to a proposal that ethylene polymerization proceeds via olefin insertion into the Ti-C bond of the electron deficient species  $\text{Cp}_2\text{TiRCl}$ . The alkyl titanocene complex ( $\text{Cp}_2\text{TiRCl}$ ) is formed by ligand exchange between titanium complex and aluminium compound. Coordination of the Lewis acid aluminium centre in  $\text{Et}_2\text{AlCl}$  to the chloride of the titanium complex polarizes the Ti-Cl bond to create an electron deficient  $\text{Cp}_2\text{TiR}$  species, which readily inserts ethylene. This mechanism is in line with the mechanism proposed by Cossee and Arlman.<sup>5</sup>

Overall metallocenes activated with alkylaluminium halides are unable to polymerize propylene and higher olefins, and that initially limited their utility in this field. The low activity of these metallocene-alkylaluminium halide based catalysts led to a new

search for more effective co-catalysts. Reichert and Meyer<sup>10</sup> reported that addition of water to the metallocene-alkyl aluminium system caused a surprising increase in the rate of ethylene polymerization by the catalyst system  $\text{Cp}_2\text{TiEtCl}/\text{AlEtCl}_2$ . Prior to this water was considered to be a poison for olefin polymerization catalysts. Subsequent studies by Long and Breslow showed that addition of water to the inactive system  $\text{Cp}_2\text{TiCl}_2/\text{Me}_2\text{AlCl}$  gives some activity.<sup>11</sup> They suggested that a dimeric aluminoxane with the structure  $\text{ClMeAl-O-AlMe}$  was formed, which was believed to be a stronger Lewis acid than  $\text{Me}_2\text{AlCl}$ . They also concluded that dimeric aluminoxane was a more efficient activator and was responsible for enhanced ethylene polymerization activity.

Sinn and Kaminsky also added water to the halogen free, polymerization inactive  $\text{Cp}_2\text{ZrMe}_2/\text{AlMe}_3$  system and observed high activity for ethylene polymerization.<sup>12</sup> The combined effort of the above researchers led to the discovery of the highly effective activator, an oligomeric methylaluminoxane, (MAO).<sup>12</sup> For example metallocene catalysts (**A** and **B**) are now routinely activated with MAO and are capable of polymerizing propylene and other higher olefins, in contrast to aluminium halide activated systems.<sup>13</sup> Catalyst activities between 890 and 111900 kg of polyethylene per mol of metallocene per hour (kg/mol h) are achieved with these catalysts.<sup>13</sup> The discovery of MAO rejuvenated Ziegler-Natta catalysis and along with major advances achieved in controlling polymer stereochemistry and architecture, began what is called "single site" polymerization catalysis. These catalysts are called single site catalysts because they have a general formula  $\text{L}_n\text{MR}$ ,

where  $L_n$  is an organic ligand part that remains bound and thus modifies the reactivity of the active metal center (M) during the entire chemical reaction and R is a growing polymer chain.



The polymers obtained from metallocene catalysts show different microstructures and properties compared to those produced by conventional Ziegler-Natta catalysts. Due to their efficiency, versatility and flexibility, metallocene/MAO catalysts have made possible the production of polyolefins, homopolymers and copolymers with narrow molecular weight distribution, raised degrees of density, low amount of extractables, high degree of tacticity and uniform co-monomer distribution.<sup>14</sup> One of the shortcomings of metallocene catalysts is their inability to polymerize polar olefins, because of the oxophilic nature of early transition metals used in metallocenes. To address this shortcoming, there has been a renewed focus on late

transition metal complexes as olefin polymerization catalysts, since these metals are less oxophilic.

### *1.3.1 Co-catalysts for ethylene polymerization by single site catalysts*

The discovery of methylaluminoxane and the extent to which it is used as a co-catalyst has been described above. MAO as an activator is thought to (i) replace halides from a dihalide precursor complex with methyls, (ii) abstract a  $\text{CH}_3^-$  from a transition metal complex, forming a weakly coordinating counterion, and (iii) scavenge or scrub impurities. Even though the methylaluminoxane activated polymerization catalysts are promising future catalysts, they suffer from two shortcomings. Firstly, large amounts of MAO (Zr:Al, 1:3000) are required to obtain satisfactory catalytic activity. Secondly, the exact molecular composition and structure of MAO are not entirely clear, making it difficult to study its activation pathway. In metallocene olefin polymerization catalysis, MAO is the mostly used activator, but there are other co-catalysts based on perfluoroaryl boron compounds such as  $\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{Ph}_3\text{C}^+\text{B}(\text{C}_6\text{F}_5)_4^-$ . The different types of olefin polymerization co-catalysts has recently been reviewed by Chen and Marks.<sup>15</sup> This review describes suitable co-catalysts for different catalysts from metallocene based to non-metallocene based catalysts. Hence it appears that the problem of larger amount of co-catalyst might be solved in the industrial process soon.



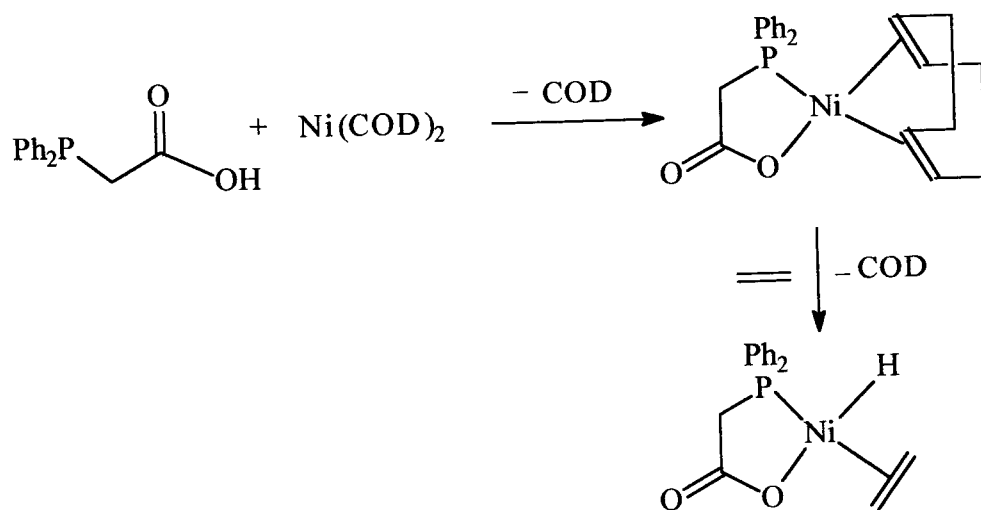
## 1.4 Late transition metals as olefin polymerization catalysts

### 1.4.1 Nickel complexes as olefin oligomerization and polymerization catalysts

One of the best known late transition metal catalyzed processes is the Shell High Olefin Process (SHOP) developed by Keim,<sup>16,17</sup> which uses nickel complexes as catalysts. This process involves the oligomerization of ethylene to linear  $\alpha$ -olefins in the C<sub>4</sub>-C<sub>20</sub> range, which are converted to detergents, plasticizers, lubricants and a variety of fine chemicals. The nickel complex used in the SHOP process is a P-O anionic chelate complex that can be prepared *in situ* from the ligand and (COD)<sub>2</sub>Ni (Scheme 1.2). The scale in which this process is applied is about 1 million tons per year, and makes it one of the widely used process for the production of linear  $\alpha$ -olefins.<sup>18</sup> The distribution of molecular weights is essentially a Schulz-Flory distribution.<sup>19</sup>

Oligomerization reactions industrially are mostly carried in polar solvents such as polyols, which are largely immiscible with the  $\alpha$ -olefins formed,<sup>20</sup> a sign that late transition metals can tolerate polar solvents. In 1987 Klabunde<sup>21</sup> showed that using a nickel catalysts similar to those used by Keim<sup>16,17</sup> for olefin oligomerization, it was possible to prepare high molecular weight polymers by removing a phosphine with a phosphine sponge or phosphine scavenger. The removal of a phosphine in these complexes opens a vacant site for ethylene to coordinate and subsequently insert into a methyl alkyl bond. The effect of this is the transformation of a catalyst meant for the production of  $\alpha$ -olefins, to a catalyst for the production of polyolefins, a development that showed late transition metal complexes could catalyze the

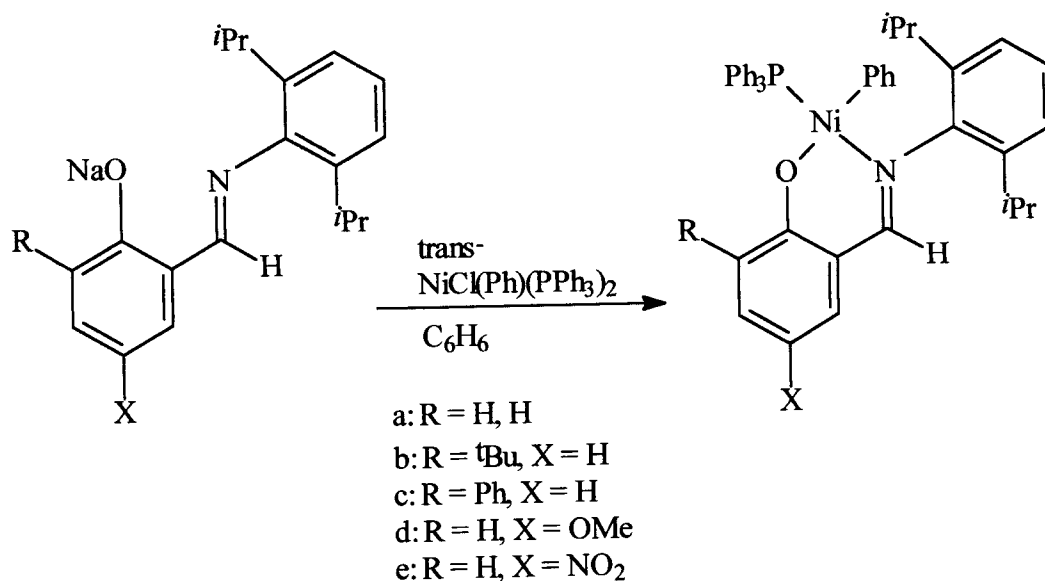
polymerization of olefins. The most useful phosphine scavengers used by Klabunde were  $\text{Rh}(\text{acac})(\text{C}_2\text{H}_2)$  and  $\text{Ni}(\text{COD})_2$ . Although these catalysts are tolerant to polar substrates, they are still poisoned by water.



**Scheme 1.2:** Synthesis of P,O chelated nickel complexes

Another interesting  $\alpha$ -iminocarboxamidato-nickel catalyst system has recently been reported by Bazan and coworkers,<sup>22</sup> for the production of branched polyethylene and treatment of this complex with  $\text{B}(\text{C}_6\text{F}_5)_3$  results in high catalytic activity. This catalyst system can also be used for ethylene oligomerization<sup>23</sup> and copolymerization<sup>24</sup> with higher olefins under certain conditions. Recently Grubbs<sup>25</sup> and coworkers reported neutral Ni(II) salicylaldiminato complexes (Scheme 1.3), which are highly active catalysts for the polymerization of ethylene to high molecular weight polymers under moderate conditions. Catalyst activities of about

250 kg/mol Ni h are obtained using these catalysts and molecular weights of around 360 000 g/mol. They chose the salicylaldiminato ligands because they are easy to synthesize and simple modification of both steric and/or electronic effects is possible.



**Scheme 1.3:** Synthesis of Grubbs catalyst

But by far the single most important discovery for late transition metal olefin polymerization catalysts was made by Brookhart and co-workers in 1995.<sup>26</sup> The Brookhart catalyst system is based on  $\alpha$ -diimine palladium and nickel complexes and will be discussed with other nitrogen ligand complexes in section 1.4.2. It is believed that the introduction of bulky substituents on the ketimine nitrogen and the phenolic ring of the salicylaldiminato ligand could block the axial faces of the metal centre, retarding the rate of associative displacement, similar to what is observed for