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19/07/2004

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# The Design of Non-Metallocene Analogues as Polymerization Catalysts

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MSc. ( Polymer Science and Technology )

December, 2001

## ABSTRACT

The main aim of this project was to prepare novel "non-metallocene" complexes and to test their ability to act as catalysts for the polymerisation of ethylene.

To do this, firstly, two new polyamine ligands, 1,4-bis(2-aminophenyl)piperazine **L2** and 1,7-bis(2-aminophenyl)-1,4,7,10-tetraazacyclododecane **L5** have been prepared and fully characterised. A preliminary investigation into the co-ordination chemistry of these potentially tetra- and hexa-dentate ligands with first row transition metals, such as Ti, Zr and Nb have been studied.

**L2** has been silylated at the aniline nitrogens by treatment with *n*-BuLi and Me<sub>3</sub>SiCl to give 1,4-bis(2-trimethylsilylamino-phenyl)piperazine **L3** in good yield. The co-ordination of **L3**, as it's dianion, with TiCl<sub>4</sub>, ZrCl<sub>4</sub>.2thf and NbCl<sub>4</sub>.2thf has been investigated. However, no tractable metal complex was formed with Ti(IV), while the Zr and Nb systems resulted in the elimination of Me<sub>3</sub>SiCl in solution and deposition of **L2**, as shown by <sup>1</sup>H-NMR.

Secondly, with the aim of testing suitable oxalic amidine 'non-metallocene' type catalyst system to use with co-catalysts of methylaluminoxane (MAO) and selected Lewis acids, in polymerization of ethylene has been studied.

The oxalic amidine ligand C<sub>6</sub>H<sub>5</sub>N=C(NH<sup>t</sup>Bu)-C(NH<sup>t</sup>Bu)=NC<sub>6</sub>H<sub>5</sub> **L6** and C<sub>6</sub>H<sub>5</sub>N=C[N(<sup>t</sup>Bu)(SiMe<sub>3</sub>)]-C[N(<sup>t</sup>Bu)(SiMe<sub>3</sub>)]=NC<sub>6</sub>H<sub>5</sub> **L7** are described. Treatment of **L6** with Ti(NMe<sub>2</sub>)<sub>4</sub> gives bimetallic complex of [Ti(NMe<sub>2</sub>)<sub>3</sub>.C<sub>6</sub>H<sub>5</sub>N.C(N<sup>t</sup>Bu)-]<sub>2</sub> **C8**. The activity towards ethylene polymerization has been investigated for ligand **C8**.

# LIST OF CONTENTS

	Page No.
Acknowledgment	vii
Abstract	viii
List of Abbreviations	ix
List of Tables	x
List of Figures	xi
List of Schemes	xii
<b>Chapter One - Introduction and Literature Review</b>	
1.1 Historical Aspects	2
1.2 Catalysis	2
1.3 Types of Catalyst	3
1.3.1 Heterogeneous $\text{TiCl}_3$ based Ziegler-Natta Catalyst	3
1.3.1.1 Historical Development	5
1.3.1.2 Polymer Structures	6
1.3.1.3 Polymer Properties	8
1.3.1.4 Reactions Occurring During Polymerization	9
1.3.1.5 The Mechanism of Ziegler-Natta Polymerization	13
1.3.1.5.1 Nature of the active sites and mechanism of propagation	14
1.3.1.5.2 Propagation at the Activator Alkyl	15
1.3.1.5.3 Propagation at the Transition Metal Alkyl	18
1.3.1.6 Limitations	21
1.3.2 Heterogeneous Catalysts using either $\text{Cr}_2\text{O}_3$ impregnated-on silica (Phillips Marlex Catalyst) or $\text{Cp}_2\text{Cr}$ on silica (Union Carbide catalyst)	26

1.3.3 Homogeneous Group 4 Metallocene Catalyst	28
1.3.3.1 Historical Development	28
1.3.3.2 Polymer Structure and Properties	29
1.3.3.3 The Role of the Co-catalyst	31
1.3.3.4 General Aspects of Metallocene Catalysts	33
1.3.3.4.1 Activation of the Catalyst Precursors	34
1.3.3.4.2 Function of Organoaluminoxanes	35
1.3.3.4.3 Additional Parameters	38
1.3.3.4.4 Olefin Polymerization Mechanism and Stereoselectivity	38
1.3.3.4.5 Chain Termination and Transfer	41
1.3.3.4.6 General Considerations and some of the Examples	43
1.3.4 Homogeneous Non-metallocene Catalysts	47
1.3.4.1 Non-metallocene Phosphine Catalysts	47
1.3.4.2 Non-metallocene Amide Catalysts	48
<b>Chapter Two- Experimental</b>	
2.1 Materials and Instrumentation	49
2.2 Syntheses of 1,4 diazacyclo hexane (Piperazine) based Ligands	50
2.2.1 1,4-Bis(2-nitrophenyl)piperazine <b>L1</b>	50
2.2.2 1,4-Bis(2-aminophenyl)piperazine <b>L2</b>	50
2.2.3 1,4-Bis(2-trimethylsilylamino phenyl)piperazine <b>L3</b>	50
2.3 Synthesis of Piperazine based Co-ordination Compounds	51
2.3.1 First Row Transition Metal Complexes	51
2.3.2 Titanium Metal Complex	51
2.3.3 Zirconium Metal Complex	51
2.3.4 Niobium Metal Complex	52
2.4 Syntheses of 1,4,7,10-tetraazacyclododecane (Cyclen) based Ligands	52
2.4.1 1,7-Bis(2-nitrophenyl)-1,4,7,10-tetraazacyclododecane <b>L4</b>	52
2.4.2 1,7-Bis(2-aminophenyl)-1,4,7,10-tetraazacyclododecane <b>L5</b>	53
2.5 Syntheses of Cyclen based Titanium Metal Complex	53

2.6 Syntheses of Amidinate based Ligands	53
2.6.1 $C_6H_5N=C(NH^tBu)-C(NH^tBu)=NC_6H_5$ L6	53
2.6.2 $C_6H_5N=C[N(^tBu)(SiMe_3)]-C[N(^tBu)(SiMe_3)]=NC_6H_5$ L7	54
2.6.3 $[Ti(NMe_2)_3.C_6H_5N.C(N^tBu)-]_2$ C8	54
2.7 Crystal Structure Analysis	54
2.8 Polymerization Studies	55
2.9 Co-catalyst MAO-Lewis Acid System Stage	56
<b>Chapter Three - Results and Discussion</b>	
3.1 Piperazine based Ligands	57
3.1.1 1,4-Bis(2-nitrophenyl)piperazine L1	57
3.1.2 1,4-Bis(2-aminophenyl)piperazine L2	60
3.1.3 1,4-Bis(2-trimethylsilylamino)phenyl)piperazine L3	63
3.1.4 Co-ordination Chemistry	63
3.2 1,4,7,10-tetraazacyclododecane (Cyclen) based Ligands	66
3.2.1 1,7-Bis(2-nitrophenyl)-1,4,7,10-tetraazacyclododecane L4	66
3.2.2 1,7-Bis(2-aminophenyl)-1,4,7,10-tetraazacyclododecane L5	70
3.2.3 Co-ordination Chemistry	71
3.3 Amidinate based Ligands	72
3.3.1 $C_6H_5N=C(NH^tBu)-C(NH^tBu)=NC_6H_5$ L6	72
3.3.2 $C_6H_5N=C[N(^tBu)(SiMe_3)]-C[N(^tBu)(SiMe_3)]=NC_6H_5$ L7	74
3.3.3 $[Ti(NMe_2)_3.C_6H_5N.C(N^tBu)-]_2$ C8	75
3.3.4 Co-ordination Chemistry of Metal Complex $[Ti(NMe_2)_3.C_6H_5N.C(N^tBu)-]_2$ C8	76
3.3.5 Ethylene Polymerization Studies with Co-catalyst MAO and Lewis Acids	77
4.4 Conclusion	80
References	81-83
Appendix 1, 2 & 3	84-94