Ligand Frameworks for Olefin Polymerisation Catalysts

By

Rebecca E. Baghurst

A thesis submitted to the University of Wales in accordance with the requirements for the degree of Doctor of Philosophy in the Faculty of Science,

Department of Chemistry, University of Wales, Cardiff

Feburary 2005

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

Acknowledgements

Firstly I must thank my supervisors Dr Simon Aldridge and Dr Ian Fallis for their help and ideas throughout this research.

Thanks to Miss J. K. Day for the further research on selected complexes.

Thanks to EPSRC and Synetix for the sponsorship of this project.

Thanks to Rob Jenkins for obtaining the GC-MS data for the polymerisation studies.

Thanks to the RAPRA service for the data on polymerisation products.

A big thank you to the technical staff in the department without you all the department would grind to a halt!

A *huge* thanks to Pauly Rog, thanks for your patience! A *very very* special thank you to Mam and Dad for their endless support throughout *everything, always* - putting up with the moaning during bad times, all the washing, ironing, home cooking (Mam!!), DIY, cars and removals (Dad!!) to mention but a few things you've done for me. Without all your help, support and encouragement over the years I'd have never have found myself where I am today. Diolch yn fawr iawn a Llawer o gariad XXxx.

Contents

List of Abbreviations

Å Angstroms

APCI Atmosphereic pressure chemical ionisation

Ar Aromatic

br Broad

^{13}C Carbon thirteen isotope

cm^{-1} Reciprocal centimetres

$CDCl_3$ Deuterated chloroform

C_6D_6 Deuterated benzene

CGC Constrained Geometry Catalysts

CYCLEN 1,4,7,10-tetraazacyclononane

δ NMR Chemical shift

d Doublet

dd Double Doublet

DCM Dichloromethane

DMSO Dimethylsulphoxide

EI Electron Impact Ionisation

Et Ethyl

FAB Fast atom bombardment

GPC Gel permeation chromatography

g Grams

GC Gas chromatography

^1H Proton

IR Infra red

J NMR Coupling constant

KBr Pottasium Bromide

KF Potassium fluoride

MAO Methylaluminoxane

M Multiplet

md Medium

mg Milligram

MHz Megahertz

mol Mole

ml Millilitre

mmol Millimole

m/z Mass/charge ratio

Mw Molecular weight

R Definition of absolute configuration

s Singlet

S Definition of absolute configuration

st Strong

t Tertiary

TACN 1,4,7-triazacyclononane

THF Tetrahydrofuran

TMS Trimethylsilane

UV Ultra violet

w Weak

Abstract

The synthesis and characterisation of ligands which have the potential to support olefin polymerisation catalysts has been investigated. The syntheses are presented of a range of mixed tertiary amine/alkoxide donor ligands formed by the ring opening of (+/-)-3,3-dimethyl-1,2-epoxybutane by linear and cyclic amines, including *N,N'-di*methylethylenediamine, 1,4-diazacycloheptane, 1,4-diazacyclohexane, monoazacyclohexane, 1,4,7,10-tetraazacyclododecane and 1,4,7-triazacyclononane. A series of ligands derived from *trans*-1,2-diaminocyclohexane, 1,4-diazacyclohexane and 1,4-diazacycloheptane has also been synthesised via substitution chemistry.

The coordination chemistry of *N,N'*-bis(2-hydroxy-3,3-dimethylbutyl)--1,4-diazacycloheptane has been investigated. Monometallic complexes with nickel and aluminium have been characterised. Two examples of bimetallic titanium complexes with *N,N'*-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacycloheptane, synthesised from titanium ethoxide and titanium isopropoxide are also reported; the structure of each has been determined by X-ray crystallography. A discussion of how the choice of titanium alkoxide starting material affects the outcome of the ligand substitution chemistry is presented. The syntheses of related complexes containing the more flexible ligand *N,N'-bis*(2-hydroxy-3,3-dimethylbutyl)-dimethylethyleneamine in conjunction with zirconium and titanium are presented and the crystal structures reported. Furthermore, complexes of the macrocyclic ligands *N,N',N''*-(2-hydroxy-3,3-dimethylbutyl)-1,4,7-triazacyclononane with titanium and *N,N',N'',N'''*-(2-hydroxy-3,3-dimethylbutyl)-1,4,7,10-tetraazacyclododecane with zirconium are reported.

The activity of selected complexes towards olefins including ethylene and 1-hexene using methylaluminoxane as an activator has been determined. Investigation into the nature of the reaction products has been undertaken using gel permeation chromatography and GC-MS. In general the complexes synthesized during the course of this study show low activites towards olefin polymerisation.

Chapter 1

Introduction to Olefin Polymerisation by Group 4 Systems

1.1 Overview

The polymerisation of α-olefins is a huge industry worldwide. In 1995, world production of polyolefins was estimated at 53.6 million tonnes, twice the figure estimated for 1983 and it is predicted that by the end of 2005 the production will grow by a further 50 %. [1] At first glance one could be forgiven for thinking that polyethylene is a rather uninteresting polymer. The simple structure consists entirely of long saturated hydrocarbons, with no functional groups, which seems to offer little scope for the research chemist. However, despite their simple structures, polyethylene and related polymers of higher α-olefins are in fact versatile materials, with a range of properties which make them suitable for a vast number of industrial and domestic applications. This versatility arises from the variation of structure possible through branching along the hydrocarbon backbone.

1.2 A Brief History of Olefin Polymerisation

Prior to the advent of transition metal co-ordination catalysts, polyethylene was manufactured via a high temperature, high-pressure, free radical polymerisation process, [2] which typically gives highly branched products. The 1950's saw the dawn of transition metal catalysts in the form of the Ziegler-Natta, ($TiCl_4/AlClEt_2$) and Philips silica-

supported chromium heterogeneous catalyst systems. Both of these systems are active polymerisation catalysts but as with many heterogeneous systems they have a common problem, namely the difficulty in controlling polymer structure. Control is difficult due to the unknown nature and distribution of active polymerisation sites within the catalyst structure.

The discovery of the polymerisation activity of titanium and zirconium complexes resulted from an investigation by Karl Ziegler and co-workers into the multiple insertion of ethene into aluminium alkyl bonds to give long chain aluminium alkyls.[3] Interest in the effects of transition metals on this insertion process was stimulated by an observation that small amounts of nickel inhibit the insertion/polymerisation reaction. This discovery not only led to nickel being developed as an ethene oligomerisation catalyst, but also to an extensive study into the effects of other transition metals on the insertion of ethene into aluminium alkyl bonds. These studies led to the discovery that certain transition metal complexes (e.g. zirconium acetylacetonate) can, in the presence of an aluminium alkyl (e.g. $AlEt_2Cl$), catalyse polymerisation of ethene under mild conditions (e.g. 50°C/10 atm). This result contrasted starkly with radical polymerisation processes available at the time, which typically required pressures in excess of 1000 atm and temperatures of the order of 200°C. By 1952, Guilio Natta extended Ziegler's work to the polymerisation of higher α-olefins.

Commercial Ziegler –Natta catalysts are prepared by the treatment of $TiCl_4$ or $TiCl_3$ with $AlEt_3$ or $AlEt_2Cl$. The polymerisation reaction is thought to take place on exposed edges

of $TiCl_3$ crystals and is a coordination polymerisation process.[2] Mechanisms for this process have been suggested by Cossee and Arlman, and by Green and Rooney (*vide infra).*

The first group 4 metallocenes were synthesised by Geoffrey Wilkinson et al. in 1953, [4] and shortly afterwards their potential to act as polymerisation catalysts was investigated. In 1957, Natta and Breslow reported that Cp_2TiCl_2 (activated by Et_3Al or Et_2AlCl) is active for ethene polymerisation but inactive towards higher α-olefins.[5,6] These metallocene catalysts were prone to reduction to Ti(III) species and as such could not compete with the highly active, stereoselective heterogeneous Ziegler–Natta catalysts. As a result of these shortfalls, the metallocene complexes, at least at this point in time, found no industrial application. However, they proved useful as homogeneous models of the original heterogeneous Ziegler-Natta systems, as they are more amenable to study by methods such as NMR and IR. This allowed investigation into mechanisms of initiation, propagation and termination.

It was a serendipitous discovery that eventually led to group 4 metallocenes becoming industrial viable polymerisation catalysts. The 1980's saw the dawn of a new activator, from partially hydrolysed Me_3Al, which yielded highly active catalysts from group 4 metallocenes.[7] Chemists were aware that Ziegler–Natta catalysts were sensitive to hydrolysis, so it came as some surprise when Kaminsky, Sinn and co workers noticed that traces of water actually increased the rate of polymerisation in titanocene/aluminium alkyl mixtures.[7,8,9] They also discovered that adding a trace of water to the normally

inactive system $[ZrCp_2Me_2]/AlMe_3$ caused it to become highly active for polymerisation. Further investigation showed that the same effect could be achieved by adding water to the $AlMe_3$, prior to the addition of the metallocene. Another consequence of this result was that metallocenes were then able to polymerise propylene and higher α-olefins under these conditions.

It has been suggested that partial hydrolysis of the aluminium alkyl generates an exceptionally strong Lewis acid that is a potent activator for polymerisation catalysis. This strong Lewis acid was identified as methylaluminoxane (MAO), which although poorly characterised is thought to consist of linear, cross linked and cyclic oligomers with molecular weight in the range 900-1200 and approximate composition $(MeAlO)_n$. It is thought to contain both three- and four-coordinate aluminium centres and probably contains $OAlMe_2$ end groups.[8,9] It is fair to say that the momentous discovery of MAO led to tremendous headway being made in polymerisation catalyst discovery.

1.3 Classification of Polymers

Polyethylenes can be classified by their structure as follows:

High Density Polyethylene (HDPE): this material has a high molecular weight and narrow molecular weight distribution; it is tough with a high impact strength and melting

point. The structure is essentially linear with negligible branching along the hydrocarbon backbone.

Low Density Polyethylene (LDPE): this differs from HDPE by the branching along the hydrocarbon backbone. It is less durable than HDPE and finds different applications e.g. in packaging.

Linear Low Density Polyethylene (LLDPE): this class of polymer has properties between LDPE and HDPE. It has less branching than LDPE, and has a similar molecular weight to HDPE but is more flexible.

Polymers of higher α-olefins, e.g. polypropylene, can be divided into main three classes. The basis of this classification is the alkyl groups attached to the alkene functionality in the monomer arranging themselves in different orientations along the hydrocarbon backbone in the resulting polymer. The classes are therefore:

Atactic: the alkyl branches along the hydrocarbon backbone are randomly arranged (Figure 1).

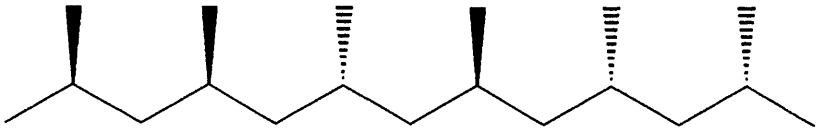


Figure 1: Atactic polypropylene.

Syndiotactic: the alkyl branches are arranged in an alternating fashion along the backbone (Figure 2).

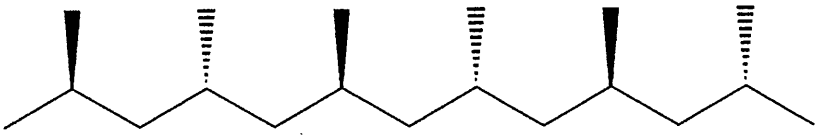


Figure 2: Syndiotactic polypropylene.

Isotactic: the alkyl branches are arranged so that they all point in the same direction with respect to the polymer backbone (Figure 3).

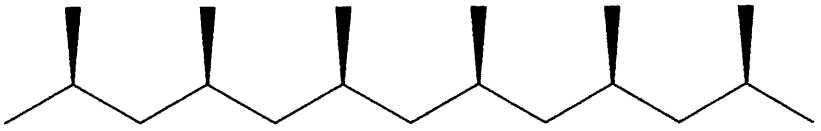


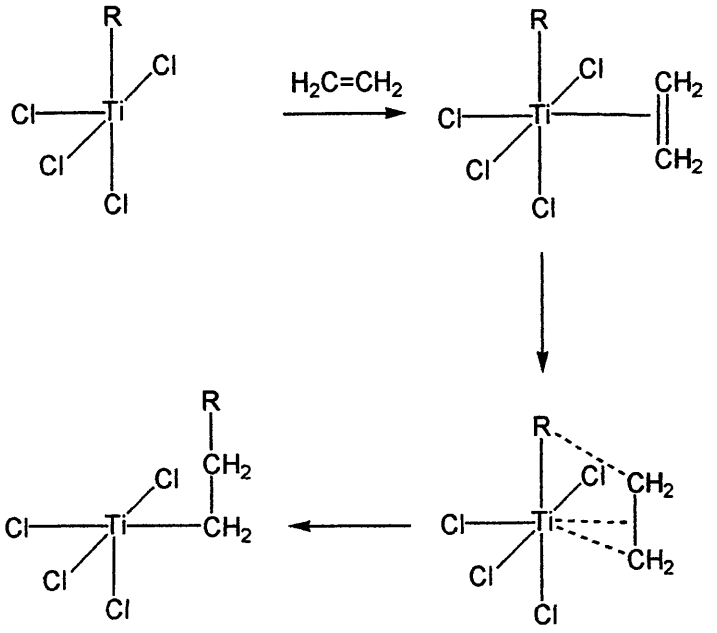
Figure 3: Isotactic polypropylene.

Small structural differences can have dramatic effects on the properties of polymers, and the development of new catalyst systems is driven by the desire of the chemical industry to control structural attributes (such as stereochemistry and incorporation of new functional groups) and to tailor the polymer for specific applications. The key to this control is catalysis.

1.4 Mechanisms, Stereoselective Polymerisation and the Origins of Polymer Stereochemistry

1.4.1 Mechanisms

For a titanium chloride heterogeneous catalyst system it was originally thought that two metal centres were required for polymerisation to occur, [10,11]one to accommodate the monomer the other to carry the alkyl group. Cossee suggested that the reaction occurs at a single titanium ion,[12] and that the empty d-orbitals are responsible for the catalytic activity. The polymerisation reaction occurs at a titanium ion at the surface layer of a α-$TiCl_3$ lattice. An alkyl group replaces one surface Cl atom in the octahedral coordination sphere; an adjacent Cl has also been completely removed so that the monomer can be accommodated. The mechanism proposed by Cossee is illustrated in Scheme 1. After the insertion process the vacancy and titanium bound alkyl have been retained, although in opposite coordination sites.



Scheme 1: The Cossee mechanism for polymerization at the surface of α-$TiCl_3$.

The olefin monomer bonds to titanium through a σ-bond formed by the overlap of bonding π orbitals with the metal d_x^2-$_y^2$ orbital; there is an addition titanium-olefin π bond formed by the overlap of the metal d_{xy} orbital with the olefin anti-bonding π* orbital. The metal alkyl bond is located along the y-axis and is σ bonded to the metal using its d_x^2-$_y^2$ orbital; electron density from this bond is donated in the π back bonding interaction of the metal with the olefin and causes weakening of both the titanium alkyl bond and the olefin π bond (Figure 5). This weakening of the titanium alkyl bond facilitates its migration.

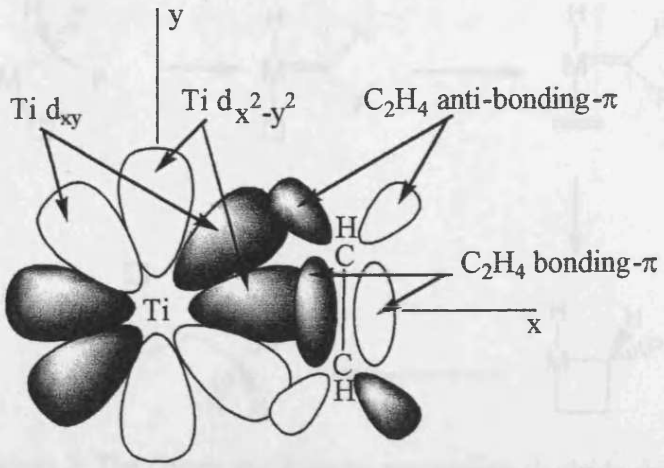
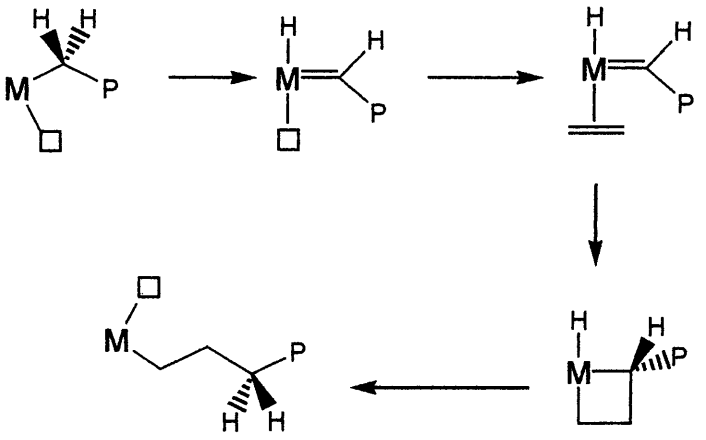


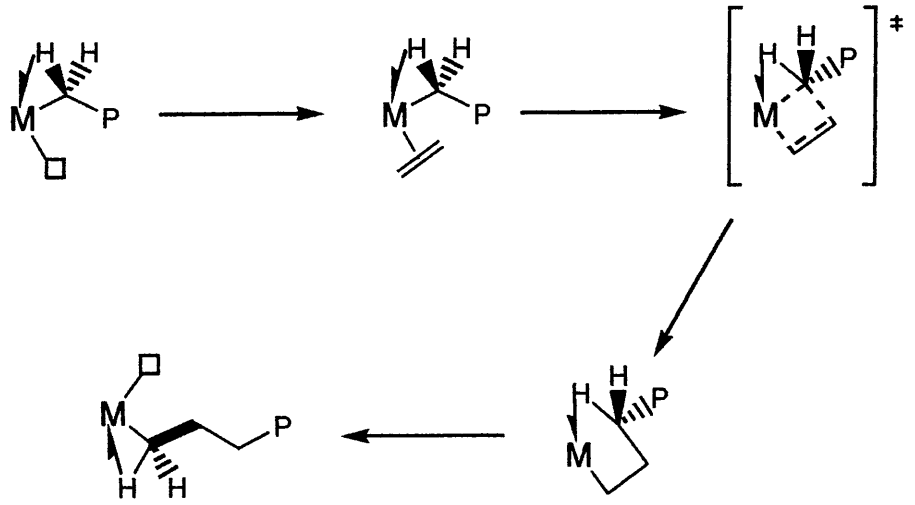
Figure 5: Bonding of the alkyl and alkene ligands in the Cossee model.

Cossee's model further explained the isotactic nature of polypropylene by suggesting that the propylene monomers are forced to coordinate at the $TiCl_3$ surface with the more bulky $=C(CH_3)H$ end of the molecule outermost, and the least bulky $=CH_2$ end innermost either pointing towards an octahedral vacancy in the lattice or towards a titanium atom. This model could not, at the time, predict which orientation was energetically most favourable. This mode of coordination ensures that attack of the alkyl group is always to the $=C(CH_3)H$ end of the molecule (head to tail).[12] A second mechanism for polymerisation was proposed by Green and Rooney (Scheme 2). An oxidative 1,2-hydrogen shift from the α-carbon of polymer to the metal generates a metal-alkylidene hydride. This then reacts with an olefin molecule to generate a metallacyclobutane, with a reductive elimination step completing the propagation. [13,14]



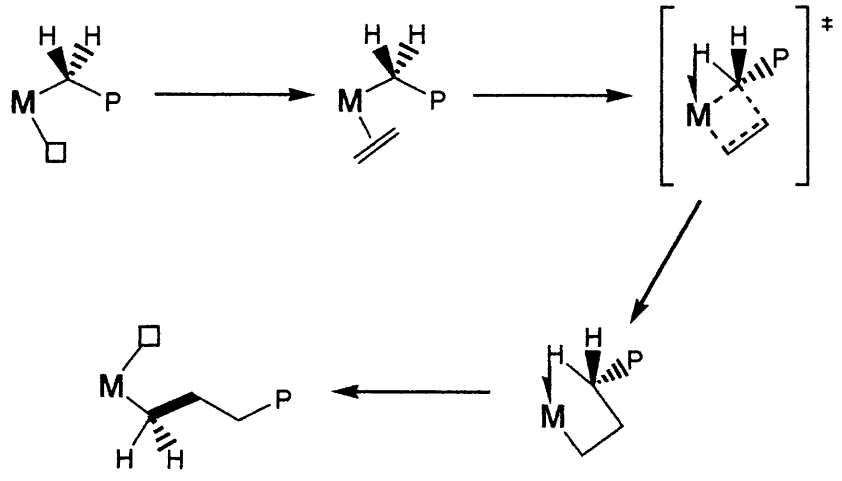
Scheme 2: The Green and Rooney mechanism (hydride shift).

Suggestions that α-agostic interactions stabilise the transition state during polymerisation gave rise to two other proposed mechanisms. The modified Green and Rooney mechanism (Scheme 3), intermediate between the original Green-Rooney and the Cossee-Arlman mechanisms, (proposed by Green, Rooney and Brookhart) involves a hydrogen atom on the α-carbon of the polymer interacting with the metal centre throughout the catalytic cycle. This three-centre, two-electron covalent bond (or "agostic" interaction) occurs when a hydrogen atom is simultaneously bonded to both a carbon and the metal centre.[15,16,17,18]



Scheme 3: The modified Green and Rooney mechanism (ground state agostic interaction).

Another suggestion is that the α-hydrogen interacts with the metal centre only during the transition state of the carbon-carbon bond-forming step (Scheme 4); this is a hybrid of the Cossee-Arlman and the modified Green-Rooney mechanisms.[19]



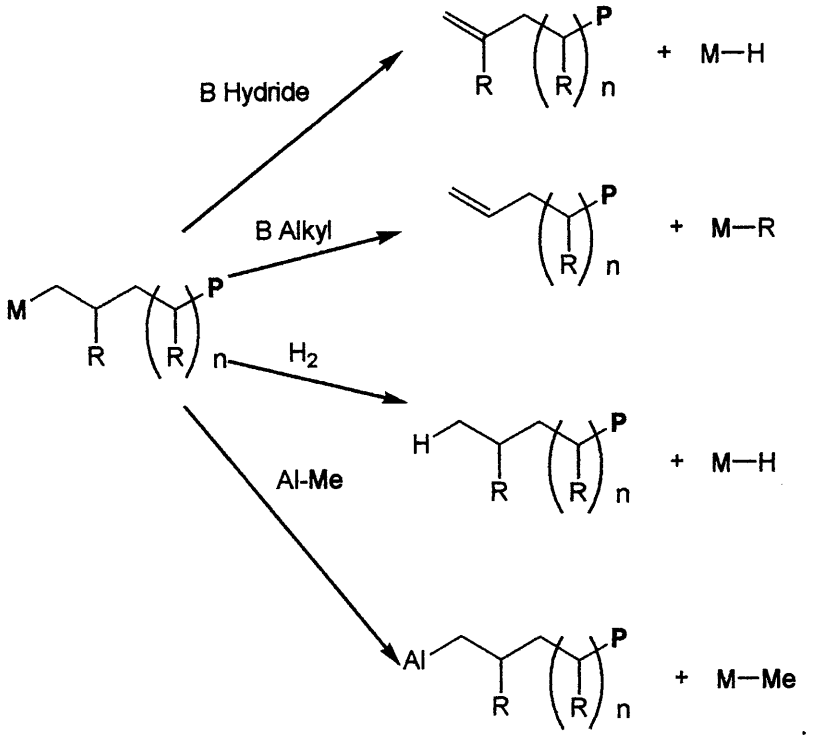
Scheme 4: The transition state α-agostic mechanism.

α-Agostic interactions are thought to be important as they may lead to a dramatic lowering of the activation barrier to olefin insertion and may therefore influence the stereochemical outcome of the reaction.[20,21,22,23]

Through studies of a homogeneous group 4 catalyst system, Grubbs et al. ruled out the modified Green and Rooney mechanism for this particular system by showing that there was no significant effect due to α-agostic interactions on either the rate of reaction or the stereochemistry of the resulting polymer.[24] The Green and Rooney mechanism has been ruled out for catalytically active 14-electron group 3 and cationic group 4 metallocene alkyls, since these d^0 catalysts cannot undergo formal oxidative addition at the metal centre.[25] Therefore, for catalysts such as these, the Cossee-Arlmann direct insertion and transition state α-agostic assisted insertion mechanisms are the leading proposals. For other catalyst systems all four mechanistic proposals are possibilities.

1.4.2 Catalyst Deactivation and Side Reactions

The repeated insertion of an alkene into the metal-alkyl bond (the propagation reaction), is not the only reaction that occurs at the catalyst, and many other competing side reactions are possible (Scheme 5)



Scheme 5: Possible competing reactions during polymerisation.

Intramolecular β-hydride elimination may occur in which transfer of a β-hydrogen from the growing polymer chain to the metal gives a allyl terminated polymer chain and a catalytically active hydride complex.[26] In the absence of β-hydrogens on the polymer chain, an intermolecular β-alkyl elimination is feasible, resulting in an active metal alkyl species and an allyl terminated polymer.[27] Hydrogen can also act as a chain transfer agent; in this case the result is a catalytically active hydride and a polymer with a saturated end group.[28] Consequently, the addition of hydrogen is used in some cases to control the average molecular weight of the resulting polymer. Alkylaluminium compounds, often employed as activators/co-catalysts, can also act as chain transfer agents. Transmetallation produces an aluminium terminated polymer and an active metal

alkyl catalyst.[29] In general terms, the rate of these chain transfer reactions relative to the rate of the chain propagation reaction is key in determining the molecular weight of a polymer.

1.4.3 Polymer Stereochemistry

Well-defined homogeneous catalysts can be systematically modified to study the effects of catalyst structure on the stereo-selectivity of polymerisation. The tacticity of a polyalkene concerns the relative configuration of adjacent stereocentres of the polymer main chain. A "dyad" i.e. two neighboring stereocentres, is described as meso *m* if they are of the same configuration and racemic *r* if they are opposite. An isotactic polymer has the relative configuration of sequential stereocentres identical (*m*), in syndiotactic polymers they are regularly alternating (*r*) and an atactic polymer is totally random. The stereoregularity of a polymer is determined by its "pentad content" or the percentage composition of the ten possible sequences of five consecutive stereocentres e.g. *mmmm* isotactic and *rrrr* syndiotactic.[30] The first experiments reported by Natta in 1954 with $TiCl_3$ systems yielded mixtures of pure atactic and pure isotactic polymers. Shortly afterwards purely isotactic material was produced by modifying the composition of the heterogeneous catalyst.[31]

Prior to the mid 1980's only atactic polypropylene had been produced from Cp_2MCl_2 systems.[32] In 1984, Ewen produced a partially isotactic polymer from Cp_2TiPh_2/MAO, having a pentad content *mmmm* 52% (c.f. 6.25% for a purely atactic polymer).[33] Ewen

also discovered that chiral ansa metallocenes first prepared by Brintzinger are capable of producing isotactic polypropylene.[34,33,35]

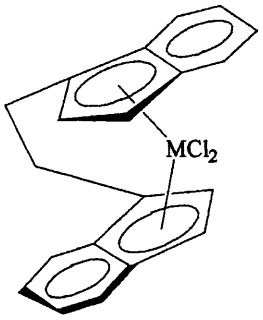
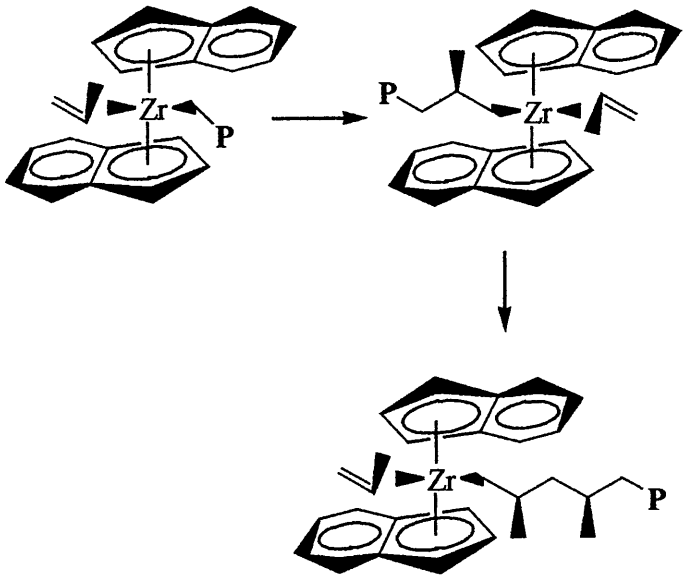
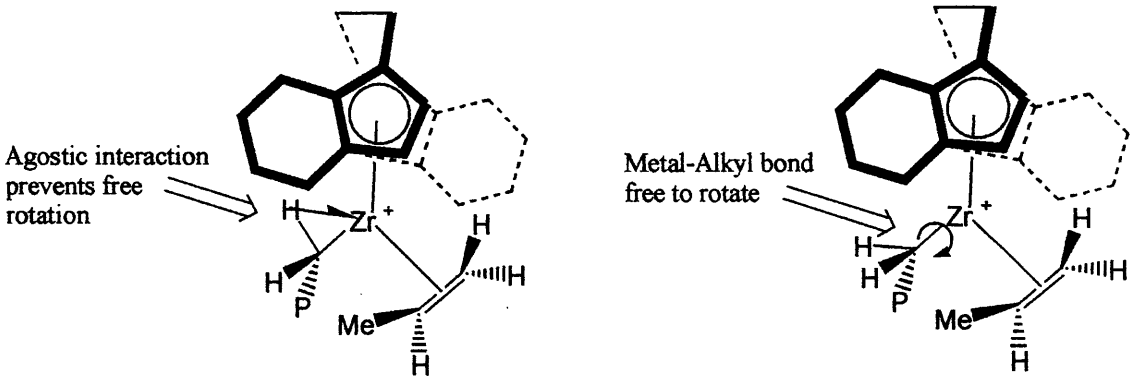


Figure 6: A C_2 symmetric ansa metallocene.

C_2 symmetric ansa metallocenes (such as that shown in Figure 6) polymerise by an enantiomorphic site control mechanism in which the geometry of the catalyst controls the stereochemistry of alkene insertion. Conformational modeling by Corradini suggested that the polymer chain is forced into an open region of the metallocene, thereby relaying the chirality of the metallocene to the incoming monomer through the orientation of the β carbon of the alkyl chain (Scheme 6).[36] Brintzinger proposed that an α-agostic interaction rigidifies the transition state of C_2 symmetric catalyst, orientating the polymer into the open area of the catalyst (Scheme 7), and thereby increases the isotacticity of the polymer.[37,38] As these chiral metallocenes are C_2 symmetric, both possible reaction sites are homotopic and therefore selective for the same enantioface. Hence the resulting polymer is isotactic.



Scheme 6: Origins of polymer stereochemistry for C_2 symmetric catalysts.



Alpha Agostic Interaction - More Rigid

No Alpha Agostic Interaction - Less Rigid

Scheme 7:Brintzinger's proposal for agostic control of stereochemistry.

Natta and Zambelli produced syndiotactic polypropylene at low temperature from a vanadium based catalyst mixture.[39] In later work, Ewen reported a metallocene catalyst that is highly active towards propylene and higher α-olefins, producing a syndiotactic

polymer at 50°C with an *rrrr* pentad content of 81% being indicative of high stereocontrol.[40]

Research by Rausch et al. has shown certain C_1 symmetric ansa metallocenes to be capable of polymerisation to give isotactic material.[41] Thus the complex illustrated in Figure 7 produces highly isotactic polypropylene (mmmm = 91%) in high yield.

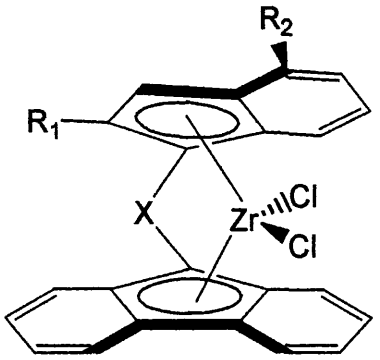


Figure 7: Rausch's C_1 symmetric system.

Although these substituted asymmetric indenyl-fluorenyl metallocenes have two possible monomer coordination sites, which are diastereotopically related, one of them is effectively blocked by the large substituents at the 2- and 4- positions of the indenyl moiety, thereby preventing the growing polymer chain from occupying that site, and leaving only one site available for monomer coordination.

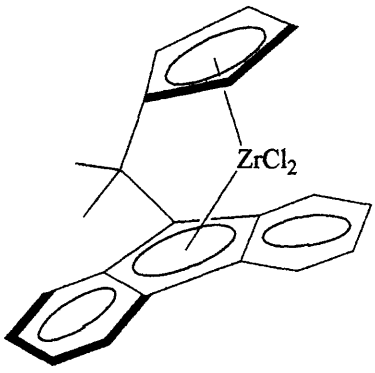
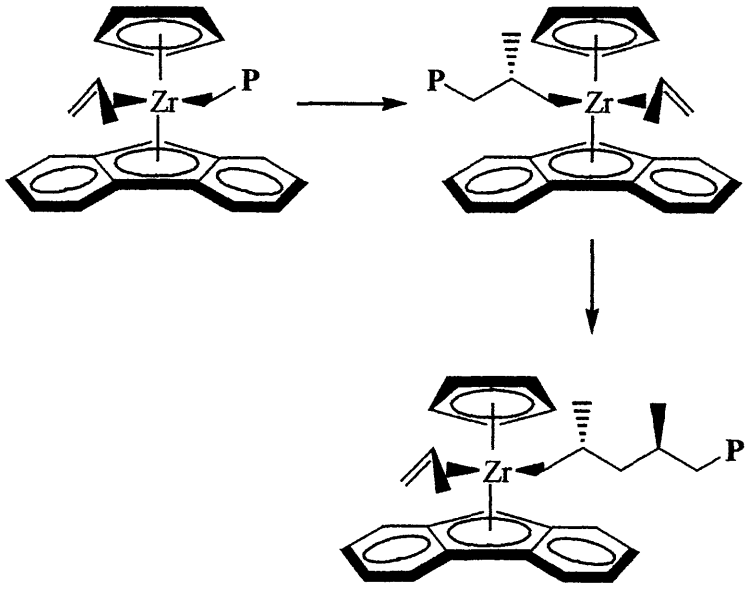


Figure 8: A C_s symmetric ansa meatllocene system.

Regularly alternating insertion of alkenes at heterotopic sites of a C_s symmetric complex (Figure 8) results in the formation of a syndiotactic polymer through the mechanism shown below (Scheme 8).



Scheme 8: Origins of polymer stereochemistry for C_s symmetric catalysts.

Guerra proposed that the high syndiospecificity of C_s catalysts results from γ-agostic interactions in the structure; this interaction is thought to stabilize the catalyst species both geometrically and electronically.[42]

1.5 The Basic Catalyst Model

A Ziegler-Natta type catalyst can be thought of as possessing three main components L, S and R around a metal centre M (Figure 9).[43]

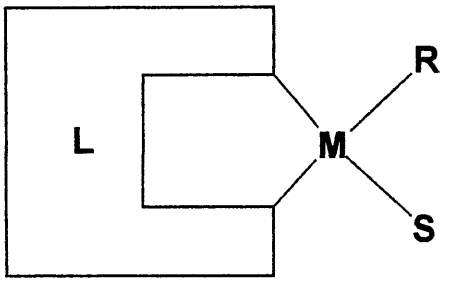


Figure 9: A basic Ziegler-Natta catalyst model.

L, the primary ligand or ligands, has four important functions, these are: (a) control over the co-ordination number of M; (b) control over the co-ordination geometry around M; (c) control over the oxidation state of M; and (d) influence on polymer stereochemistry by sterics and steric protection of the active site. S, the spectator ligand are bound loosely in an effective catalyst. S can be a solvent molecule or, after abstraction of an alkyl group by the cocatalyst/activator to form the active catalyst, it may be an anionic counter ion. Eventually this site will be occupied by the monomer molecule prior to insertion into the M–R bond. R in the activated catalyst will be an alkyl group; it is this metal–alkyl (M–R)

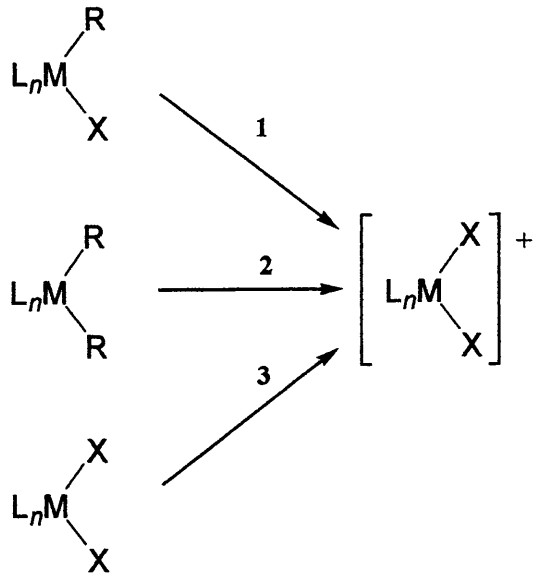
bond into which the olefin monomer will insert during first step of the polymerisation process. In the precatalyst R may be a different atom or molecule, common examples being Cl or NMe_2.[43] For an active catalyst R and S must be mutually cis so that insertion can occur.[43]

A good catalyst requires an electron deficient L_nM fragment, but an electron deficient metal centre will be prone to attack by other species, which could lead to deactivation.[43] A ligand or group of ligands L must therefore be selected which can create an electron deficient L_nM fragment whilst simultaneously providing both an environment which protects the active catalyst from deactivation reactions and directs the monomer, during insertion into the M-R bond, to give desirable stereochemistry in the resulting polymer.

1.6 Activation of precatalyst

The catalytically active species in olefin polymerisation is generally regarded to be a coordinatively unsaturated cationic alkyl complex $[L_nMR]^+$ which is stabilized by several ligands or a chelating ligand L. The topic of cocatalysts for metal catalysed polymerisation has been reviewed extensively by Marks and Chen.[44]

There are three main routes to the catalytically active species as shown in Scheme9.[43]



Scheme 9: Activation of precatalyst.

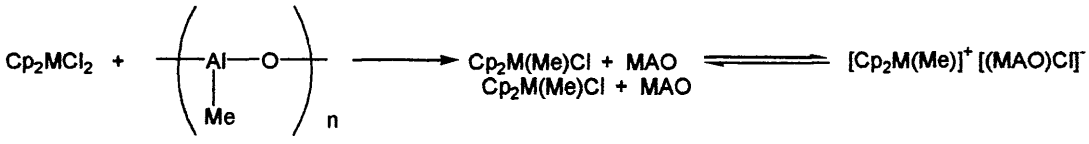
(1) Abstraction of an anionic ligand, usually a halide, and substitution with a weakly coordinating anion by a salt elimination reaction. Examples of common reagents for this purpose are $Na[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$, $AgBF_4$ or for later transition metals AgOTf.

(2) Abstraction of an alkyl anion. Reagents commonly used for this include approach include the trityl salt $[Ph_3C][B(C_6F_5)_4]$ which abstracts the alkyl anion, the anilinium salt $[PhNhMe_2][B(C_6F_5)_4]$ and the acid $[H(OEt_2)_2][B\{3,5\text{-}(CF_3)_2C_6H_3]_4]$ which remove the alkyl ligand by protonation, and $B(C_6F_5)_3$ which only partially abstracts the alkyl ligand resulting in a 'cation-like' active species. MAO is also employed for abstraction.

(3) A combined alkylation and abstraction approach using a dihalide precatalyst. This is achieved by reacting the precatalyst with a trialkylaluminium compound and one of the

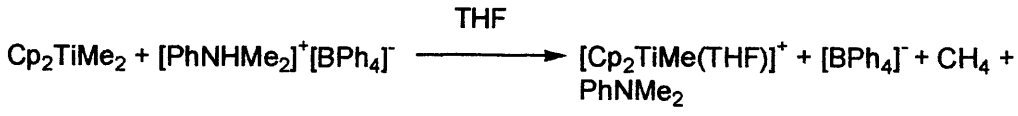
aforementioned abstraction agents. Alternatively, both steps can be performed with one reagent, as is the case with MAO.

MAO is by far the most commonly employed cocatalyst either for abstraction alone or to carry out a combined alkylation/abstraction methodology. It is used in a large excess, usually at around a 1000:1 molar ratio, as it is thought that such an excess is required to shift the equilibrium involving a metal alkyl and MAO to the active cationic species (Scheme 10).[45] High catalyst activity suggests that the MAO-derived anion is labile and easily displaced by the alkene monomer.



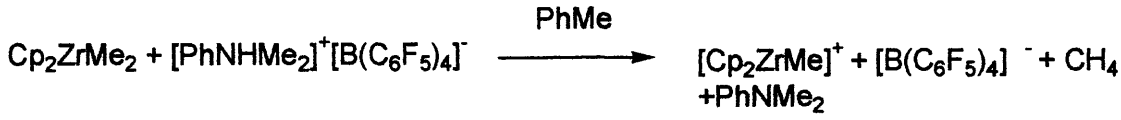
Scheme 10: Activation of a precatalyst by MAO.

Active polymerisation catalysts have been reported where MAO is replaced by a stoichometric amount of another compound, the first examples being anilinium tetraphenylborate salts.[46,47] In this case, the resulting cationic titanocene complex exhibits low activity as a result of the highly electrophilic metal centre reacting with the anion and also solvent binding (Scheme 11)



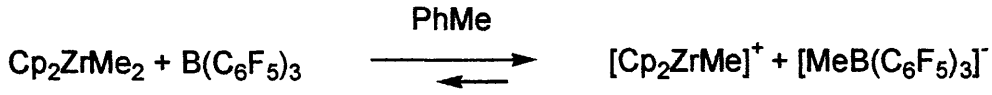
Scheme 11: Activation by an anilinium tetraphenylborate salt.

Turner and Hlatky found that solvent/counter ion interactions with the active cationic species could be dramatically reduced with perfluoronated anions and toluene as the solvent, to produce a highly active catalyst (Scheme 12).[48]

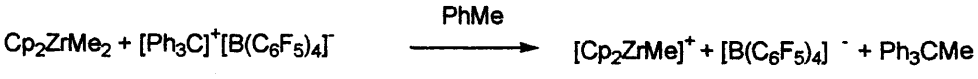


Scheme 12: Activation by an anilinium tetrafluoroborate salt.

Marks later reported the use of the Lewis acid $B(C_6F_5)_3$ as an activator for dimethylzirconocene by methyl abstraction (Scheme 13).[49] In a similar fashion the trityl cation activates dimethylzirconocene by methyl abstraction (Scheme 14).[50,51,52]



Scheme 13: The Lewis acid $B(C_6F_5)_3$ as an activator.



Scheme 14: Activation by the trityl cation.

In addition to the classical activation methods, alternative strategies have been developed in the form of 'zwitterionic metallocenes'.[53,54]

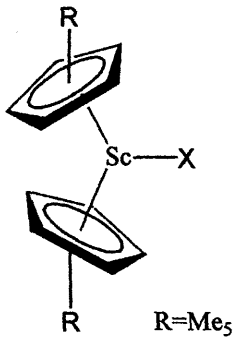
1.7 Overview of Past and Current Research in Precatalyst Synthesis

The field of olefin catalysis is vast and as a result a comprehensive review of the area is beyond the scope of this thesis. However, there are many detailed reviews available in the literature [55-60] For the purposes of this thesis the milestones and recent advances related to this project are to be highlighted. The main focus of this thesis is group 4 catalysts, so particular attention will be paid to these in the discussion that follows.

1.7.1 Group III and IV Metallocenes

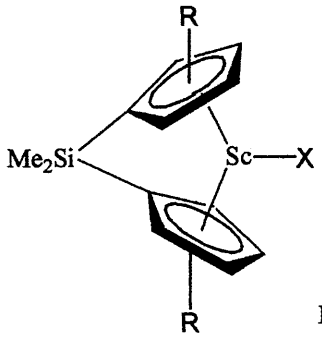
Group three neutral alkyl complexes (e.g. Cp_2ScR) are isoelectronic with group 4 cationic alkyl complexes of the type $[Cp_2ZrR]^+$. These neutral alkyl species $[L_2MR]$ tend to act as single component catalysts i.e. they require no cocatalyst to activate them. They commonly exist as dimers, $[L_2MR]_2$, in the solid state and solution, although monomeric species have been achieved by replacing L with a bulky ligand or by introducing an additional donor ligand.[60] Most ligand systems used to create group 3 catalysts are based on ligands that have been successful for group 4 metals. Examples include complexes **1-3** where the same variation of Cp/Cp* sterics and electronics that have been reported for group 4 have been examined for scandium. Scandium complexes generally have low polymerization activity, which has enabled detailed studies of the mechanism of the polymerization process to be carried out, as some of the intermediates could actually be

isolated.[61,62,26,63,64] Higher activities toward ethylene have been observed for the yttrium catalysts **4**(42 g $mmol^{-1}bar^{-1}h^{-1}$)[65] and **5** (584 g $mmol^{-1}bar^{-1}h^{-1}$).[66,67,68,69]



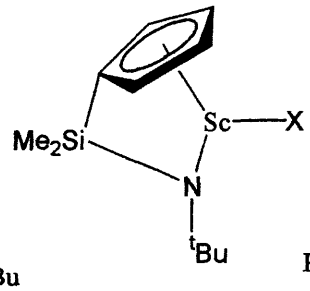
R=Me_5

1



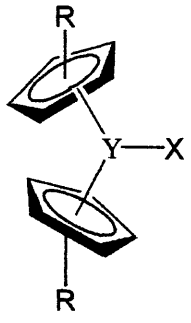
R=Me_4,^{t}Bu

2



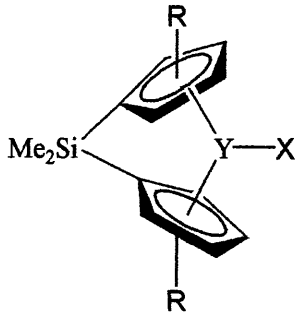
R=Me_4

3



R=H_5,Me_5,$SiMe_3$

4

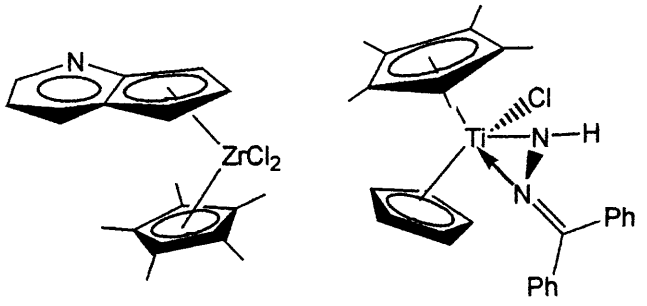


R=Me_4, $(SiMe_3)_2$

5

The group 4 metallocenes Cp_2TiCl_2 and Cp_2ZrCl_2 when activated with MAO to give $[Cp_2MR]^+$ are capable of very high polymerisation activities (ca 30,000 g $mmol^{-1}$ $bar^{-1}h^{-1}$)[43] Modification of the Cp rings can cause dramatic changes to polymerisation activities and behavior. Thus, complex **6** containing a cyclopentadienyl ligand with a

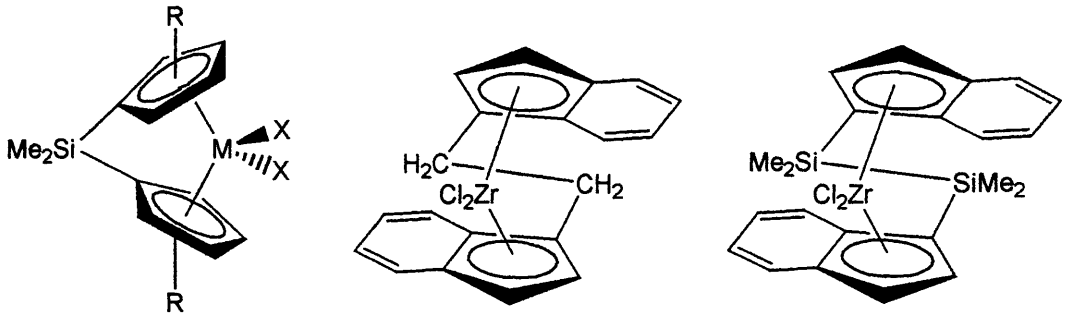
fused pyridine ring [70] has been shown, on activation with MAO, to polymerise ethylene and copolymerise ethylene and 1-hexene. The relatively narrow polydispersities of the polymers indicate that the traditional single site polymerization behavior is occurring.



6 **7**

Titanocene hydrazonide derivatives are active for olefin polymerisation.[71] Among such species, complex **7** is the most active reported and is capable of producing polyethylene (66 g $mmol^{-1}$ bar^{-1} h^{-1}) and polypropylene (1 g $mmol^{-1}$ $bar^{-1}h^{-1}$). Variation of the Cp substituents produces complexes which polymerise styrene.

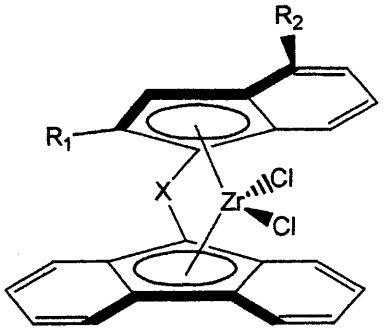
Group 4 ansa metallocenes (Figure 10) have been at the forefront in the quest to find catalysts that allow reliable control over polymer stereochemistry. Tethering of Cp rings effectively locks the rings in only one possible conformation by preventing free rotation of metal-Cp bond. This is especially important when substituents are added to the Cp ring as they can be locked in positions such that they may make attack by a monomer at a particular polymerisation site more or less favorable *vide supra.*



8 **9** **10**

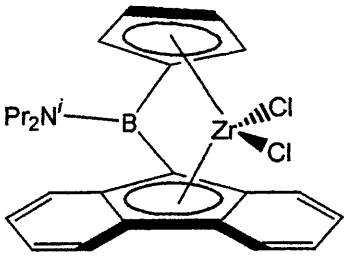
Figure 10: Examples of ansa-metallocenes.

The size of the ansa bridge has been shown to be very important; the optimum size appears to feature one (most active) or two atoms in the bridge [e.g. $(Me_2Si)_2$ or $(CH_2)_2$].[72,73] Metallocenes with three or four atom bridges, although active for the small ethylene monomer, have been found to be inactive towards propylene.[74,75,76,77,78] It has been suggested that shorter ansa bridges hold back the Cp rings and open up the coordination gap for the incoming monomer.[79,80] Thomas et al. have synthesized a series of asymmetric indenyl-fluorenyl metallocenes **11**, which are highly efficient catalysts for Ziegler Natta type polymerisation of ethylene and propylene.[41] Interestingly, for these catalysts it has been noted that raising the polymerisation temperature increases the stereoregularity of the resulting polymeric material.



R_1=Me, R_2=Ph, X=C_2H_4
R_1= R_2=Ph, X=$SiMe_2$
R_1=Me, R_2=Ph, X=$SiMe_2$

11



12

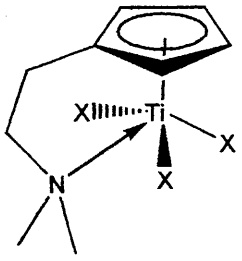
Atoms from groups other than group 14 have also been incorporated into the ansa bridge, with boron-based systems having been reported recently by both Braunschweig and Ashe. When activated by MAO complex **12**, for example, shows high activity towards the copolymerisation of 1-octene and ethylene, and is also highly active for the polymerisation of propylene, producing monodisperse, syndiotactic polymer.[81]

1.7.2 Half Sandwich Complexes

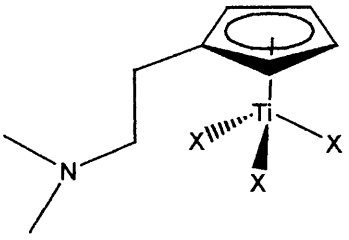
1.7.2.1 'Piano Stool' Complexes

Complexes having piano stool structures generally have low polymerisation activities than traditional metallocenes. [82,83,84] However, the addition of a pendant neutral donor can substantially increase polymerisation activity. Precatalysts **13**,[85] **14**,[86] **15a**, **15b**, [87] and **16** [88] are examples of such complexes. The pendant phenyl moiety in **15a** and **15b** has been shown not to be coordinated to the metal in the precatalyst, but becomes a donor in the cationic species formed by methyl abstraction using a Lewis acid. [87] The related

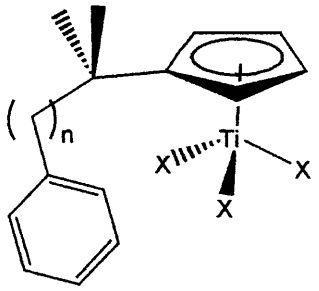
complex **16** shows high activity, and the proposed active species is a low valent Ti species stabilized by coordination of the pendant phenyl donor.[88]



13



14

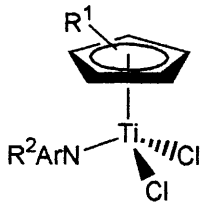


15a (n = 0, X = Me)

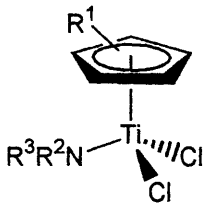
15b (n = 1, X = Me)

16 (n = 0, X = Cl)

The addition of amide donors to these 'piano stool' complexes has yielded some useful catalysts. Nomura et al. have introduced some simple amide ligands in place of the X substituent in complexes of the type $CpMX_3$.[89]



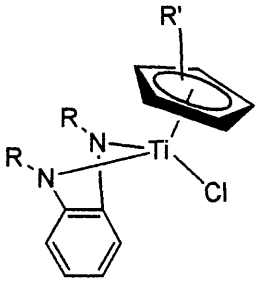
17(R^1 = Me_5, Me_2, H_5; R^2 = $SiMe_3$; Ar = 2,6-$Me_2C_6H_3$)



18 (R^1 = Me_5, Me_2; R^2 = Me, Cy; R^3 = Me, Et, Cy)

Activities of up to 1000 g $mmol^{-1}$ bar^{-1} h^{-1} towards ethylene for anilide complexes of the type **17** have been observed for the Cp* complex.[89] The molecular weight of the resulting

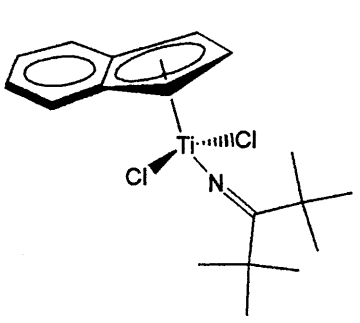
polymer is high with a low polydispersity suggesting that a single site mechanism is in operation. Activity towards hex-1-ene was reported to be substantially lower. In general, the activities of these anilide complexes are significantly lower than their aryloxide counterparts (*vide infra*). Alkyl substituted amide complexes of the type **18** have been shown to be highly active for the polymerisation of ethylene and styrene and for the copolymerisation of ethylene and hex-1-ene. The nature of the Cp and the amide substituents has been shown to affect the reactivity towards different monomers.[90]



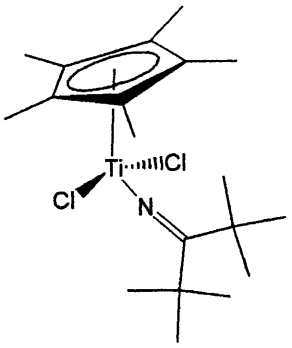
19

Further variations of amide ligands have recently been reported. A series of half sandwich complexes of the type **19** were synthesized with two chelating amides tethered by an aryl backbone.[91] Reactions with propylene were unsuccessful yielding minimal traces of polymer. Ethylene polymerisation runs showed moderate activities ranging from 70-150 g $mmol^{-1}$ bar^{-1} h^{-1} and, as observed for the mono amide complexes **17** and **18**,the activity of the complexes was highly dependant on the Cp substituents.

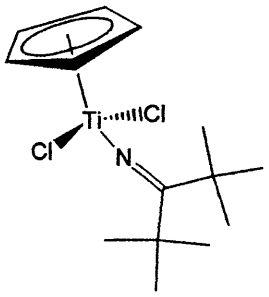
Other nitrogen donors such as imides have been successfully exploited in generating active olefin polymerisation catalysts.



20a

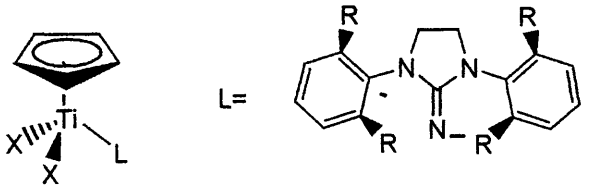


20b



20c

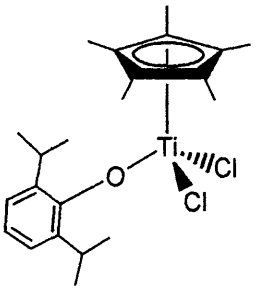
Ketimide ligands in combination with indenyl, Cp* or Cp derivatized titanium centres, give a range of complexes, which when activated with MAO, act as catalysts with low to moderate activity.[92] Complex **20a** shows the highest activity (123370 g $mmol^{-1}$ bar^{-1} h^{-1} for ethylene and 50770 g $mmol^{-1}$ bar^{-1} h^{-1} for propylene) which is about six times higher than that observed for **20b** which in turn has an activity four times higher than that recorded for **20c**. This difference in activity has been explained by the differing abilities of the ligands to stablise the active cationic species (i.e indenyl>Cp*>Cp). Interestingly, the order of reactivity changes in the case of propylene polymerisation with **20a>20c>20b**; in this case activity is thought to be determined by stereochemical factors. **20a-20c** are also able to copolymerise ethylene with unsaturated alcohols. More recently Martins et al have syntheised complexes with an additional ketimide giving complexes of the type $CpM(N{=}C^tBu)_2Cl$. The most active of these complexes was $CpZr(N{=}C^tBu)_2Cl$ (270000 g $mmol^{-1}$ bar^{-1} h^{-1}).[93]



21

Kretschemer and coworkers have shown that the incorporation of a monoanionic 1,3-bis(xylyl)iminomidazolidide into a cationic mono(cyclopentadienyl)titanium alkyl complex **21** yields efficient catalyst for homo (896 g $mmol^{-1}$ bar^{-1} h^{-1}) and copolymerisation (1600 g $mmol^{-1}$ bar^{-1} h^{-1}) of olefins.[94]

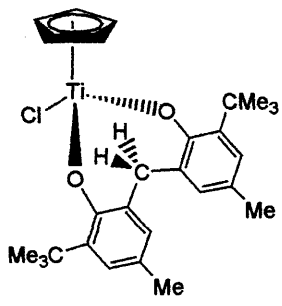
Amides and imides are not the only anionic ligands to be used in place of halogens and alkyls in the original $CpMX_3$ complexes. Alkoxide based ligands have been incorporated successfully and have resulted in some active catalysts.



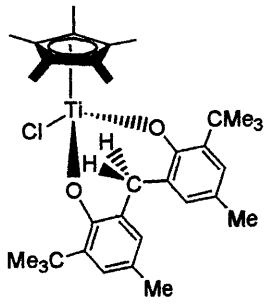
22

Normura et al. have applied the non bridged approach with aryloxides in the same way as they did with amides (*vide supra*).[89] Thus Cp* complex **22** exhibits exceptionally high polymerisation activity not only for ethylene but also for ethylene/α-olefin copolymerisation. Moreover, the complex can be transformed into an efficient styrene

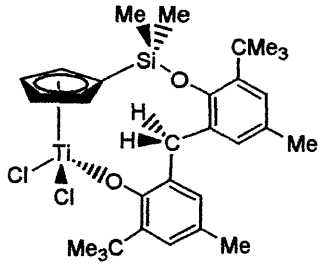
and ethylene/styrene polymerisation catalyst by changing the Cp* ligand for $C_5H_3Me_2$ [95,96,97,98].



23a

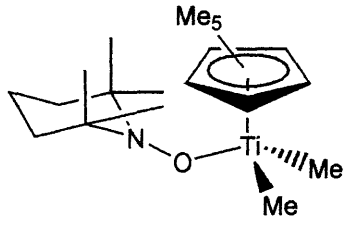


23b

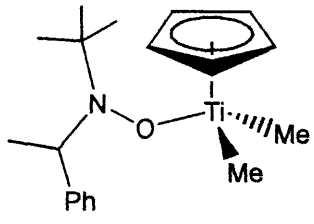


23c

The complexes **23a-23c** with chelating alkoxide donors[99] are active for the polymerisation of propylene, styrene and isoprene; the polypropylene produced contains large isotactic stereoblocks. The data shows that activity is highly influenced by the substituents on the Cp ring, a recurring theme with these 'piano stool' complexes.



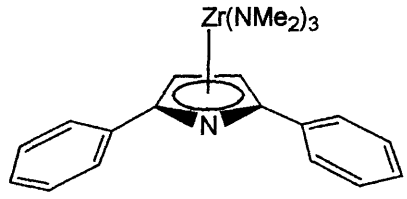
24a



24b

Waymouth et al. have reported active half sandwich catalysts with a combination of Cp and nitroxide donors.[100] Complexes **24a** and **24b** are active for the copolymerisation of ethylene and hex-1-ene. The polymer molecular weights produced by **24b** are slightly lower than for **24a** which is likely due to the less electron rich nature of the Cp ligand in

24b. The molecular weight distribution of copolymers is broad, compared to those observed for single site catalysts, which is thought to be indicative of secondary reactions including chain transfer.



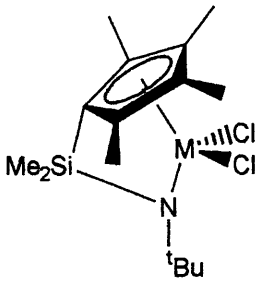
25

A variation on the typical Cp half sandwich complex is the zirconium Pyrrolyl complex **25** where the heterocycle binds in a η^5 fashion to the metal.[101] On activation with MAO the complex does polymerise ethylene, but the activity is substantially lower than that observed for Cp_2ZrCl_2/MAO systems.

1.7.2.2 Constrained Geometry Catalysts

The combination of a Cp ring and a pendant anionic donor gives highly active "constrained geometry catalysts" (CGC's), and has resulted in their development for commercial exploitation. Some have been found to be viable alternatives to the original Ziegler-Natta systems. For instance the half sandwich catalyst $[Me_2Si(Cp)(N^tBu)]ZrCl_2$ **26**, which produces α-olefin oligomers on activation with MAO, is one of the few examples of commercially exploited "non-metallocene" catalysts.[102] Reaction with propylene gives oligomers which, it is proposed, coat the catalyst; when propylene

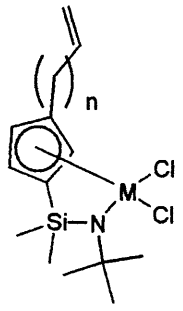
oligomerisation ceases, the introduction of ethylene causes further polymerization, however the reactivity of the coated catalyst towards ethylene is far higher than that of the original $[Me_2Si(Cp)(N^tBu)]ZrCl_2$/MAO combination. Even more surprisingly this oligomer 'coated' catalyst also survives treatment with typical catalyst poisons such as water and hydrochloric acid, and remains active.



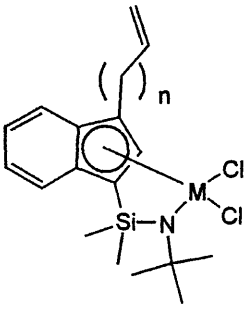
26

Alt et al have investigated the possibility of developing a 'self-immobilising catalyst'.[103] The design of the ligands was based on half sandwich constrained geometry systems but with the addition of alkenyl side chains on the Cp ring. The logic of this approach is that the double bond of the alkenyl chain is thought to copolymerise with ethylene, thereby forming a heterogeneous catalyst. Three basic types of complex were synthesized **27**, **28** and **29**. Data on homogenous ethylene polymerisation shows that in general indenylidene complexes show higher activities (9000 g $mmol^{-1}$ bar^{-1} h^{-1}) than cyclopentadienylidene compounds (ca 1000 g $mmol^{-1}$ bar^{-1} h^{-1}), perhaps due to the weaker π donor effect of the indenyl increasing the Lewis acidity at the metal. Highest activities were observed for catalysts of type **28**, with activity increasing with increasing chain length in the case of zirconium, but with the reverse being true of titanium. For complexes of type **27** the trend seen was that of increasing activity with increasing chain length for titanium complexes

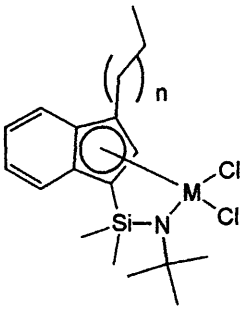
with the opposite trend for zirconium. Complexes of the type **29** were generally lower in activity but nonetheless efficient catalysts (of the order of 2000 g $mmol^{-1}$ bar^{-1} h^{-1}). Heterogenous catalyst runs were carried out with complexes of the type **28** and showed that there is an optimum chain length for maximum activity. Alt et al have also studied phenylalkyl substituted half sandwich complexes **30**[104] and have found activity to increase with the length of the chain linking the Cp and Ph components, with activities for zirconium complexes being higher than for titanium (10000 vs. 5000 g $mmol^{-1}$ bar^{-1} h^{-1}).



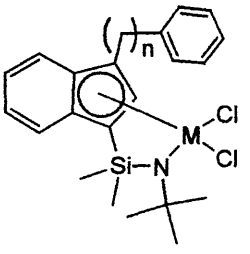
27



28



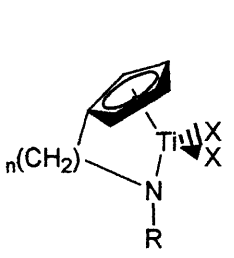
29



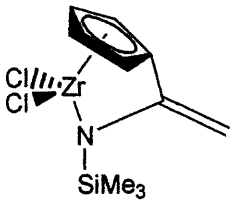
30

Many developments on the theme of constrained geometry catalysts which have been reviewed by McKnight and Waymouth.[105] Noteworthy examples include those where the nature of the linkage between the Cp ring and the anionic donor has been varied. For example, complex **31** reported by Teuben and Green has a carbon based tether instead of silicon.[106,107] Catalysts with linkers containing an alkene functionality (e.g. **32**) have been reported with polymerisation activity comparable to that of **26** .[108] Another variation on

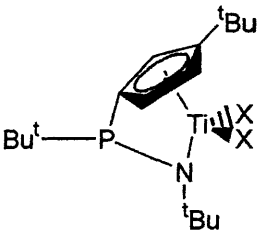
this theme is the introduction of a phosphorus bridge (as in **33**) which gives a catalyst with high activity (100 g $mmol^{-1}$ bar^{-1} h^{-1}).[109]



31

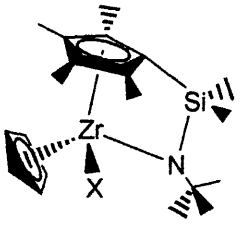


32

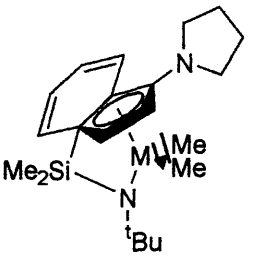


33

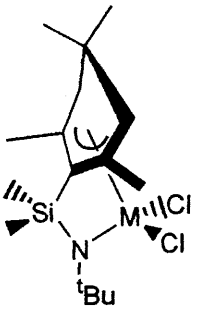
Variation in the nature of the Cp ring has also yielded some active catalysts. Thus the heteroatom substituted complex **35** is active for the copolymerisation of ethylene and 1-octene, producing a higher molecular weight polymer than observed for **26** although the activity is very much dependant on the position of the substituents on the Cp ring.[110] Replacement of the Cp ring with a cyclohexadienyl fragment (as in **36**) gives a highly active catalyst for the copolymerisation of ethylene and 1-octene with the zirconium complexes being more active than their titanium counterparts. [111,112]



34



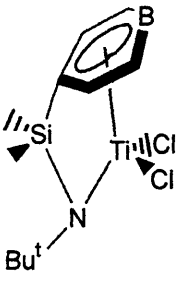
35



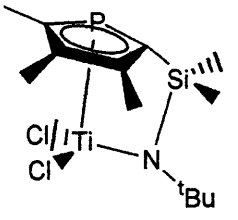
36

Ashe and co-workers have shown bridged boratobenzene-amido titanium and zirconium complexes such as **37** to have high activity for thecopolymerisation of ethylene and oct-1-ene[113] The phospholyl-amido complex **38** shows comparable ethylene polymerisation

activity to **26** but with lower molecular weight.[114]More recently Chen and co-workers have published results relating to a new class of monoalkyl/monohalide, chiral-at-metal constrained geometry catalysts **34.** [115]These complexes give highly active polymerisation catalysts upon activation with aluminium co-catalysts, being capable not only of the polymerisation of olefins but also methyl methacrylate. They are thought to function by a different mechanism i.e. attack by the aluminium activator on the polarized olefin and formation of a Zr-CH_2(R)-Al bond. This bimetallic mechanism is similar to that proposed by Natta and Mazzanti.[116] This discovery that complexes containing a single insertable/abstractable metal-alkyl bond can be activated for olefin polymerisation adds a new class of monoalkyl and mono-chloro metal complexes to the ever-expanding polymerisation catalyst library.



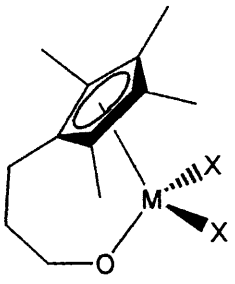
37



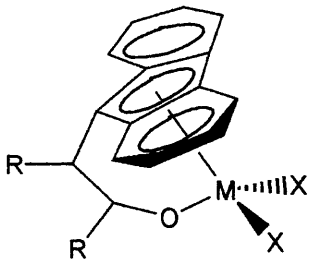
38

There is also a number of constrained geometry type complexes with an alkoxide in place of the usual amide donor. Hessen and co-workers reported the Cp-alkoxide titanium complex **39** to be capable of the polymerisation of propylene.[117] Similarly, the fluorenyl alkoxide zirconium dichloride complex **40** was shown by Rieger to be an active catalyst when activated by MAO.[118] Furthermore, a highly active (2100 g $mmol^{-1}$ bar^{-1} h^{-1})

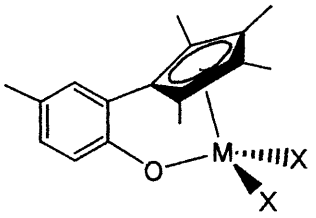
complex (**41**) for the polymerisation of ethylene has also been synthesised by Marks et al., containing a pendant aryloxide function.[119]



39

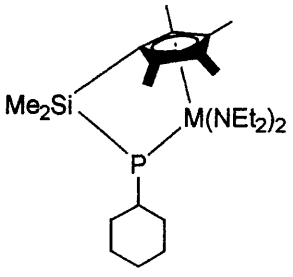


40



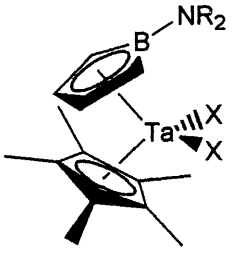
41

In addition to amides and alkoxides, constrained geometry catalysts have also been synthesized which employ phosphido ligands.[120] Thus, on activation with MAO, complex **42** gives a moderately active catalyst for the polymerisation of ethylene; for this particular system zirconium is found to give the more active catalyst (66 g $mmol^{-1}$ bar^{-1} h^{-1}). **42** is also active for the copolymerisation of ethylene and oct-1-ene, although in this case the titanium analogue performs slightly better (16 g $mmol^{-1}$ bar^{-1} h^{-1}).

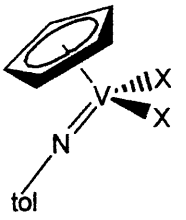


42

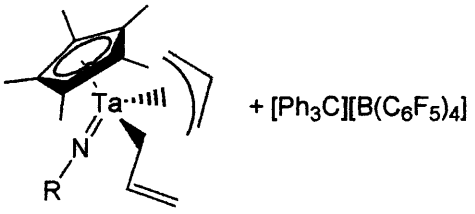
Finally, piano stool and constrained geometry type complexes are not restricted to group 4 metals. Cp ligand frameworks and dianionic fragments such as imides have been combined to produce neutral group 5 complexes. Substitution of a CH group by BNR_2 in a Cp ring gives a borollide ligand which when complexed to tantalum gives a catalyst [Cp*Ta^{V}(η^5-borollide)Cl_2], **43**, which shows low polymerisation activity.[121] Vanadium complex **44**, when activated with MAO, yields a complex with activity 27 g $mmol^{-1}$ bar^{-1} h^{-1};[122] an analogous niobium complex, although isolobal with zirconocene, is less active than **44**. Complex **45**, an η^1,η^3 – diallyl tantalum compound,[123] can be treated with a trityl fluoroborate salt to give a catalyst with low ethylene polymerisation activity. The resulting polyethylene is of high molecular weight and a high polydispersity. The allyl substitution pattern is required to stabilise the complex. An analogous compound **46** supported by a very bulky silyl imido ligand shows moderate activity when activated with MAO (14 g $mmol^{-1}$ bar^{-1} h^{-1}). The resulting polymer is similar in molecular weight to that produced by **45** but has a lower polydispersity. Niobium complex **47** shows a moderate activity of 39 g $mmol^{-1}$ bar^{-1} h^{-1} giving polyethylene with molecular weight over 100 000 and narrow polydispersity.[124,125,126] An analogous tantalum complex has been reported.[125]



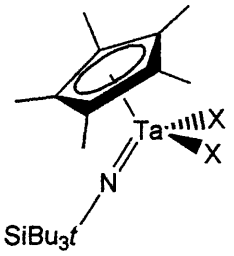
43



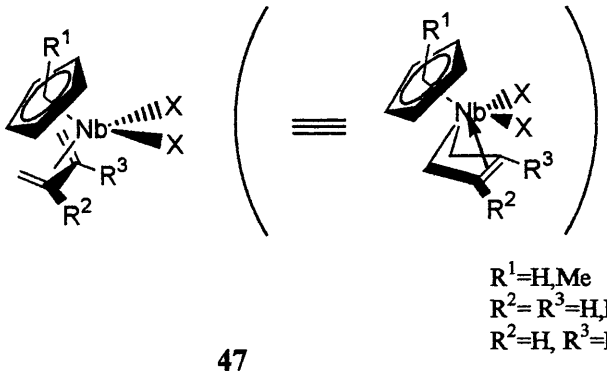
44



45



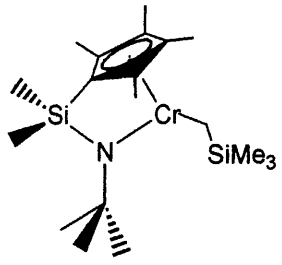
46



47

R^1=H,Me
R^2= R^3=H,Me
R^2=H, R^3=Me

The Cp-amido ligand framework has been applied to chromium based catalysts. Although complex **48** shows low activity towards α-olefins,[127] catalyst **49** shows activities of 8300 g $mmol^{-1}$ bar^{-1} h^{-1} when activated with as little as 100 equivalents of MAO.



48

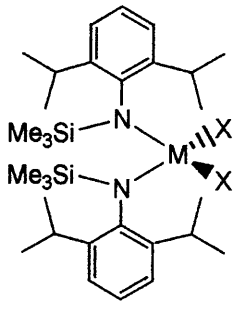
49

1.7.3 Group 4 metals incorporating nitrogen and oxygen donors

Through research over the last ten years it has emerged that group 4 metal complexes containing amide spectator ligands are promising systems for olefin polymerisation.[43,59] These systems have a lower formal electron count; $[(R_2N)_2ZrR]^+$ for example, is a 10 electron species compared with the 14 electron $[Cp_2ZrR]^+$. The lower electron count is likely to result in a more electrophilic, and as a result a potentially more active, catalyst fragment.

1.7.3.1 Nitrogen Donors

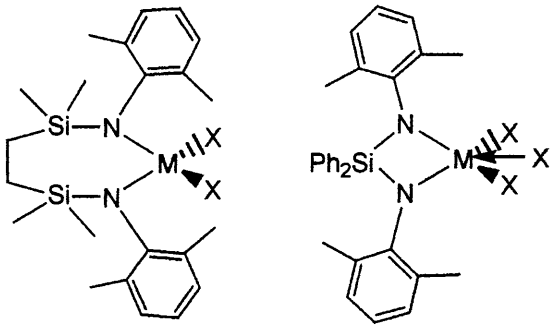
Reported amide catalysts include those containing the spectator ligands as a pair of monodentate or single bidentate ligand (bis(amido) complexes), the latter having received far more attention.



50

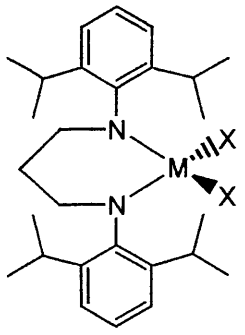
Structures **50-63** are examples of such compounds. Compound **50**, an example incorporating monodentate anilide ligands, has been shown to have moderate activity when using MAO as a cocatalyst (13 g $mmol^{-1}$ bar^{-1} h^{-1}).[128,129] Complex **51** reported by Gibson shows a high activity towards ethylene (490 g $mmol^{-1}$ bar^{-1} h^{-1}),[130] in contrast to

complex **52**, reported in the same paper, which has a much lower activity (3 g $mmol^{-1}$ bar^{-1} h^{-1}). The main difference between these complexes is the 'bite-angle' of the ligand. Incorporation of a $Si(CH_2)_2Si$ bridge in complex **51** means the angle at which the amide ligand chelates to the zirconium centre is much larger than that in complex **52**. This causes the aryl groups to fall into a position which protects the metal centre, in contrast to **52** where the aryl groups are drawn back, due to the more acute bite-angle of the chelate. This close positioning of the aryl rings in **51**, protecting the metal from attack by small molecules which could block the active site, is thought to be the reason that it is more active than **52**. These complexes are a good example of how steric protection of the metal centre in a catalyst can promote higher polymerization activities.[130]



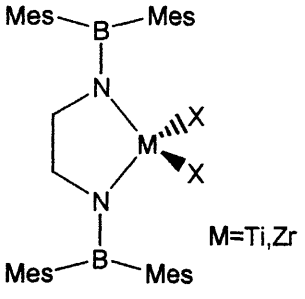
51 **52**

The diamide complex illustrated in **53**, which was developed by McConville and co workers, is reported to show very high activity for α-olefin polymerisation although no ethylene polymerisation results were reported.[131,132,133]

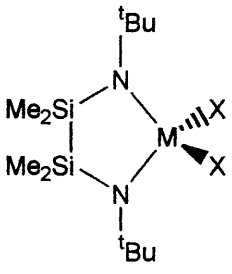


53

The design principles behind complex **54** include bulky mesityl groups, locked in position by N-B π-bonding to protect the metal centre, and a strongly π-accepting boryl group designed to increase the electrophilicity of the metal complex. The polymerisation activity of **54** was tested using $B(C_6F_5)_3$ as the activator but it showed little activity towards ethylene. This is thought to be a consequence of strong anion binding.[134] Complex **56** is also reported to have low ethylene polymerization activity,[135] in contrast to complex **55** which contains a silicon-based backbone and displays an activity of 100 g $mmol^{-1}$ bar^{-1} h^{-1}.[136]

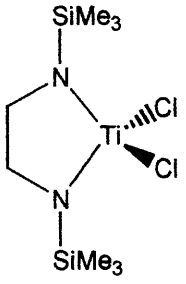


54

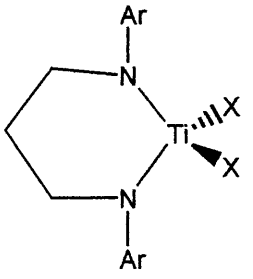


55

Complex **57a** has been reported to polymerise 1-hexene in a living fashion at room temperature with activation from $B(C_6F_5)_3$. [137] By varying the cocatalyst **57b** can catalyse the co-polymerisation of ethylene and 2-butene [138] as well as polymerizing propylene itself [139,140] but both with low activity.

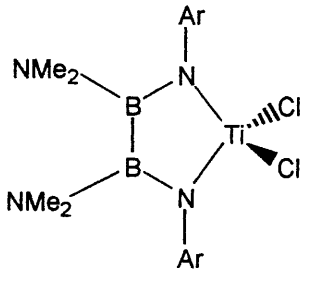


56

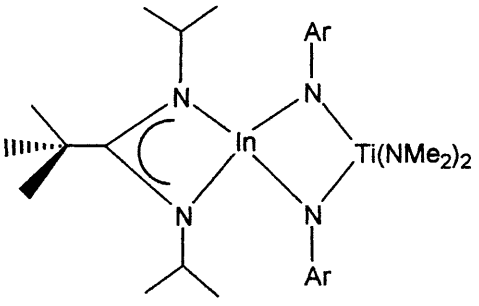


57a M=Ti, X=Me
b M=Ti X=Cl

Patton and co workers have reported high activity and production of a high molecular weight polymer from **58** [141]The research into these Lewis acid bridged bis (amido) complexes has been extended by introducing an indium bridge in compound **59.** [141] Although active for ethylene polymerization, **59** does not compare with Cp based single site catalysts.

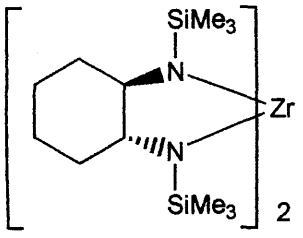


58

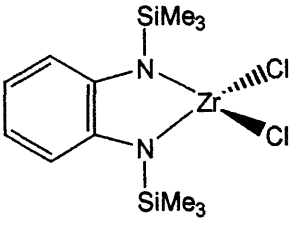


59

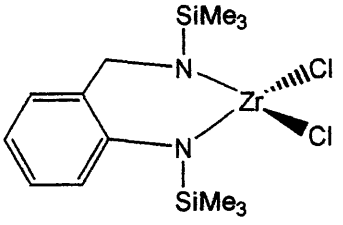
Complex **60** is reported by Bochmann to have a moderate activity towards ethylene (50 g $mmol^{-1}$ bar^{-1} h^{-1});[142] replacing the cyclohexane ring with a benzene ring gives low activity catalysts **61** [143,144] and **62.** [145]



60

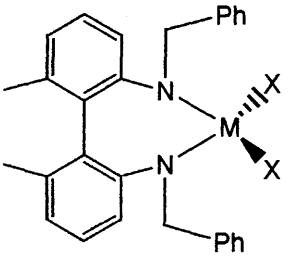


61

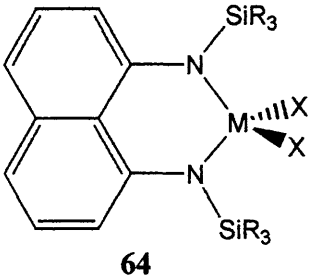


62

The biphenyl complex **63** investigated by Cloke et al shows moderate polymerisation activity (13 g $mmol^{-1}$ bar^{-1} h^{-1}).[146] The rather rigid complex **64** shows ethylene polymerisation activities of up to several hundred g $mmol^{-1}$ bar^{-1} h^{-1}. [147,148]



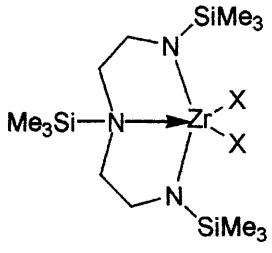
63



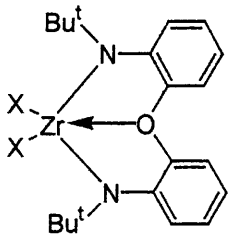
64

Group 4 bis(amido) complexes containing an additional amine, pyridyl, or ether donor have also been reported. Horton et al. developed catalyst **65**, which shows moderate polymerisation activity (46 g $mmol^{-1}$ bar^{-1} h^{-1}) and contains an amine donor in addition to the main amide donors.[149] Catalyst **66**, with an additional ether donor, shows moderate polymerisation activity (100 g $mmol^{-1}$ bar^{-1} h^{-1}).[150]

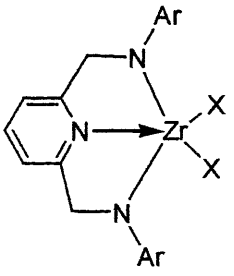
Addition of a pyridyl donor, as in complex **67**, increases the activity, generating a highly active catalyst (1500 g $mmol^{-1}$ bar^{-1} h^{-1}).[151] The titanium analogue shows low activity towards ethylene polymerization, an observation which is probably due to reduction of the Ti(IV) centres to Ti(III). Complexes **68** and **69** have been reported by Bochmann;[152] **69** has been shown to have only low polymerization activity towards ethylene (5.2 g $mmol^{-1}bar^{-1}h^{-1}$) whereas **68** has moderate polymerization activity (40 g $mmol^{-1}$ bar^{-1} h^{-1}). In related work complexes of the type **70** (which is structurally similar to **67**) have been shown to be active towards hex-1-ene polymerization at temperatures below 10°C on activation with $[Ph_3C][B(C_6F_5)_4]$.[153]



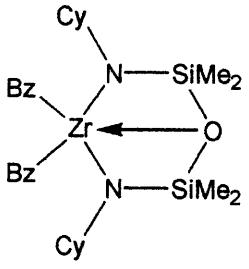
65



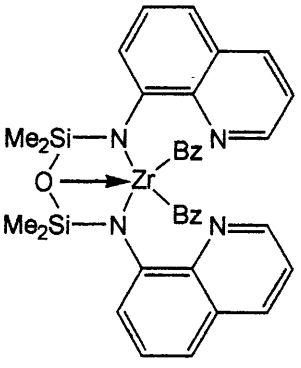
66



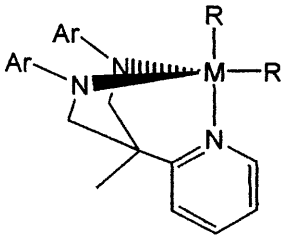
67



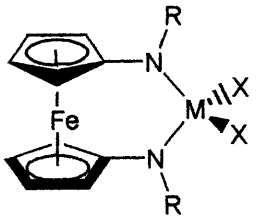
68



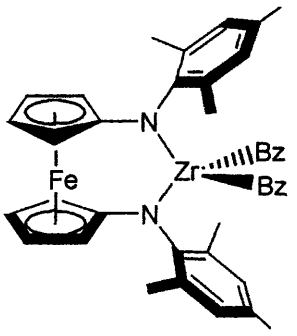
69



70



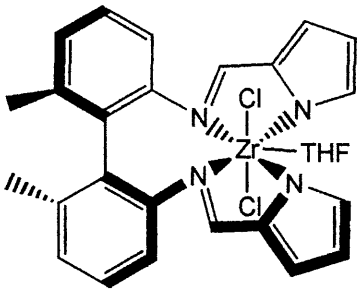
71a R=Ph X=N(Me)$_2$
71b R=SiMe$_3$ X=Me



71c

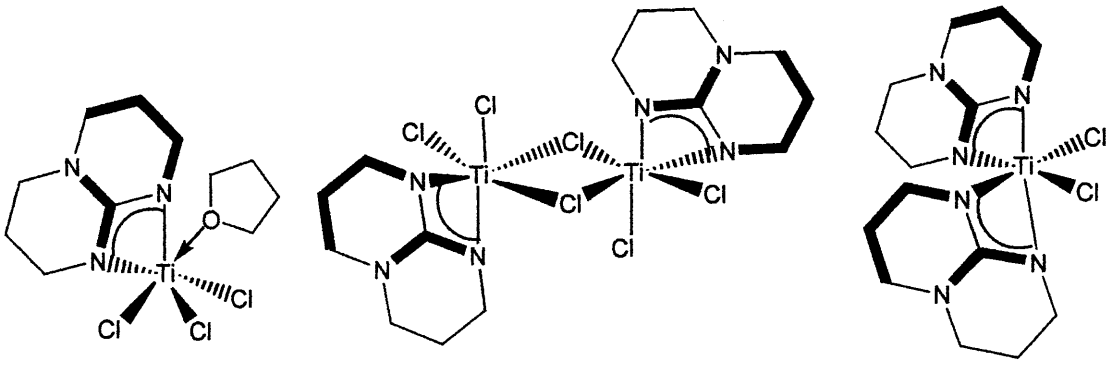
Ferrocenyl-bridged chelating amides of the type **71** [154] are active for the polymerisation of ethylene. Thus **71a**, on activation with $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$, has been shown to oligomerise ethylene with an activity of up to 100 g mmol^{-1} bar^{-1} h^{-1}. [155,156] More recently Arnold et al. have extended this work to aryl substituted ferrocenyl-bridged diamides such as **71c.** [157] This complex is not viable 1-hexene polymerisation catalyst when activated with $B(C_6F_5)_3$, but activation with $[Ph_3C][B(C_6F_5)_4]$ gives poly-1-hexene with low polydispersities.

In addition to the amide donors, a wide range of other nitrogen based ligand sets have been reported.



72

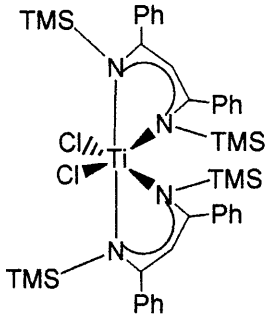
Brintzinger et al. have reported a moderately active bis-aniline based complex **72.** [158] On activation with MAO this complex is capable of the polymerisation of ethylene (6.2 g $mmol^{-1}$ bar^{-1} h^{-1}) and propylene (7.8 g $mmol^{-1}$ bar^{-1} h^{-1}). The propylene obtained from the polymerisation is partially isotactic.



73a **73b** **73c**

The bicyclic guanidinates **73a-73c** were synthesised by Coles et al. [159] **73a** and **73b** on activation with MAO show low activities towards ethylene (7.4 and 7.1 g $mmol^{-1}$ bar^{-1} h^{-1}, respectively), which may be due to the titanium precatalyst retaining THF (**73a**) or adopting a dimeric structure (**73b**) thus hindering either the activation or monomer coordination step. **73c** was predicted to show higher activity but surprisingly the opposite was true and the complex was less active than both **73a** and **73b** (2.2 g $mmol^{-1}$ bar^{-1} h^{-1}) under the same conditions. To investigate this lower activity for **73c** the complex was reacted with trimethyl aluminium and the resulting complex showed that the guanidinate ligands are not in fact simply supporting ligands, but have the ability to interact with aluminium centres. Although not demonstrated conclusively this reaction with an aluminium alkyl is thought to be the same as occurs when the complex is reacted with MAO and therefore gives a possible explanation for the lower activity of **73c**. The benzyl

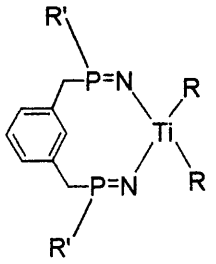
analogue of **73c** was synthesised and tested for its activity but during the activation step a similar problem with interaction of the guanidinate was witnessed.



74

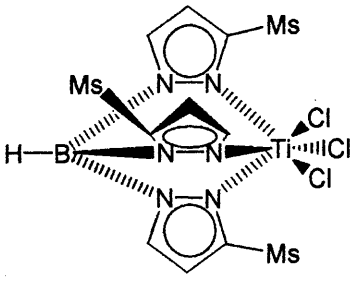
Group 4 β-diketiminate complexes have proved successful for the polymerisation of propylene.[160] Catalytic runs with **74**/MAO produced remarkably high molecular weight elastomeric propylene at activities of 130000 g $mmol^{-1}$ bar^{-1} h^{-1}. Interestingly, the zirconium analogue is inactive for catalysis.

The use of titanium fluorides as catalysts for organic reactions has been limited due to their lack of solubility in common organic solvents However Waymouth et al. have synthesised $[TiF_2(NMe_2)_2]_4$ and tested its activity towards the polymerization of ethylene, propylene and styrene.[161] The complex showed a modest activity towards olefins with activities some 10-100 times lower than titanocene catalysts.

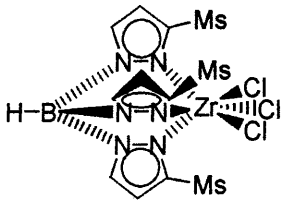


75
R'=^{t}Bu R=Me
R'=^{t}Bu R= Bz
R'=Cy R= Bz

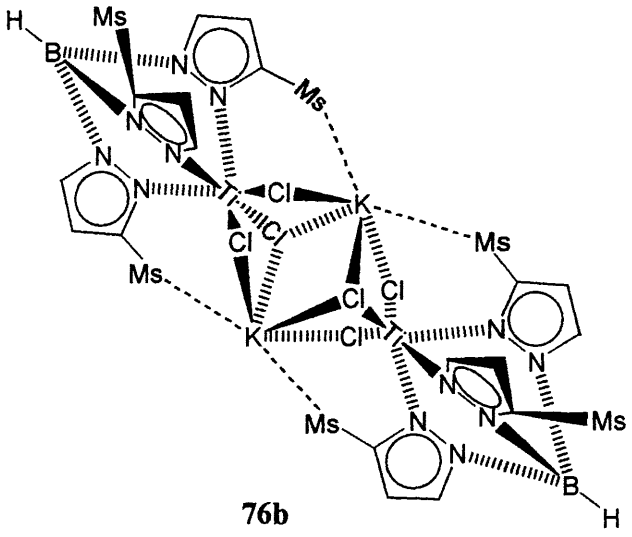
Phospinimide complexes of titanium e.g. $CpTi(NPR_3)X_2$ and $(R_3PN)_2TiX_2$ (R=alkyl, halide, X= halide, alkyl) are highly active for polymerisation provided a non-aluminium activator is used. [162,163] Stephan et al have carried out preliminary investigations into the possibility of group 4 bis-phosphinimide complexes such as **75** as polymerisation catalysts.[164] Only very low activities were observed at this point. Further work into phosphimide ligands by this research group involved an investigation into the effect of activators on polymerisation performance.[165] On this occasion a combination of Cp and phosphimide ligands were employed. The ethylene polymerisation activities showed that the typical MAO activation gave only moderate activity, however using $B(C6F_5)_3$ as a cocatalyst significantly increased activity. The highest activities for these complexes were obtained by using $[Ph_3C][B(C_6F_5)_4]$ as the activator.



76a



76c

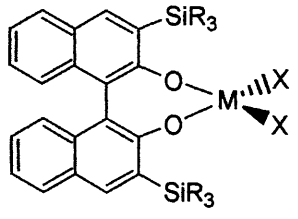


76b

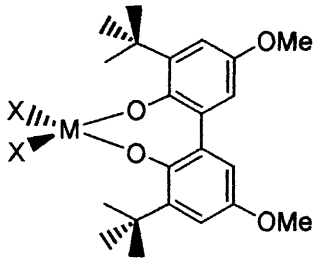
Titanium complexes with tris(pyrazolyl)borate ligands (e.g. **76a** and **b**) are active as polymerisation catalysts [166] with activities comparable to those published for zirconocene dichloride under similar conditions.[167] Both catalysts produce ultra high molecular weight polyethylene. Zirconium and hafnium complexes containing tris(pyrazolyl)borate ligands have also been investigated for their polymerisation activity.[168] The main focus of this research was to investigate the effect of steric crowding of the tris(pyrazolyl)borate ligands on activity. As expected, the less crowded complex **76c** gave the highest activity; activities towards ethylene polymerization (15700 g $mmol^{-1}$ bar^{-1} h^{-1}) and ethylene/hex-1-ene copolymerisation are extremely high, producing narrow M_w distributions and thereby suggesting a single site mechanism is in operation.

1.7.3.2 Oxygen Donors

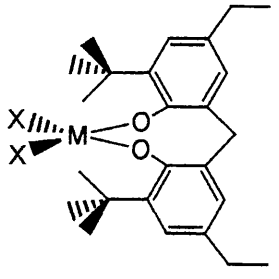
Terminal oxygen donor ligands have been used successfully in polymerisation catalysts. Schaverien et al. presented a study of chelating phenoxide complexes of titanium and zirconium as polymerisation catalysts[169] Thus, complexes **77** and **78** are only moderately active towards ethylene, but complex **79** with a methylene linker gives a higher activity (130 g $mmol^{-1}$ bar^{-1} h^{-1}). An ethylene-bridged analogue of **79** has been synthesized by Okuada et al (**80**), which has been shown to be a successful copolymerisation catalyst for ethene and styrene. ([170,171]



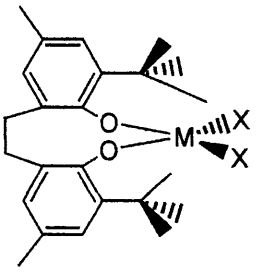
77



78

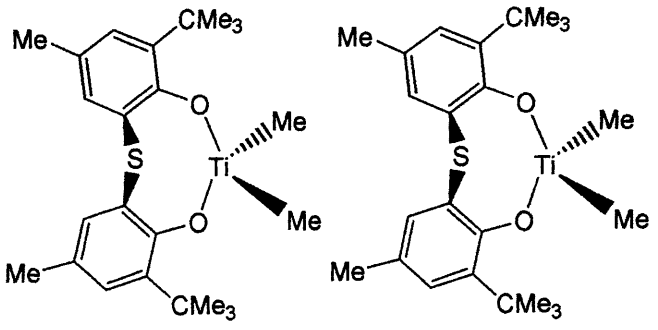


79



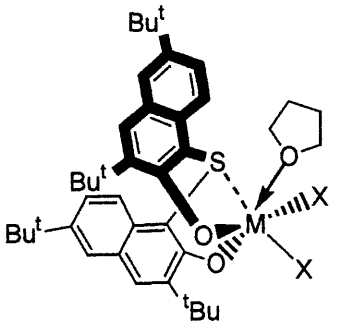
80

As observed for amide systems, group 4 alkoxides can also be combined with additional neutral donors.



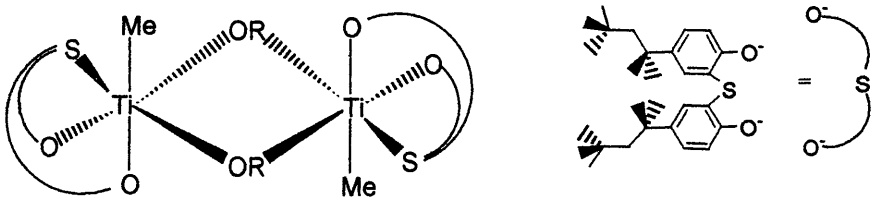
81 **81**

Thus, complex **81**, a thioether linked bis(phenolato) complex, has been reacted with the Lewis acidic activators $B(C_6F_5)_3$, $[NPhMe_2H][B(C_6F_5)_4]$ and $[Ph_3C][B(C_6F_5)_4]$. The dark red solutions so formed reproducibly polymerised ethylene, albeit in low yield.[172]



82a M=Zr X= Cl
82b M=Ti X= Cl
82c M=Zr X= Bz

Similarly complexes of type **82** [173] containing dianionic binaphtholate ligands show moderate activity towards polymerisation of ethylene, with **82b** and **82c** giving 29 and 26 g $mmol^{-1}$ bar^{-1} h^{-1} respectively. In comparison, the zirconium chloride complex **82a** shows a much lower activity (1 g $mmol^{-1}bar^{-1}h^{-1}$). Under conditions identical to those used for ethylene polymerisation, **82b** shows moderate activity for polymerisation of propylene.

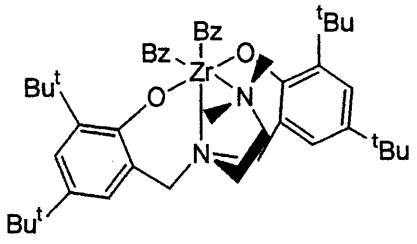


83

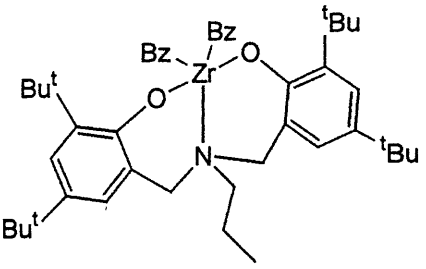
Bimetallic titanium complexes supported by bis(aryloxo) ligands have shown very high activities for the polymerisation of ethylene. Complex **83**, for example, has an activity of 204760 g $mmol^{-1}$ bar^{-1} h^{-1}, with the narrow Mw distribution observed suggesting that a single site mechanism is in operation.[174]

Amine bis(phenolate) zirconium complexes **84** and **85** have been synthesised and their hex-1-ene polymerisation activity tested with $B(C_6F_5)_3$ as an activator.[175]It was shown that the donor arm in complex **84** made it an extremely active catalyst (15500 g $mmol^{-1}$ bar^{-1} h^{-1}), in contrast to **85** which yielded oligo(hex-1-ene) chains at much lower activity (23 g $mmol^{-1}$ bar^{-1} h^{-1}). The extra donor arm is thought to lower the electrophilicity of the complex. Hence it seems that the electrophilicity of catalyst **84** does not play a major role in determining its activity. It is suggested that the extremely high activity of **84** is as a result of steric effects i.e. a narrow angle between the growing polymer chain and the coordinated olefin as well as electronic effects induced by the N-donors being *trans* to the active positions. Kol et al. have extended this work by investigating the effect of a pendant thf moiety in place of the amine in **84**. The complexes **86, 87** and **88** were synthesized and their activity towards hex-1-ene was tested.[176] The zirconium (**86**) and hafnium (**87**) complexes show very high activities for polymerization (21000 g $mmol^{-1}$ bar^{-1} h^{-1} and 4000 g $mmol^{-1}$ bar^{-1} h^{-1} respectively). Although it shows a moderate activity

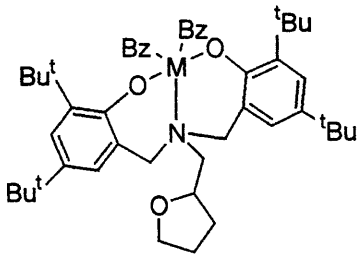
in comparison (12 g $mmol^{-1}$ bar^{-1} h^{-1}), the titanium complex **88** polymerises hex-1-ene in a living fashion. In addition the polymer produced was of the highest molecular weight ever obtained by polymerization of hex-1-ene in a living fashion.



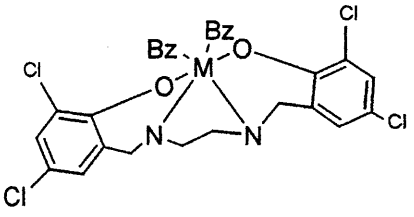
84



85



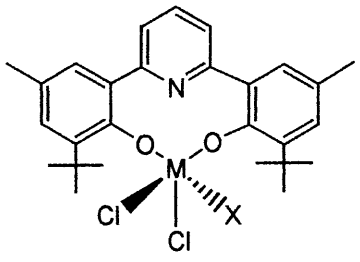
86 M=Zr
87 M=Hf
88M=Ti



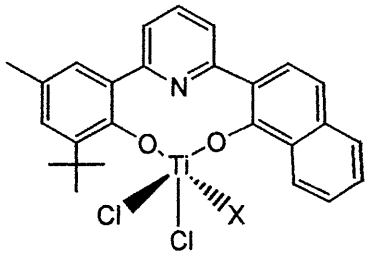
89 M=Zr
90M=Ti

A very recent publication by Kol et al. reports complexes of the type **89** and **90** into which electron withdrawing chlorine substituents have been introduced onto the phenolate rings.[177] The zirconium complex **89** is highly active (5400 g $mmol^{-1}$ bar^{-1} h^{-1}) towards the polymerisation of hex-1-ene but produces low M_w atactic polymers. However, the titanium analogue **90** is also highly active (200 g $mmol^{-1}$ bar^{-1} h^{-1}) but is

capable of producing ultra high M_w poly(1-hexene) with differing isotacticity depending on the nature of the phenolate substituents.



91a M=Zr, X=THF
91b M=Zr X=OEt_2
91c M=Ti X=THF

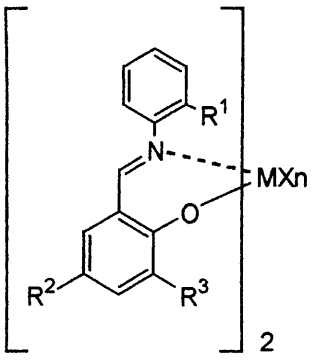


92

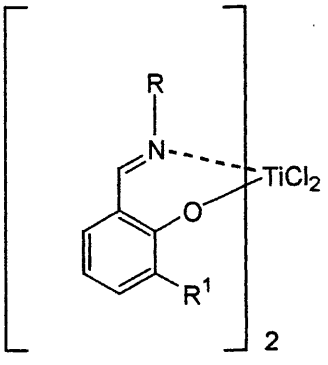
Complexes **91a–91c** and **92**[178] show similarities to Kol's bis(phenolate) complexes. **91a** shows very high activity for ethylene polymerisation (5850 g $mmol^{-1}bar^{-1}h^{-1}$), which is surprising given the presence of the coordinated THF molecule. Complex **91c** with an ethoxide ligand also shows comparable activity to **91a**. It was suggested that the chelating solvent (THF or ether) was perhaps playing a similar role to the pendant donors reported by Kol.[175] The titanium complexes **91b** and **92**, on the other hand, show only very low activities with or without the chelating solvent.

The highly active alkoxide/imine donor complex **93** has been synthesized by Mitsui Chemicals, Inc. of Tokyo.[179] The zirconium and hafnium complexes afforded high activities of 3300 g $mmol^{-1}$ bar^{-1} h^{-1} and 6500 g $mmol^{-1}$ bar^{-1} h^{-1} respectively, but the titanium counterpart exhibited a substantially higher activity of 519000 g $mmol^{-1}$ bar^{-1} h^{-1}. Further investigation into the zirconium complex showed that the nature of substituents in the R^1, R^2 and R^3 positions have major detectable effects on polymerisation activity and M_w of resulting polymer. The bulkier alkyl groups at R^1 were reported to give higher

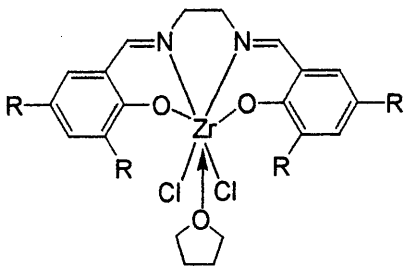
M_w polymer. Bulky alkyls at R^2 lower polymerisation activity whereas bulky alkyls at R^3 increase activity. Further work on bis(phenoxy-imine) titanium complexes has yielded a new cocatalyst system $MgCl_2/i\text{-}Bu_mAl(OR)_n$.[180] When activated with this magnesium containing cocatalyst, complexes of the type **94** have been shown to have high activities for ethylene polymerisation (20800 -36300 g $mmol^{-1}$ bar^{-1} h^{-1}). These values are comparable to or exceed that found for Cp_2TiCl_2/MAO under similar conditions. Activation of these complexes with $i\text{-}Bu_mAl(OR)_n$ or $i\text{-}Bu_3Al$ alone gave no activity proving that $MgCl_2$ does in fact have a pivotal role. Cp_2TiCl_2 activated with $MgCl_2/i\text{-}Bu_mAl(OR)_n$ gives only low activities which may be related to the fact that the N and O heteroatoms are required for electronic interaction with $MgCl_2$. Polyethylene formed by using this new activator has a narrow polydispersity, suggesting a single site Mechanism is in operation.



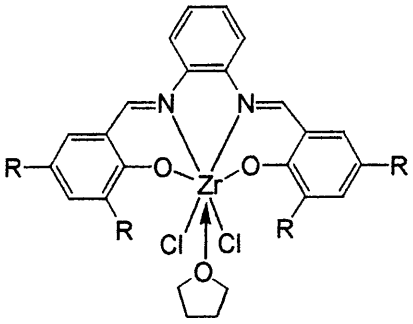
93



94
R=Ph or Cy
R^1=^{t}Bu or H

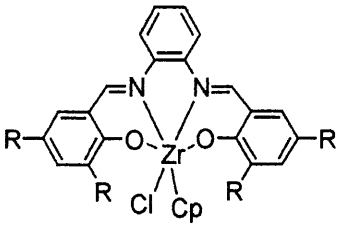


95

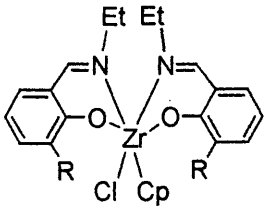


96

The salen type complexes **95** and **96** are active for the oligomerisation of ethylene.[181] The highest activities are observed for the complexes of type **95**, but in both cases the *tert*-butyl substituted species (R = ^{t}Bu) show low activity; it is thought that the bulky groups prevent the close interaction of the π electrons of the ethylene monomer and the zirconium centre. Subsequent research by Scott et al.[182] showed that the nature of the group occupying the position ortho to the oxygen atom on the phenyl ring is important for activity. This is due to the imine units of such ligands being prone to intramolecular reactions (1,2-migratory insertion with metal bound alkyls). Bulky ortho alkyls cause the metal bound alkyl in the activated species to be pushed closer to the imines making this insertion more likely.

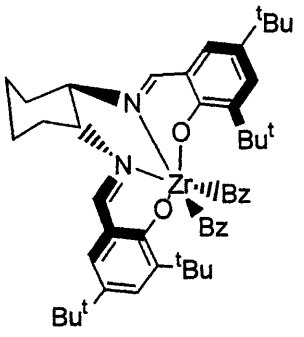


97 R=^{t}Bu

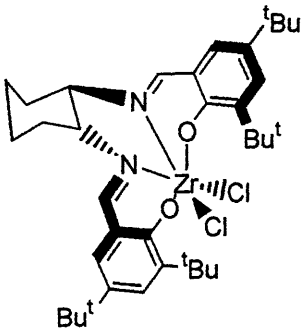


98R=^{t}Bu

Further more recent research into salen type ligands by Bochmann et al. has yielded the complexes **97** and **98.**[183] Upon activation with MAO higher activities for ethylene polymerisation are observed for **97**(462 g mmol^{-1} bar^{-1} h^{-1}) than **98** (18 g mmol^{-1} bar^{-1} h^{-1})

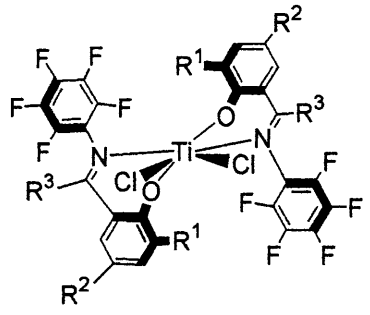


99



100

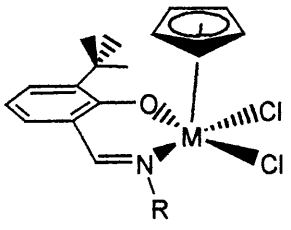
C_2 symmetric systems based on trans-1,2-cyclohexanediamine have also been reported in 2004. When complexes **99** and **100** are activated with MAO they give moderately active ethylene polymerisation systems (50-150 g mmol^{-1} bar^{-1} h^{-1}),[184] with the benzyl complex **100** being the most active.



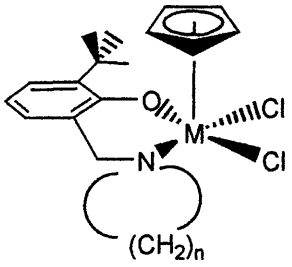
101

Recently Coates et al. have reported new phenoxyketimine titanium complexes of type **101**, which are active polymerisation catalysts capable of producing substantially isotactic polypropylene, with a narrow M_w distribution that is thought to be indicative of

living polymerisation behaviour.[185] The paper also reports that the substituents R^1-R^3 have a marked influence on activity.



102a

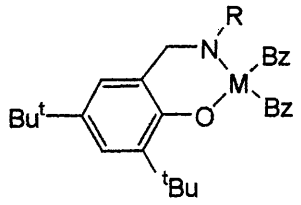


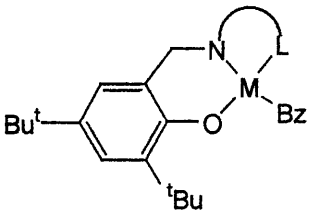
102b

Bott et al. chose to combine phenoxy-imine **102a** or phenoxy-amine **102b** ligands with a Cp ring.[186] The design theory was that by necessity complexes of this type would be chiral-at-metal and therefore have the potential for stereoselective polymerisation. For comparison the bis(phenolate) analogues of **102a** and **102b** were synthesised but in polymerisation runs these yielded no polymer. For the complexes of the type **102a**, activities for zirconium and titanium were remarkably similar. In contrast for complexes of the type **102b** the titanium complexes are about two orders of magnitude less active than their zirconium counterparts.

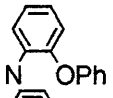
The advantage of incorporating soft donors, which are usually restricted to mid and late transition metals, into early transition metal complexes has been illustrated in a communication by Gibson et al.[187] The dianionic complexes **103a-b** were synthesized along with four analogues (**104a-d**) incorporating neutral donors. Ethylene polymerization tests revealed that **103a-b** were not particularly active catalysts (22 and 32 g $mmol^{-1}$ bar^{-1} h^{-1}, respectively). In comparison there was marked enhancement of

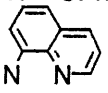
activity towards ethylene polymerization for complexes **104a-b** containing additional neutral donors (affording activities <100 g $mmol^{-1}$ bar^{-1} h^{-1}. Under the same conditions **104c** showed a greater activity (3530 g $mmol^{-1}$ bar^{-1} h^{-1}) but this was surpassed by the diphenylphosphine complex **104d** (195000 g $mmol^{-1}$ bar^{-1} h^{-1}).

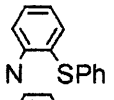


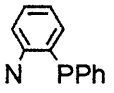


103a M=Ti, R= 2,6-$Me_2C_6H_3$
103b M=Ti, R= 2,6-$Me_2C_6H_3$

104a M=Ti, L= 

104bM=Ti, L= 

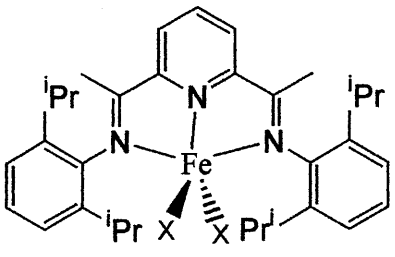
104c M=Ti, L= 

104d M=Ti, L= 

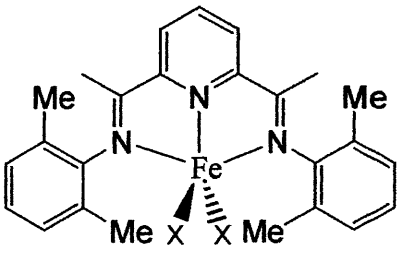
1.7.4 Late transition metals

Although early transition metal polymerization catalysts are often very active, they suffer a drawback in that they are highly oxophilic. This typically makes them air- and moisture-sensitive and renders them incompatible with monomers which are more functionalised than simple olefinic hydrocarbons. Later transition metals are less oxophilic, but most of these metal systems produce low molecular weight oligomers from ethylene and α-olefins because polymer chain termination reactions compete with polymer growth reactions. The key to producing high molecular weight polymers is using extremely bulky ligands, which greatly retard the chain termination mechanisms that predominate for late transition metal catalysts.

A number of highly reactive, non-metallocene iron(II) complexes have been reported. Complexes **105** and **106** are based on a five-coordinate iron center with a neutral tridentate 2,6-bis(imino)pyridine ligand.[188] When activated with MAO they are extremely active catalysts for the polymerization of ethylene to linear, high-density polyethylene. Activities are comparable to those reported for group 4 metallocenes under similar conditions. It is interesting to note that increasing the steric bulk of the *ortho* aryl substituents and placing substituents in both *ortho* positions increases the molecular weight of the polymer produced (complex **102**, R=^{i}Pr, M_w=7.1 x 10^4 c.f. complex **103,** R=Me, M_w=3.3 x 10^4).

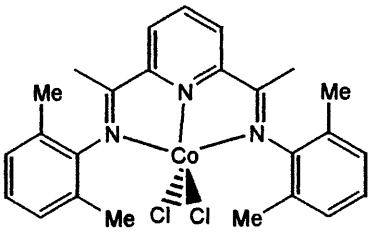


105

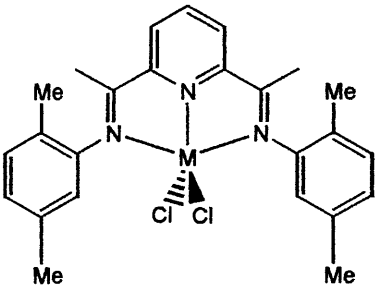


106

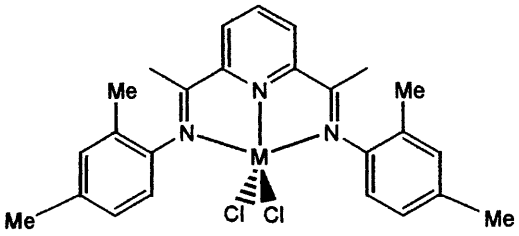
In addition to iron(II), there have been similar bis(imino)pyridine catalysts reported for Co(II). Cobalt catalysts such as **107** show the highest reported activities for group 9 systems[189] although activities are an order of magnitude lower than for analogous iron complexes. As with iron (II), the incorporation of bulky *ortho* aryl substituents has the effect of increasing the molecular weight of the resulting polymer, although in general cobalt bis(imino)pyridine complexes produce lower molecular weight polymers than their iron analogues. The polyethylene obtained is end-capped with a vinyl group, consistent with β-hydride elimination being the predominant chain termination process.[188]



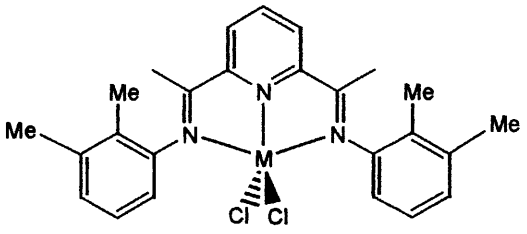
107



108a M=Co
108b M=Fe



109a M=Co
109b M=Fe

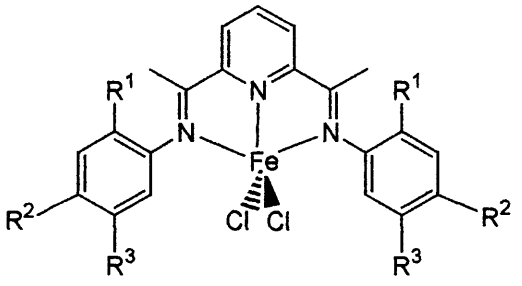


110a M=Co
110b M=Fe

The effect of substituent position on ethylene polymerization activity in cobalt and iron bis(imino)pyridine complexes has been studied extensively by Kim et al.[190] For the purposes of this study complex **106** was synthesized in addition to **107**, **108a** and **b**, **109a** and **b** and **110a** and **b**, these complexes varying in the position of the methyl groups on the phenyl rings. The study showed that the protective effect of the *ortho* substituents of the phenyl rings, above and below the active centre, was critical to the molecular weight of resulting polymers. Only complexes **106** and **107** yielded high M_w polymers, with iron giving higher molecular weights than cobalt.

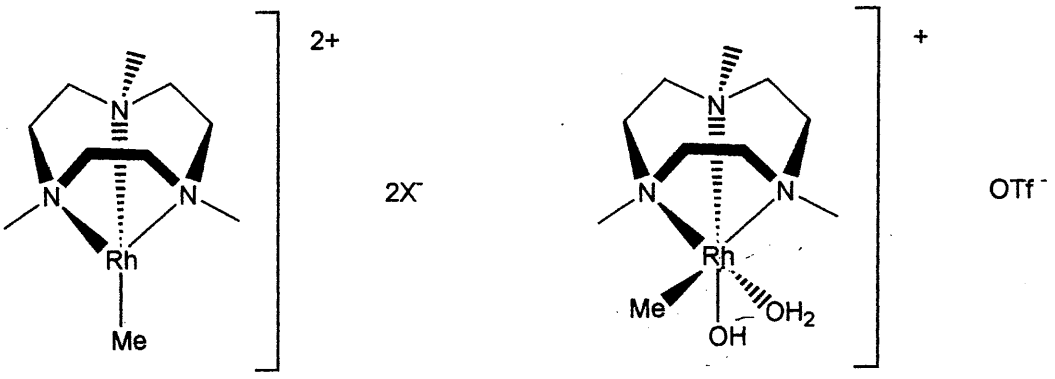
Zhang et al have synthesized a series of compounds (**111**) with a halogen atom in the ortho position.[191] Earlier work has shown that halogen substituents and the positive charge of the metal center are important factors which greatly influence the activity of complexes.[192,193] The introduction of bromine in the para position of the aryl rings has

also been reported to improve catalytic activity.[194] The halogen atoms in combination with the bulky alkyl groups reported by Gibson were employed in complexes of the type **111**. The complex with R^1=Cl and R^2 or R^3 = CH_3 show the highest activity towards ethylene oligomerisation.



111

Complex **112**, a dicationic rhodium(II) complex supported by a hard triazacyclononane triamine donor, is an active ethylene polymerisation catalyst which is capable of polymerisation of ethylene in water.[195,196] The active species is believed to be formed by dissociation of H_2O from complex **113**; the turnover is low and the catalyst is sensitive to pH.

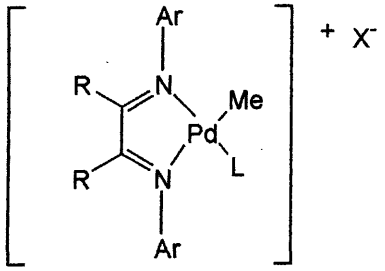


112 **113**

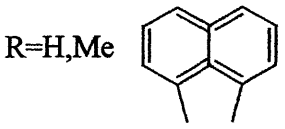
Complexes **114** and **115** incorporate an aryl-substituted α-diimine ligand framework and, as with the analogous iron complexes, bulkier substituents on the aryl rings are found to lead to higher molecular weights for the resulting polymer. Palladium complex **114** polymerizes ethylene, propylene and 1-hexene; a dibromide derivative of α-diimine complex **114** when treated with MAO shows very high polymerization activity (11000 g $mmol^{-1}$ bar^{-1} h^{-1}).[197] Similarly nickel complexes **115** also catalyse the polymerization of ethylene and α-olefins; the dibromide precursor when activated with MAO shows an activity comparable to metallocenes.[197,198] By varying reaction conditions it was found that an increase in temperature caused an increase in the branching of the polymer; conversely increasing pressure reduced branching. In addition, changing the steric bulk of the aryl groups, (e.g. swapping *ortho* methyl for *ortho* isopropyl groups) resulted in a less branched polymer of decreased molecular weight. These systems were the first reported catalysts where simple variation of temperature, pressure and ligand substituents allowed access to an ethylene polymer whose structure varied from a highly branched, completely amorphous material to a linear, semi crystalline, high density material. In a later

publication Brookhart reported the aforementioned palladium α-diimine complexes to be the first transition metal complexes capable of the copolymerisation of ethylene or propylene with functionalised vinyl monomers, early transition metal systems have previously been shown to be too oxophilic to polymerize functionalised vinyl polymers.[199] Thus complexes **116** and **117** on exposure to ethylene or propylene in the presence of methyl acrylate catalyse the formation of high molar mass random copolymers.

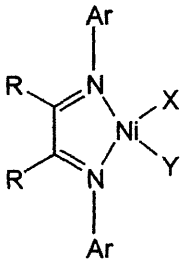
There are also reports of nickel oligomerisation catalysts bearing mixed P,O donor chelate ligands. The earliest of these systems to be investigated was a nickel ylide system introduced by Keim and et al.[200] Recently, papers published from the Gibson group report nickel complexes of type **118** featuring mixed P,O donors.[201] As with the nickel α-diimine complexes, introduction of bulky substituents (especially at the site adjacent to the oxygen donor) dramatically enhances polymerisation activity. Catalysts of this type are also capable of the polymerisation of polar monomers such as methyl methacrylate with activities in the range 80 –418 g $mmol^{-1}$ h^{-1} with narrow molecular weight distributions.[202]



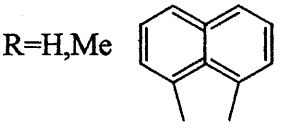
114



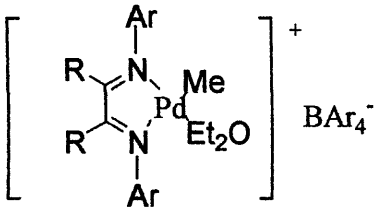
X=B[3,5-$(CF_3)_2C_6H_3]_4$, SbF_6
L=Et_2O, MeCN



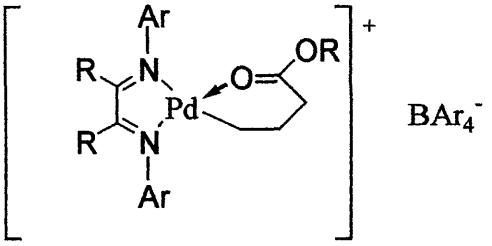
115



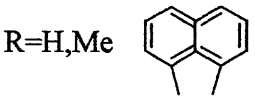
X=Y=Br
X=B[3,5-$(CF_3)_2C_6H_3]_4$.Et_2O, Y=Me
Ar=2,6-$iPrC_6H_3$, 2,6-$Me_2C_6H_3$, 2-$tBuC_6H_4$



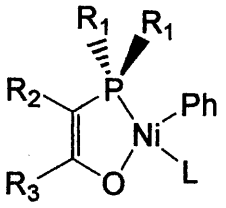
116



117

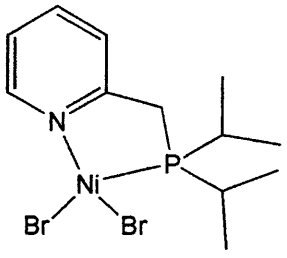


Ar=2,6-$iPrC_6H_3$, 2,6-$Me_2C_6H_3$, 2-$tBuC_6H_4$

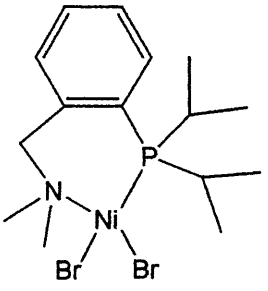


118

Bluhm et al. have investigated new nitrogen and phosphorus donor nickel(II) complexes for ethylene oligomerisation.[203] Thus complex **119** produces predominantly butanes and hexenes but has low selectivity, whereas **120** is less active but shows better selectivity.

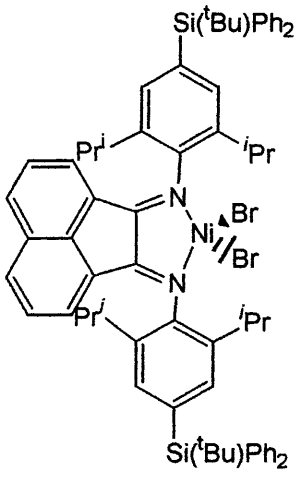


119

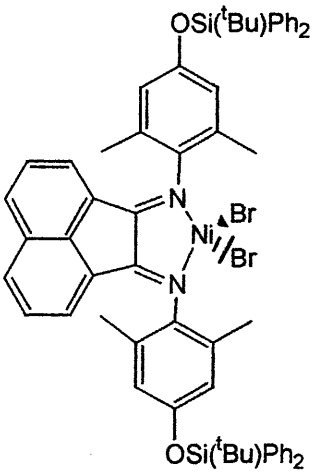


120

More recently, a silyated α-diimine has been synthesized and coordinated to nickel (complex **121**).[204] The activity of **121** towards ethylene and propylene polymerization has been determined, and activities are found to be comparable with those of α-diimine complexes published previously. A similar complex (**122**) has been shown to be active for the living polymerisation of hex-1-ene and propylene and can be considered as one of the most active Brookhart type catalysts yet reported.[205]

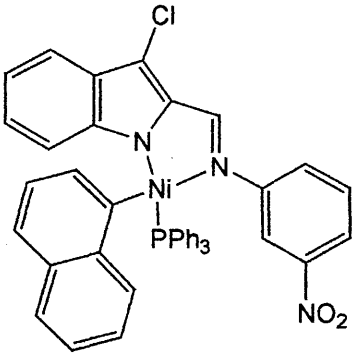


121



122

In related work a 2-imino-indole complex of nickel (**123**) has been synthesized and shows activity of 20 g $mmol^{-1}$ bar^{-1} h^{-1} towards the oligomerisation of ethylene without the need for an activator/cocatalyst.[206]



123

1.8 Aims of Current Research

At the outset the aims of the research reported in this thesis were threefold:

(a) Given that current research in the area of polymerisation catalysis has been aimed towards alternatives to metallocene primary ligand systems, it was decided to investigate the synthesis of new non-metallocene primary ligand frameworks. The emphasis was on simplicity, both in ligand design and synthetic strategies, in order to make the research more appealing to the industries whom this research might ultimately benefit. Research has been confined to the synthesis of ligands containing amine and alcohol functionalities in order to give access to a range of complexes containing alkoxide, amide, amine and imine functionalities. Previous research has shown that these primary ligand systems can give rise to highly effective olefin polymerization catalysts.

(b) Synthesis of metal complexes of the ligands produced. Although the focus of the research reported here is on group 4 metals, it has not been restricted to these. Complexation with metals from most d-block groups has been attempted, since it has been frequently reported in the recent literature that transition metals other than those from group 4 give highly active polymerisation catalysts.

(c) Preliminary investigation into the catalytic activity of the complexes synthesized was to be attempted in order to build a picture of how the steric and electronic features of

these new primary ligand frameworks affect polymer molecular weight and catalyst activity. Comparison of the activities of complexes synthesized during this research with data for previously published catalysts was also to be attempted.

References

1. M. Bochmann, *J.Chem.Soc., Dalton Trans.*, 1996, 225-270

2. Encyclopedia of polymer science and engineering 2nd Edition, Wiley-interscience, Editors H. F. Marks, N. M. Bikales, C.G. Overberger, G. Menges, J. I. Kroschwitz

3. J. P. Coleman, L. S. Hegedus, J. R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Sausalito California USA, 1987, 355-428

4. G. Wilkinson, *J. Am. Chem. Soc.*, 1953, **75,** 1011

5. G. Natta, P. Pino, G. Mazzanti, U. Giannini, *J. Am. Chem. Soc.*, 1957, **79**, 2975

6. D.S. Breslow, N. R. Newburg, *J. Am. Chem. Soc.*, 1957, **79**, 5072

7. H. Sinn, W. Kaminsky, H. J. Vollmer, R. Woldt, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 390

8. H. Sinn, W. Kaminsky, *Adv. Organometallic Chem.*, 1980, **18**, 99

9. M. R. Mason, J. M. Smith, A. R. Barron, *J. Am. Chem. Soc.*, 1993, **115**, 4971

10. Ulezmann, *J. Polymer Sci.*, 1958, **32**, 457

11. Patat, H. Sinn, *Angew. Chem., Int. Ed. Engl.*, 1958, **70**, 496

12. Cossee, *Tetrahedron Lett.*, 1960, **17**, 12-16

13. M. L. H. Green, *Pure Appl. Chem.*, 1978, **50**, 27-35

14. K. J. Ivin, J. J. Rooney, C. D. Stewart, M. L. H. Green, R .J. Mahtab, *J. Chem. Soc., Chem.Comm.* 1978, 604-606

15. Z. Dawoodi, M. L. H. Green, V. S. B. Mteetwa, K. Prout, *J. Chem. Soc., Chem. Comm.*, 1982, 1410-1411

16. D. T. Laverty, J. J. Rooney, *J.Chem. Soc., Faraday Trans. 1*, 1983, **79**, 869-878

17. M. Brookhart, M. L. H. Green, *J.Organometallic Chem.*, 1983, **250**, 395-408

18. M. Brookhart, M. L. H. Green, L. L. Wong, *Prog. Inorg. Chem.*, 1988, **36**, 1-124

19. R. H. Grubbs, G. W. Coates, *Acc. Chem. Res.*, 1996, **29**, 85-93

20. M. H. Prosenc, C. Janaik, H. H. Brintzinger, *Organometallics,* 1991, **11**, 4036-4041

21. I. -M. Lee, W.J. Galithier, J. M. Ball, B. Iyengar, S. Collins, *Organometallics,* 1992, **11**, 2115-2122

22. B. J. Burger, W. D. Cotter, E. B. Coughlin, S. T. Chacon, S. Hajela, T. A. Herzog, R. Kohn, J. Mitchell, W. E. Piers, P. J. Shapiro, J. E. Bercaw in Ziegler catalysts G. Fink, R. Mullhaupt, H. H. Brintzinger Eds.;Springer-Verlag:berlin 1995;pp317-331

23. Z. Yu, J.C.W. Chien, J. *Polymer Sci., part A*, 1995, **33**, 125-135

24. L. Clawson, J. Soto, S. L. Buchwald, M. L. Steigerwald, R. H. Grubbs, *J. Am. Chem. Soc.,* 1985, **107**, 3377-3378

25. M. B. Brookhart, M. L. H. Green, *J. Organometallic Chem.,* 1983, **250**, 395-408

26. B. J. Burger, M. E. Thompson, W. D. Cotter, J. E. Bercaw *J. Am. Chem. Soc.,* 1990, **112**, 1566

27. P. L. Watson, D. C. Roe, *J. Am. Chem. Soc.,* 1982, **104**, 6471

28. R. F. Jordan, *Adv. Organometallic Chem.,* 1991,**32**,325

29. A. L. Mogstad, R. M. Waymouth, *Macromolecules,* 1992, **25**, 2282

30. A. Zambelli, P. Locatell, G. Bajo, F. A. Bovey, *Macromolecules,* 1975, **8**, 687

31. P. Pino, R. Mullhaupt, *Angew. Chem., Int. Ed. Engl.,* 1980, **19**,857

32. W. Kaminsky, Handbook of Polymer Synthesis, Ed; Kricheldorf & Dekker, New York 1991, Vol 1, Page 1

33. J. A. Ewen, *J. Am. Chem. Soc.,* 1984, **106**, 6355

34. F. R.W. P. Wild, L. Z. Solnai, G. Hutter, H. H. Brintzinger, *J. Organometallic Chem.,* 1982, **232**, 233

35. K. Kulper, H. H. Brintzinger, F.R.W. P. Wild, *Angew., Chem. Int. Ed. Engl.,* 1985, **24**, 507

36. P. Corradini, G. Guerra, *Prog. Polymer Sci.,* 1991, **16**, 239

37. M. H. Prosenc, C. Janiak, H. H. Brintzinger, *Organometallics*, 1992, **11**, 4036-4041

38. W. Roll, H. H. Brintzinger, B. Reiger, R. Zolk, *Angew. Chem., Int. Ed. Engl.,* 1990, **29**, 279-280

39. G. Natta, I. Pasquon, A. Zambelli, *J. Am. Chem. Soc.*, 1962, **84**, 1488

40. J. A. Ewen, R. L. Jones, A. Razavi, J. D. Ferrara *J. Am. Chem. Soc.*, 1988, **110**, 6255

41. E. J. Thomas, M. D. Rausch, J. C. W. Chein, *Organometallics,* 2000, **19**,4077- 4083

42. L. Cavallo, G. Guerra, M. Vacatello, P. Corradini, *Macromolecules,* 1991, **24**, 1784-1790

43. V. C. Gibson, G. J. P. Britovsek, D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**, 428-447

44. E. Y. Chen, T. J. Marks, *Chem. Rev.*, 2000, **1000,** 1391-1434

45. D. Fischer, R. Mullhaupt, *J. Organometallic Chem.*, 1991, **417**,C7

46. R. Taube, L. Krukowka , *J. Organometallic Chem.*, 1988, **347**, C9

47. M. Bochmann, L. M. Wilson, *J. Chem. Soc., Chem. Commun.*, 1986, 1610

48. H. W. Turner (Exxon) Eur. Pat. 0 277 004 (1988), *Chem. Abs.*, 1989, **110**, 58, 290 a

49. X. Yang, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.*, 1991, **113**, 3623

50. J. W. C. Chein, W. M. Tsai, M. D. Rausch, *J. Am. Chem. Soc.*, 1991, **113**, 8570.

51. D.A. Straus, C. Zhang, T. D. Tilley, *J. Organometallic Chem.*, 1989, **369**, C13

52. J.A. Ewen, M J. Elder (Fina) Eur. Pat. 0 426 637 (1991) *Chem. Abstracts,* 1992 **115**

136 988 d

53. L. W. M Lee, W. E. Piers, M. Parvez, S. J. Rettig, V. G. Young, *Organometallics,* 1999, **18,** 3904-3912

54. W. E. Piers, Y. M. Sun L.W. M. Lee, *Topics in Catalysis*, 1999, **7**, 133-143

55. A.L. McKnight, R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587-2598

56. H. H. Brintzinger, D. Fischer, R. Mullhaupt, B. Reiger, R. M. Waymouth, *Angew. Chem., Int Ed. Engl.*, 1995, **34**, 1143-1170

57. G. W. Coates, *Chem. Rev.*, 2000, **100**, 1223-1252

58. W. Kaminsky, *Advances in catalysis,* **46**, 2001, 89-159

59. V. C. Gibson, S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283-315

60. J. Gromada, J. F. Carpentier, A. Mortreux, *Coordination Chem. Rev.*, **248**, 2004, 397-410

61. P. J. Shapiro, W. D. Cotter, W. P. Schaefer, J. A. Labinger, J. E. Bercaw, *J. Am. Chem. Soc.*, 1994, **116**, 4623-4640.

62. P. J. Shapiro, E. E. Bunel W. P. Schaefer, J. E. Bercaw, *Organometallics*, 1990, **9**, 867-869

63. S. Hajela, J. E. Bercaw, *Organometallics*, 1994, **13**, 1147-1154.

64. W. E. Piers, P. J. Shapiro, E. E. Bunel, J. E. Bercaw, *SynLett*, 1990, 74-84

65. D. G. H. Ballard, A. Courtis, J. Holton, J. McMeeking, R. Pearce, *J. Chem. Soc., Chem. Commun.*, 1978, 994-995

66. J. P. Mitchell, S. Hajela, S. K. Brookhart, K. I. Hardcastle, L. M. Henling, J. E. Bercaw, *J. Am. Chem. Soc.*, 1996, **118**, 1045-1053.

67. E. B. Coughlin, J. E. Bercaw *J. Am. Chem. Soc.*, 1992, **114**,7606-7607.

68. H. Yasuda, E. Ihara, *Tetrahedron*, 1995,**51**,4563-4570.

69. H. Yasuda, E. Ihara, M. Morimoto, M. Nodono, S. Yoshioka, M. Furo, *Macromol. Symp.*,1995, **95**, 203-216

70. A. N. Yabov, V. V. Izmer, A. A. Borisenko, J. A. M. Canich, L. G. Kuzmina, J. A. K. Howard, A. Z. Voskoboynikov, *J. Chem. Soc., Dalton Trans*, 2002, 2995-3000

71. V. Tabernero, T. Cuenca, E. Herdtweck *J. Organometallic Chem.*, **663**, 2002, 173-182

72. J. A. Ewen, M. J. Elder, R. L. Jones, L. Haspeslagh, J. L. Attwood, S. G. Bott, K. Robinson, *Makromol. Chem. Macromol. Symp.*, 1991, **48/49**, 253

73. W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, *Makromol. Chem.*, 1992, **193**, 1643

74. W. A. Herrmann, J. Rohrmann, E. Herdtweek, W. Spaleck, A. Winter, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**,1511

75. W. Roll, L. Zsolnai, G. Huttner, H. H. Brintzinger, *J. Organometallic Chem.*, 1987, **322**, 65

76. J. A. Vol, M. L. H. Green, I. M. Gardiner, K. Prout, *J. Chem. Soc., Dalton trans.*, 1991, 2207

77. M. E. Huttenloch, J. Diebold, U. Rief, H. H. Brintzinger, A. M. Gilbert, T. J. Katz, *Organometallics*, 1992, **11**, 3600

78. W. Mengele, J. Diebild, C. Troll, W. Roll, H. H. Brintzinger, *Organometallics*, 1993,**12**,1931

79. K. Hortmann, H. H. Brintzinger, *New J. Chem.*, 1992, **16**, 51

80. P. Burger, K. Hortmann, H. H. Brintzinger, *Makromol. Chem. Macromol Symp.*, 1993, **66**, 127

81. A. J. Ashe, X. Fang, A. Hokky, J. W. Kampf, *Organometallics*, **23**, 2004, 2197-2200

82. M. Bochmann., S. J. Lancaster, *Organometallics*, 1993, **13**, 633-640

83. J. C. Flores, J. C. W. Chein, M. D. Rausch, *Organometallics*, 1994, **13**, 4140-4142

84. S. J. Skoog, C. Mateo, G. G. Lavoie, F. J. Hollander, R. G. Bergman, *Organometallics*, 2000, **19**, 1406-1421

85. J. C. W. Chien, Z. T. Yu, M. M. Marques, J. C. Flores, M. D. Rausch, *J. Polym Sci. Polym. Chem.*, 1998, **36**, 319-328

86. M. S. Blais, J. C. W. Chien, M. D. Rausch, *Organometallics*, 1998, **17**, 3775-3783

87. J. Sassmannshausen, A. K. Powell, C. E. Anson, S. Wocaldo, M. Bochmann, *J. Organometallic Chem.*, 1999, **592**, 84-94

88. P. J. W. Deckers, B. Hessen, J. H. Teuben , *Angew. Chem. Int. Ed.*, 2001, **40**, 2516-2519

89. K. Nomura, K. Fujii, *Organometallics*, 2002, **21**, 3042-3049

90. K. Nomura, K. Fujii, *Macromolecules*, 36, **8**, 2003

91. V. Tabernero, T. Cuenca, E. Herdtweck, *Eur. J. Inorg. Chem.*, 2004, 3154-3163

92. A. R. Dias, T. Duarte, A. C. Fernandes, S. Fernandes, M.M. Marques, A.M. Martins, J. F. da Silva, S.S. Rodrigues, *J. Organometallic Chem.*, **689**, 2004, 203-213

93. A. M. Martins, M. M. Marques, J. A. Ascenso, A. R. Dias, M. T. Duarte, A. C. Fernades, S. Fernandes, M. J. Ferreira, I. Matos, M. C. Oliveira, S. S. Rodrigues, C. Wilson, *J. Organometallic Chem.*, **690**, 2005, 874-884

94. W. P. Kretschmer, C. Dijkhuis, A. Meetsma, B. Hessen, J. H. Teuben, *Chem. Commun.* 2002, 608-609

95. K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, *Organometallics*, 1998, **17**, 2152

96. K. Nomura, N. Naga, M. Miki, *Macromolecules*, 1998, **31**, 7588

97. K. Nomura, K. Oya, T.Komatsu, Y. Imanishi, *Macromolecules*, 2000, **33**, 3187

98. K. Nomura, K. Oya, Y. Imanishi, *J. Mol. Catal A*, 2001, **174**, 127

99. M. G. Maupoey, T. Cuenca, *Organometallics*, 2003, **22**, 2694-2704

100. M. K. Mahanthappa, A. P.Cole, R.M. Waymouth, *Organometallics*, 2004, **23**, 836-845

101. J. M. Tanski, G. Parkin, *Organometallics*, 2002, **21**, 587-589

102. A. Eisenhardt, W. Kaminsky, *Catalysis Communications*, **5**, 2004, 653-657

103. H. G. Alt, A. Reb, W. Milius, A. Weis, *J. Organometallic Chemistry*, **628**, 2001, 169-182

104. H. G. Alt, A. Reb, K. Kundu, *J. Organometallic Chemistry*, **628**, 2001, 211-221

105. A. L. Mcknight, R. M. Waymouth, *Chem. Rev.*, 1998, **98**, 2587-2598

106. P. J. Sinnema, L. van der Veen, A. L. Spek, N. Veldman, J. H .Teuben, *Organometallics*, 1997, **16**, 4245-4247.

107. P.T. Gomes, M.L.H. Green, A. M. Martins, P. Mountford, *J. Organometallic Chem.*, 1997, **541**, 121-125

108. L. Duda, G. Erker, R. Frolich, F. Zippel, *Eur. J. Org. Chem.*, 1998, **551**, 133-138

109. V. V. Kotov, E. V. Avtomonov, J. Sundermeyer, K. Harms, D. A. Lemenovskii, *Eur. J. Inorg. Chem.*, 2002, 678-691

110.J. Klosin, W. J. Kruper, P. N. Nickias, G. R. Roof, P. De Waele, K. A. Abboud, *Organometallics*, 2001, **20**, 2663-2665

111. S. G. Feng, J. Klosin, W. J. Kruper, M. H. McAdon, D. R. Neithamer, P. N. Nicklas, J. T. Patton, D. R. Wilson, K. A. Abboud, C. J. Stern, *Organometallics*, 1999, **18**, 1159-1167.

112. D. R. Wilson, D. R. Neithamer, P. N. Nickias, W. J. Kruper Jr., (Dow Chemical Co. USA).PCT Int. Appl. WO9608498, 1996, *Chem. Abstr.*, 1996, **125**, 34355

113. A. J. Ashe, X. G. Fang, J. W. Kampf, *Organometallics*, 1999, **18**, 1363-1365

114. S. J. Brown, X. L. Gao, D. G. Harrison, L. Koch, R. E. V. Spence, G. P. A. Yap, *Organometallics*, 1998, **17**, 5445-5447

115. J. Jin, D. R. Wilson, E. Y. -X. Chen, *Chem. Commun.*, 2002, 708-709

116. G. Natta, G. Mazzanti , *Tetrahedron*, 1960, **8**, 86

117. E. E .C. Gielens, J .Y. Tiesnitsch , B. Hessen , J .H. Teuben, *Organometallics* , 1998, **17**, 1652-1654

118. B. Rieger, *J. Organometallic Chem.*, 1991, **420** C17-C20

119. Y .X. Chen, P. F. Fu, C. L. Stern, T. J. Marks, *Organometallics*, 1997, **16**, 5958-5963

120. G. Altenhof, S. Bredeau, G. Erker, G. Kehr, O. Kataeva, R. Frohlich, *Organometallics*, 2002, **21**, 4084-4089

121. G. C. Bazan, S .J. Donnelly, G. Rodrigeuz, *J. Am. Chem. Soc.*, 1995, **117**, 2671-2672

122. M. P. Coles, V. C. Gibson, *Polym. Bull.*, 1994, **33**, 529-533

123. D. M. Antonelli, A. Leins, J. M. Styker, *Organometallics*, 1997, **16**, 2500-2502

124. K. Mashima, S. Fujikawa, H. Urata, E. Tanaka, A. Nakamura, *J. Chem. Soc., Chem. Commun.*, 1994, 1623

125. K. Mashima, S. Fujikawa, Y. Tanaka, H. Urata, T. Oshiki, E. Tanaka, A. Nakamura, *Organometallics*, 1995, **14**, 2633-2640

126. K. Mashima, Y. Tanaka, M. Kaidzu, A. Nakamura, *Organometallics*, 1996, **15**, 2431-2433

127. Y. Liang, G. P. A. Yap, A. L. Rheingold, K. H. Theopold, *Organometallics*, 1996, **15**, 5284-5286

128. S. A. A. Shah, H. Dorn, A. Voight, H. W. Roesky, E. Parisini, H. -G. Schmidt, M. Noltemeyer, *Organometallics*, 1996, **15**, 3176-3181

129. J. A. M. Canich, H. W. Turner, (Exxon), WO-A 92/12162, 1992, *Chem. Abstracts*. 1993, **118**, 81615j

130. V. C. Gibson, B. S. Kimberely, A. J. P. White, D. J. Williams, P. Howard *Chem.Commun.*, 1998, 313-314

131. J. D. Scollard, D. H. McConville, J. *Am. Chem. Soc.*, 1996, **118**, 10008-10009

132. J. D. Scollard, D. H. McConville, S. J. Rettig, *Organometallics*, 1997, **16**, 1810-1812

133. J. D. Scollard, D. H. McConville, J. J. Vittal, *Organometallics*, 1997, **156**,4415-4420

134. H. Warren, R. R. Schrock, W. M. Davis, *Organometallics*, 1996, **15**, no2, 562-569

135. S. Tinkler, R. J. Deeth, D. J. Duncalf, A. McCamley, *Chem. Commun.*, 1996, 2623-2624

136. F. Jager, H. W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H .-G. Schmidt, *Chem. Berichte*, 1999, **130**, 399-403

137. J. D. Scollard, D. H. McConville, J. J. Vittal, N. C. J. Payne, *J. Mol. Catal.,A: Chem.*, 1998, **128**, 201-214

138. C. H. Ahn, M. Tahara, T. Uozumi, J. Jin, S. Tsubaki, T. Sano, K. Soga, *Macromol. Rapid Commun.* 2000, **21**, 385-389

139. T. Uozumi, S. Tsubaki, J. Z. Jin, T. Sano, K. Soga, *Macromol. Chem. Phys.*, 2001, **202**, 3279-3283

140. S. Tsubaki, J. Jin, C. H. Ahn, T. Sano, T. Uozumi, K. Soga, *Macrolmol. Chem. Phys.* 2001, **202**, 482-487

141. J. T. Patton, M. M. Bokota, K. A. Abboud, *Organometallics*, 2002, **21**, 2145-2148

142. N. A. H. Male, M. Thornton-Pett, M. Bochmann, *J.Chem.Soc, Dalton Trans*, 1997, 2487-2494

143. Y. M. Jeon, J. Heo, W. M. Lee, T. H. Chang, K. Kim, *Organometallics*, 1999, **18**, 4107-4113

144. R. M. Gauvin, C. Lorber, R. Choukroun, B. Donnadieu, J. Kress, *Eur. J. Inorg. Chem.*, 2001, 2337-2346

145. S. Daniele, P. B. Hitchcock, M. P. Lappert, P. G. Merle, *J. Chem. Soc., Dalton Trans.*, 2001, 13-19

146. F. G .N. Cloke, T. J .Geldbach , P. B. Hitchcock, J. B. Love, *J. Organometallic Chem.*, 1996, **506**, 343-345

147. K. Nomura, N. Naga, K. Takaoki, *Macromolecules*, 1998, **31**, 8009-8015

148. C. H. Lee, Y. H. La, S. J. Park, J. W. Park, *Organometallics*, 1998, **17**, 3643-3655

149. A .D. Horton, J. de With, A .J. van der Linden, H .van de Weg, *Organometallics*, 1996, **15**, 2672-2674

150. R. Baumann, W. M. Davis, R. R. Schrock, *J. Am. Chem. Soc.*, 1997, **119**, 3830-3831

151. F. Guerin, D .H. McConville, J .J. Vittal, *Organometallics*, 1996, **15**, 5586-5590

152. M. Bochmann, *J.Chem.Soc, Dalton Trans.*, 1997, 2487-2494

153. P. Mehrkhodavandi, R. R. Schrock, L. L. Pryor, *Organometallics*, 2003, **22** 4569-4583

154. M. Herberhold, *Angew. Chem., Int. Ed.*, 2002, **41**, 6, 956-958

155. A. Shafir, M. P. Power, G. D. Whitener, J. Arnold, *Organometallics*, 2001, **20** 1365-1369

156. A. Shafir, J. Arnold, *J. Am. Chem. Soc.*, 2001, **123**, 9212-9213

157. A. Shafir, J. Arnold, *Inorganica Chimica Acta*, **345**, 2003, 216-220

158. M. Kettuenen, C. Vedder, F. Schaper, M. Leskela, I. Mutikainen, H. H. Brintzinger, *Organometallics*, 2004, **23**, 3890-3807

159. M. P. Coles, P. B.Hitchcock, *Organometallics*, **22**, 2003, 5201-5211

160. E. Shaviv, M. Botoshansky, M. S. Eisen, *J. Organometallic Chem.*, **683**, 2003, 165-180

161. D.A. Straus, M. Kamigaito, A.P. Coles, R. M. Waymouth, *Inorganica Chimica Acta*, ***349***, 2003, 65-68

162. J.E. Kickham, F. Guerin, D.W. Stephan, *J Am. Chem, Soc.*, 2002, **124**, 11486-11494

163. D. W. Stephan, J. C. Stewart, F. Guerin, S. Courtney, J. Kickham, E. Hollink, C. Beddie, A. Hoskin, T. Graham, P. Wei, R.E.V. Spence, XW. Xu, L. Koch, X.Gao, D. G. Harrison, *Organometallics*, 2003, **22,** 1937-1947

164. E. Hollink, J. C. Stewart, P. Wei, D. W. Stephan, *Dalton Trans.*, 2003, 3968-3974

165. E. Hollink, P. Wei, D. W. Shapiro, *Organometallics,* 2004, **23**, 1562-1569

166. K. Michiue, R. F. Jordan, *Macromolecule,s* 2003, **36**, 9707-9709

167. P. T. Matsunaga, R.S. Schiffino, PCT Int. Appl. WO 9929739 1999

168. K. Michiue, R. F. Jordan, *Organometallics*, 2004, **23,** 460-470

169. A. van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G .Orpen , *J. Am. Chem. Soc.*, 1995, **117**, 3008-3021

170. S. Fokken, T. P. Spaniol, J. Okuda, F. G. Sernetz, R. Mullhaupt, *Organometallics,* 1997, **16**, 4240-4242.

171. F. G. Sernetz, R. Mullhaupt, S. Fokken, J. Okuda, *Macromol.*,1997, **30**, 1562-1569

172. S. Fokken, F. Reichwald, T. P. Spaniol, J. Okuda, *J. Organometallic Chem.*, **663** 2002, 158-163

173. L. S. Natrajan, C. Wilson, J. Okuda, P. L. Arnold, *Eur. J. Inorg. Chem.*, 2004, 3724-3732

174. Z. Janas, L. B. Jerzykiewiez, K. Przybylak, P. Sobota, K. Szezegot *Eur. J. Inorg. Chem.*, 2004 1639-1645

175. E. Y. Tshuva, I. Goldberg, M. Kol, Z. Goldschmidt, *Inorg. Chem. Commun.*, **3**, 2000, 611-614

176. S. Groysman, I. Goldberg, M. Kol, E. Genizi, Z. Goldschmidt, *Inorganica Chimica Acta*, **345**, 2003, 137-144

177. S. Sengal, I. Goldberg, M. Kol, *Organometallics,* 2005, **24,** 200-202

178. M. C. W. Chan, K. H. Tam, Y. L. Pui, N. Zhu, *J. Chem. Soc. Dalton Trans.*, 2002, 3085-3087

179. S. Matsui, T. Fujita, *Catalysis Today,* **66,** 2001, 63-73. Mitsui Chemicals, inc. Tokyo EP 0874 005 A1

180. Y. Nakayama, H. Bando, Y. Sonobe, H. Kaneko, N. Kashiwa, T. Fujita, *J. Catal.*, **215**, 2003, 171-175

181. M. Wang, H. Zhu, K. Jin, D. Dai, L. Sun, *J. Catal.* **220**, 2001, 392-398

182. P. D. Knight, A. J. Clarke, B. S. Kimberely, R. A. Jackson, P. Scott, *Chem. Commun.*, 2002, 352-353

183. M. Sanz, T. Cuenca, M. Galakhov, A. Grassi, R. K. J. Bott, D. L. Hughes, S. J. Lancaster, M. Bochmann, *Organometallics*, 2004, **23**, 5324-5331

184. C. Cuomo, M. Strianese, T. Cuenca, M. Sanz, A Grassi, *Macromolecules*, 2004, **37**, 7469-7476

185. A. F. Mason, G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 16326-16327

186. R. K. J. Bott, D. L. Hughes, M. Schormann, M. Bochmann, S. J. Lancaster, *J. Organometallic Chemistry*, **665**, 2003, 135-149

187. D. C. H. Oakes, B. S. Kimberley, V. C. Gibson, D. J. Jones, A. J. P. White, D. J. Williams, *Chem. Commun.*, 2004, 2174-2175

188. B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**,4049-4050

189. G. J .P. Britovsek, V. C. Gibson, B. S. Kimberely, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.*, 1998, 849-850.

190. I. Kim, B. H. Han, Y. S. Ha, C. S. Ha, D. W. Park, *Catalysis Today*, **93-95**, 2004, 281-285

191. Z. Zhang, S. Chen, X. Zhang, H. Li, Y. Ke, Y. Lu, Y. Hu J. *Mol. Catal. A: Chem.*, **230**,2005,1-8

192. Y. Chen, C. Qian, J. Sun, *Organometallics*, **22**, 2003, 1231-1236

193. Y. Chen, R. Chen, C Qin, X. Dong, J. Sun, *Organometallics*, **22**, 2003, 4312-4321

194. J. S. Paulino, R. Schnchardt, *J. Mol. Catal. A: Chem.* **211**, 2004, 55-58

195. L. Wang, T. C. Flood, *J. Am. Chem. Soc.*, 1992, **114**, 3169-3170

196. L. Wang, R. S. Lu, R. Bau, T.C. Flood, *J. Am. Chem. Soc.*, 1993, **115**, 6999-7000

197. L. K. Johnsom, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.*, .1995, **117**, 6414-6415

198. J. Feldman, S. J. McClain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics*, 1997, **16**, 1514-1516

199. L. K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 267-268

200. W. Keim, F. H. Kowaldt, R. Goddard, C. Kruger, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 446

201. V. C. Gibson, A. Tomov, A. J. P. White, D. J.Williams, *Chem. Commun.* , 2001, 719-720

202. V. C. Gibson, A. Tomov, *Chem. Commun.*, 2001, 1964-1965

203. M. E. Bluhm, C. Folli, O. Walter, M. Doring *J. Mol. Catal A: Chemical* **229,** 2005, 117-181

204. H. R. Liu, P. T. Gomes, S. I. Costa, M. T. Duarte, R. Branquinho, A. C. Fernandes, J. C. W. Chien, R. P. Singh, M. M. Marques, *J. Organometallic Chem.*, 2004, article in press

205. J. C. Yuan, L. C. Silva, P. T. Gomes, P. Valgera, J. M. Campos, M. R. Ribeiro, J. W. Chein, M. M. Marques, *Polymer,* received September 2004, article in press

206. J. Li, T. Gao, W. Zhang, W. H. Sun, *Inorg. Chem. Commun.*, **6**, 2003, 1372-1374

Chapter Two

Experimental Techniques

2.1 Manipulation of Air Sensitive Compounds

Some of the compounds described in this thesis are air and moisture sensitive, such that conventional bench top methods were not suitable for their preparation or manipulation. In the case of such compounds Schlenk, glove box and high vacuum techniques were employed. A brief description of each of these techniques is given here and a more detailed discussion can be found in any number of reviews and books currently in existence.[1]

2.1.1 Inert Atmosphere Techniques

Exclusion of air using an inert atmosphere is one of the most widely employed methods for the manipulation of air sensitive compounds. The compounds described were handled using either (i) Schlenk line techniques, where bench top operations are performed with specially designed glassware or (ii) glove box techniques, involving the handling of compounds under an inert atmosphere in a sealed unit.

(i) Schlenk Line Techniques

The Schlenk line is ideally suited to the manipulation of large or small quantities of liquids, solutions and solids. The line used during the course of the research described in this thesis is illustrated in Figure 2.1, and provided, in effect, a reaction system

secure from the atmosphere. Construction of the Schlenk line was from Pyrex glass incorporating ground glass joints and two-way stopcocks lubricated with "Dow-Corning High Vacuum" grease. Evacuation of the line and attached reaction vessels was achieved by an oil-sealed rotary pump, which was protected from volatile contaminants by a low temperature trap cooled with liquid nitrogen. This system enabled evacuation to a pressure of typically 10^{-2} Torr, monitored quantitatively by a Pirani pressure gauge. Pure inert gas (generally Argon) introduced from a cylinder was passed through a column packed with molecular sieves to remove any trace moisture; excess pressure was vented via a mercury bubbler. The design of the line allowed several pieces of apparatus to be purged simultaneously with the two-way stopcocks providing a means of alternating between inert gas and vacuum. By a series of several cycles of pumping followed by filling with inert gas an effectively oxygen- and moisture-free environment was achieved. When more rigorous exclusion of moisture was required, this was achieved by 'flaming' reaction vessels with a blue Bunsen flame while under vacuum. Transfer of liquids and solutions between Schlenk vessels was achieved by basic cannula and syringe techniques using rubber septa.

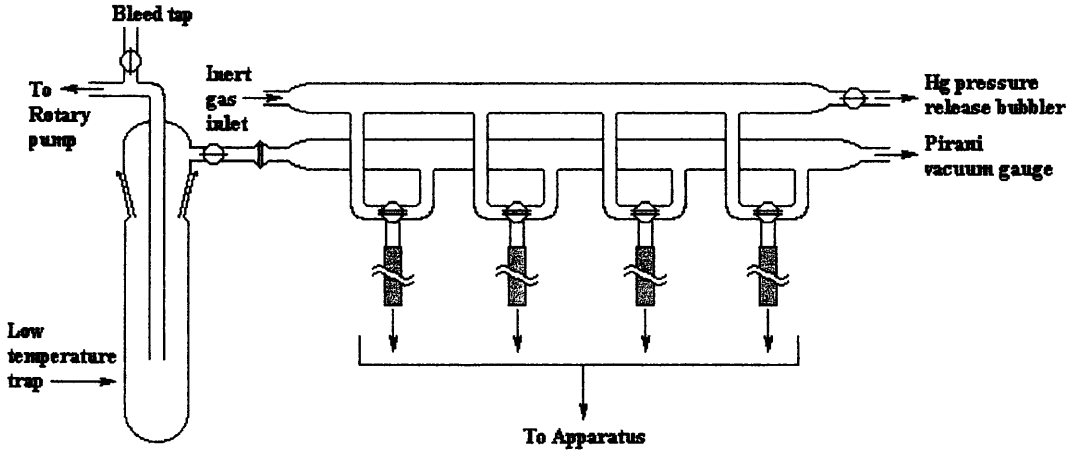


Figure 2.1: Schematic diagram of the Schlenk line apparatus used in this study.

(ii) Glove Box Techniques

Operations involving air-sensitive solids, such as weighing of reagents and preparation of samples (e.g. for infra-red spectrometry or mass spectrometry), also required an inert atmosphere. The solid air-sensitive precursors and reaction products were manipulated in a 'Saffron Scientific Omega' glove box.[2] This unit is constructed from stainless steel incorporating a toughened glass viewing panel. Access to the glove box is through two neoprene gloves and a stainless steel side port, which can be pumped and purged to allow introduction of chemicals and equipment to the main box with minimal disturbance to the atmosphere within. A B.O.C cylinder supplied the nitrogen atmosphere, re-circulated internally through catalyst, molecular sieve and solvent scrubbing columns to provide an atmosphere with oxygen and moisture levels typically less than 5 ppm and 10 ppm respectively.

2.1.2 High Vacuum Techniques

Operations such as vacuum sublimation or removal of trace solvent (where the rotary pump on the Schlenk line provides insufficient vacuum) were carried out on a basic high vacuum line. This simple system was constructed from Pyrex glass incorporating Young's greaseless stopcocks. Evacuation of the system was achieved by the combination of a mercury diffusion pump and a rotary pump, thereby achieving a pressure of *ca.* 10^{-4} Torr. Here too, the pumps were protected from volatile contaminants by a cold trap at –196°C (liquid nitrogen). The quality of the vacuum was monitored using a Tesla coil that produces a high frequency discharge at pressures between 1 and 10^{-3} Torr.

2.2 Physical Measurements

2.2.1 NMR Spectroscopy

NMR spectra were recorded on either a Bruker AM-400 or a Jeol Eclipse 300 Plus FT-NMR spectrometer. The residual signal(s) of the solvent were used for ^{1}H and ^{13}C NMR while $BF_3.OEt_2$ was used as an external reference for ^{19}F NMR. Solution samples of air sensitive compounds were prepared by preconditioning a Young's NMR tube to an inert atmosphere on a Schlenk line and transferral of solution by cannula methods.

2.2.2 Infrared Spectroscopy

Infrared spectra were measured for compounds as a KBr disk on a Nicolet 5000 FT-IR spectrometer. Disks of moisture-sensitive solid samples were prepared in the glove box, the KBr being pre-conditioned by heating under continuous pumping on the high vacuum line prior to use.

2.2.3 Mass Spectrometry

Mass spectra were measured at the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea and by the departmental service at Cardiff University. Perfluorotributylamine and polyethylenimine were used as standards for high resolution EI and CI mass spectra respectively.

2.2.4 Chemical Analysis

Elemental analysis was performed by the departmental analysis service of the Cardiff School of Chemistry, and by Warwick Analytical Services.

2.2.5 X-Ray Crystallography

Data collection was carried out on either an Enraf Nonius Kappa CCD diffractometer (EPSRC Crystallography Service, Southampton University or Cardiff School of Chemistry) or on a CAD4 four-circle diffractometer (Cardiff School of Chemistry). Structure solution and refinement were carried out by Prof. C. Jones, Dr. K.M.A. Malik or Dr. M.E. Light

2.3 Purification and Preparation of Solvents and Reagents

Some compounds synthesised during the course of this research had as precursors, compounds which were not themselves readily available. Such starting materials therefore had to be prepared from commercially available reagents, the preparations of which are included in this chapter. In addition it was also necessary to purify some commercially available reagents and solvents prior to use. Table 2.1 shows the sources and procedures for purification of commercially available precursors.

Table 2.1: Sources of chemicals.

Compound	**Source**	**Purity**	**Procedure**
Reagents			
Trimethylchlorosilane	Aldrich	98%	Used as supplied
n-Butyllithium (2.5 M in hexanes)	Aldrich	*a*	Used as supplied
n-Butyllithium (1.6 M in hexanes)	Lancaster	*a*	Used as supplied
1,2–*Trans* – Diaminocyclohexane	Aldrich	99%	Sublimed onto cold finger held at -78°C at 10^{-2} Torr
2-Fluoronitrobenzene	Avocado	98%	Used as supplied
4-Fluoronitrobenzene	Aldrich	98%	Used as supplied
2-Chloro-6-nitropyridine	Avocado	99%	Used as supplied
2-Fluoropyridine	Aldrich	98%	Used as supplied
Homopiperazine	Lancaster	98%	Used as supplied
Piperazine	Avocado	99%	Used as supplied
Piperidine	Aldrich	99%	Used as supplied
(+/-)-3,3-dimethyl-1,2-epoxybutane	Lancaster	98%	Used as supplied
t-Butyldimethylchlorosilane	Lancaster	97%	Used as supplied
n-Butyldimethylchlorosilane	Lancaster	97%	Used as supplied
*Di*methylamine hydrochloride	Aldrich	99%	Used as supplied
Benzaldehyde	Aldrich	99.5+%	Used as supplied
*N,N'-Di*methylethylenediamine	Aldrich	99%	Used as supplied

N,'N, N'',N''''-tris [2-hydroxy-3-dimethylbutyl]-1,4,7-cyclen	*b*	*a*	Used as supplied
Benzyl chloride	Aldrich	99%	Used as supplied
$AlMe_3$	Aldrich	97%	Used as supplied
Titanium(IV) isopropoxide	Lancaster	97%	Used as supplied
Zirconium(IV) propoxide 70% wt solution in 1-propanol	Aldrich	*a*	Used as supplied
Titanium(IV) Ethoxide	Aldrich	*a*	Used as supplied
Titanium(IV)chloride	Lancaster	98+%	Used as supplied
Zirconium(IV)chloride	Riedel-De Haen	*a*	Used as supplied
Nickel chloride	Aldrich	*a*	Used as supplied
Pd/C catalyst	Avocado	*a*	Used as supplied
Methylaluminoxane, 10%wt in toluene	Aldrich	*a*	Used as supplied
1-Hexene	Aldrich	*a*	Used as supplied
Chromium(III)chloride tristetrahydrofuran	*c*	*a*	Used as supplied

Solvents			
Toluene	Fischer	>99%	Heated under reflux over potassium followed by distillation.
Dichloromethane	Fischer	>99%	Heated under reflux over CaH_2, followed by distillation.
Hexane	Fischer	>99%	Heated under reflux over potassium followed by distillation.
THF	Fischer	>99.5%	Heated under reflux over potassium followed by distillation.
Acetonitrile	Fischer	>99%	Used as supplied

Deuteriated Solvents			
Benzene-d_6	Goss Scientific Instruments Ltd	99.6 atom %	Stored under argon over potassium mirror
Chloroform-*d*	Aldrich	99.8 atom %	Stored under argon over dried molecular sieves
Dichloromethane-d_2	Aldrich	99.8 atom %	Stored under argon over dried molecular sieves

Gases			
Argon	B.O.C	*a*	Used as supplied
Nitrogen	B.O.C	*a*	Used as supplied
Hydrogen	B.O.C	*a*	Used as supplied
Ethylene	B.O.C	*a*	Used as supplied

a Data not available.
b Courtesy of Dr. R. Strevens, Cardiff School of Chemistry.
c Courtesy of Dr. W. Perkins, Cardiff School of Chemistry.

2.3.1 Preparation of Precursors

In addition to the above reagents, the precursors benzylmagnesium bromide, tetrabenzylzirconium, tetrachloro*bis*(tetrahydrofuran)titanium(IV), and tetrachloro-*bis*(tetrahydrofuran)zirconium(IV) were prepared using published literature methods with minor modifications.[3,4]

References

1. See, for example, (a) D. F. Shriver, M. A. Drezdzon, *The Manipulation of Air Sensitive Compounds*, 2nd edn., Wiley-Interscience, 1986. (b) R.E. Dodd, P.L. Robinson, *Experimental Inorganic Chemistry*, Elsevier, 1954

2. Saffron Scientific Equipment Ltd., glove box operation manual

3. U. Zucchini, E. Albizzati and U. Giannini, *J. Organomet. Chem.*, 1971, **26**, 357

4. L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 135

Chapter Three

The Synthesis of New Ligand Frameworks for Olefin Polymerisation Catalysts

3.1 Introduction

In recent years there has been much research into new non-metallocene ligand frameworks for supporting active transition metal olefin polymerisation catalysts.[1,2] Publications from many groups report an assortment of new ligands incorporating donors such as amides [3], imines [4] and alkoxides [5] which when complexed to a suitable transition metal give active polymerisation catalysts. Thus, for example, a number of iron (II) complexes have been reported containing a neutral tridentate 2,6-bis(imino) pyridine ligand,[6,7] which when activated with MAO, give rise to extremely active catalysts. Similar diimine catalysts have also been reported for cobalt (II), nickel (II) and palladium (II).[6,8] Schiff base (imine) ligands are also known to support highly active polymerisation catalysts based on group 4 metals, for example containing mixed imine / alkoxide donor sets.[9]

3.1.1 Aims of the current research

Over the past 20-30 years, extensive research into polymerisation catalysis has revealed much information about how the nature of spectator ligands can greatly influence both the efficacy of the catalyst and the structure of the polymer generated.[1] Amine bis(phenolate) zirconium complexes[4] illustrate how labile pendant donors can act as a shield for the active polymerisation site, thereby preventing potentially

deactivating side reactions which can slow rates and decrease polymer molecular weights. Furthermore, the stereochemistry and steric bulk of the coordinated ligand has been shown to be important in influencing the stereochemistry of the polymer it produces; this characteristic is clearly illustrated by the case of propylene polymerisation by ansa-metallocenes (*vide supra*). With these previously employed and successful principles of complex design as a basis, a series of ligands was to be designed and syntheses attempted. Two basic backbones were to be employed:

(i) Ligands containing a cyclohexane backbone

A number of ligands based on a *trans*-1,2-disubstituted cyclohexane backbone with amine or amide functionalities were synthesised during this project. This backbone was chosen mainly because of its ready availability and C_2 symmetry; it was hoped that the functionalised cyclohexane ring could be coordinated to suitable metals, thereby imparting its symmetry to the complexes formed. A catalytically active metal complex with a C_2 symmetric diamide ligand, for example, could conceivably act in a similar manner to the well-documented ansa metallocenes, in producing isotactic polymers from α-olefins (*vide supra*). *Trans*-1,2-diaminocyclohexane is also cheap, readily available and easily resolvable to its enantiomers.

(ii) Ligands derived from linear and macrocyclic amines

During this research linear, cyclic and macrocyclic amines were also to be employed as backbones for ligands. Although in most cases these lack the rigidly defined C_2 symmetry of the *trans*-1,2-disubstituted cyclohexane backbone, their ready availability and ease of functionalization, meant that they were attractive alternative targets. Numerous complexes of group 4 metals with such ligands have been

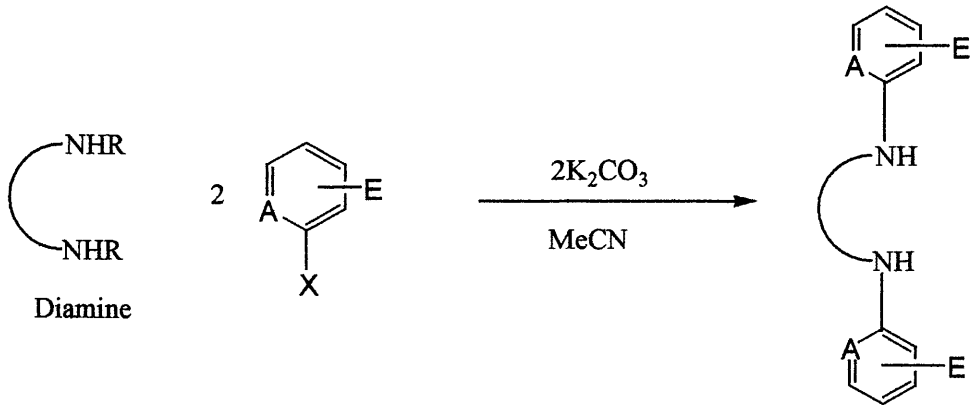
reported,[8] and functionalisation of amines is achieved relatively easily, allowing for incorporation of additional donor groups such as alkoxides and imines. Furthermore, variation in the nature of the ligand backbone (e.g from a linear to a macrocyclic framework) offers the potential for interesting comparisons of coordination chemistry as a function of donor architecture and rigidity.

3.2 Experimental

(a) Synthesis via nucleophilic aromatic substitution

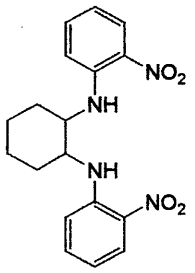
(i) Diamines

The generic synthetic strategy employed for the syntheses (or attempted syntheses) of ligands H_2L^1 - L^5 is outlined in the scheme below. In the case of ligands H_3L^3 and H_3L^4, however, only mono-substitution of the diamine could be achieved despite significant variation in reaction conditions.



***Trans*-1,2-di(2-nitrophenylamino)cyclohexane**

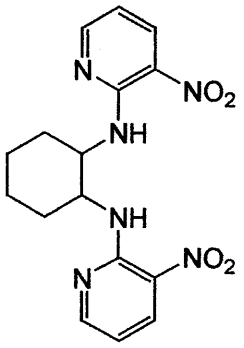
$C_{18}H_{20}N_4O_4$ (H_2L^1)



Trans-1,2-diaminocyclohexane (2.00 g, 0.018 mol) and 2-fluoronitrobenzene (4.93 g, 0.035 mol) were dissolved in acetonitrile (100 ml) containing K_2CO_3 (4.84 g, 0.035 mol), and this mixture was refluxed (81-82°C) for 12 h. The reaction mixture was filtered while warm to remove potassium fluoride. Acetonitrile was removed from the filtrate yielding a crystalline bright orange solid, which was recrystallised from hot toluene to yield clean orange crystals (5.02 g, 78.3 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 1.44-3.61 (overlapping m, 10H,cyclohexyl ring), 6.47 (m, 2H, aromatic), 6.88 (m, 2H, aromatic), 7.20 (m, 2H, aromatic), 7.87 (m, 2H, aromatic), 8.07 (broad s, 2H, N*H*). ^{13}C NMR ($CDCl_3$, 25°C): δ 24.7, 32.5, 56.8 (cyclohexyl ring), 114.2, 115.9, 127.1, 132.1, 136.4, 145.3 (aromatic CHs and quaternary Cs). Elemental analysis, calculated for $C_{18}H_{20}N_4O_4$ 60.66 % C, 5.66 % H, 15.72 % N, measured 60.49 % C, 5.46 % H, 15.66 % N. Mass spec. (APCI) 357.4, $(M+H)^+$. IR (KBr disk, cm^{-1}) 2872 (w), 1600 (md), 1505 (md), 1338 (md), 1301(md), 1224 (md) and 1043 (md).

***Trans*-1,2-di(2-nitro-6-pyridylamino)cyclohexane**

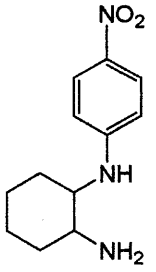
$C_{16}H_{18}N_6O_4$ (H_2L^2)



H_2L^2 was prepared from *trans*-1,2-diaminocyclohexane (2.00 g, 0.018 mol) and 2-chloro 6-nitropyridine (5.55 g, 0.035 mol) using the method detailed above for H_2L^1 and isolated as yellow/brown acicular crystals (4.74 g, 73.6 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 1.45-4.41 (overlapping m, 10H, cyclohexyl ring), 6.51 (broad s, 2H, N*H*), 8.22 (m, 2H, aromatic), 8.34 (m, 4H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.3, 33.2, 55.2 (cyclohexyl ring), 112.2, 127.9, 135.6, 152.9, 156.2 (pyridyl CHs and quaternary Cs). Elemental analysis, calculated for $C_{16}H_{18}N_6O_4$ 53.63 % C, 5.06 % H, 23.45 % N, measured 53.55 % C, 5.00 % H, 23.23 % N. Mass spec. (APCI) 359.3, $(M+H)^+$.

***Trans*-1-(4-nitrophenylamino)-2-amino-cyclohexane**

$C_{12}H_{17}N_3O_2$ (H_3L^3)

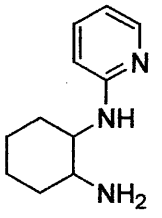


H_3L^3 was prepared from *trans*-1,2-diaminocyclohexane (2.00 g, 0.018 mol) and 4-fluoronitrobenzene (4.94 g, 0.035 mol) using the method detailed above for H_2L^1 and

isolated as a bright yellow solid (3.17 g, 74.9 %). ^{1}H NMR ($CDCl_3$, 25°C): δ1.1-3.03 (overlapping m, 10H, cyclohexyl ring), 4.18 (overlapping N-H) 6.52 (m, 2H, aromatic), 7.97 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.2, 25.3, 32.5, 35.8, 56.2, 59.9 (cyclohexyl ring), 111.9, 126.9, 138.1, 153.5 (aromatic CHs and quaternary Cs). Elemental analysis, calculated for $C_{12}H_{17}N_3O_2$ 61.26 % C, 7.28 % H, 17.86 % N, measured 61.05 % C, 7.10 % H, 17.74 % N. Mass spec. (APCI) 236.3 $(M+H)^+$. IR (KBr disk, cm^{-1}) 3350 (w), 3230 (w), 2928 (w), 1594 (st), 1550 (md), 1464 (st), 1299 (st), 1182 (md), and 1113 (md).

***Trans*-1-(2-pyridylamino)-2-amino cyclohexane**

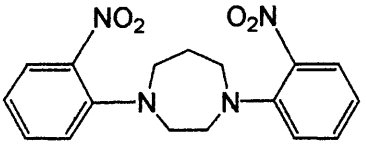
$C_{11}H_{17}N_3$ (H_3L^4)



H_3L^4 was prepared from *trans*-1,2-diaminocyclohexane (2.00 g, 0.018 mol) and 2-fluoronitropyridine (3.4 g, 0.035 mol) using the method detailed above for H_2L^1 and isolated as a cream coloured solid (2.32 g, 67.4 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 1.07-3.32 (overlapping m, 10H, cyclohexyl ring), 4.23 (broad s, 2H, N*H*), 6.38 (m, 1H, aromatic), 6.48 (m, 1H, aromatic), 7.20 (m, 1H, aromatic), 7.33 (m, 1H, aromatic), 7.99 (broad s, 1H, N*H*). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.4, 25.7, 33.2, 35.4, 56.2, 58.6 (cyclohexyl ring) 107.7, 113.3, 137.8, 148.5, 159.6 (aromatic CHs and quaternary Cs). Elemental analysis, calculated for $C_{11}H_{17}N_3$ 69.07 % C, 8.96 % H, 21.97 % N, measured 68.74 % C, 8.72 % H, 21.67 % N. Mass spec. (APCI) 192.3 $(M+H)^+$.

Bis(2-nitrophenyl)-1,4-diazacycloheptane

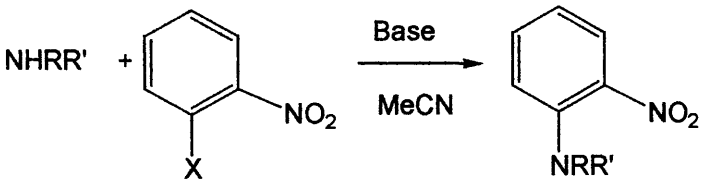
$C_{17}H_{18}N_4O_4$ (L^5)



L^5 was prepared from 1,4-diazacycloheptane (2.00 g, 0.02 mol) and 2-fluoronitrobenzene (6.0 g, 0.04 mol) using the method detailed above for H_2L^1. The orange solid obtained from the filtered reaction mixture was recrystallised from hot toluene to yield orange crystals (5.39 g, 78.7 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 2.03 (m, 2H, $NCH_2CH_2CH_2N$), 3.28 (m, 4H, $NCH_2CH_2CH_2N$), 3.42 (s, 4H, NCH_2CH_2N), 6.89 (m, 2H, aromatic), 7.07 (m, 2H, aromatic), 7.36 (m, 2H, aromatic), 7.64 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 29.3, 53.8, 54.1 (1,4-diazacycloheptane ring), 120.4, 121.0, 126.6, 133.5, 141.9, 146.4 (aromatic CHs and quaternary Cs). Elemental analysis, calculated for $C_{17}H_{18}N_4O_4$ 59.64 % C, 5.30 % H, 16.37 % N, measured 59.71 % C, 5.44 % H, 15.99 % N. Mass spec. (APCI) 343.3 $(M+H)^+$. IR (KBr disk, cm^{-1}) 2873 (w), 1600 (md), 1565 (md), 1505 (st), 1445 (md), 1428 (md), 1397 (md), 1338 (md), 1300 (md), 1224 (md), 1181 (md), 1104 (md), 1043 (md) and 931 (md).

(ii) **Mono amines**

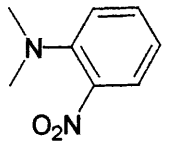
Mixed nitro/amino ligand precursors H_2L^6 and L^7 were synthesized according to the following scheme:



6 R=R'=Me, X= Cl
7 RR'=C_4H_8, X=F

Dimethyl-2-nitrophenyl amine

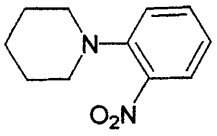
$C_8H_{10}N_2O_2$ (H_2L^6)



To a solution of 2-fluoronitrobenzene (4.00 g, 0.028 mol) in acetonitrile (50 ml), in a pressure tube, was added dimethylamine hydrochloride (4.60 g, 0.028 mol) and K_2CO_3 (11.7 g, 0.084 mol). This mixture was heated at 130°C for 4 days then cooled and filtered. Acetonitrile was removed under vacuum to give a bright orange oil and any unreacted dimethylamine hydrochloride was removed by washing the oil with water (yield 5.20 g, 59.8 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 2.88 (s, 6H, NMe_2), 6.79 (m, 1H, aromatic), 7.01 (m, 1H, aromatic), 7.37 (m, 1H, aromatic), 7.72 (m, 1H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 40.6 (NMe_2), 116.0, 116.3, 124.9, 131.5, 137.4, 144.4 (aromatic CHs and quaternary Cs). Mass spec. (APCI) 167 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

***N*-(2-nitrophenyl)azacyclohexane**

$C_{11}H_{14}N_2O_2$ (L^7)



2-Fluoronitrobenzene (6.00 g, 0.043 mol), azacyclohexane (10.80 g, 0.043 mol) and KF (2.40 g, 0.043mmol) were sealed in a pressure tube and heated to 130°C for 12 h. The resulting bright orange reaction mixture was cooled to room temperature, acetonitrile (10 ml) was added and the solution filtered to remove the white solid formed. The acetonitrile was removed under vacuum to give an orange solid, which

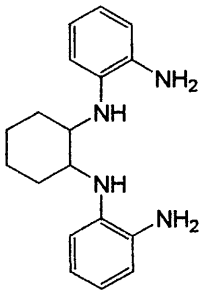
was recrystallised from hot toluene to give large, acicular bright orange crystals (yield 5.20 g, 32 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 1.54 (m, 2H, $CH_2CH_2CH_2N$), 1.63 (m, 4H, $CH_2CH_2CH_2N$), 2.94 (m, 4H, $CH_2CH_2CH_2N$), 6.91 (m, 1H, aromatic), 7.05 (m, 1H, aromatic), 7.36 (m, 1H, aromatic), 7.69 (m, 1H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 22.9, 24.9, 51.8 (azacyclohexane ring), 119.5, 119.8, 124.9, 132.4, 141.5, 146.0 (aromatic CHs and quaternary Cs). Elemental analysis, calculated for $C_{11}H_{14}N_2O_2$ 64.06 % C, 6.84 % H, 13.58 % N, measured 63.72 % C, 6.72 % H, 13.18 % N. Mass spec. (APCI) 207.0 $(M+H)^+$. IR (KBr disk cm^{-1}) 1603 (w), 1567 (md), 1504 (md), 1343 (md), 1297 (md), 1234 (md), 1167 (md), 1130 (md), 1027 (md) and 927 (md).

(b) Hydrogenation reactions

Hydrogenation reactions using a palladium on carbon catalyst were typically employed to convert the nitro-substituted ligand precursors $H_2\mathbf{L}^1$ - $\mathbf{L}^7$ into the corresponding amino derivatives.

***Trans*-1, 2-di(2-aminophenylamino) cyclohexane**

$C_{18}H_{24}N_4$ ($H_6\mathbf{L}^8$)

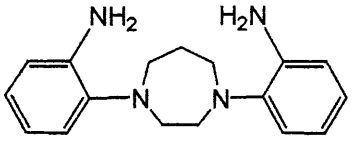


A solution of $H_2\mathbf{L}^1$ (2.00 g, 0.056 mol) in toluene was stirred with a 5 % palladium on carbon catalyst (0.20 g) under an atmosphere of dihydrogen until the solution became colourless. The solution was filtered to remove the catalyst, concentrated to

approximately one third original volume and cooled to give a white crystalline solid (1.24 g, 74.6 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 0.78-3.10 (overlapping m, 10H, cyclohexyl ring), 3.45 (broad, overlapping N-H signals), 6.51-6.80 (overlapping m, 8H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 23.8, 30.8, 55.8 (cyclohexyl ring), 111.9, 115.6, 117.8, 118.9, 134.4, 135.2 (aromatic). Elemental analysis, calculated for $C_{18}H_{24}N_4$ 72.94 % C, 8.16 % H, 18.90 % N, measured 72.91 % C, 8.08 % H, 19.04 % N. Mass spec. (APCI) 297.9 $(M+H)^+$. IR (KBr disk cm^{-1}) 3377 (md), 3295 (md), 3169, 2920 (md), 2863 (md), 1638 (md), 1597 (md), 1505 (st), 1449 (md), and 1271 (st).

Bis(2-aminophenyl)- 1,4-diazacycloheptane

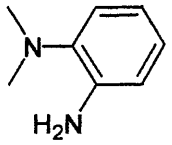
$C_{17}H_{22}N_4$ (H_4L^9)



H_4L^9 was synthesised using the method detailed above for H_6L^8 but using L^5 (3.70 g, 0.01 mol), and 0.37 g of catalyst. The product was isolated as a very pale pink crystalline solid (1.60 g, 55 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 2.07 (m, 2H, $NCH_2CH_2CH_2N$), 3.26 (m, 8H, $NCH_2CH_2CH_2N$), 4.08 (broad s, 2H, N*H*), 6.78 (m, 4H, aromatic), 6.95 (m, 2H, aromatic), 7.09 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 30.5, 54.6, 57.4 (1,4-diazacycloheptane ring), 115.6, 119.0, 121.9, 124.9, 142.1, 142.2 (aromatic CHs and quaternary Cs). Elemental analysis, calculated for $C_{17}H_{22}N_4$ 72.31 % C, 7.85 % H, 19.84 % N, measured 72.15 % C, 7.64 % H, 19.61 % N. Mass spec. (APCI) 282.7 $(M+H)^+$. IR (KBr disk cm^{-1}) 3392 (md), 2945 (w), 2823 (w), 1606 (md), 1496 (md), 1451 (md), 1379 (w), 1360 (w), 1323 (w), 1260 (md), 1202 (md), 1156 (md), 920 (w), 900 (w) and 747 (md).

Dimethyl-2-[phenyl-2-amino] amine

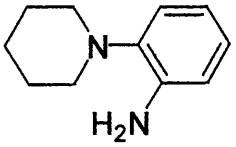
$C_8H_{12}N_2$ (H_2L^{10})



H_2L^{10} was synthesised using the method detailed above for H_6L^8 but using L^6 (2.00 g, 0.01 mol) and 0.20 g of catalyst. The product was isolated as a light pink oil (yield 0.81 g, 49.2 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 2.43 (s, NMe_2, 6H), 3.67 (broad s, 2H, N*H*), 6.47 (m, 1H, aromatic), 6.71 (m, 1H, aromatic), 6.88 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 43.3 (NMe_2), 115.2, 118.4, 119.3, 124.5, 140.6, 141.0 (aromatic CHs and quaternary Cs). Mass spec. (APCI) 136.9 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

***N*-(2-aminophenyl)azacyclohexane**

$C_{11}H_{16}N_2$ (H_2L^{11})



H_2L^{11} was synthesised using the method detailed above for H_6L^8 but using L^7 (3.00 g, 0.01 mol) and 0.30 g of catalyst. The product was isolated as a white crystalline solid (1.72 g, 67.3 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 1.49 (broad m, 2H, $CH_2CH_2CH_2N$), 1.64 (m, 2H, $CH_2CH_2CH_2N$), 2.76 (broad m, 2H, $CH_2CH_2CH_2N$), 3.89 (broad s, 2H, N*H*), 6.71 (m, 2H, aromatic), 6.86 (m, 1H, aromatic), 6.93 (m, 1H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 23.3, 25.9, 51.6 (azacyclohexane ring), 113.9, 117.5, 118.8, 123.1, 139.7, 140.5 (aromatic CHs and quaternary Cs). Mass spec. (APCI) 177.0 $(M+H^+)$.

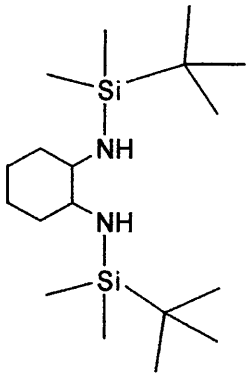
Despite repeated attempts, satisfactory elemental analyses for this compound could not be obtained.

(c) Synthesis of silyl substituted amine ligands

The silyl substituted amines H_2L^{12} - HL^{16} were synthesized by a standard protocol involving deprotonation with an appropriate equivalence of *n*-butyllithium and subsequent reaction of the lithium amide with a chlorosilane.

***Trans*-1,2-di[(*t*-butyldimethylsilyl)amino]cyclohexane**

$C_{18}H_{42}N_2Si_2$ (H_2L^{12})

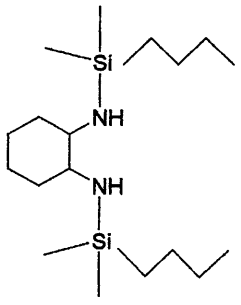


To a solution of *trans*-1,2-diaminocyclohexane (1.50 g, 0.013 mol) in diethyl ether (100 ml) cooled to –78°C, was added *n*-butyllithium in hexane (5.30 ml of a 2.5 M solution). The solution was warmed to room temperature and stirred for 1 h. The solution was then cooled back to -10°C and a solution of *t*-butyldimethylsilylchloride (3.96 g, 0.026 mol) in diethyl ether (50 ml) was added. The solution was warmed to room temperature and stirred for 12 h. The orange/brown solution was separated from the white precipitate by filtration and the solvent removed from the filtrate in vacuo to yield a dark brown oil. This was redissolved in hexane, filtered and the hexane then

removed under vacuum to yield an orange/brown oil (2.45 g, 54.4 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 0.04 (s, 12H, SiMe), 0.88 (s, 18H, ^{t}Bu), 1.14-2.21 (overlapping m, 10H, cyclohexyl ring). ^{13}C NMR ($CDCl_3$, 25°C): δ -3.4 (SiMe), 18.0 (Me of ^{t}Bu), 25.1 (cyclohexyl ring), 26.8 (quaternary of ^{t}Bu), 37.3, 59.2 (cyclohexyl ring). Mass spec. (APCI) 343.1 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

***Trans*-1,2-di[(*n*-butyldimethylsilyl)amino]cyclohexane**

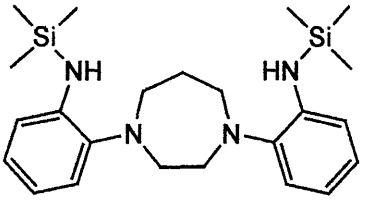
$C_{18}H_{42}N_2Si_2$ (H_2L^{13})



H_2L^{13} was synthesised using the method detailed above for H_2L^{12} but using *trans*-1,2-diaminocyclohexane (1.50 g, 0.013 mol), *n*-butyllithium in hexane (5.3 ml of a 2.5 M solution) and *n*-butyldimethylsilylchloride (3.96 g, 0.026 mol) in diethyl ether (50ml). The compound was isolated as a straw-coloured oil (2.91 g, 65.4 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 0.07 (s, 12H, SiMe), 0.54 (m, 4H, $CH_2(CH_2)_2CH_3$), 0.95 (m, 6H, $CH_2(CH_2)_2CH_3$), 1.12 (m, 4H, cyclohexyl ring), 1.16 (m, 2H, cyclohexyl ring), 1.35 (m, 8H, $CH_2(CH_2)_2CH_3$), 1.56 (m, 4H, cyclohexyl ring). ^{13}C NMR ($CDCl_3$, 25°C): δ -0.8 (SiMe), 17.3, 17.5 (^{n}Bu), 26.3 (cyclohexyl ring), 26.8 (^{n}Bu), 36.7 (cyclohexyl ring), 37.8 (^{n}Bu), 58.9 (cyclohexyl ring). Mass spec. (APCI) 343.2 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

1,4-*bis*[2-(trimethylsilylamino)phenyl])-1,4-diazacycloheptane

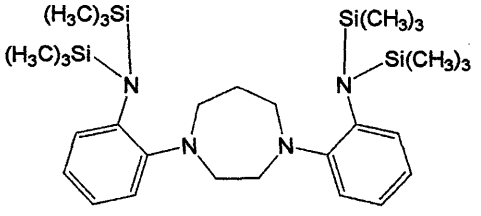
$C_{23}H_{38}N_4Si_2$ (H_2L^{14})



H_2L^{14} was synthesized using the method detailed above for H_2L^{12}, but using H_2L^{10} (1.00 g, 0.004 mol) *n*-butyllithium (4.40 ml of a 1.6 M solution) and trimethylsilylchloride (1.00 ml). The product was isolated as a straw coloured oil (0.80 g, 53 %). ^{1}H NMR (C_6D_6, 25°C): δ 0.26 (s, 18H,SiMe), 1.70 (m, 2H, $NCH_2CH_2CH_2N$), 2.92 (s, 4H, NCH_2CH_2N), 2.98 (m, 4H, $NCH_2CH_2CH_2N$), 5.02 (broad s, 2H, N*H*), 6.77(m, 2H, aromatic), 6.92(m, 2H, aromatic), 6.98(m, 4H, aromatic). ^{13}C NMR (C_6D_6, 25°C): δ 1.16 (SiMe), 30.6, 54.6, 57.7 (1,4-diazacycloheptane ring), 114.6, 117.7, 122.1, 125.1, 142.9, 143.3 (aromatic CHs and quaternary Cs). Mass spec. (APCI) 428.7 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

1,4-bis[2-bis(trimethylsilylamino)phenyl])-1,4-diazacycloheptane

$C_{29}H_{54}N_4Si_4$ (L^{15})

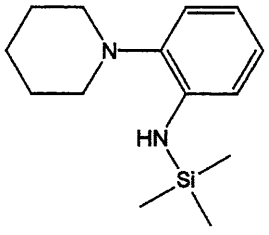


L^{15} was synthesized using the method detailed above for H_2L^{12}, but using H_2L^{11} (0.50 g, 0.001 mol), *n*-butyllithium (3.00 ml of a 1.6 M solution) and trimethylsilylchloride (0.5 ml). The product was isolated as a pink/brown oil (0.39 g, 58.6 %). ^{1}H NMR

(C_6D_6, 25°C): δ 0.17 (s, 36H, SiMe), 1.83 (m, 2H, $NCH_2CH_2CH_2N$), 2.11 (s, 4H, NCH_2CH_2N), 3.23 (m, 4H, $NCH_2CH_2CH_2N$), 6.85, 6.94, 7.01, 7.11 (m, 8H, aromatic CHs). ^{13}C NMR (C_6D_6, 25°C): δ 2.8 (SiMe), 28.6, 52.6, 53.9 (1,4-diazacycloheptane ring), 121.7, 122.5, 124.2, 130.1, 142.9, 150.5 (aromatic CHs and quaternary Cs). Mass spec. (APCI) 571.6 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

***N*-[2-(trimethylsilylamino)phenyl]azacyclohexane**

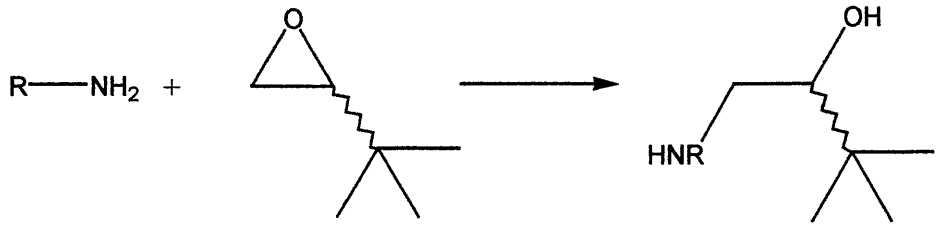
$C_{14}H_{24}N_2Si$ (HL^{16})



HL^{16} was synthesized using the method detailed above for H_2L^{12}, but using HL^{17} (0.60 g, 0.004 mol), *n*-butyllithium (2.8 ml of a 1.6 M solution) and trimethylsilylchloride (0.5 ml, 0.004 mol). The product was isolated as a pink/brown oil (0.55 g, 64.8 %). ^1H NMR ($CDCl_3$, 25°C): δ 0.31 (s, 9H, SiMe), 1.57 (m, 6H, $CH_2CH_2CH_2N$), 2.87 (m, 2H, $CH_2CH_2CH_2N$), 4.98 (broad s, 1H, N*H*), 6.93 (m, 1H, aromatic), 6.99 (m, 1H, aromatic), 7.11 (m, 2H, aromatic). ^{13}C NMR ($CDCl_3$, 25°C): δ 0.3 (SiMe), 24.5, 27.3, 53.2 (azacyclohexane ring), 114.6, 117.8, 120.6, 125.1, 142.0, 143.0 (aromatic CHs and quaternary Cs). Mass spec. (APCI) 249.5 $(M+H)^+$. No satisfactory elemental microanalysis was obtained for this oil.

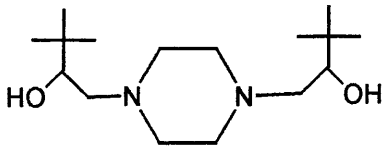
(d) Ring opening reactions of epoxides

H_2L^{17} - HL^{23} were synthesized according to the following scheme:



***N,N'*-bis(2-hydroxy-3,3-dimethylbutyl)-1,4-diazacyclohexane**

$C_{16}H_{34}N_2O_2$ (H_2L^{17})

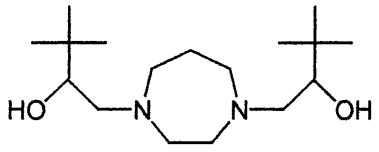


To a solution of 1,4-diazacyclohexane (0.77 g, 0.009 mol) in acetonitrile (10 ml), contained in a pressure tube, was added excess (+/-)-3,3-dimethyl-1,2-epoxybutane (2.69 g, 0.026 mol). The reaction mixture was stirred at 80°C for 24 hours, and the white crystals which formed on cooling of the reaction mixture were filtered and washed with cold acetonitrile (1.15 g, 40.0 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 0.90 (s, 18H, ^{t}Bu), 2.32 (overlapping m, 12H, NC*H*$_2$ and NC*H*$_2$CHOH), 2.72 (s br, 2H, O*H*), 3.33 (m ,2H, C*H*(OH)). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.7 (CH_3 of ^{t}Bu), 33.3 (^{t}Bu quaternary), 53.4 (1,4-diazacyclohexane ring), 58.9 (*C*H$_2$CHOH), 72.9 (*C*HOH). Mass spec. (APCI) 287.1, $(M+H)^+$. IR (KBr disk, cm^{-1}) 3218 (br), 2953 (br), 2361 (w), 1482 (md), 1456 (md), 1411 (md), 1383 (md), 1358 (md), 1326 (md), 1267 (md), 1243 (md), 1187 (md), 1151 (md), 1100 (md), 1054 (md), 1017 (md), 995 (md) and

945 (md). No satisfactory elemental analysis could be obtained despite repeated attempts.

***N,N'*-bis(2-hydroxy-3-dimethylbutyl)-1,4-diazacycloheptane**

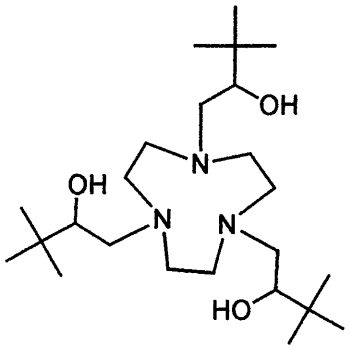
$C_{17}H_{36}N_2O_2$(H_2L^{18})



H_2L^{18} was synthesized using the method detailed above for H_2L^{17} but using 1,4-diazacycloheptane (0.90 g, 0.009 mol). The product was isolated as a white crystalline solid (2.30 g, 85.0 %). ^{1}H NMR ($CDCl_3$, 25°C): δ 0.9 (s, 18 H, ^{t}Bu), 1.82 (m, 2H, NCH_2CH_2 CH_2N), 2.27 (m, 2H, C(H)(*H*)CHOH), 2.52 (m, 2H, C(*H*)(H)CHOH), 2.55 (m,4H, NCH_2), 2.82 (m, 4H, NCH_2), 3.22 (m, 2H, C*H*OH), 3.82 (br s, 2H, CHO*H*). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.7 (CH_3 of ^{t}Bu), 56.2 (NCH_2), 33.2 (NCH_2CH_2), 28.2 (^{t}Bu quaternary), 54.4 (NCH_2CH_2), 59.5 (CH_2CHOH), 73.7 (*C*HOH). Elemental analysis, calculated for $C_{17}H_{36}N_2O_2$ 67.95 % C, 12.08 % H, 9.32 % N, measured 68.31 % C, 12.55 % H, 8.99 % N. Mass spec. (APCI) 301.6 $(M+H)^+$. IR (KBr disk, cm^{-1}) 3417 (br), 2955 (br), 2855 (w), 1653 (w), 1467 (md), 1410 (md), 1362 (md), 1244 (md), 1154 (w), 1088 (st), 1013 (md), 944 (md), 863 (md) and 821 (md).

***N,'N, N''-tris* [2-hydroxy-3,3-dimethylbutyl]-1,4,7-triazacyclononane**

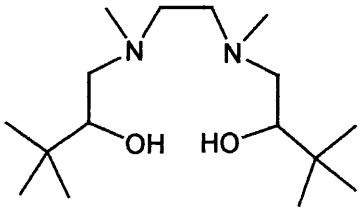
$C_{24}H_{51}N_3O_3$ (H_3L^{19})



H_2L^{19} was synthesized using the method detailed above for H_2L^{17} but using 1,4,7-triazacyclononane (2 g, 0.009 mol), as reported originally by Fallis and Strevens.[10] The (R,R,S)/(S,S,R) pair of isomers were isolated as white crystals, leaving the (R,R,R)/(S,S,S) pair in the supernatent solution (yield: 2.00 g, 48.0 %). Spectroscopic data were in accordance with those reported previously.[11]

N,N'-*bis*(2-hydroxy-3,3-dimethylbutyl)-dimethylethylenediamine

$C_{16}H_{36}N_2O_2$ (H_2L^{20})

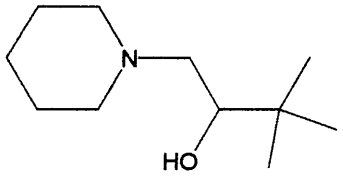


H_2L^{20} was synthesized using the method detailed above for H_2L^{17} using *N,N'*-dimethylethylenediamine (0.50 g, 0.006 mol) with excess (+/-)-3,3-dimethyl-1,2-epoxybutane (2.30 g, 0.023 mol) as the solvent. Excess epoxide was removed under vacuum to yield the product as a clear oil containing a mixture of (R,R/S,S and R,S/S,R) diastereoisomers at room temperature (waxy solid at -25°C). Yield: 0.63 g, 59.0 %) ^{1}H NMR ($CDCl_3$, 25°C): 0.87 ($C(CH_3)_3$), 2.24-2.66 (broad unresolvable

signals, aliphatic hydrogens signals), 3.25 (m, HOC*H*). ^{13}C NMR ($CDCl_3$, 25°C): δ 25.8,25.9 (C(CH_3)$_3$), 33.39, 33.41 (*C*(CH_3)$_3$), 42.5, 43.5 (NCH_3), 54.7, 55.8 (NCH_2), 58.6, 59.2 (*C*H_2CHOH), 74.6, 74.7 (*C*HOH). Mass spec. (APCI) 289.1 $(M+H)^+$. Exact mass: calc. for $C_{16}H_{36}N_2O_2$ 289.2855, measured 289.2859. IR (KBr disk, cm^{-1}) 2957 (br, md), 1463 (md), 1363 (md), 1217 (md), 1090 (st), 1017 (md), 937 (md). No satisfactory elemental analysis was obtained for this oil.

***N*-(2-hydroxy-3-dimethylbutyl)monoazacyclohexane**

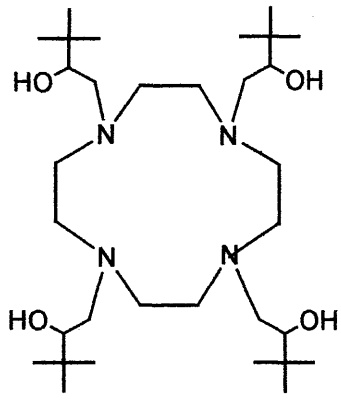
$C_{11}H_{23}NO$ (HL^{21})



HL^{21} was synthesized using the method detailed above for H_2L^{17} using Monoazacyclohexane (2.00 g, 0.023 mol). The product was isolated as straw coloured oil (2.90 g, 67.0 %). ^{1}H NMR (DMSO, 25°C): δ 0.82 (s, 9H, ^{t}Bu), 1.38 (m br, 2H, C*H*$_2$CH$_2$CH$_2$N), 1.48 (m br, 4H, CH$_2$C*H*$_2$CH$_2$N), 2.18 (m br, 4H, CH$_2$CH$_2$C*H*$_2$N), 2.54 (m br, 2H, NC*H*$_2$CH), 3.24 (double doublet, 9.63Hz & 4.63Hz 1H, NCH$_2$C*H*), 3.91 (s br weak, 1H, O*H*). ^{13}C NMR (DMSO, 25°C): δ 25.0 (CH_3 of ^{t}Bu)(C(CH_3)$_3$), 26.2, 26.3 (azacyclohexane ring), 34.1 (^{t}Bu quaternary), 55.0 (NCH_2 of azacyclohexane ring), 61.3 (C*H*$_2$CHOH), 73.8 (*C*HOH),. Mass spec. (APCI) 186.1, $(M+H)^+$. No satisfactory elemental analysis was obtained for this oil.

***N, N',N'',N'''-tetra* [2-hydroxy-3,3-dimethylbutyl]-1,4,7,10-tetrazacyclododecane**

(H_4L^{22})

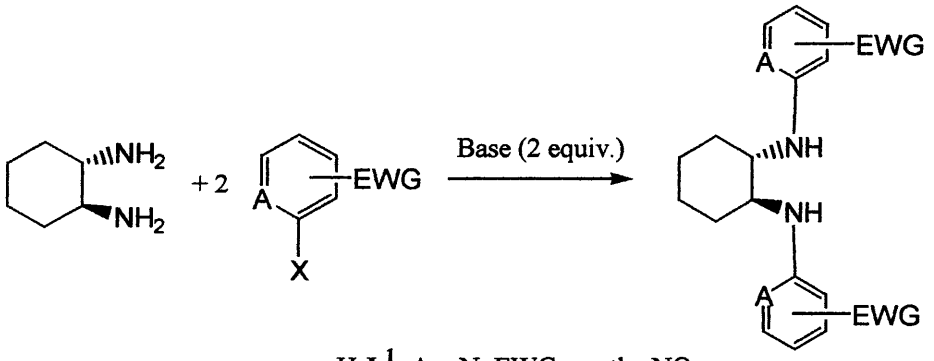


Kindly donated by R. Strevens.

3.3 Results and Discussion

3.3.1 Ligands Based on a Diaminocyclohexane Backbone

Functionalisation of *trans*-1,2-diaminocyclohexane was readily achieved through substitution chemistry. Thus, ligands H_2L^1 and H_2L^2 were synthesised by nucleophilic aromatic substitution (S_NAr) of a chloride or fluoride substituent on a nitrobenzene or nitropyridine ring under refluxing acetonitrile conditions (Scheme 3.1).



H_2L^1: A = N, EWG = ortho NO_2
H_2L^2: A = CH, EWG = ortho NO_2

Scheme 3.1

Nucleophilic aromatic substitution reaction may only occur if the aromatic reagent has an electron-withdrawing group in the ortho or para position [9]. The HX by-product is neutralised by potassium carbonate to form potassium halide, which precipitates as a white solid from the reaction mixture thereby helping to drive the equilibrium in favour of the desired product. Filtration of the hot acetonitrile reaction solution followed by controlled cooling allowed isolation of clean crystalline products $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$. $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ have been characterised by multinuclear NMR and IR spectroscopies, mass spectrometry and elemental analysis. In addition, ligand $H_2\mathbf{L}^1$, was isolated as bright orange crystals suitable for X-ray diffraction. The structure obtained together with selected bond length and angles are shown in Figure 3.1 and Table 3.1 respectively. The crystal structure of a different polymorph of $H_2\mathbf{L}^1$ has recently been reported.[11] Ligand $H_2\mathbf{L}^2$, on the other hand is isolated as brown acicular crystals and its X-ray structure illustrated in Figure 3.2. Selected bond lengths and angles are listed in Table 3.2.

The crystal structures of both $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ show approximate C_2 symmetry with bond lengths and angles being typical for such systems. [11]

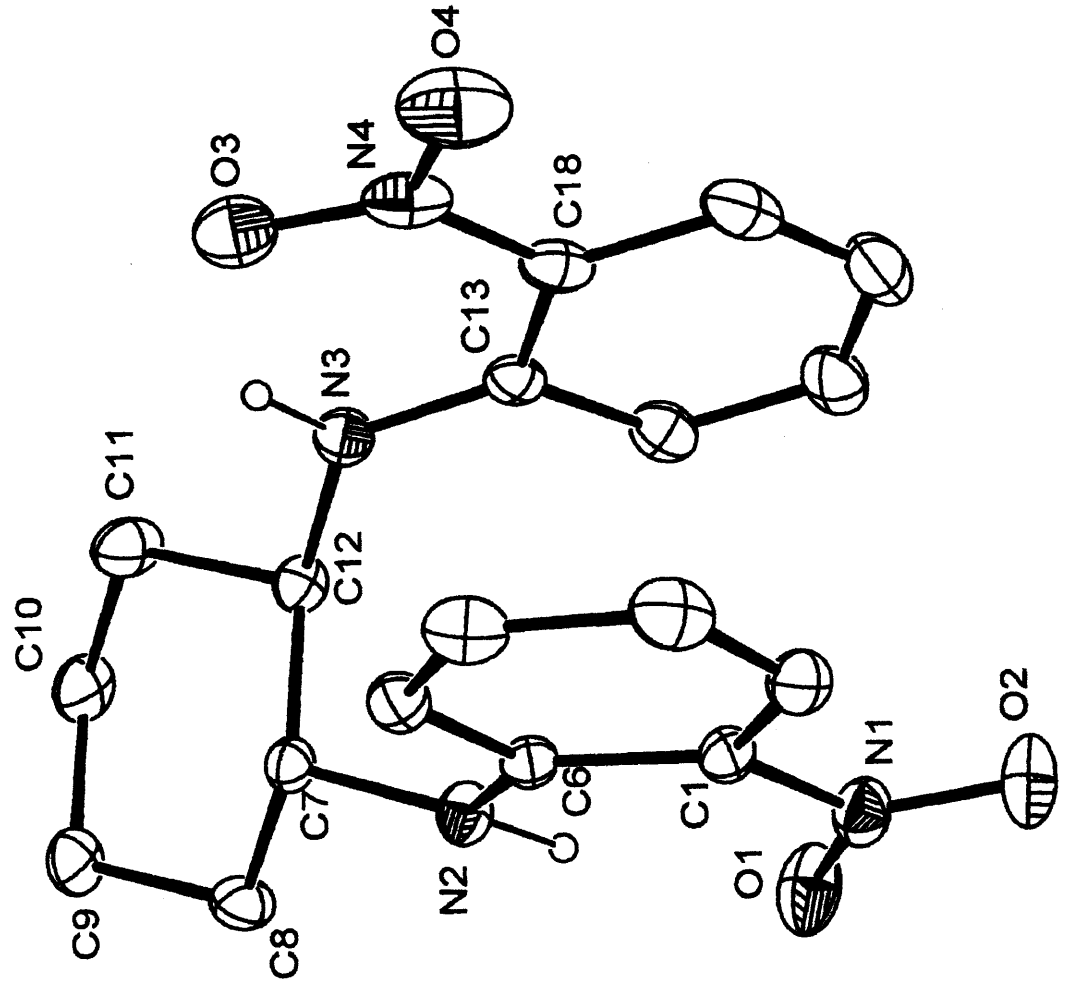


Figure 3.1: Crystal structure of H_2L^1, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except those attached to N(2) and N(3) omitted for clarity.

Table 3.1 Selected bond distances (Å) and angles (°) for H_2L^1

C(1) -N(1) 1.427(8)	C(18) –N(4) 1.437(8)
N(3) –C(13) 1.357(9)	N(2) –C(6) 1.364(7)
N(3) –C(12) 1.456(8)	N(2) –C(7) 1.455(7)
C(13)-N(3)-C(12) 126.8(1)	C(6)–N(2)–C(7) 125.9(1)
N(2)–C(7)–C(12) 111.9(1)	N(3)–C(12)–C(7) 111.6(1)
N(2)–C(7)–C(8) 109.3(1)	N(3)–C(12)–C(11) 109.1(1)

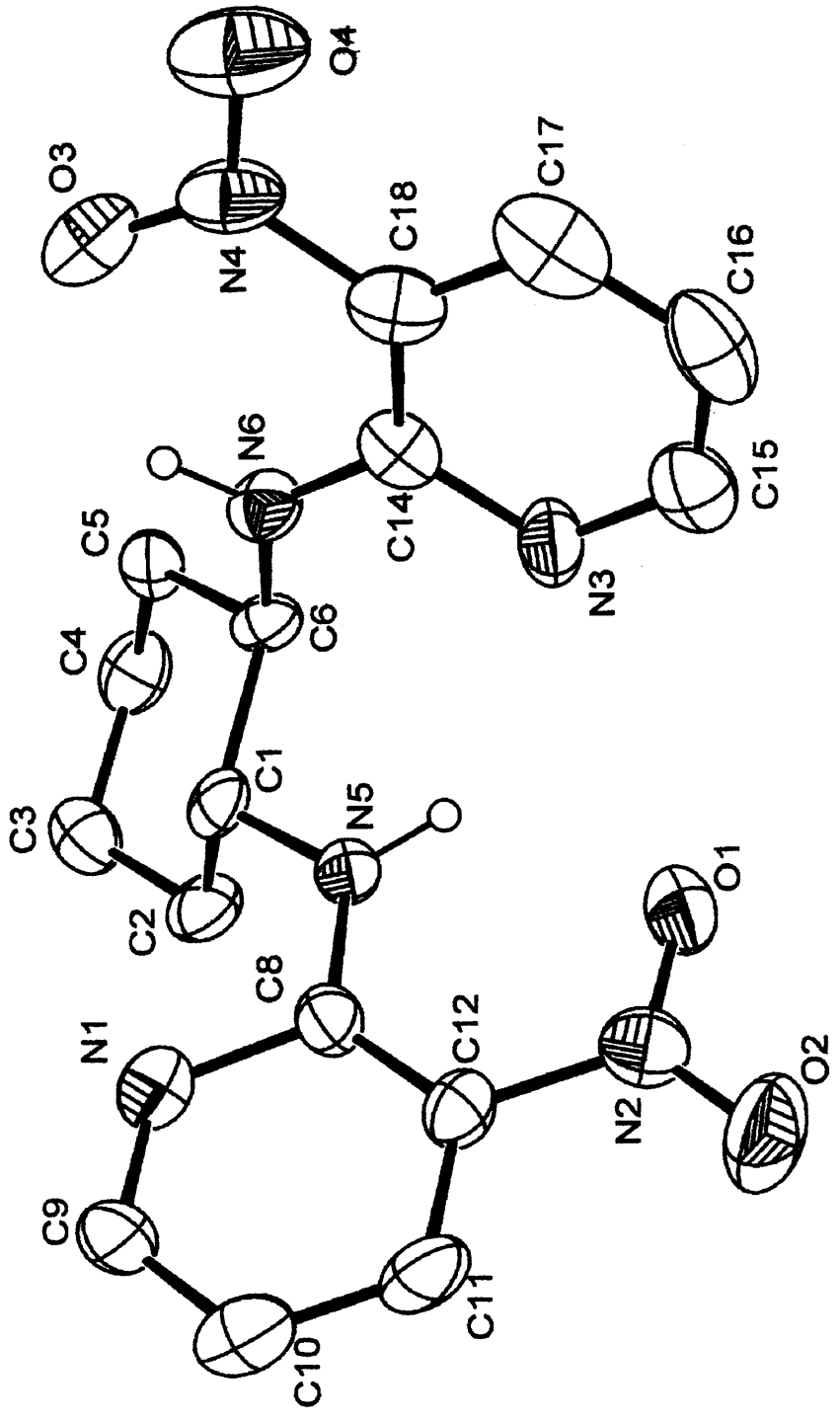
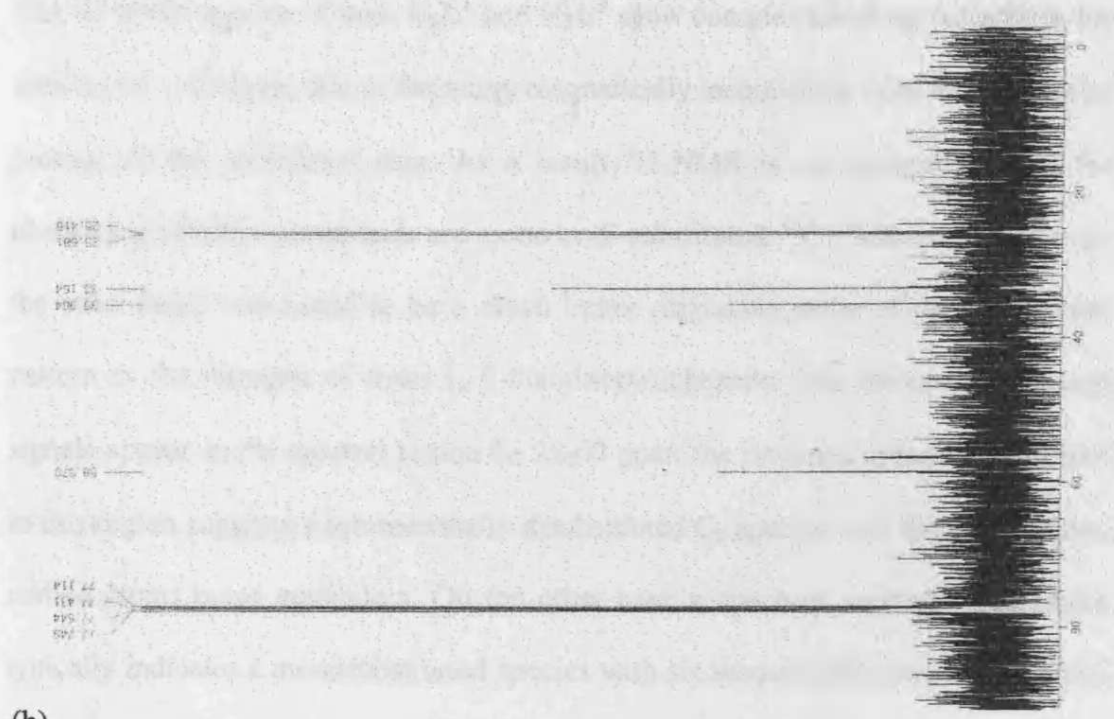


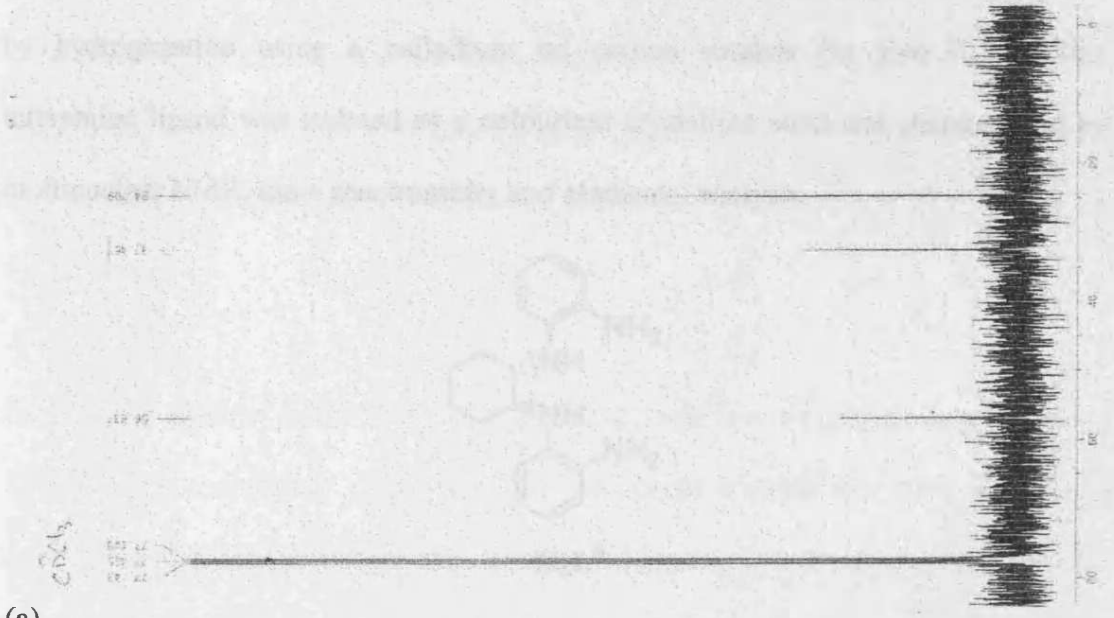
Figure 3.2: Crystal structure of H_2L^2, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except those attached to N(5) and N(6) omitted for clarity.

Table 3.2 Selected bond distances (Å) and angles (°) for H_2L^2.

C(12)–N(2) 1.432(10)	C(18)–N(4) 1.465(12)
N(1)–C(9) 1.325(8)	N(1)–C(8) 1.393(9)
N(3)–C(14) 1.350(9)	N(3)–C(15) 1.324(10)
C(1)–N(5) 1.471(8)	N(5)–C(8) 1.342(9)
C(6)–N(6) 1.424(8)	N(6)–C(14) 1.316(9)
C(1)–N(5)–C(8) 125.3(1)	C(6)–N(6)–C(14) 128.3(1)
N(5)–C(1)–C(6) 113.5(1)	N(6)–C(6)–C(1) 112.3(1)
N(5)–C(1)–C(2) 112.2(1)	N(6)–C(6)–C(5) 112.9(1)



(b)

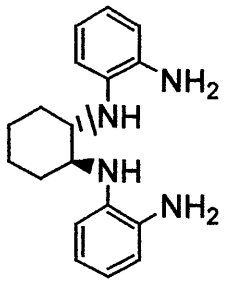


(a)

Figure 3.3: Examples of the ^{13}C NMR spectra in the cyclohexyl region for (a) symmetrically disubstituted; and (b) monosubstituted *trans*-1,2-diaminocyclohexane derivatives.

The ^{1}H NMR spectra of both $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ show complex coupling patterns in the area δ_H 1.0 - 4.5 ppm, due to the many magnetically inequivalent axial and equatorial protons of the cyclohexyl ring. As a result ^{1}H NMR is not generally useful for identifying whether compounds are mono or di-substituted. ^{13}C NMR spectroscopy on the other hand, was found to be a much better diagnostic probe of the substitution pattern at the nitrogen of *trans*-1, 2-diaminocyclohexane. The relevant cyclohexyl signals appear in the spectral region δ_C 25-60 ppm; the presence of three resonances in this region suggests a symmetrically disubstituted C_2 species with three sets of two carbon atoms being equivalent. On the other hand a spectrum containing six peaks typically indicates a monosubstituted species with six inequivalent cyclohexyl carbon atoms (Figure 3.3).

Ligand $H_2\mathbf{L}^1$ was further modified by converting the nitro groups to primary amines by hydrogenation using a palladium on carbon catalyst (to give $H_6\mathbf{L}^8$). This tetraamine ligand was isolated as a colourless crystalline solid and characterised by multinuclear NMR, mass spectrometry and elemental analysis.



$\mathbf{H_6L^8}$

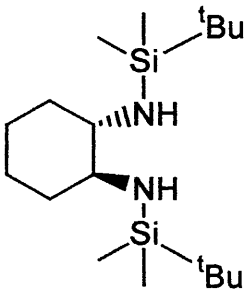
Reaction of 4-fluoronitrobenzene with *trans*-1,2-diaminocyclohexane under the same conditions applied to the synthesis of $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ however, yields the *mono*-substituted species $H_2\mathbf{L}^3$ as a bright yellow powder. Several attempts were made to synthesise the disubstituted species. Firstly, 4-fluoronitrobenzene and potassium

carbonate were used in greater excess (four equivalents rather than two). A second strategy was to raise the temperature of the reaction from 81-82°C (refluxing acetonitrile) to 132°C (refluxing chlorobenzene). These methods proved to be unsuccessful as determined from analysis of the ^{13}C NMR spectra of the isolated reaction products. In both cases these showed the characteristic six cyclohexyl peaks of the *mono*-substituted species $H_3\mathbf{L}^3$. In a final attempt to synthesise the disubstituted species, $H_3\mathbf{L}^3$ was reacted with one equivalent of *n*-butyllithium at -78°C, followed by one equivalent of 4-fluoronitrobenzene at room temperature in thf. No further substitution occurred. Raising the temperature to 60°C for several hours after the addition of 4-fluoronitrobenzene did not induce substitution to the disubstituted species. A possible reason for the observed lack of further reactivity is that the secondary amine in $H_2\mathbf{L}^3$ is likely to be more acidic than the target primary amine. If deprotonation takes place at the (nitrobenzene substituted) secondary amine, subsequent attack by a further fluoronitrobenzene molecule would be hindered by the steric bulk of the existing aryl functionality. It should be noted that an alternative synthesis for $H_3\mathbf{L}^3$ using different reaction conditions has been reported previously by Smith et al.[12]

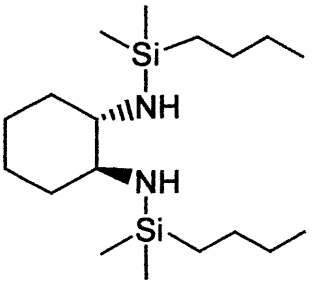
In a similar manner, reaction of 2-fluoropyridine with *trans*-1,2-diaminocyclohexane in refluxing acetonitrile with potassium carbonate yielded the *mono*-substituted species $H_3\mathbf{L}^4$. Attempts to form the disubstituted species by utilising similar strategies employed for $H_3\mathbf{L}^3$ again proved unsuccessful. The ^{13}C NMR spectrum of the isolated product in each case showed the six cyclohexyl peaks characteristic of a mono-substituted *trans*-1,2-diaminocyclohexane species. Synthesis of $H_3\mathbf{L}^4$ from the

corresponding aryl bromide using a palladium catalysed route has been reported in the literature.[13]

Bochmann has reported a bis(trimethylsilyl) substituted *trans*-1,2-diaminocyclohexane species, synthesised from chlorotrimethylsilane, which when complexed to zirconium gives a complex which shows moderate polymerisation activity towards ethylene.[14] It therefore seemed logical to explore analogous compounds, as there are many readily available chlorosilanes which allow for significant variation in steric properties. For this purpose *n*-butyldimethylsilylchloride and *t*-butyldimethylsilylchloride were chosen. Using substitution reactions analogous to those described by Bochmann,[14] *t*-butyldimethylsilylchloride and *n*-butyldimethylsilylchloride where reacted with diaminocyclohexane to yield H_2L^{13} and H_2L^{14} respectively. Both compounds are oils at room temperature, typically pink/brown in colour, which were characterised by multinuclear NMR and mass spectrometry.



H_2L^{12}



H_2L^{13}

Once again ^1H NMR spectroscopy was not useful in identifying the substitution pattern of the products, although the prochiral methyl groups, which are bonded to the silicon, are easily identified. In the case of H_2L^{13}, the signals due to the *n*-butyl group appear in the same spectral region as the cyclohexyl protons and as a result, overlapping of some signals occurs making interpretation especially difficult. The ^{13}C

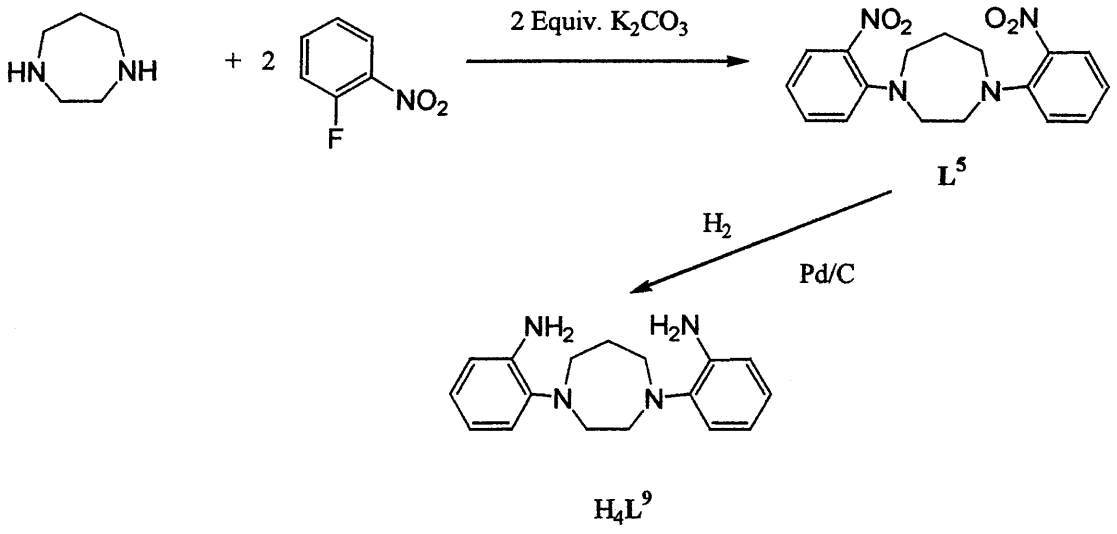
NMR spectrum is more useful for characterising $H_2\mathbf{L}^{12}$ and $H_2\mathbf{L}^{13}$. However, the ^{13}C NMR for $H_2\mathbf{L}^{13}$ is again complicated due to the overlap of the cyclohexyl and C_4H_9 signals. Both $H_2\mathbf{L}^{12}$ and $H_2\mathbf{L}^{13}$ give very clean mass spectra with the molecular ion being evident as the strongest peak in each case.

3.3.2 Ligands Based on Linear, Cyclic and Macrocyclic Amine Derivatives

3.3.2.a Ligands from Azacycloamines

A number of compounds were synthesised based around a 1,4-diazacycloheptane (homopiperazine) backbone. Unlike *trans*-1,2-diaminocyclohexane, homopiperazine does not offer the possibility for C_2 symmetric systems but it was chosen as a potential ligand backbone as it is easy to functionalise at the amine nitrogens to produce a variety of donor sets. The starting point for such ligands was compound $\mathbf{L}^5$ illustrated in Scheme 3.2, which was synthesised by nucleophilic aromatic substitution (S_NAr) of the fluorine substituents of 2-fluoronitrobenzene.

Once again ^{13}C NMR spectroscopy allied to mass spectrometry gives the clearest information as to the nature of the product. Three peaks in the spectral region δ 30-60 ppm indicate a disubstituted 1,4-diazacycloheptane compound. $\mathbf{L}^5$ is an orange crystalline compound which has been characterised by multinuclear NMR and IR spectroscopies, mass spectrometry and elemental analysis.



Scheme 3.2

$\mathbf{L^5}$ was subsequently hydrogenated to convert the nitro groups to primary amines thereby giving $H_4\mathbf{L^9}$. This functional group conversion was achieved by using a palladium on carbon catalyst and an atmosphere of hydrogen. $H_4\mathbf{L^9}$ is a pale pink crystalline solid which has been characterised by multinuclear NMR and IR spectroscopies, mass spectrometry and elemental analysis. In addition, the crystal structure of $H_4\mathbf{L^9}$ is depicted in Figure 3.4 and relevant bond lengths and angles listed in Table 3.3

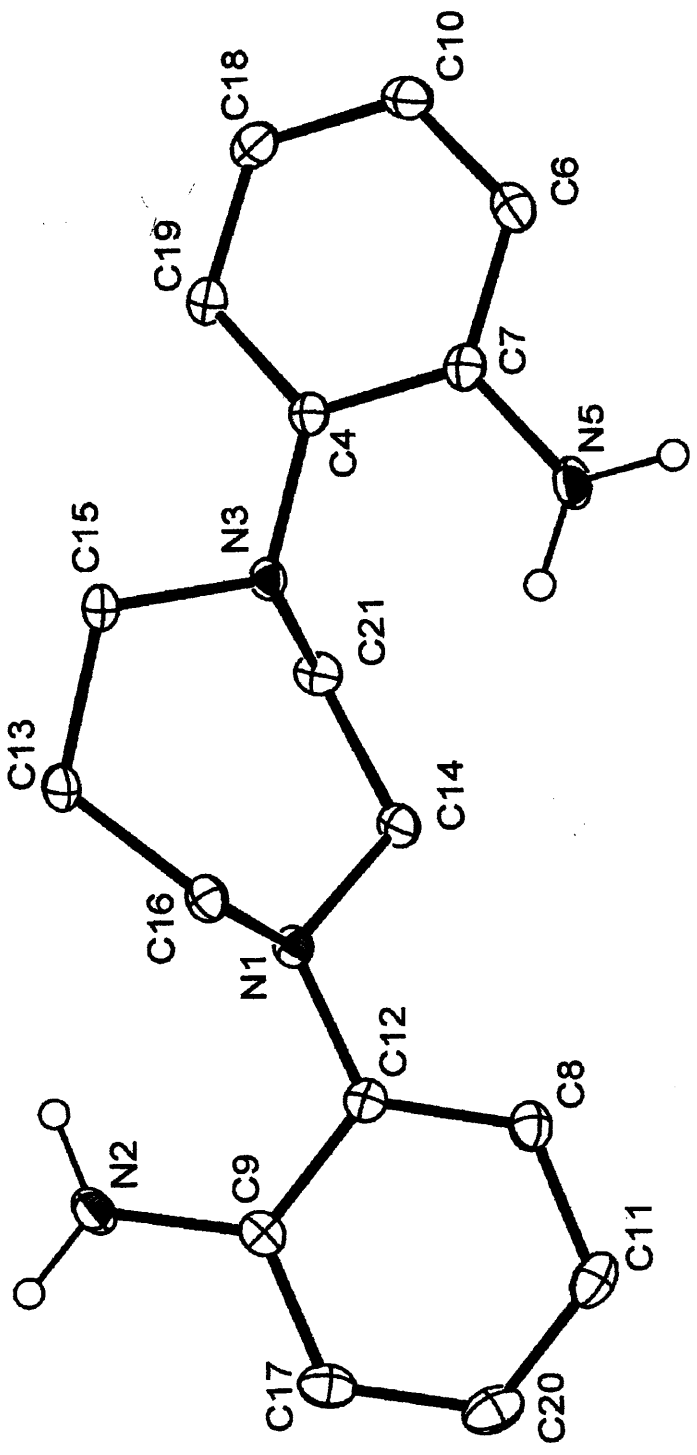
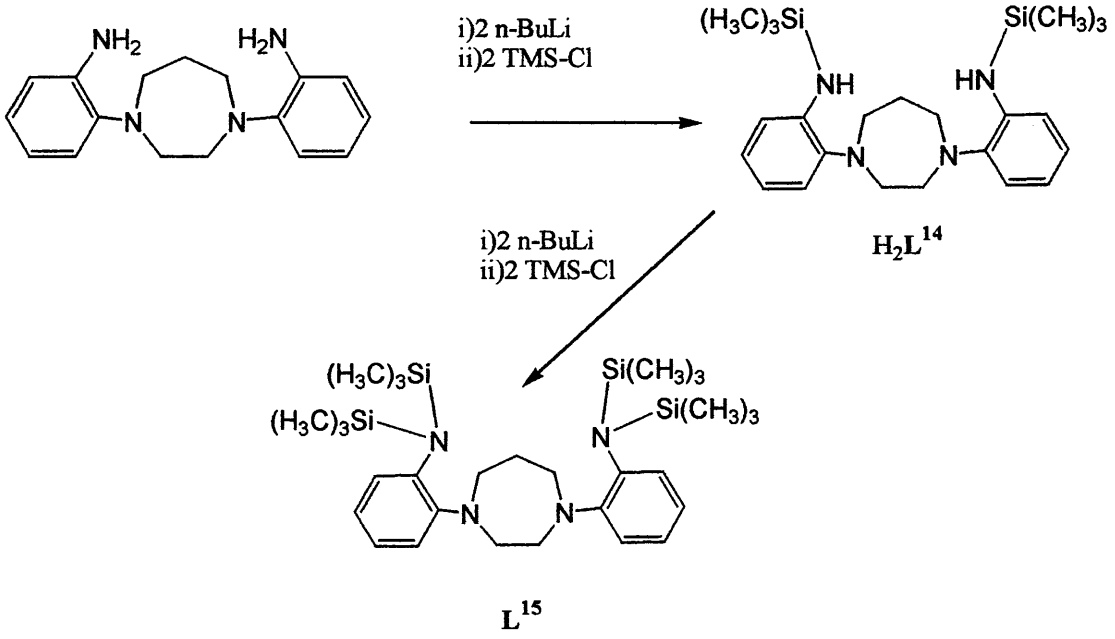


Figure 3.11: Crystal structure of H_4L^9, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except those attached to N(2) and N(5) omitted for clarity.

Table 3.3 Selected bond distances (Å) and angles (°) for H_4L^9

N(2)–C(9) 1.407(2)	N(5)–C(7) 1.399(2)
N(1)–C(12) 1.433(2)	N(3)–C(4) 1.434(2)
N(1)–C(14) 1.459(2)	N(3)–C(21) 1.478(2)
N(1)–C(16) 1.483(19)	N(3)–C(15) 1.463(19)
N(2)–C(9)–C(12) 119.9 (2)	N(5)–C(7)–C(4) 119.2 (2)
C(12)–N(1)–C(16) 112.8 (1)	C(15)–N(3)–C(21) 114.9 (1)
C(16)–N(1)–C(14) 112.0 (1)	C(4)–N(3)–C(15) 114.7(1)

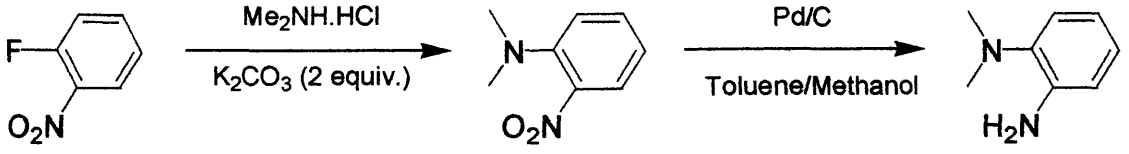
Further functionalisation of the primary amines leads to the formation of two new compounds, H_2L^{14} and L^{15} (Scheme 3.3). The introduction of bulky trimethylsilyl groups was designed to probe steric effects on coordination properties. Both H_2L^{14} and L^{15} are oils and have been characterised by multinuclear NMR and mass spectrometry.



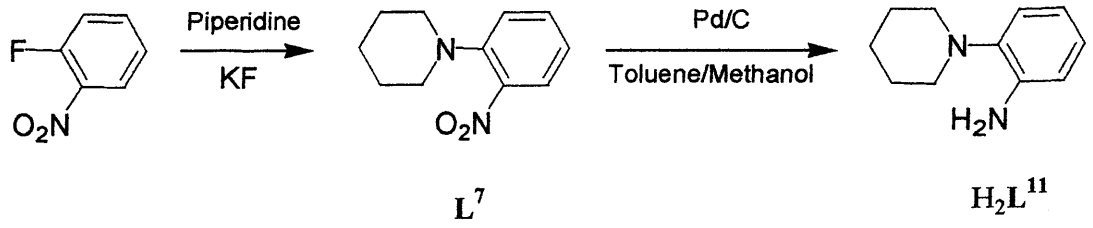
Scheme 3.3

The functionalisation of the amine with trimethylsilyl groups was achieved by reacting H_4L^9 with *n*-butylithium followed by chlorotrimethylsilane. Compound L^{15} was synthesised from H_2L^{14} by repeating the addition with a further two equivalents of *n*-butyllithium and chlorotrimethylsilane. Substitution of the second hydrogen atom of the amine required a longer reaction time (72 h as opposed to 12 h). This presumably reflects the somewhat more sterically shielded environment in H_2L^{14} compared to that in H_4L^9.

The use of azacyclohexane as a ligand backbone was also invesigated, in order to provide bidentate systems to contrast with the tetra-dentate ligands based on 1,4-diazacycloheptane. Another reason for this choice of framework was to create new ligands which would have similar features (i.e. a combination of neutral and anionic donors) to those reported by Mitsui Chemicals,[8] which are known to give highly active titanium-based polymerisation catalysts. Compounds $H_2\mathbf{L}^6$ and $\mathbf{L}^7$ were synthesised from 2-fluoronitrobenzene and the appropriate amine (Schemes 3.4 and 3.5). Both reactions were achieved by heating the starting materials and a base, K_2CO_3 or KF, to 130°C in a pressure tube. The synthesis of $\mathbf{L}^7$ was performed under solvent free conditions, as both 2-fluoronitrobenzene and monoazacyclohexane are liquids. $\mathbf{L}^7$ was recrystallised from acetonitrile as a bright orange solid. On the other hand, reaction of 2-fluoronitrobenzene and dimethylamine hydrochloride yields $H_2\mathbf{L}^6$ as a bright orange oil. The hydrochloride salt was used for convenience, as dimethylamine is a gas a room temperature and is much more difficult to handle. This reaction is very low yielding presumably because deprotonation of $Me_2NH_2^+$ requires a stronger base. Other methods of synthesis for H_2L^6 [15,16] and L^7 [17,18] have been reported. $H_2\mathbf{L}^6$ was characterised by multinuclear NMR and IR spectroscopies, mass spectrometry and elemental analysis. The same characterising data was collected for the oil $\mathbf{L}^7$ with the exception elemental analysis which could not be obtained



$H_2\mathbf{L}^6$ $H_2\mathbf{L}^{10}$

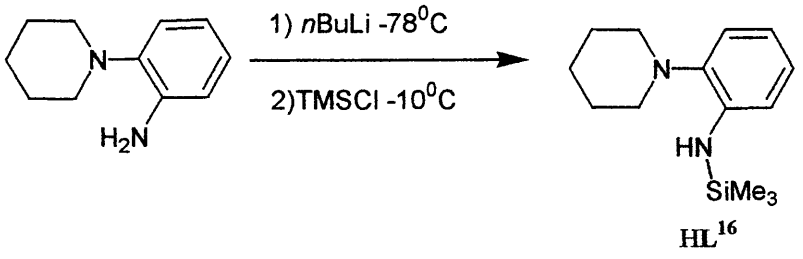


L^7 H_2L^{11}

Schemes 3.4 and 3.5

H_2L^6 and L^7 were subsequently hydrogenated using a palladium on carbon catalyst to give the respective primary amines H_2L^{10} and H_2L^{11}. A similar palladium catalysed hydrogenation of 2-nitrophenyl derivatives of dimethylamine and piperidine was published during the course of research.[20] H_2L^{10} and H_2L^{11} were characterised by multinuclear NMR and mass spectrometry.

Reaction of H_2L^{11} with *n*-butyllithium followed by chlorotrimethylsilane (Scheme 3.6) yielded HL^{16} as a pale pink oil which was characterised by multinuclear NMR and mass spectrometry.

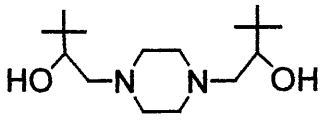


HL^{16}

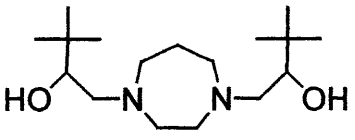
Scheme 3.6

3.3.2.b Alkoxides via ring opening of 3,3-dimethyl-1, 2-epoxybutane

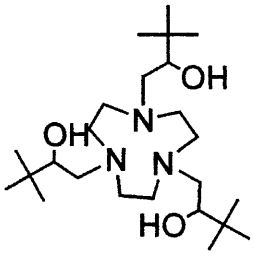
A series of compounds H_2L^{17}- HL^{21} was synthesised by ring opening of 3,3-dimethyl-1, 2-epoxybutane by a secondary amine. All reactions were performed under forcing conditions in a pressure tube with an excess of racemic epoxide at 100°C. [12] For cyclic amines it was found that the larger ring sizes required longer the reaction times. Thus synthesis of H_2L^{17} required 24 h for completion, in contrast to HL^{21}, which took 72 h to give comparable yields. Compounds H_2L^{17} and H_2L^{18} are white crystalline solids and have been characterised by multinuclear NMR, IR spectroscopy and mass spectrometry, for H_2L^{18} elemental analysis was also obtained. In addition, the crystal structure of H_2L^{17} is shown in Figure 3.5 and selected bond lengths and angles listed in Table 3.4. The unit cell of H_2L^{17} contains both S,S and R,R enantiomers. The ^1H and ^{13}C NMR spectra of crystalline H_2L^{17} show only one *tert*-butyl peak, which, when supported by the crystal structure data, indicates that it is the R,R/S,S pair of enantiomers that crystallise out of the reaction mixture with the diastereoisomeric pair R,S/S,R remaining in solution.



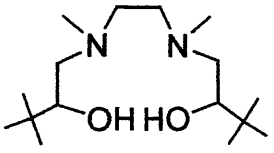
H_2L^{17}



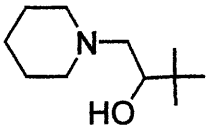
H_2L^{18}



H_3L^{19}



H_2L^{20}



HL^{21}

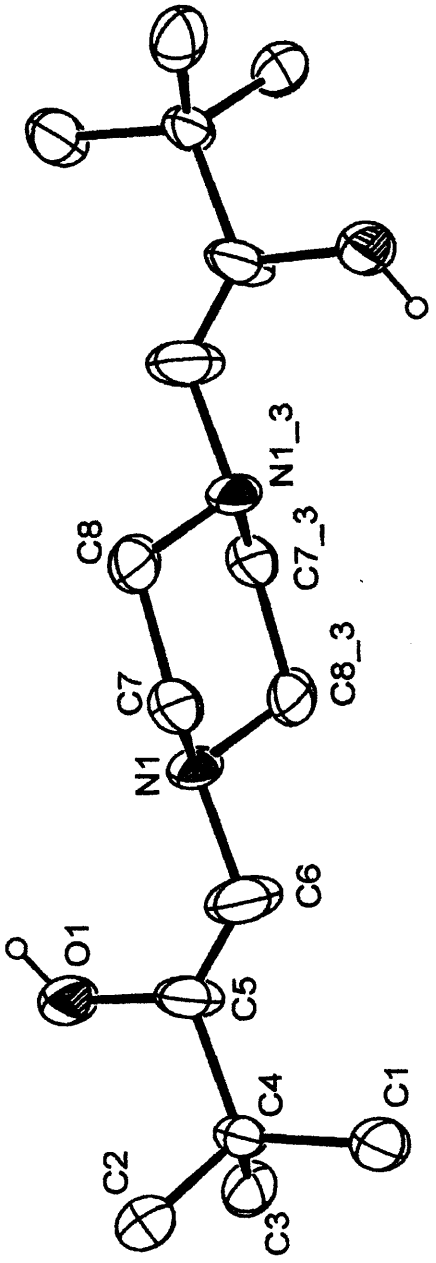


Figure 3.5: Crystal structure of H_2L^{17}, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms except those attached to O(1) and O(1_3) omitted for clarity. The molecule sits on a centre of inversion, with one half comprising the asymmetric unit.

Table 3.4 Selected bond lengths (Å) and angles (°) for H_2L[17]

N(1)–C(7) 1.457(14)	N(1)–C(6) 1.457(15)
O(1)–C(5) 1.423(10)	C(4)–C(1) 1.527(11)
C(7)–N(1)–C(6) 111.2 (1)	C(6)–C(5)–O(1) 121.8 (1)
C(2) –C(4) –C(3) 109.2 (7)	

Although H_2L^{18} was also obtained as a white crystalline solid, the crystals obtained were not suitable for X-ray diffraction. The absolute configuration of H_2L^{18} was determined from the crystal structure of a complex obtained by the reaction with nickel perchlorate (*vide infra*). Once again the presence of only one *tert*-butyl peak in the ^{1}H and ^{13}C NMR spectra indicated that one set of diastereomers was present. Examination of the X-ray diffraction data showed that the coordinated ligand was of either the R,R or S,S stereochemistry.

H_2L^{20} and HL^{21} are liquids at room temperature and were characterised by multinuclear NMR and mass spectrometry. Alternative methods for the synthesis of HL^{21} have been published previously.[20,21] Cooling of H_2L^{20} to -25°C causes it to become a waxy solid. Compound H_2L^{20} was synthesised from *N,N'*-dimethylethylenediamine and racemic 3,3-dimethyl-1,2-epoxybutane. The ^{13}C NMR spectrum of isolated H_2L^{20} clearly shows the presence of two diastereoisomers. Separation of these diastereoisomers was not attempted, as fractional crystallisation was impractical due to the compound being a liquid at room temperature. It was felt that reaction of H_2L^{20} (as a mixture of diastereoisomers) with metal precursors might lead to diastereomeric complexes which (being solids) would be easier to separate by fractional crystallisation.

3.4 Conclusions

The syntheses of two groups of ligand have been successfully achieved:

i) Precursors to amide ligands, based on C_2 symmetric *trans*-diaminocyclohexane and also cyclic amines such as 1,4-diazacycloheptane.

ii) A related group of ligands containing pendant alkoxide donors has been synthesised from both linear and cyclic amine precursors.

Properties such as ring size and number and spatial distribution of donors have been systematically modified to give a series of related ligands whose coordination chemistry can now be investigated.

References

1. G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem., Int. Ed.*, 1999, **38**,428-447

2. V.C. Gibson, S. K. Spitzmesser, *Chem. Rev.*, 2003, **103**, 283-315

3. V. C. Gibson, B. S. Kimberley, A. J. P. White, D. J. Williams, P Howard, *Chem.Commun.*, 1998, 313.

4. G. J. P. Britovsek, V. C. Gibson, B. S. Kimberley, P. J. Maddox, S. J. McTavish, G. A. Solan, A. J. P. White, D. J. Williams, *Chem. Commun.*, 1998, 849-850

5. E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.*, 2000,379.

6. B. L. Small, M. Brookhart, A. M. A. Bennett, *J. Am. Chem. Soc.*, 1998, **120**, 4049.

7. G. J. P. Britovsek, *Chem. Commun.*, 1998, 849.

8. J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshall, J. C. Calabrese, S. D. Arthur, *Organometallics*, 1997, **16**, 1514.

9. S. Matsui, T. Fujita, *Catalysis Today*, **66**, 2001, 63-73. Mitsui Chemicals, Inc. Tokyo *EP 0874 005 A1.*

10. R. R. Strevens, PhD thesis, Cardiff University, 2002.

11. S. M. S. V Wardell, J. L. Wardell, M. F. Ward, J. N. Low, C. Glidewell, *Acta Cryst.allographica*, 2000, **C56**, 865.

12. H.E. Smith, W.I. Cozart, T. De Paulis, F. M. Chen, *J. Am. Chem. Soc.* 1997, **101**, 18..

13. C.G. Frost, P. Mendonca. *Tetrahedron: Asymmetry* 1999, **10**, 1831.

14. N. A. H. Male, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans*, 1997,2487-2494

15. H. Firouzabadi, N. Iranpoor, H. Alinezhad, *Bull. Chem. Soc. Japan*, 2003, **76**, 143.

16. A. H. Khuthier, J. M. A. Al-Rawi, A. K. Al-Kazzaz, M. A. Al-Iraqi, *Org. Magn. Reson,*, 1982, **18**, 104.

17. M. Abou-Gharbia, M.E. Freed, R.J. M^{c}Caully, P.J. Silver, R.L. Wendt, *J. Med. Chem.* 1984, **27** 1743.

18. C. Boga, P. Guardia, *Gazz. Chim. Ital.*, 1997, **127**, 259.

19. S. DeCastro, R. Chicharro, V.J. Aran, *J. Chem. Soc., Perkin Trans. 1*, 2002, 790.

20. D. W. Hoard, E. J. Moher, J.A. Turpin, *Organic Process Research and Development* 1999, **3,** 64.

21. M. Hayashi, F. Okamura, T. Toba, N. Oguni, B. Sharpless, *Chem. Lett.* 1990, **4,** 547.

Chapter Four

Complexation Studies

4.1 Introduction

In general, for a complex to be active for olefin polymerisation it must possess an electrophilic metal centre combined with two mutually cis coordination sites that are suitable for coordination of the monomer starting material and an alkyl ligand or growing polymer chain. A primary ligand is one that remains bound to the metal throughout activation and polymerisation, and can thereby control the electrophilicity of the metal; a more electrophilic metal centre would be expected to have greater affinity for coordination of the incoming monomer. A further function of the primary ligand is to protect the electron deficient metal centre (e.g. by steric factors) from undesirable deactivating side reactions.

Complexes of group 4 metals incorporating primary ligands with amide and alkoxide donors have been reported to be active for olefin polymerisation catalysis.[1-8] More specifically, the combination of amide or alkoxide donors with other softer and/or potentially hemi-labile donors such as thioethers or amines, can give catalysts with higher activities.[7,8,9,10]

4.1.1 Aims of Research

The aims of the research outlined in this chapter were to investigate the coordination chemistries of some of the ligands synthesised in chapter three with two main aims:

(i) To create a better understanding of the coordination chemistry of mixed amide/amine and alkoxo/amine donors with group 4 metals.

(ii) To produce precatalysts for olefin polymerisation with mutually cis coordination sites and, preferably also with C_2 symmetry.

A number of synthetic approaches to these complexes were to be investigated, including (i) direct reaction of the protonated forms of the ligands with appropriately basic group 4 precursors such as alkyls or alkoxides, and (ii) initial deprotonation of the ligand by an external base such as *n*-butyllithium, followed by metal-centred substitution of existing chloride ligands. In addition, the coordination chemistry of these ligand systems towards other transition metals such as nickel and towards the main group metal aluminium were investigated for comparative purposes.

4.2 Experimental

4.2.1 Complexes of the group 4 metals titanium and zirconium

Reactions with tetrabenzyl zirconium

Under Schlenk conditions, a toluene solution of the ligand was added dropwise to a toluene solution of tetrabenzyl zirconium at -78°C. When addition was complete the reaction mixture was allowed to warm to room temperature and stirred for a further 12

h. This method was applied to ligands $H_2\mathbf{L}^1$, $H_2\mathbf{L}^2$, $H_2\mathbf{L}^{12}$, $H_2\mathbf{L}^{13}$, $H_2\mathbf{L}^{14}$ and $\mathbf{L}^{15}$ but no tractable products were obtained. In all cases a dark brown powder was isolated. The ^1H and ^{13}C NMR spectra of each sample gave no recognisable pattern of signals.

Reactions with tetrachloro*bis*(tetrahydrofuran)zirconium(IV)

Under Schlenk conditions, ^{n}BuLi was added to an ether or thf solution of the ligand at -78°C. This solution was allowed to warm to room temperature and stirred for a further 1 h. The reaction mixture was then added to a thf or ether solution of tetrachloro*bis*(tetrahydrofuran)zirconium(IV) at -78°C, allowed to return to room temperature and stirred for a further 12 h. This method was applied to ligands $H_2\mathbf{L}^1$, $H_2\mathbf{L}^2$, $H_2\mathbf{L}^{12}$, $H_2\mathbf{L}^{13}$, $H_2\mathbf{L}^{14}$ and $\mathbf{L}^{15}$ but no tractable products were obtained. In each case the ^1H and ^{13}C NMR spectra showed broad unidentifiable signals.

Reactions with tetrachloro*bis*(tetrahydrofuran)titanium(IV)

The same reaction conditions were used as outlined above but using tetrachloro*bis*(tetrahydrofuran)titanium(IV) in place of its zirconium analogue. This method was applied to ligands $H_2\mathbf{L}^1$, $H_2\mathbf{L}^2$, $H_2\mathbf{L}^{12}$ and $H_2\mathbf{L}^{13}$ but no tractable products were obtained. ^1H and ^{13}C NMR spectra showed unidentifiable signals or unreacted ligand.

The ligands $\mathbf{L}^5$-$\mathbf{L}^7$ and $H_2\mathbf{L}^{10}$ which were synthesised in the previous chapter were precursors for other ligands and as such reactions with metals were not attempted. $H_6\mathbf{L}^8$ and $H_4\mathbf{L}^9$ were reacted with benzaldehyde in an attempt to form Schiff base type ligands, but these reactions proved unsuccessful as the products were oils which were only formed in extremely low yields and were very 'dirty'.

$L^{18}Ti_2(O^iPr)_6$

Under Schlenk conditions, neat titanium tetrakis(isopropoxide) (0.50 ml, 1.76 mmol) was added to a sample of *N,N'-bis*(2-hydroxy-3,3-dimethylbutyl)-diazacycloheptane H_2L^{18} (0.50 g, 1.66 mmol). The reaction mixture was stirred until it became solid, isopropanol formed during the reaction was then removed in vacuo and the resulting solid redissolved in dry hexane. Colourless crystals were grown by cooling the hexane solution to -30°C (0.79 g, 64 %). ^{1}H NMR (C_6D_6, 25°C): δ 1.00 (s, 18H, C(CH_3)$_3$), 1.37 (d, J = 6.0 Hz, 36H, CH(CH_3)$_2$), 1.85 (m, 2H, NCH$_2$CH_2CH$_2$N), 2.55 (m, 2H, NCH(H)CHOH), 2.84 (m, 2H, NCH(H)CHOH), 3.50 (b overlapping m, 8H, NCH$_2$ of diazacycloheptane), 4.08 (m, 2H, C(H)O), 4.92 (septet, J = 6.0 Hz, 6H, CH(CH$_3$)$_2$). ^{13}C NMR (C_6D_6, 25°C): 26.3 (CH$_3$ of C(CH_3)$_3$), 27.8 (CH$_3$ of CH(CH_3)$_2$), 31.1 (NCH$_2$CH$_2$CH$_2$N), 35.6 (quaternary of C(CH$_3$)$_3$), 58.1 (NCH$_2$CH$_2$CH$_2$N), 60.1 (NCH$_2$CH$_2$N), 62.3 (NCH$_2$C(H)OH), 77.4 (CH of CH(CH$_3$)$_2$). Elemental analysis, calculated for $C_{35}H_{76}N_2O_8Ti_2$ 56.15 % C, 10.23 % H, 3.74 % N, measured 55.61 % C, 10.01 % H, 3.89 % N. Mass spec (FAB) 747.3 (M-H)$^+$.

$[L^{18}Ti(OEt)]_2(\mu_2\text{-}O)$

L^{18}Ti(OEt)]$_2$(μ_2-O) was prepared from titanium tetrakis(ethoxide) (0.40 ml, 1.75 mmol) and H_2L^{18} (0.50 g, 1.66 mmol) using the method detailed above for $L^{18}Ti_2(O^iPr)_6$. The product was isolated in very low yield as colourless crystals obtained from hexane solution. Complete characterization was frustrated in this case by the small amount of crystalline compound obtained. ^{1}H NMR (C_6D_6, 25°C): δ 0.99 (s, 36H, C(CH_3)$_3$), 1.21 (t, J = 8.0 Hz, 6H, OCH$_2$CH_3), 1.88 (m, 4H, NCH$_2$CH_2CH$_2$N), 2.68 (b m, 4H, NCH(H)CHOH), 2.78 (m, 4H, NCH(H)CHOH),

3.20-3.68 (b overlapping m, 16H, NCH_2 of diazacycloheptane), 3.91 (q, J = 8.0 Hz, 4H, OCH_2CH_3), 4.15 (m, 2H, C(*H*)O). Mass spec. (FAB) 799.6$(M\text{-}H)^+$.

$(L^{20})_2Zr$

$(L^{20})_2Zr$ was prepared from zirconium tetrakis(propoxide) (0.9 ml of a 70% wt solution in propanol, 1.92 mmol) and N,N'-*bis*(2-hydroxy-3,3-dimethylbutyl)dimethylethylenediamine, H_2L^{20} (0.50 g, 1.74 mmol) using the method detailed above for $L^{18}Ti_2(O^iPr)_6$, and isolated as colourless crystals from a concentrated hexane solution (0.88 g, 69 %). ^1H NMR (C_6D_6, 25°C): δ 1.08 (s, 18H, $C(CH_3)_3$), 1.10 (s, 18H, $C(CH_3)_3$), 3.14 (t, J = 12.0 Hz, 2H, OC*H*) 3.29 (t, J = 11.6 Hz, 2H, OC*H*), 2.14 (s, 6H, NCH_3), 2.18-2.87 (broad unresolvable signal, 8H, NCH_2CHO), 2.91 (s, 6H, NCH_3), 3.78 (dd, J = 2.6, 11.1 Hz, 2H, NCH_2CH_2N), 4.06 (dd, J = 4.1, 11.1 Hz, 2H, NCH_2CH_2N), 4.09 (dd, J = 5.1, 11.4 Hz, 2H, NCH_2CH_2N), 4.37 (dd, J = 4.4 Hz, 11.5 Hz, 2H, NCH_2CH_2N). ^{13}C NMR (C_6D_6, 25°C): δ 26.9, 27.2 ($C(CH_3)_3$), 35.2, 35.3 ($C(CH_3)_3$), 43.4 (NCH_3), 48.6 (NCH_3), 57.2 (*C*HO) 58.9 (*C*HO),60.4 (CH_2CHO), 64.5 (CH_2CHO), 78.9 (NCH_2), 83.9 (NCH_2). Elemental analysis, calculated for $C_{32}H_{68}N_4O_4Zr$ 57.87 % C, 10.32 % H, 8.44 % N, measured 57.41 % C, 10.00 % H, 8.59 % N. Mass spec. (EI) 661.3 $(M\text{-}H)^+$. Exact mass: calc. for $ZrC_{32}H_{68}N_4O_4$ 661.4204, meas. 661.4187.

$L^{20}Ti(O^iPr)_2$

$L^{20}Ti(O^iPr)_2$ was prepared from titanium tetrakis(isopropoxide) (0.50 ml, 1.76 mmol) and H_2L^{20} (0.50 g, 1.74 mmol) using the method detailed above for $L^{18}Ti_2(O^iPr)_6$, and isolated as colourless crystals after two recrystallizations from concentrated hexane solution (0.90g, 64 %). Although the oily precursor H_2L^{20} was used as a mixture of

rac (R,R/S,S) and meso (R,S) isomers, X-ray diffraction analysis of the crystalline product reveals that it contains solely the C_2 symmetric (R,R/S,S) pair of enantiomers. The remaining oily residue can be shown by ^1H and ^{13}C NMR to be the C_1 symmetric complex derived from the R,S ligand precursor. Characterizing data for crystalline product (R,R/S,S): ^1H NMR (C_6D_6, 25°C): δ 1.15 (s, 18H, C(CH_3)$_3$), 1.39 (d, J = 6.3 Hz, 6H, C(CH_3)$_2$), 1.54 (d, J = 6.0 Hz, 6H, C(CH_3)$_2$), 2.14 (dd, J = 10.7, 4.1 Hz, 2H, NCH_2CH_2N), 2.22 (s, 6H, NCH_3), 2.42 (d, J = 9.0 Hz, 2H, NCH_2CHO), 2.73 (d, J = 9.0 Hz, 2H, NCH_2CHO), 3.09 (t, J = 12.0 Hz, 2H, OCHCH_2N), 3.83 (dd, J = 10.6, 4.1 Hz, 2H, NCH_2CH_2N), 5.14 (sept, J = 6.0 Hz, 2H, CH(CH_3)$_2$). ^{13}C NMR (C_6D_6, 25°C): δ 26.0, 26.4 (C(CH_3)$_3$), 36.5 (C(CH_3)$_3$), 45.3 (NCH_3), 51.9 (NCH_2 backbone), 62.8 (NCH_2 ligand arm), 74.6 (C(CH_3)$_2$), 84.2 (CHO). Elemental analysis, calculated for $C_{22}H_{48}N_2O_4Ti$ 58.40 % C, 10.69 % H, 6.19 % N, measured 58.01 % C, 10.14 % H, 6.24 % N. IR (KBr disk, cm^{-1}) 2958(s), 2855 (s), 1465 (md), 1390 (md), 1320(md), 1261 (md) and 1100(s).

^1H and ^{13}C NMR data for oily product (R,S): ^1H NMR (C_6D_6, 25°C): δ 0.96 (s, 9H, C(CH_3)$_3$), 1.11 (s, 9H, C(CH_3)$_3$), 1.31 (d, J = 3.6 Hz, 6H, C(CH_3)$_2$), 1.48 (d, J = 5.1 Hz, 6H, C(CH_3)$_2$), 1.67 (dd, J = 12.1, 4.1 Hz, 1H, NCH_2CH_2N), 1.82 (dd, J = 13. 9, 4.0 Hz, 1H, NCH_2CH_2N), 2.21 (s, 6H, NCH_3), 2.42 (d, J = 6.2 Hz, 2H, NCH_2CHO), 3.08 (t, J = 10.7 Hz, 1H, OCH), 3.15 (t, J = 10.6 Hz, 1H, OCH), 3.83 (dd, J = 10.4, 4.3 Hz, 1H, NCH_2CH_2N), 4.38 (dd, J = 9.5, 5.2 Hz, 1H, NCH_2CH_2N), 5.11 (sept, J = 6.1 Hz, 2H, CH(CH_3)$_2$). ^{13}C NMR (C_6D_6, 25°C): δ 25.9, 26.0 (C(CH_3)$_3$), 26.2, 26.3 (C(CH_3)$_3$), 26.6, 26.9 ((CH_3)$_2$C), 34. 7 ((CH_3)$_2C$), 47.9, 57.2 (NCH_3), 56.7, 59.2 (NCH_2 backbone), 59.4, 66.0 (NCH_2 ligand arm), 74.8, 74.9 (C(CH_3)$_2$), 84.8, 85.1 (CHO).

Reaction of H_3L^{19} with titanium tetrakis(isopropoxide)

The reaction of neat titanium tetrakis(isopropoxide) (0.60 ml, 1.32mmol) and N,N',N''-(2-hydroxy-3-dimethylbutyl)-triazacyclononane, $H_3\mathbf{L}^{19}$, (0.50 g, 1.16 mmol) was carried out using the method detailed above for $\mathbf{L}^{18}Ti_2(O^iPr)_6$. The product was isolated as a white powder in yields of 0.34 g (56 %). ^{1}H NMR (C_6D_6, 25°C): δ 0.95 (s, 9H, $C(CH_3)_3$), 1.05 (s, 9H, $C(CH_3)_3$), 1.18 (s, 9H, $C(CH_3)_3$), 2.50-2.91 (b overlapping m, 6H, NCH_2CHOH), 3.41-3.99 (b overlapping m, 12H, NCH_2CH_2N), 4.15 (b m, 2H, C(*H*)O). No ^{13}C NMR data was obtained due to the low solubility of complex. Mass spec. (APCI) 473.9 $(M+H)^+$.

Reaction of H_4L^{22} with zirconium tetrakis(propoxide)

The reaction of zirconium tetrakis(propoxide) (0.7 ml of a 70% wt solution in propanol, 1.5mmol) and N,N',N'',N'''-(2-hydroxy-3-dimethylbutyl)-1,4,7,10-tetraazacyclododecane, $H_4\mathbf{L}^{22}$, (0.10 g, 0.17 mmol) was carried out using the method detailed above for $L^{18}Ti_2(O^iPr)_6$. The product was isolated as a white powder in yields of 0.05 g (52 %). ^{1}H NMR (C_6D_6, 25°C): δ 0.89 (s, 18H, $C(CH_3)_3$), 0.91 (s, 18H, $C(CH_3)_3$), 2.38-2.66 (b overlapping m, 8H, NCH_2CHOH), 3.22-4.01 (b overlapping m, 16H, NCH_2CH_2N), 4.38 (b m, 4H, C(*H*)O). ^{13}C NMR (C_6D_6, 25°C): 26.2, 27.4 (CH_3 of $C(CH_3)_3$), 35.6, 37.8 (quaternary of $C(CH_3)_3$), 58.9, 60.4 (NCH_2CH_2N), 62.3, 62.8 ($NCH_2C(H)OH$), 76.6, 77.4 (CH_2CHO). Mass spec. (FAB) 659.0 $(M+H)^+$.

4.2.2 Complexes of nickel

$[H_2L^{18}Ni(OH_2)_2]^{2+}[ClO_4^-]_2$ and $[H_2L^{18}Ni(OH_2)_2]^{2+}[Cl^-]_2$

To a solution of nickel (II) perchlorate (0.050 g, 0.14 mmol) in the minimum quantity of ethanol required for dissolution was added an ethanol solution of $H_2\mathbf{L}^{18}$ (0.040 g,

0.13 mmol). The solution changed colour from light to dark green and X-ray quality crystals were grown by diffusion of diethyl ether into the reaction solution. Complete characterization was frustrated in this case by the small amount of crystalline compound obtained

$[H_2\mathbf{L}^{18}Ni(OH_2)_2]^{2+}[Cl^-]_2$ was prepared from nickel(II) chloride hexahydrate (0.050 g, 0.21 mmol) and $H_2\mathbf{L}^{18}$ (0.63 mg, 0.21 mmol) using the method detailed above for the corresponding *bis*-perchlorate salt . Ethanol was removed under vacuum and the product was isolated as a yellow-green solid in yields of 0.07 g (67 %). Mass spec. (APCI) 357.0 $(M+H)^+$. UV/vis 439 nm (22779 cm^{-1}). IR (KBr disk, cm^{-1}) 3355 (br st), 2959 (st), 1636 (w), 1479 (md), 1399 (md), 1365 (md), 1079 (md) and 1016 (md).

4.2.3 Reactivity towards main group alkyls

$\mathbf{L}^{18}$AlMe

Under Schlenk conditions, a solution of $H_2\mathbf{L}^{18}$ (0.50 g, 1.66 mmol) in toluene (100 ml) was added to a solution of trimethylaluminium (0.12 ml, 1.60 mmol) in toluene (100 ml) at -78°C. The mixture was stirred at room temperature for 12 h and the solvent then removed in vacuo. Warm hexane (40°C, 100 ml) was then added and insoluble matter removed by filtration. Hexane was then removed from the filtrate under vacuum to yield the product as a white powder (0.29 g, 52 %). ^{1}H NMR (C_6D_6, 25°C): δ -0.50 (s, 3H CH_3Al), 1.22 (br s, 9H, $C(CH_3)_3$ ligand), 1.26 (br s, 9H, $C(CH_3)_3$ ligand), 1.38-3.63 (m, br, 16H, ligand signals). ^{13}C NMR: –10.5(CH_3Al), 25.9 ($C(CH_3)_3$), 26.6 ($C(CH_3)_3$), 33.8 ($C(CH_3)_3$), 34.8 ($C(CH_3)_3$),. Mass spec. (CI) 341 $(M+H)^+$. Exact mass: calc. for $C_{18}H_{37}N_2O_2AlH$ calculated mass 341.2748 measured mass 341.2745.

4.3 Results and Discussion

4.3.1 Synthetic Methods

Three main synthetic methods were used in an attempt to achieve the coordination of the ligands synthesized in chapter 3 to metal centres (predominantly from group 4); these were carried out with varying degrees of success.

(i) Substitution of one or more alkyl ligands at the metal centre by direct reaction of the protonated form of the ligand (H_yL) with a metal alkyl complex (e.g. tetrabenzyl zirconium) resulting in replacement of the metal-carbon bond with a metal-amide or metal-alkoxo linkage:

$$MR_x + H_yL \longrightarrow LMR_{x-y} + yRH$$

(ii) Substitution of one or more monodentate alkoxide ligands at the metal centre by reaction with the protonated form of the ligand:

$$M(OR)_x + H_yL \longrightarrow LM(OR)_{x-y} + yROH$$

$$M(OR)_x + 2H_yL \longrightarrow L_2M(OR)_{x-2y} + 2yROH$$

(iii) Substitution of one or more halide ligands at the metal centre by reaction of the deprotonated form of the ligand (L^{y-})with a transition metal halide.

$$MX_x + L^{y-} \longrightarrow LMX_{x-y} + yX^-$$

Research routes (i) and (iii) proved to be unsuccessful in most cases examined; however route (ii) proved to be much more promising and resulted in a range of group 4 complexes containing mixed alkoxo/amino donor ligands.

4.3.2 Reactions with group 4 metals

4.3.2.1 Amide donor ligands

Trans-1,2-di(2-nitrophenylamino)cyclohexane $H_2\mathbf{L}^1$ and *trans*-1,2-di(2-nitro-6-pyridylamino)cyclohexane $H_2\mathbf{L}^2$ were each reacted with tetrabenzyl zirconium by direct addition of a toluene solution of the ligand to tetrabenzyl zirconium itself dissolved in toluene. In both cases no coordination of the ligand was observed in the crude product mixture prior to attempted recrystallization; the signals corresponding to the ligand in the ^1H and ^{13}C NMR spectra were very close to those of the free ligand. Heating the reaction mixture to 60°C for several hours did not induce coordination in either case, with signals corresponding to the ligand still visible in the ^1H and ^{13}C NMR spectra showing that the ligand was largely unchanged and had not decomposed. A second method of coordination to titanium and zirconium was attempted by the reaction of the conjugate bases $(\mathbf{L}^1)^{2-}$ and $(\mathbf{L}^2)^{2-}$ with group 4 metal tetrachlorides. In each case the ligand was first reacted with two equivalents of *n*-butyllithium to produce the dianion *in situ*, which was then reacted with the appropriate metal chloride. Once again coordination was not observed for either compound.

The inability of $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ to coordinate to titanium or zirconium via either of these methodologies is somewhat surprising, given their widespread application in early transition metal amide synthesis. It is possible that this unusual behaviour can be attributed to the nitro group present on each ligand. The ability of certain substituents on aromatic systems to direct metalation by an organolithium reagent to the ortho position (ortho-directed metalation) is well known.[11,12] For substituted phenyl systems the following substituents have been reported to ortho-lithiate on reaction with *n*-butyllithium: $-NMe_2$,[13] $-CH_2NMe_2$,[14] $-CH_2CH_2NMe_2$,[15] -OMe,[16] -CONHR,[17] $-SO_2NHR$,[18] $-SO_2NR_2$,[19] $-CF_3$,[20,21] and –F.[22] Research on substituted anisoles has also shown that –OMe, $-CH_2NMe_2$, -CONHMe and $-SO_2NHMe$ substituents have the strongest ortho-directing abilities.[12]. The nitro group $-NO_2$ is similar in some ways to groups such as $-SO_2NHMe$ and $-SO_2NR_2$, providing as it does an oxygen donor which might coordinate to the hard lithium centre. It therefore seems feasible to suggest that the $-NO_2$ substituents in $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ might be acting in a similar way by directing ortho lithiation (or forming an intermediate before complete metalation) of the aromatic rings (Figure 4.1). Although much of the published research has been on organolithium reagents it could be possible that in the reactions of tetrabenzyl zirconium with $H_2\mathbf{L}^1$ and $H_2\mathbf{L}^2$ a similar metalation reaction occurs. At the very least, it would appear that the nitro groups in these ligands offer the potential for a competing centre of reactivity (to the secondary amine functions) in their reactions with metal alkyl reagents.

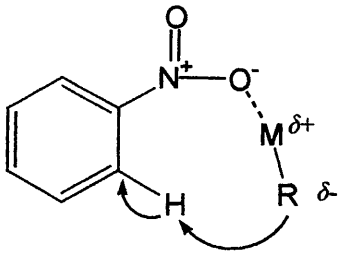


Figure 4.1: Proposed ortho metalation process for nitrophenyl compounds.

The ligands H_3L^3 and H_3L^4 were produced via incomplete nucleophilic aromatic substitution at only one of the two primary amine functions of the precursor *trans*-1,2-cyclohexanediamine (vide supra). As a result they do not possess the desired C_2 symmetry, and this fact, together with the unpromising reactivity towards metal reagents demonstrated for H_2L^1 and H_2L^2, meant that the further reactivity of H_3L^3 and H_3L^4 was not investigated.

The silyl substituted *trans*-diaminocyclohexane ligands H_2L^{12} and H_2L^{13} were reacted directly with tetrabenzyl zirconium as well as with the thf adducts of titanium and zirconium chlorides (after initial deprotonation by n-butyllithium) These reactions did not yield tractable products. However, H_2L^{12} was used in combination with tetrabenzyl zirconium in the catalytic runs outlined in chapter 5 (vide infra). In a similar fashion, HL^{16}, derived from precursor compound H_2L^{11} was not isolated in a pure form coordinated to titanium or zirconium, but was used in the catalytic runs in a mixture with tetrabenzyl zirconium. Similar attempts to coordinate the phenyl substituted diazacycloheptane based H_2L^{14} and L^{15} ligands to group 4 metals also led to the isolation of no tractable products.

4.3.2.2 Alkoxide donor ligands

(a) Ligands based around a 1,4-diazacyclohexane backbone

The reaction of $H_2\mathbf{L}^{18}$ with titanium alkoxides gives some unexpected and interesting bimetallic complexes. Reaction with titanium tetrakis(isopropoxide) at room temperature in the absence of solvent followed by removal of isopropanol under vacuum gives a white solid, which when extracted with dry hexane, concentrated and cooled to –30°C can be isolated as colourless crystals. The ^{1}H NMR spectrum of the solid clearly shows a singlet due to the *tert*-butyl groups of the $\mathbf{L}^{18}$ fragment and a doublet due to the methyl groups of the titanium-bound isopropoxide ligands. The intensity ratio suggests that for every *tert*-butyl group there are three corresponding isopropyl groups, and mass spectral data imply a molecular unit containing one ligand $\mathbf{L}^{18}$, and two $Ti(O^iPr)_3$ fragments. These spectral inferences are confirmed by the X-ray crystal structure (Figure 4.2) which shows that the complex, $\mathbf{L}^{18}Ti_2(O^iPr)_6$, does indeed contain a single ligand and two titanium atoms. Each five coordinate titanium centre is coordinated to one amine donor and one pendant alkoxide of the $\mathbf{L}^{18}$ ligand, with three isopropoxide ligands being retained from the starting material. The geometry around each titanium atom appears to be a distorted trigonal bipyramid with the $\mathbf{L}^{18}$ amine donor and one isopropoxide ligand occupying the axial sites [O(2)-Ti(1)-N(1) 171.0(1)°, O(6)-Ti(2)-N(2) 170.4(1)°]. The $\mathbf{L}^{18}$ derived alkoxide donor and the two remaining isopropoxides occupy the three approximately equatorial sites [O(4)-Ti(1)-O(3) 115.9(1)°, O(2)-Ti(1)-O(4) 100.5(1)°, O(2)-Ti(1)-O(3) 99.6(1)°]. The Ti-O bond involving the $\mathbf{L}^{18}$ derived alkoxide is somewhat longer that those featuring the isopropoxide donors [1.853(3) vs. 1.821(3) and 1.820(3) Å for compar-

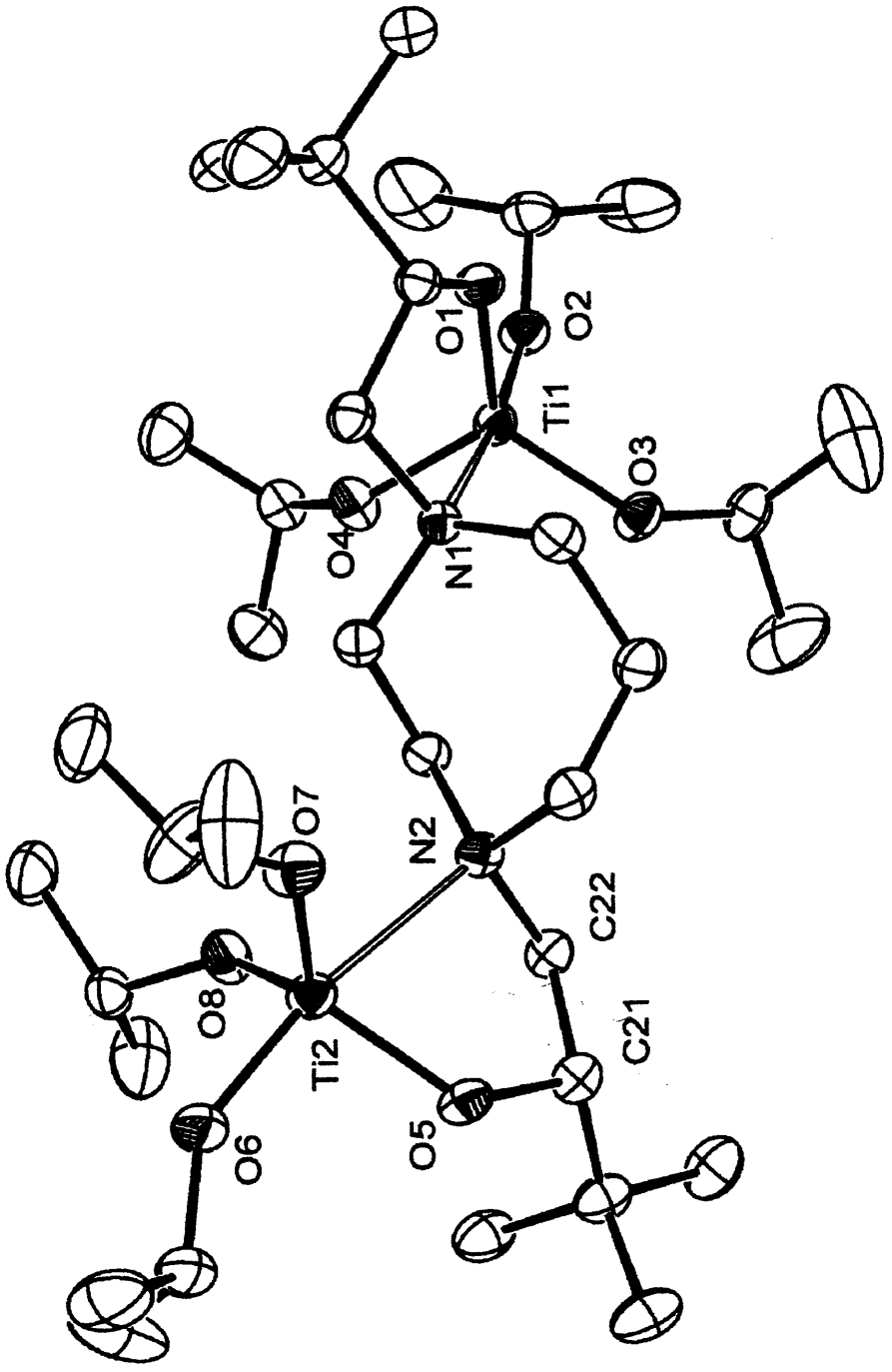


Figure 4.2: Crystal structure of $L^{18}Ti_2(O^iPr)_6$, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

Table 4.1: Selected bond distances (Å) and angles (°) for $\mathbf{L}^{18}Ti_2(O^iPr)_6$.

Ti(1)–N(1)	2.378(3)	Ti(2)–N(2)	2.391(3)
Ti(1)–O(1)	1.853(3)	Ti(2)–O(5)	1.853(3)
Ti(1)–O(2)	1.784(3)	Ti(2)–O(6)	1.792(3)
Ti(1)–O(3)	1.821(3)	Ti(2)–O(7)	1.831(3)
Ti(1)–O(4)	1.820(3)	Ti(2)–O(8)	1.820(3)
O(1)–Ti(1)–N(1)	76.0(1)	O(4)–Ti(1)–O(2)	100.5(1)
N(1)–Ti(1)–O(2)	171.0(1)	O(4)–Ti(1)–O(1)	118.4(1)
N(1)–Ti(1)–O(3)	87.3(1)	O(4)–Ti(1)–O(3)	115.9(1)
N(1)–Ti(1)–O(4)	81.5(1)	O(1)–Ti(1)–O(3)	119.3(1)

-able equatorial substituents], as might be expected both because of the restrictions imposed by the two-atom tether to the amine nitrogen function, and the steric bulk of the proximal ^{t}Bu group. In more general terms, the Ti-O distances are within the bounds expected for five-coordinate titanium complexes of this type, with the Ti-N distance [2.385 Å (mean)] being, if anything, slightly longer than those found in comparable systems. Thus, for example, a useful comparison can be made with the corresponding bond lengths found in the complexes $N[CH_2(3,5\text{-}Me_2C_6H_2)O]_3TiOR$ [R = $C_6H_3{}^{i}Pr_2$-2,6, *d*(Ti-O) = 1.833 (mean), *d*(Ti-N) = 2.305(2) Å; R = ^{i}Pr, *d*(Ti-O) = 1.831 (mean), *d*(Ti-N) = 2.295(3)] and $N[CH_2(3,5\text{-}Me_2C_6H_2)O]_2(CH_2CH_2O)TiOR$ [R = $C_6H_3{}^{i}Pr_2$-2,6, *d*(Ti-O) = 1.822 (mean), *d*(Ti-N) = 2.288(3) Å], each of which features an analogous (approximately trigonal bipyramidal) $Ti(OR)_4(NR_3)$ unit, with the amine donor occupying one of the axial positions. [23-25]

In a bid to obtain a mononuclear complex, the reaction was repeated using an excess of $H_2\mathbf{L}^{18}$; however once again the same binuclear complex was observed. It seems that under the conditions used (i.e. liquid titanium isopropoxide added to solid $H_2\mathbf{L}^{18}$) the reaction of $H_2\mathbf{L}^{18}$ with two distinct titanium centres occurs rapidly, with further reaction at either of the titanium centres presumably being prevented by the steric bulk of the isopropoxide ligands. It therefore seemed logical that reducing the steric bulk of the alkoxides in the titanium starting material might allow for the coordination of more than one $H_2\mathbf{L}^{18}$ ligand. Reaction with titanium tetrakis(ethoxide) under similar conditions yields colourless crystals in low yield after recrystallisation from hexane. The ^{1}H NMR spectrum of such a sample shows the *tert*-butyl groups as a singlet and a low field quartet that corresponds to the methylene group of the ethoxide ligands. Comparison of the intensities of these peaks gives a ratio of ethoxide to $\mathbf{L}^{18}$

of 1:1. As predicted on the basis of steric arguments, this structure (Figure 4.3) is different from that of $\mathbf{L^{18}}Ti(O^iPr)_6$ as it contains two L^{18} ligands. The bimetallic complex $[\mathbf{L^{18}}Ti_2(OEt)]_2(\mu_2\text{-}O)$ features two titanium centres which are linked via a symmetrically bridging oxide ligand [Ti(2)-O(7) 1.818(4) Å, Ti(1)-O(7) 1.826(4) Å]. The coordination sphere at each titanium is completed by of one ethoxide ligand remaining from the starting material, two alkoxide linkages (one from each $\mathbf{L^{18}}$ ligand) and a N→Ti donor/acceptor interaction.

The geometry at each titanium centre is a highly distorted trigonal bipyramid with axial amine and ethoxide donors [O(6)-Ti(2)-N(3) 165.3(2)°]. The two remaining $\mathbf{L^{18}}$ alkoxide donors and the bridging oxygen form a somewhat distorted trigonal plane for which the sum of the O-Ti-O angles is 351.0° [O(4)-Ti(2)-O(5) 109.4(2)°, O(4)-Ti(2)-O(7) 116.6(2)°, O(7)-Ti(2)-O(5) 125.0(2)°]. The Ti-O distances in $[\mathbf{L^{18}}Ti(OEt)]_2(\mu_2\text{-}O)$ are similar to those found in $\mathbf{L^{18}}Ti_2(O^iPr)_6$ and are therefore typical of alkoxide donors to five-coordinate titanium(IV).[1,2] As with $\mathbf{L^{18}}Ti_2(O^iPr)_6$, the Ti-O distances featuring the equatorial alkoxides are significantly longer than those featuring the corresponding axial ligands [e.g. Ti(1)-O(1) 1.860(3) vs. Ti(1)-O(3) 1.835(3) Å]. Finally some comment needs to be made concerning the Ti-N interactions. Each titanium centre features two disparate Ti-N distances [e.g. Ti(2)-N(3) 2.443(4), Ti(2)-N(4) 2.962(4) Å]. Even the shorter Ti-N distance must be considered long for a N→Ti donor/acceptor interaction featuring a $Ti(OR)_4$ type Lewis acid,[23,24] whereas the longer Ti-N distance falls well outside the sum of conventional covalent radii for N and Ti. [26]

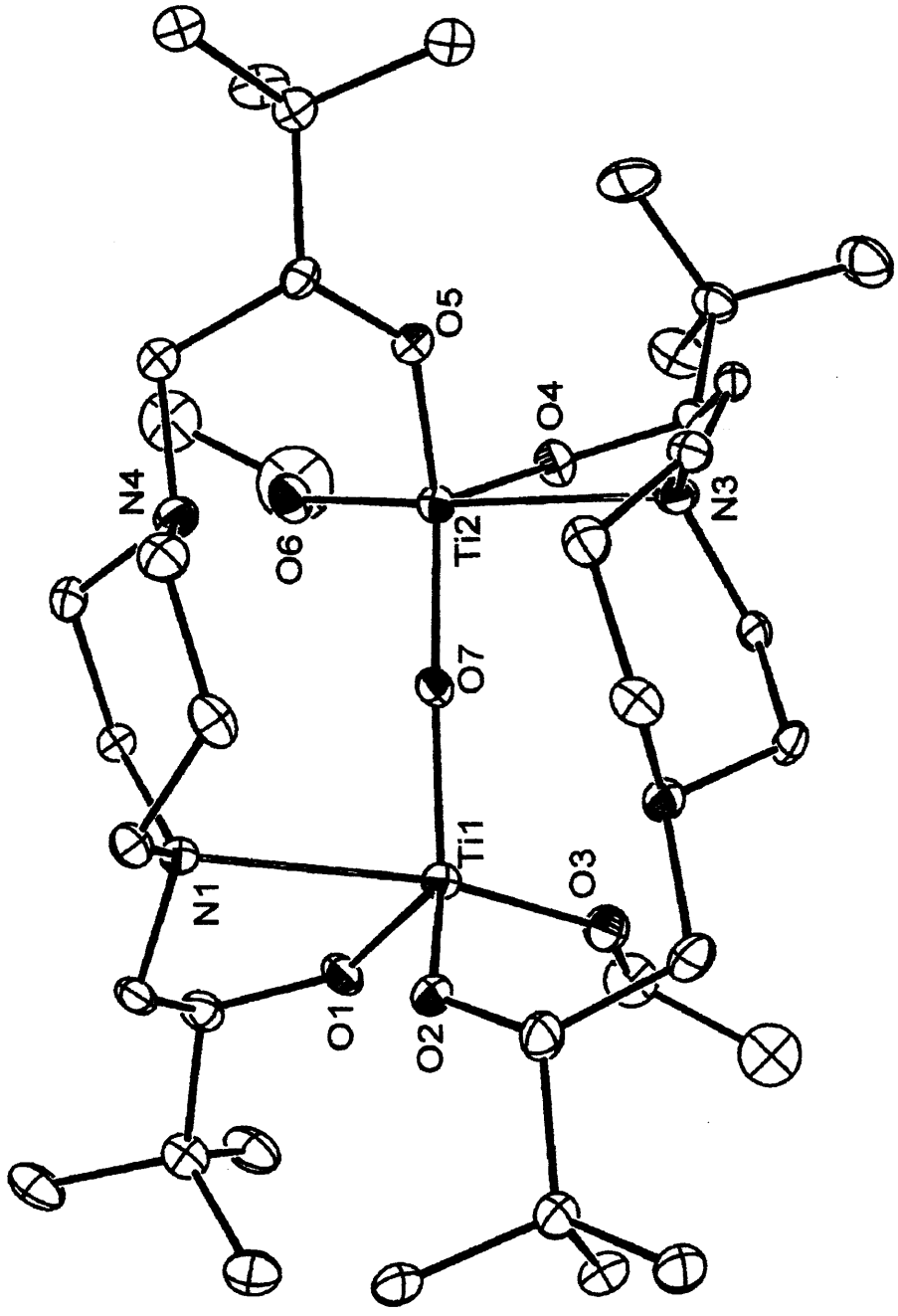
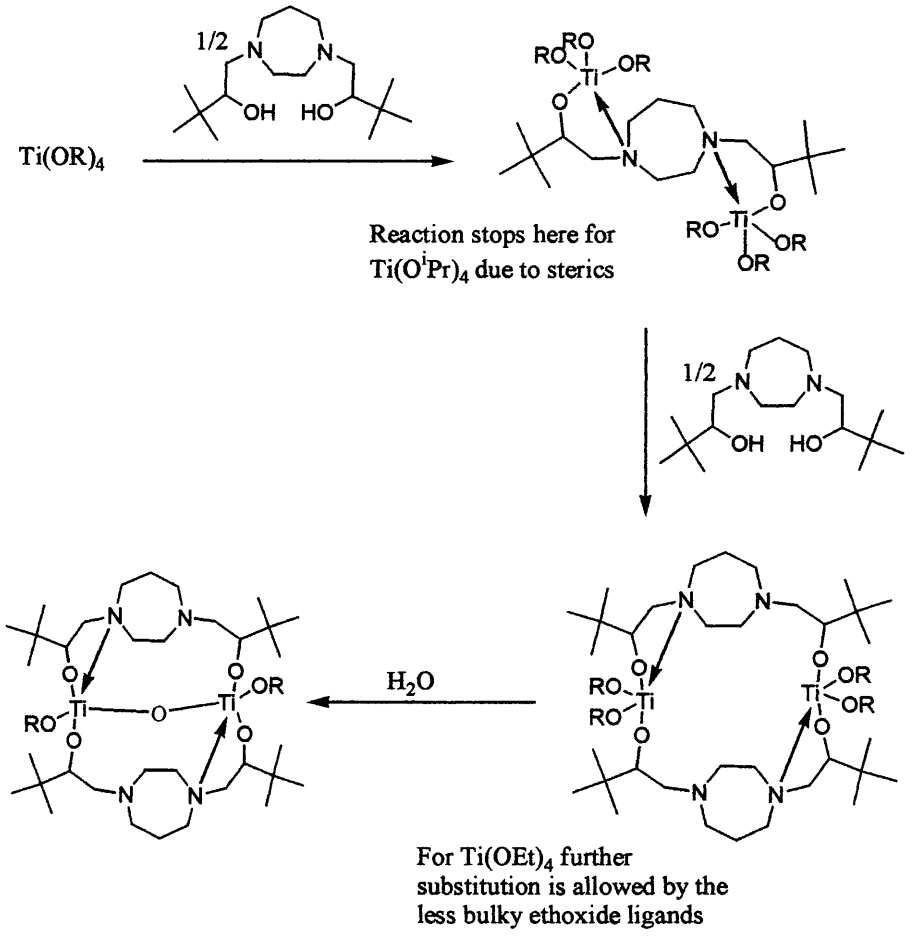


Figure 4.3: Crystal structure of $[L^{18}Ti(OEt)]_2(\mu_2\text{-}O)$, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

Table 4.2: Bond distances (Å) and angles (°) for $[\mathbf{L}^{18}Ti_2(OEt)]_2(\mu_2\text{-}O)$.

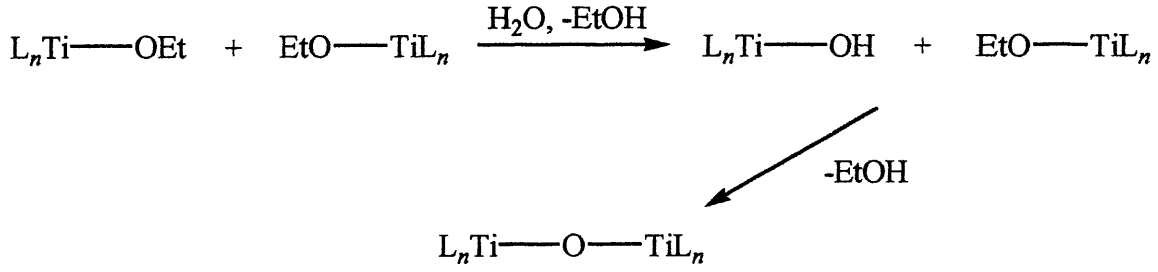
Ti(1)–O(7)	1.826(4)	Ti(2)–O(7)	1.818(4)
Ti(1)–O(1)	1.860(4)	Ti(2)–O(4)	1.852(3)
Ti(1)–O(2)	1.860(4)	Ti(2)–O(5)	1.840(4)
Ti(1)–O(3)	1.835(3)	Ti(2)–O(6)	1.827(4)
Ti(1)–N(1)	2.506(4)	Ti(2)-N(3)	2.443(4)
Ti(1)–N(2)	2.757(4)	Ti(2)-N(4)	2.962(4)
O(1)–Ti(1)–O(2)	107.60(15)	O(4)–Ti(2)–O(5)	109.42(16)
O(1)–Ti(1)–O(3)	89.93(16)	O(4)–Ti(2)–O(6)	91.36(16)
O(1)–Ti(1)–O(7)	114.34(16)	O(4)–Ti(2)–O(7)	116.57(16)
O(2)–Ti(1)–O(3)	106.14(16)	O(5)–Ti(2)–O(6)	104.41(16)
O(2)–Ti(1)–O(7)	127.62(16)	O(5)–Ti(2)–O(7)	125.04(16)
O(3)–Ti(1)–O(7)	103.87(16)	O(6)–Ti(2)–O(7)	102.94(17)

Mechanistically, the reaction of titanium tetrakis(ethoxide) with $H_2\mathbf{L}^{18}$ can formally be thought to occur in three steps as shown in Scheme 4.1. The first step involves substitution of one ethoxide ligand at each metal centre to form a bimetallic species with only one $\mathbf{L}^{18}$ ligand (with a ratio of Ti:$\mathbf{L}^{18}$ of 2:1) analogous to $\mathbf{L}^{18}Ti_2(O^iPr)_6$. A second step would then be the reaction of a second half-equivalent of $H_2\mathbf{L}^{18}$, resulting in substitution of one further ethoxide ligand at each metal centre, to give a ratio of Ti:$\mathbf{L}^{18}$ of 1:1. It is feasible to suggest that this second step would not occur in the case of reaction with titanium tetrakis(isopropoxide) due to the steric bulk of the isopropoxide groups preventing the attack of a further $H_2\mathbf{L}^{18}$ ligand.



Scheme 4.1: Effect of steric bulk of alkoxides on substitution.

Another interesting feature to note is the occurrence of a Ti-O-Ti bridge in $[\mathbf{L}^{18}Ti_2(OEt)]_2(\mu_2\text{-}O)$. This is proposed to be the result of partial hydrolysis by adventitious water. Conversion of an ethoxide ligand at each metal centre to a hydroxyl ligand followed by attack of this hydroxyl group on a remaining ethoxide ligand (Scheme 4.2).



Scheme 4.2: Proposed origins of the Ti-O-Ti bridge.

It is intriguing that both of the structurally characterized titanium complexes of $\mathbf{L}^{18}$ {i.e. $[\mathbf{L}^{18}Ti(OEt)]_2(\mu_2\text{-}O)$ and $\mathbf{L}^{18}Ti_2(O^iPr)_6$} feature this ligand coordinated in a bridging fashion between two metal centres. By contrast the *diprotonated* ligand $H_2\mathbf{L}^{18}$ forms a discrete tetradentate mono-metallic complex with Ni(II) (*vide infra*). This result is probably best attributed to the relative size of the metals and the lack of flexibility inherent in the ligand. Ni^{2+} has an ionic radius of ~0.70 Å compared to ~0.6 Å for Ti^{4+} [27] Furthermore, it seems likely that the 1,4-diazacycloheptane ring in the backbone of $\mathbf{L}^{18}$ restricts its flexibility so that there is little scope to alter the bite angle on chelation. It is thought that the ionic radius of Ti^{4+} is too small to be accommodated by a chelating $\mathbf{L}^{18}$ ligand, and in this case suitable orbital overlap can only be achieved by the ligand adopting a bridging mode of coordination. The ionic radius of Zr^{4+} is larger than that of Ti^{4+} so it is possible that it could accommodate a chelating $(\mathbf{L}^{18})^{2-}$ ligand. However, the accepted model for an active olefin

polymerisation catalyst requires two labile mutually cis ligands. By contrast, the complex $[(H_2\mathbf{L}^{18})Ni(OH_2)_2]^{2+}$shows that even when acting as a chelating ligand, $H_2\mathbf{L}^{18}$ favours coordination in an equatorial fashion which leaves the remaining ligands mutually trans. Therefore, it seems very likely that even though a monometallic complex may be conceivable with Zr^{4+} the mode of coordination of $(\mathbf{L}^{18})^{2-}$ might well be such as to produce mutually trans ancillary ligands, as seen for $H_2\mathbf{L}^{18}$ with Ni^{2+}. As a result the complexation chemistry of $\mathbf{L}^{18}$ was not pursued further.

Ligand systems which are capable of coordinating to titanium(IV) and zirconium(IV) in a chelating fashion to form mono-metallic complexes with mutually cis ancillary ligands were therefore sought. In the first instance two possibilities were examined:

(i) Use of a more flexible ligand backbone e.g. a compound in which the amine functionalities are only joined via a single alkyl bridge and therefore more able to adjust to accommodate smaller metal ions.

(ii) A macrocyclic approach i.e. using a macrocycle to obtain a mono-metallic complex by encapsulation of the metal.

(b) Ligands based around a N,N'-dimethylethylenediamine backbone

Flexible ligands based on a linear array of donors have previously been reported to give active olefin polymerisation catalysts with group 4 metals. Thus, for example, the ansa metallocene analogue $Ti(Me_3SiNCH_2CH_2NSiMe_3)Cl_2$ which contains a non-rigid linear amine is an active catalyst for ethylene polymerisation. [28]

With regard to the current set of ligands under investigation, a more flexible framework was synthesised by replacing the rigid 1,4-diazacycloheptane ring with a more flexible *N,N'*-dimethylethylenediamine backbone to give *N,N'-bis*(2-hydroxy-3-dimethylbutyl)-dimethylethylenediamine ($H_2\mathbf{L}^{20}$). $H_2\mathbf{L}^{20}$ was synthesised from *N,N'*-dimethylethylenediamine and racemic (+/-)-3,3-dimethyl-1,2-epoxybutane. The product $H_2\mathbf{L}^{20}$ was isolated as an oil, meaning that in this case fractional crystallisation to separate R,R/S,S from S,R/R,S diastereoisomers was not possible. Therefore the ligand was reacted with metal precursors as a mixture of isomers, with the hope of separating diastereomers at the metal complex stage.

Reaction of $H_2\mathbf{L}^{20}$ with zirconium tetrakis(propoxide) at room temperature resulted in a crude reaction mixture showing several ^{t}Bu and ^{i}Pr signals. Extraction into hexane and controlled cooling of the resultant solution led to the isolation of colourless crystals. The X-ray crystal structure (Figure 4.4) shows two $\mathbf{L}^{20}$ ligands coordinated to one zirconium centre, with none of the propoxide ligands from the starting material remaining in the zirconium coordination sphere. The complex so formed, $Zr(\mathbf{L}^{20})_2$, features both $\mathbf{L}^{20}$ ligands of meso (R,S) stereochemistry, with the alternative possible complexes (*R,R,R,R*; *S,S,S,S*; *R,R,S,S*; *R,R,R,S* or *S,S,R,S*) presumably being less crystalline under the conditions used, and so remaining in solution. The coordination of two molecules of $\mathbf{L}^{20}$ to the metal centre is not that surprising, as zirconium is large enough to support an eight-coordinate geometry. Coordination of two ligands to give ZrL_2 complexes has been previously reported, one such example having been reported

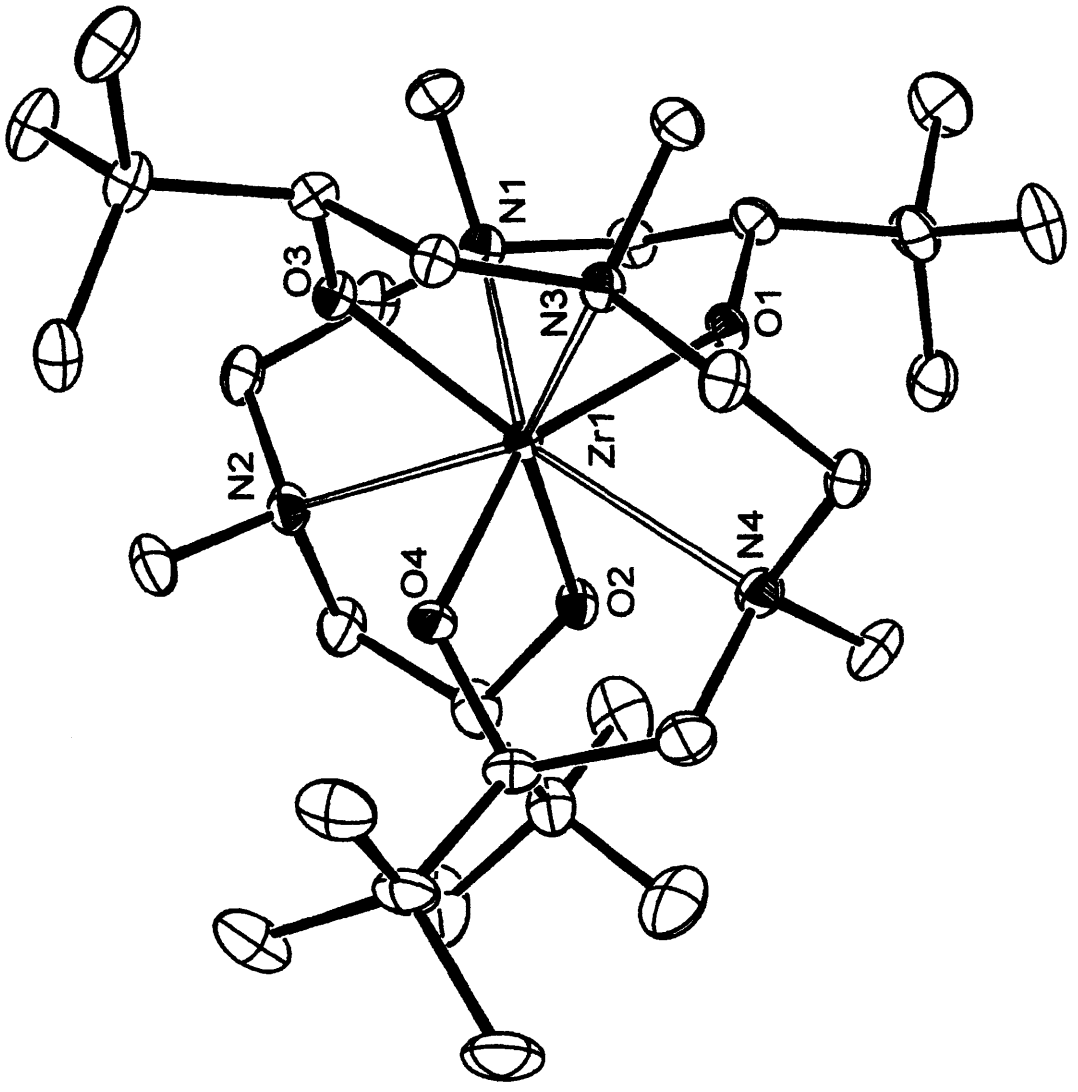


Figure 4.4a: Crystal structure of $Zr(L^{20})_2$, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

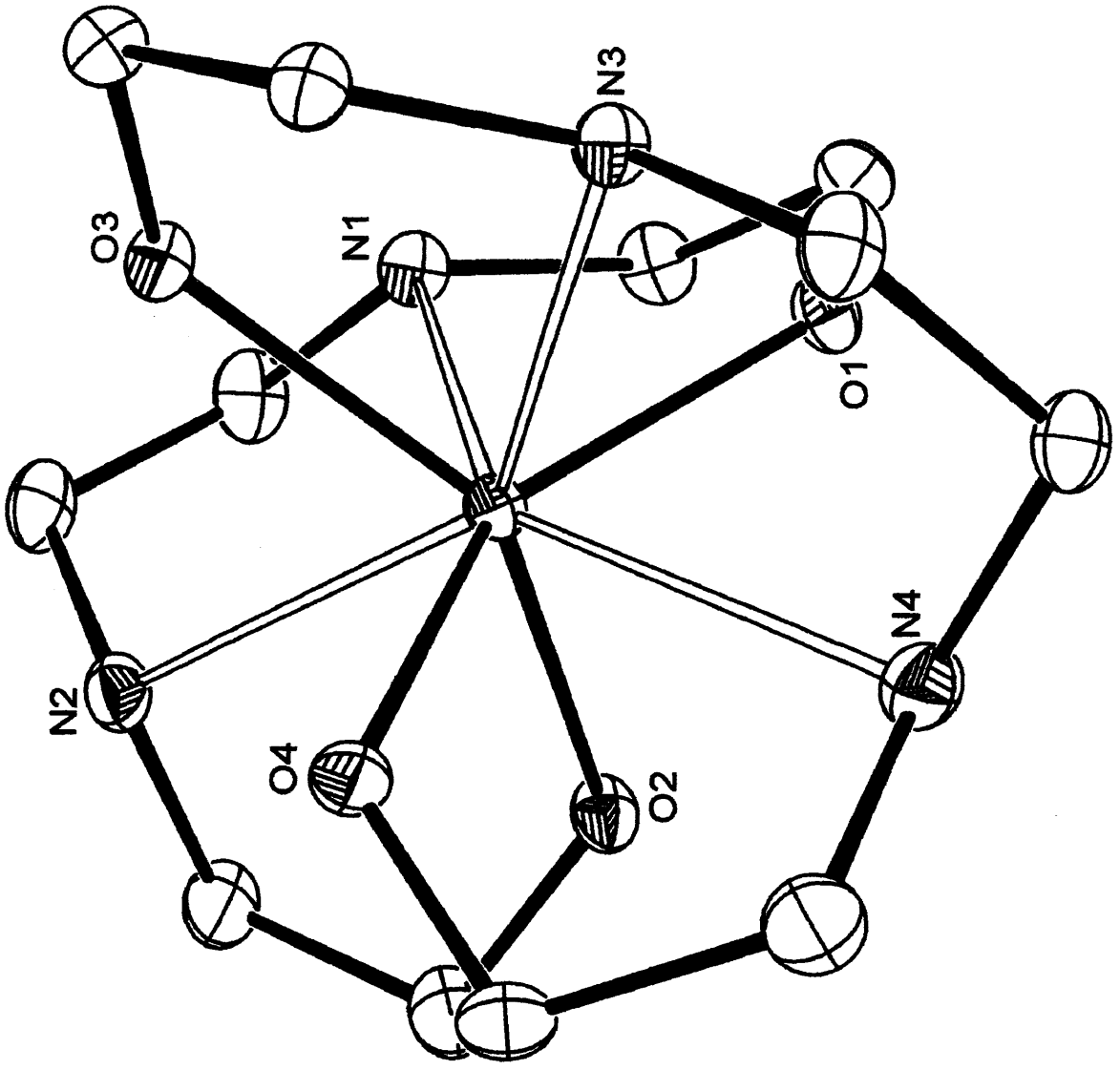


Figure 4.4b: Crystal structure of $Zr(L^{20})_2$, showing the immediate coordination environment at the zirconium centre.

Table 4.3: Selected bond distances (Å) and angles (°) for $Zr(\mathbf{L}^{20})_2$.

Zr(1) –O(1)	2.060(15)	Zr(1) –O(2)	2.058(14)
Zr(1) –O(3)	2.073(14)	Zr(1) –O(4)	2.056(16)
Zr(1) –N(1)	2.620(2)	Zr(1) –N(2)	2.621(19)
Zr(1) –N(3)	2.595(17)	Zr(1) –N(4)	2.616(2)
O(4) –Zr –O(2)	90.07(6)	O(2) –Zr –O(1)	89.00(6)
O(4) –Zr –O(1)	141.74(6)	O(2) –Zr –O(3)	141.97(6)
O(4) –Zr –O(3)	87.69(6)	O(1) –Zr –O(3)	115.17(6)

by Bochmann in which two trans-1,2-$(Me_3SiNH)C_6H_{10}$ ligands are coordinated to a single zirconium atom.[29] This paper also reports similar behaviour for the ligands $O(SiMe_2NHBu^t)_2$ and $O(SiMe_2NHC_6H_{11})_2$. Eight-coordinate zirconium complexes incorporating four oxygen and four nitrogen donors have previously been reported by a number of groups.[30]

In the case of $Zr(\mathbf{L}^{20})_2$, the eight donors conferred by the two $\mathbf{L}^{20}$ ligands adopt a distorted square anti-prismatic arrangement around the metal centre, the distortion being due to the unequal lengths of the Zr-O and Zr-N bonds. The Zr-N and Zr-O bond lengths for this structure are close to those reported by Goldschmidt for zirconium complexes of amine bis(phenolate) ligands.[31]

Attempts to synthesize a zirconium complex of composition $\mathbf{L}^{20}Zr(OR)_2$, by varying the metal/ligand stoichometry, were unsuccessful, invariably resulting in the formation of the 2:1 complex $Zr(\mathbf{L}^{20})_2$. Thus, in an attempt to obtain a 1:1 complex of the type LMX_2, reactions of $H_2\mathbf{L}^{20}$ with titanium precursors were investigated. The much smaller size of titanium compared to zirconium makes it unlikely to support an eight coordinate geometry.

The reaction of $H_2\mathbf{L}^{20}$ with titanium tetrakis(isopropoxide) gives two products, as determined from the ^1H and ^{13}C NMR spectra of the crude reaction mixture. Careful recrystallization from hexane (twice) allows the isolation of a colourless crystalline solid, for which ^1H and ^{13}C NMR and mass spectrometry indicate a formulation as $\mathbf{L}^{20}Ti(O^iPr)_2$. The ^{13}C NMR spectrum (Figure 4.5) shows only nine signals, indicating that in this complex the two halves of the ligand are symmetry related. This inference

is confirmed by the results of a single crystal X-ray diffraction study (Figure 4.6) which confirms local C_2 symmetry and that the coordinated ligands are of either R,R or S,S stereochemistry (both a present in the centro-symmetric crystal lattice).

Overall, the complex is six coordinate (a distorted octahedron) with one $\mathbf{L^{20}}$ ligand coordinated to titanium and two mutually cis isopropoxide ligands remaining from the starting material. Its C_2 symmetry and the mutually cis disposition of the isopropoxide ligands make this complex particularly interesting for olefin polymerisation. It has been shown for C_2 symmetric metallocene catalysts that C_2 symmetry can induce isotactic stereochemistry in the resulting polymer (see Chapter 1). This occurs because the C_2 symmetry of the complex causes the possible reaction sites to be homotopic. Conformational modelling has suggested that the polymer chain is forced into an open region of the metallocene thereby relaying the chirality of the metallocene to the incoming monomer.[32] The same principles should be applicable to $\mathbf{L^{20}}Ti(O^iPr)_2$ suggesting that if the complex shows activity for olefin polymerisation it may be capable of producing isotactic material.

Interestingly, the supernatent hexane solution remaining after crystallization of rac (*R,R/S,S*) $\mathbf{L^{20}}Ti(O^iPr)_2$ can be concentrated and cooled to yield a colourless highly viscous oil, which solidifies slowly on prolonged continuous evacuation (10^{-4} Torr). Examination of this oil by ^1H and ^{13}C NMR shows that it consists of an approximately 3:1 mixture, in which the minor component is (*R,R/S,S*) $\mathbf{L^{20}}Ti(O^iPr)_2$, but for which the major component gives rise to seventeen peaks in the ^{13}C NMR spectrum (Figure 4.7). It seems likely that this second component is derived from the meso (*R,S*) form of the ligand, with the resulting complex, $\mathbf{L^{20}}Ti(O^iPr)_2$, having only C_1 symmetry (no

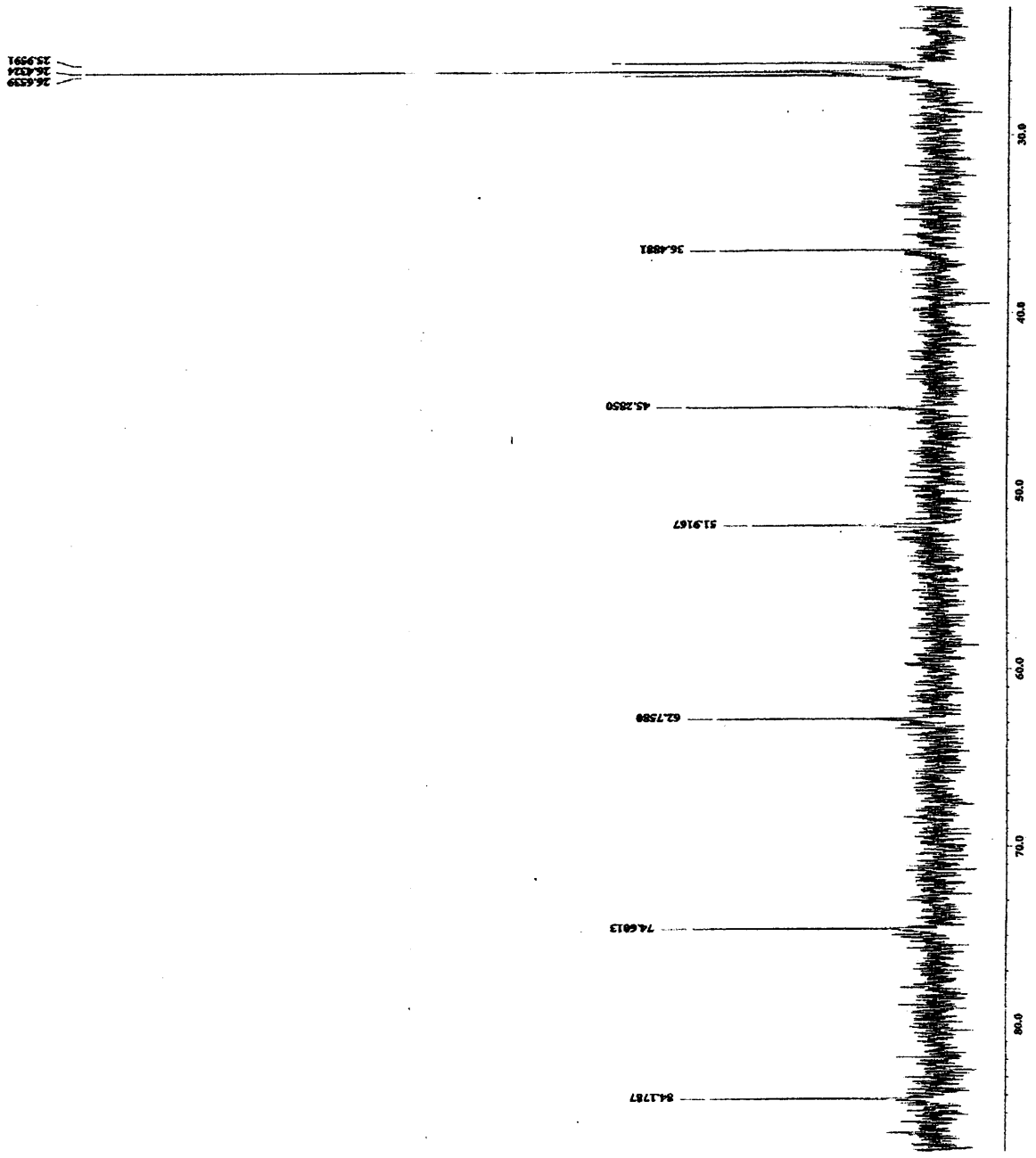


Figure 4.5: $^{13}C\{^{1}H\}$ NMR spectrum of the crystalline product obtained from the reaction of $Ti(O^{i}Pr)_4$ with $H_2\mathbf{L}^{20}$ after two recrystallizations. The nine peaks correspond to the expected signals for the crystallographically characterized C_2 symmetric [(*R*,*R*) and (*S*,*S*)] isomers of $\mathbf{L}^{20}Ti(O^{i}Pr)_2$.

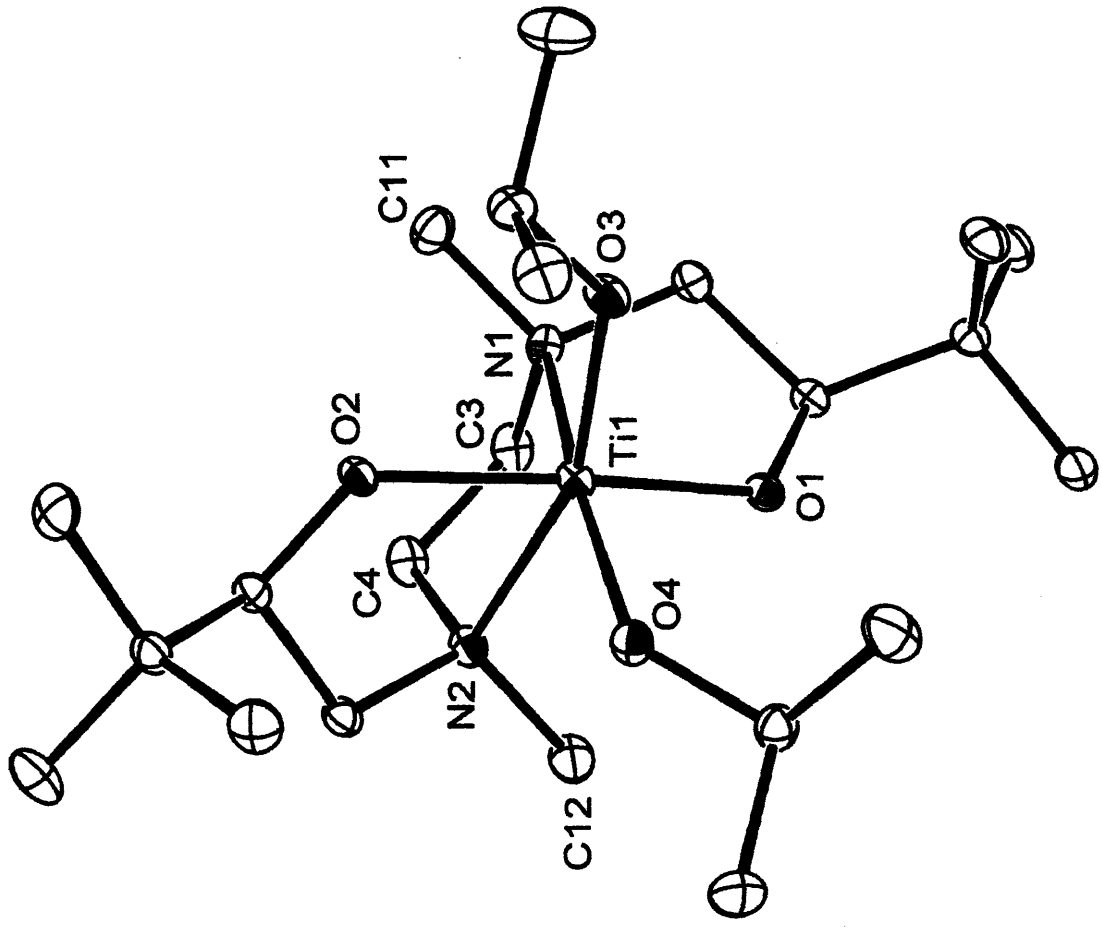


Figure 4.6: Crystal structure of $L^{20}Ti(O^iPr)_2$, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms omitted for clarity.

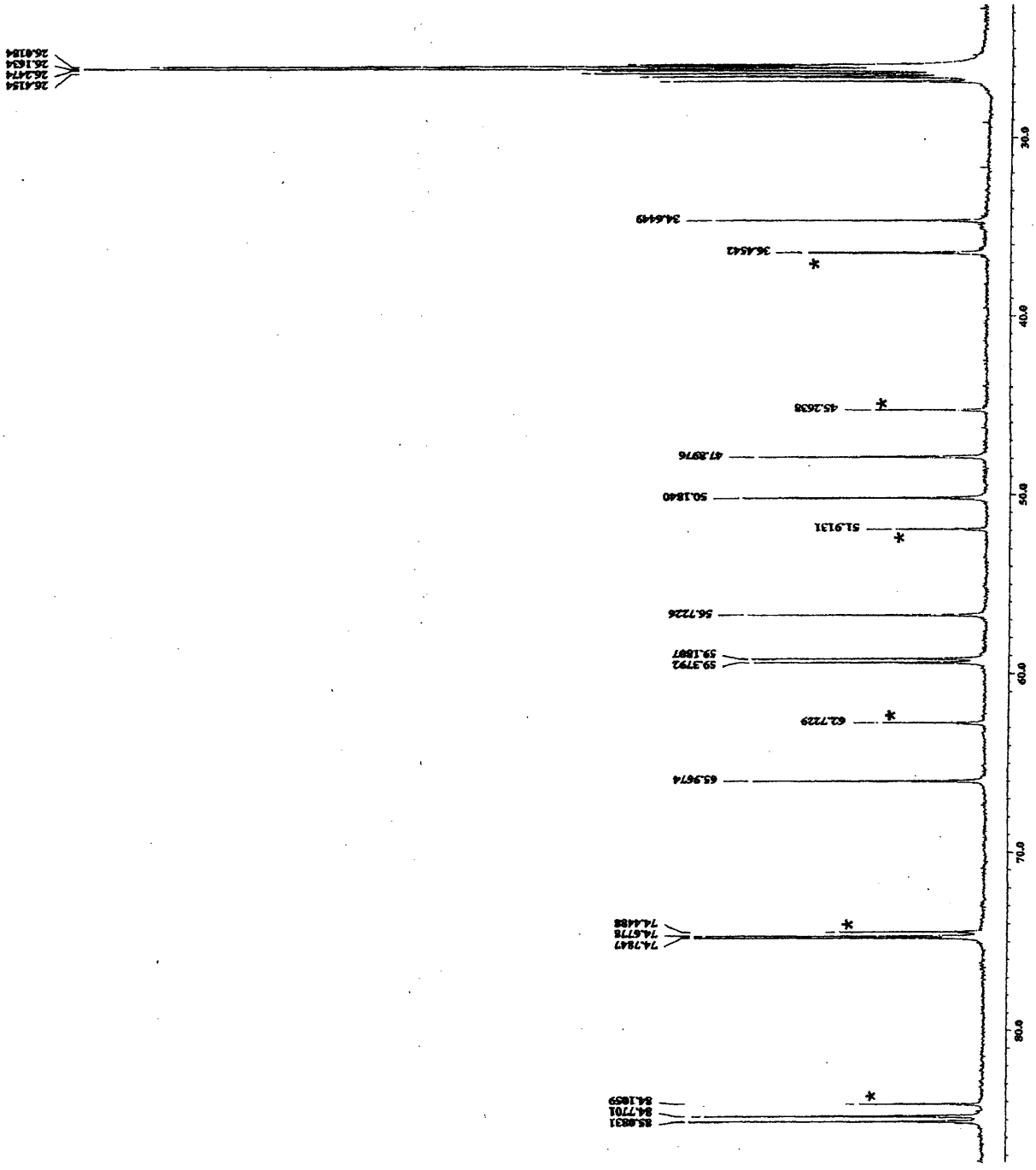
Table 4.4: Selected bond distances (Å) and angles (°) for $L^{20}Ti(O^iPr)_2$.

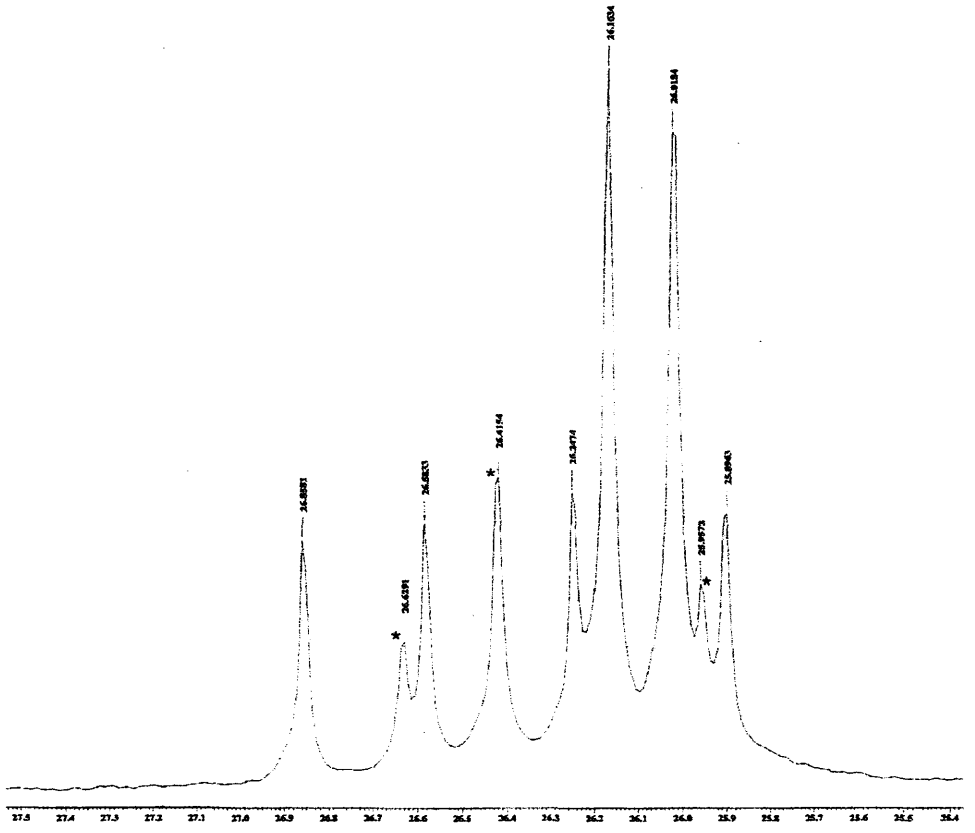
Ti(1)-N(1)	2.325(2)	Ti(1)-N(2)	2.313(2)
Ti(1)-O(1)	1.906(15)	Ti(1)-O(2)	1.901(15)
Ti(1)-O(3)	1.836(15)	Ti(1)-O(4)	1.834(16)
O(2)-Ti(1)-O(4)	98.1(1)	O(2)-Ti(1)-N(2)	74.5(1)
O(1)-Ti(1)-O(3)	99.4(1)	N(1)-Ti(1)-O(1)	74.4(1)
N(1)-Ti(1)-O(4)	159.3(1)	O(2)-Ti(1)-O(3)	91.4(1)
N(2)-Ti(1)-O(3)	159.2(1)	N(2)-Ti(1)-N(1)	76.2(1)

C_2 axis) and therefore giving rise to double the number of ^{13}C NMR resonances. That seventeen, rather than eighteen signals are observed is likely due to the overlap of the two ^{t}Bu quaternary carbon resonances. Attempts to obtain this second isomer in pure form for comparative structural and catalytic studies were frustrated by its oily nature and the difficulty in removing the last traces of the C_2 isomer.

Further research to convert $\mathbf{L^{20}}Ti(O^iPr)_2$ into a more versatile catalyst system has also been attempted. In the first case replacement of the isopropoxide ligands by chlorides was attempted by using a solution of HCl in diethyl ether. The resulting product was essentially insoluble in non polar solvents suggesting that it was either an aggregate or charged species. Dissolution in d_3-acetonitrile was possible, however, and the ^1H and ^{13}C NMR spectra of the solution confirmed the loss of isopropoxide ligands. The spectra also indicated a loss of C_2 symmetry consistent with a species such as $[\mathbf{L^{20}}TiCl(NCCD_3)]^+$. However mass spectrometric results revealed only fragmentation products, and given the sparing solubility in even relatively polar solvents, attempts to further derivatize via this route were taken no further.[33]

Attempts to directly substitute the isopropoxide ligands for methyls to give a more useful precatalyst have also been attempted. A solution of $\mathbf{L^{20}}Ti(O^iPr)_2$ was reacted with methyl lithium, but the reaction rapidly yielded a brown oil. The ^{13}C NMR spectrum of this oil was very convoluted and no products containing the $\mathbf{L^{20}}Ti$ fragment could be isolated from it.[33] Jordan and co-workers have observed a similar outcome with a similar complexes and methyl lithium, in this case the reaction products were black insoluble matter.[34]


26.4194
26.1634
26.0184
34.6449
36.4543
45.2638
47.8976
50.1840
51.9131
56.7226
59.3792
59.1807
62.7229
65.9674
74.7847
74.5778
74.4488
84.0831
84.7701
84.1059
30.0
40.0
50.0
60.0
70.0
80.0



Figures 4.7a (previous page) and 4.7b: $^{13}C\{^{1}H\}$ NMR spectra (including expansion on the ^{i}Pr and ^{t}Bu methyl region, bottom) of the oil obtained from the supernatent hexane solution in the reaction of $Ti(O^{i}Pr)_4$ with $H_2\mathbf{L}^{20}$. The peaks marked with an asterix (*) correspond to the minor component of the mixture - *i.e.* the C_2 symmetric [(*R*,*R*) and (*S*,*S*)] isomers. The remaining peaks correspond to the major component [*i.e.* the C_1 symmetric (*R*,*S*)/(*S*,*R*) isomers of $\mathbf{L}^{20}Ti(O^{i}Pr)_2$].

(c) Ligands based around macrocyclic backbones

Another possible strategy for obtaining mono-metallic complexes of titanium and zirconium is by employing macrocyclic ligand backbones. Aza macrocycles such as 1,4,7-triazacyclononane (tacn) with pendant donors have been shown to coordinate to group four metals to give discrete mono-metallic complexes.[35] Thus, for example, titanium *tert*-butyl or trimethylsilyl-imido complexes featuring single pendant-arm triazacyclononane ligands have been synthesized by Mountford and co-workers, with an alkoxide donor on the pendant arm.[35f] Similar discrete mono metallic, cationic titanium complexes containing the 1,4,7-*tris*(5-*tert*-butyl-2-hydroxybenzyl)-1,4,7-triazacyclononane ligand have been reported by Wieghardt.[36] These types of ligands generally form kinetically and thermodynamically stable complexes through the benefits of chelate and macrocycle effects; thus suitably robust pre-catalyst may well be obtainable.[37] A number of preliminary reactions have therefore been examined with macrocyclic donor ligands.

The reaction of (*R,R,S/S,S,R*)-*N,N',N''*-(2-hydroxy-3,3-dimethylbutyl)-1,4,7-triazacyclononane ($H_3\mathbf{L^{19}}$) with titanium tetrakis(isopropoxide) yields a colourless crystalline solid. The mass spectrum of this solid shows a strong peak at m/z = 473.9 (Figure 4.8) which equates to one $\mathbf{L^{19}}$ ligand and one titanium centre i.e. $[\mathbf{L^{19}}Ti]^+$. The ^1H NMR spectrum of this compound is very complex as might be expected due to the inequivalences in (and consequently couplings between) the macrocycle CH_2 protons which will be engendered upon coordination. Due to the difficulty in obtaining crystals suitable for X-ray diffraction, definitive identification of this compound (and of its counter-ion) is clearly not possible. However, based on the mass spectrum, one

possibility is [Ti(*N*,*N*',*N*''-(2-hydroxy-3-dimethylbutyl)-triazacyclononane)]$^{+}{}_{(x-4)}$ [Ti(O^{i}Pr)$_x$]$^{(x-4)-}$ where x = 5 or 6 (Figure 4.9).

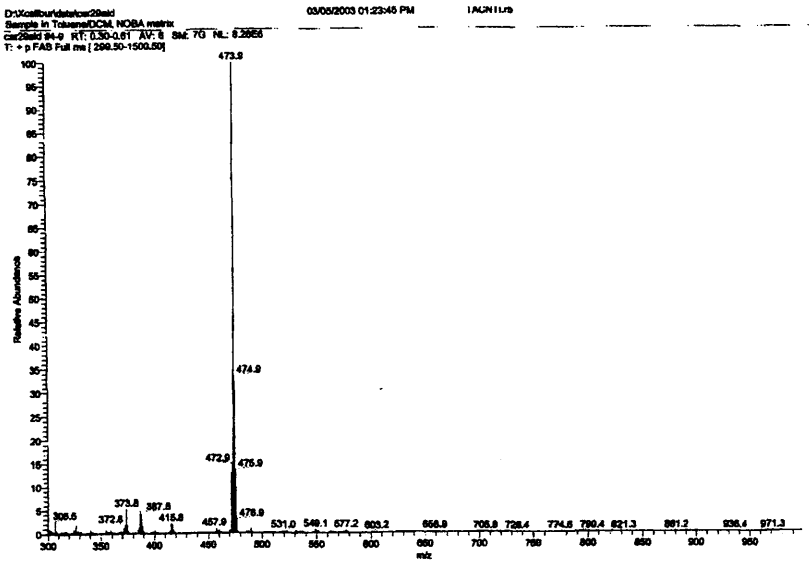


Figure 4.8: Mass spectrum of the colourless crystalline solid isolated from the reaction of $H_2\mathbf{L}^{19}$ with titanium tetrakis(isopropoxide).

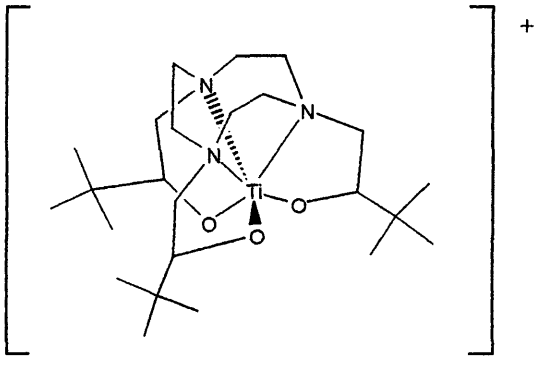


Figure 4.9: Proposed structure of [Ti(*N*, *N*', *N*''-(2-hydroxy-3,3-dimethylbutyl)-1,4,7-triazacyclononanetriazacyclononane)]$^{+}$, [$\mathbf{L}^{19}$Ti]$^{+}$.

The mass spectrum suggests the presence of the [Ti(*N*,*N*',*N*''-(2-hydroxy-3,3-dimethylbutyl)-1,4,7-triazacyclononanetriazacyclononane)]$^{+}$ unit, which would then

explain the complex nature of the ^{1}H NMR spectrum as due to the lack of symmetry causing all ligand protons to be inequivalent. A possible suggestion for the counterion would be $[Ti(O^iPr)_x]^{(x-4)-}$ (where x = 5 or 6), as $Ti(OR)_6^{2-}$ has previously been reported [36] and these anions could simply be formed by transfer of the isopropoxide ligand from the incipient cationic complex to unreacted $Ti(O^iPr)_4$. At the very least these tentative results suggest that reaction of aza-macrocyclic ligands possessing pendant alcohol functions with group 4 alkoxides is a promising route to amine stabilized titanium alkoxide complex formation.

A very similar result is achieved by the reaction of (R,R,S,S/S,S.R,R) *N,N',N'',N'''*(2-hydroxy-3,3-dimethylbutyl)-1,4,7,10-tetrazacyclododecane ($H_4\mathbf{L}^{22}$) with zirconium tetrakis(propoxide). Here too the product can be isolated as a white powder, the mass spectrum of which shows a peak envelope centred at m/z = 659.0 (Figure 4.10). This observation is consistent with one $\mathbf{L}^{22}$ ligand bound to zirconium

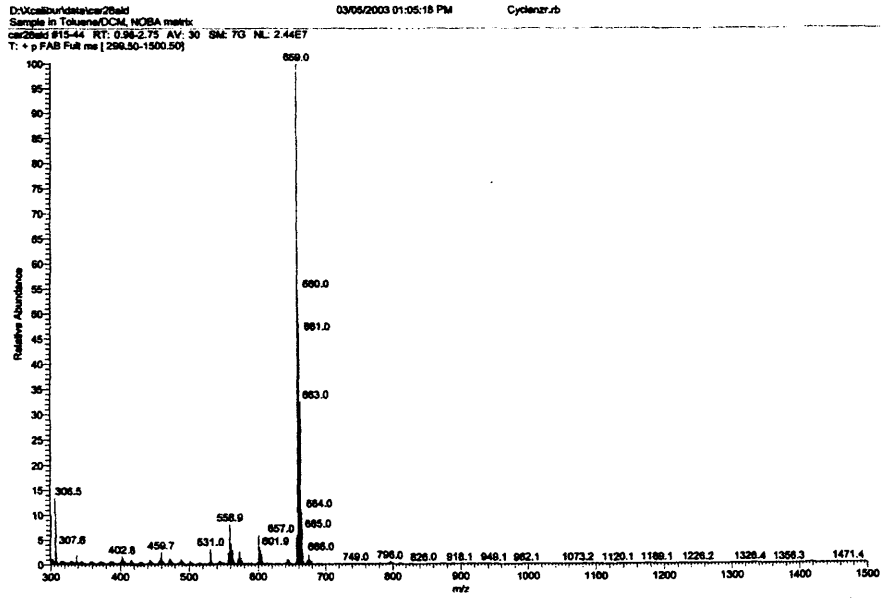
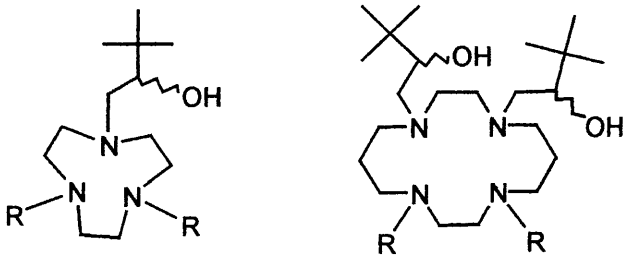


Figure 4.10: Mass spectrum of the colourless solid isolated from the reaction of $H_4\mathbf{L}^{22}$ with zirconium tetrakis(propoxide).

with all propoxide ligands substituted (i.e. with the ion $[\mathbf{L}^{22}Zr]^{+}$). As with the experiment reported above for zirconium the complex nature of the ^{1}H NMR spectrum and the difficulty in obtaining single crystals has prevented definitive characterization, although given the propensity of zirconium to achieve eight-fold coordination, a fully encapsulated species, $\mathbf{L}^{22}Zr$, incorporating four amine and four alkoxide donors is a distinct possibility.

Given the likely formation of macrocycle-tethered alkoxide linkages which these preliminary results imply, a potentially fruitful further avenue of research would involve the syntheses of the ligands $\mathbf{L}^{23}$ and $\mathbf{L}^{24}$ (Figure 4.11) and investigation of their complexation chemistries with titanium and zirconium, respectively. Such ligand frameworks might offer the possibility not only for the isolation of mono-metallic systems, but also for the availability of mutually cis ancillary ligand sites.



HL^{23} HL^{24}

Figure 4.11: Possible macrocyclic amine / alkoxide ligands for further study.

4.3.3 Nickel complexes of H_2L^{18}

Unlike its counterpart *N,N'-bis*(2-hydroxy-3-dimethylbutyl)-1,4 diazacyclohexane, containing a six-membered ring backbone ($H_2\mathbf{L}^{17}$), attempts to grow crystals of *N,N'*-

bis(2-hydroxy-3-dimethylbutyl)-1,4-diazacycloheptane ($H_2\mathbf{L}^{18}$) of suitable quality for X-ray diffraction have proved unsuccessful (see chapter 3). Given that $H_2\mathbf{L}^{18}$ is synthesized from 1,4-diazacyclohexane and *racemic* (+/-)-3,3-dimethyl-1,2-epoxybutane, a mixture of rac (R,R/S,S) and meso (R,S) diastereomers is presumably formed in this reaction. An X-ray structure of the crystals of this ligand obtained from hexane was therefore particularly desirable, as it would allow the determination of the relative stereochemistries at the two chiral centres in the crystalline product. Given the poorly diffracting nature of crystals of the pure ligand, complexation studies with metal sources bearing readily displaced ligands were attempted. Thus it was hoped that, albeit indirectly the stereochemistry of the crystalline product isolated from the ligand synthesis could be determined.

$H_2\mathbf{L}^{18}$ was therefore reacted with nickel (II) perchlorate hexahydrate. The structure of the small pale green crystals grown from diffusion of ether into the filtered reaction mixture is shown in Figure 4.12; relevant bond lengths and angles are listed in Table 4.5. Although the quality of the data was not optimal, the structure solution is of sufficient quality to determine that the complex features a distorted octahedral coordination environment containing one $H_2\mathbf{L}^{18}$ ligand coordinated to nickel through two oxygen and two nitrogen atoms. Furthermore the tetradentate $H_2\mathbf{L}^{18}$ ligand is coordinated in an equatorial fashion leaving two water molecules coordinated in the axial positions. The structure shown in Figure 4.11 confirms that both chiral centres are of the same handedness and this together with the non-chiral space group indicates, that the ligand exists as the *(R,R/S,S)* pair of enantiomers.

$H_2\mathbf{L}^{18}$ was also reacted with nickel chloride hexahydrate. Although no crystalline material was isolated from this reaction a mass spectrum was obtained of the green solid obtained after removing the solvent. The main peak in the mass spectrum at 357.0 equates to a $H_2\mathbf{L}^{18}$ ligand and a nickel atom. Also observed is a peak at 395.2 which may be attributed to a $[(H_2\mathbf{L}^{18})Ni(OH_2)_2]$ fragment. An alternative possibility for this fragment ion is $[(H_2\mathbf{L}^{18})NiCl]^+$, given the similarity in mass of one chloride and two water ligands. This is thought to be unlikely for several reasons: (i) the observed envelope intensity pattern is inconsistent with the presence of ^{35}Cl and ^{37}Cl isotopes; (ii) aqueous or wet alcoholic solutions of $NiCl_2$ are commonly known to act as precursors for complexes in which all nickel-bound chloride ligands have been removed, in some cases to be replaced by (mass spectroscopically characterized) nickel(II) aquo species;[38] and (iii) the stronger binding of H_2O (over Cl^-) to Ni(II) is well known from the spectrochemical series and illustrated by the purple form of Lifschitz's salt $[L_2Ni(OH_2)_2]Cl_2$ (L = *trans*-1,2-cyclohexanediamine).[39]

The UV/vis spectrum of this solid shows absorbances at 439 nm (22779 cm^{-1}) and 580 nm (17241 cm^{-1}) which are highly indicative of an octahedral nickel (II) complex.[40] On the basis of the mass spectrum and UV data the suggested formula for this complex is $[(H_2\mathbf{L}^{18})Ni(OH_2)_2]^{2+}[Cl^-]_2$. From the data available the coordination mode of the $H_2\mathbf{L}^{18}$ ligand cannot be conclusively stated, but the previously synthesised perchlorate salt of the same complex ion strongly suggests tetradentate binding with equatorial coordination of the N_2O_2 donor set.[40]

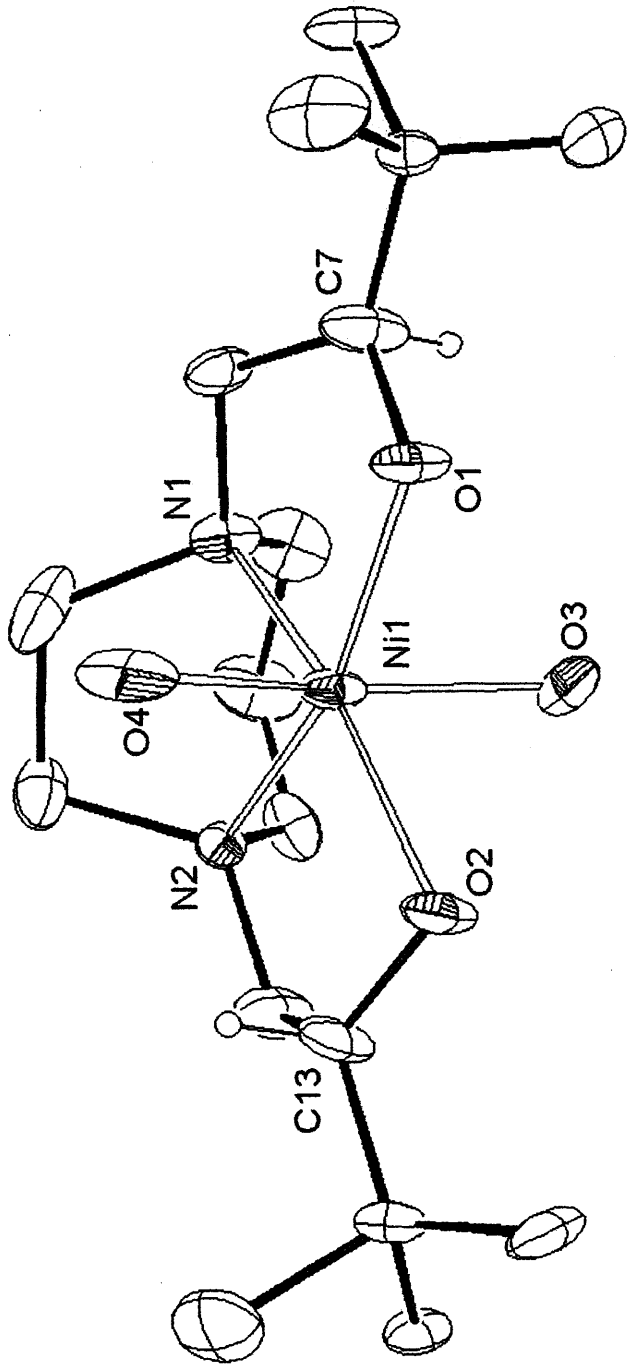


Figure 4.12: Crystal structure of the cationic component of $[(H_2L^{18})Ni(OH_2)_2][ClO_4]_2$, with thermal ellipsoids drawn at the 30% probability level. Hydrogen atoms and perchlorate counter-ions omitted for clarity.

Table 4.5: Selected bond distances (Å) and angles (°) for $[(H_2\mathbf{L}^{18})Ni(OH_2)_2][ClO_4]_2$.

N(1) –Ni(1)	2.031(6)	N(2) –Ni(1)	2.054(5)
O(1) –Ni(1)	2.087(5)	O(2) –Ni(1)	2.096(6)
O(3) –Ni(1)	2.061(13)	O(4) –Ni(1)	2.101(9)
N(1) –Ni(1) –N(2)	78.9(1)	N(1) –Ni(1) –O(1)	81.7(1)
N(2) –Ni(1) –O(2)	82.19(1)	O(3) –Ni(1) –O(4)	160.7(1)
O(1) –Ni(1) –O(2)	117.3(1)	O(1) –Ni(1) –O(3)	83.8(1)
O(1) –Ni(1) –O(4)	83.3(1)	O(4) –Ni(1) –N(1)	94.2(1)

4.3.4 Reactivity of H_2L^{18} towards aluminium alkyls

The reactivity of H_2L^{18} towards trimethylaluminium has also been investigated. Unfortunately, despite many attempts with different solvent systems, no single crystals could be obtained, only a fine white mircocrystalline precipitate. Two singlet resonances attributable to the *tert*-butyl groups of the L^{18} ligand and a further signal corresponding to an aluminium bound methyl group are easily identified in the ^1H NMR spectrum of this compound. Integration of these two peaks suggests a ratio of ligand *tert*-butyl:aluminium bound methyl of 2:1. This ratio is consistent with a formulation, L^{18}AlMe, in which one of the three aluminium methyl groups is retained. This inference is supported by the mass spectral data, which shows a prominent peak corresponding to the molecular ion (m/z = 341) which has the correct accurate mass and isotope distribution.

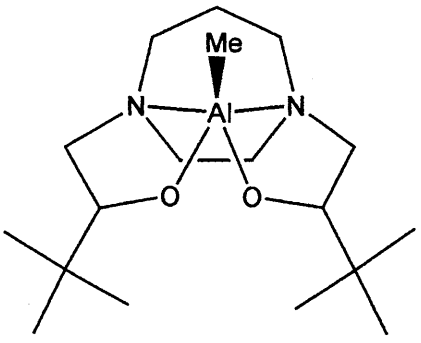
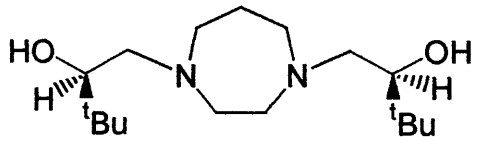


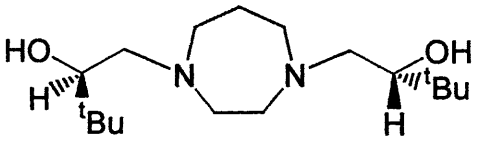
Figure 4.13: Possible structure for L^{18}AlMe

The ^1H NMR spectrum of L^{18}AlMe shows two signals at δ 1.22 and 1.26 that correspond to the *tert*-butyl groups of the ligand. The presence of these two signals indicates two different *tert*-butyl environments and therefore enables some tentative

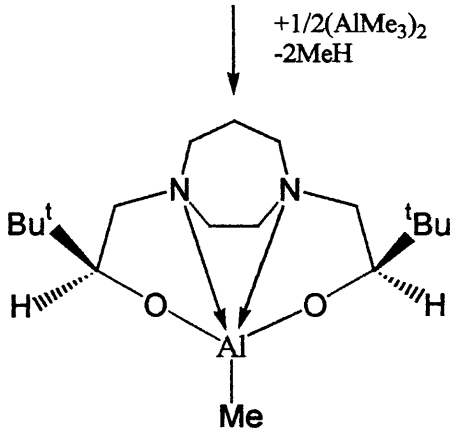
conclusions to be reached concerning the coordination of the ligand to aluminium. Coordination of either the R,S or S,R diastereomer would be expected to give only one signal for the *tert*-butyl group in the ^{1}H and ^{13}C NMR spectra (Figure 4.14), whereas two signals would be expected for the two inequivalent *tert*-butyl groups in the R,R/S,S isomers. Although an alternative explanation involving, for example, different states of aggregation cannot entirely be ruled out, this NMR data is consistent with the structural inferences obtained from coordination of the same ligand to nickel(II) - i.e. that the ligand used is of the in R,R/S,S pair of enantiomers.



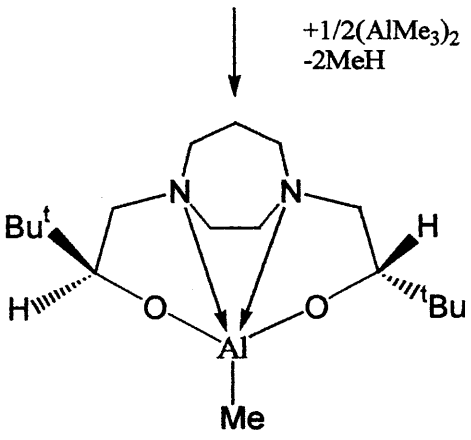
R,S and S,R



R,R and S,S



Tert-butyl Groups equivalent in NMR
- one signal.



Tert-butyl Groups not equivalent in NMR
- two signals.

Figure 4.14: Different numbers of tert-butyl environment stemming from the coordination of **L**[18] to aluminium.

4.4 Conclusions

Unfortunately attempts to coordinate $H_2\mathbf{L}^1$ (*trans*-1, 2-*di*(2-nitrophenylamino) cyclohexane) and $H_2\mathbf{L}^2$ (*trans*-1,2-di(2-nitro-6-pyridylamino)cyclohexane) to group 4 metals proved unsuccessful. This was thought to be due to the nitro groups causing ortho-directed lithiation of the benzene or pyridyl ring. Reaction of ligands $H_2\mathbf{L}^{12}$, $H_2\mathbf{L}^{13}$, $H_2\mathbf{L}^{14}$ and $\mathbf{L}^{15}$ with group 4 metal benzyls and chlorides also proved unsuccessful.However, two interesting bimetallic titanium complexes have been synthesised from group 4 alkoxide precursors, these being $\mathbf{L}^{18}Ti_2(O^iPr)_6$and $[\mathbf{L}^{18}Ti_2(OEt)]_2(\mu_2\text{-}O)$. There appears to be a simple relationship between the number of $(\mathbf{L}^{18})^{2-}$ ligands which can be introduced into the metal coordination sphere and the size of the alkoxides substituents of the $Ti(OR)_4$ starting material. Thus, titanium tetrakis(ethoxide) undergoes substitution of two ethoxide ligands at each titanium centre, whereas titanium tetrakis(isopropoxide) undergoes substitution of only one isopropoxide. Coordination of the related, but more flexible tetradentate ligand *N,N'-bis* (2-hydroxy-3-dimethylbutyl)dimethylethylenediamine ($H_2\mathbf{L}^{20}$) to zirconium and titanium was also successful. Coordination of two $(\mathbf{L}^{20})^{2-}$ ligands was observed for zirconium, but coordination of only one occurs for the smaller titanium centre. In the latter case, the compound so synthesized, $\mathbf{L}^{20}Ti(O^iPr)_2$ crystallizes with approximate C_2 symmetry and two mutually *cis* isopropoxide ligands. It is therefore comparable to the ideal model for active olefin polymerisation catalysts.

References

1. G. J. P. Britovsek, V. C. Gibson, D. F. Wass, *Angew Chem. Int. Ed.*, 1999, **38**, 428

2. V. C. Gibson, B. S. Kimberly, A. J. P. White, D. J. Williams, P. Howard *Chem. Commun.*, 1998, 313

3. F. Jager, H. W. Roesky, H. Dorn, S. Shah, M. Noltemeyer, H.-G. Schmidt, *Chem. Ber.*, 1999, **130**, 399

4. A. Van Der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, *J. Am. Chem. Soc.*, 1995, **117**, 3008

5. S. Fokken, T. P. Spaniol, J. Okuda, F. G. Sernetz, R. Mullhaupt, *Organometallics*, 1997, **16**, 4240

6. F. G. Sernetz, R. Mullhaupt, S. Fokken, J. Okuda, *Macromol.*, 1997, **30**, 1562

7. S. Fokken, F. Reichwald, T. P. Spaniol, J. Okuda, *J. Organomet. Chem.*, 2002, **663**, 158

8. S. Groysman, I. Goldberg, M. Kol, E. Genizi, Z. Goldschmidt, *Inorg. Chim. Acta*, 2003, **345**, 137

9. F. Guerin, D. H. McConville, J. J. Vittal, *Organometallics*, 1996, **15**, 5586

10. M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2487

11. E. M. Kaiser, D. W. Slocum in *Organic Reactive Intermediates*, S. P. McManus Ed., Academic Press, New York, NY, 1973, chapter 5

12. D. W. Slocum, C. A. Jenning, *J. Org. Chem.*, 1976, **41**, 23

13. A. R. Lepley, W. A. Khan, A. B. Giumanini, A. G. Guimanini, *J. Org. Chem.*, 1966, **31**, 2047

14. F. N. Jones, C. R. Hauser, *J. Org. Chem.*, 1962, **27**, 70

15. N. S. Narasimhan, A. C. Ranade, *Tetrahedron Lett.*, 1966, **7**, 603

16. D. A. Shirley, J. R. Johnson, Jr., J. P. Hendrix, *J. Organomet. Chem.*, 1968, **11**, 217

17. W. H. Puterbaugh, C. R. Hauser, *J.Org.Chem*, 1968, **33**, 900

18. H. Watanabe, R. L. Gay, C. R. Hauser *J.Org.Chem.*, 1964, **29**, 900, 853

19. H. Watanabe, R. A. Schwartz, C. R. Hauser, J. Lewis, D. W. Slocum, *Can. J. Chem.*, 1969, **47**, 1543

20. J. D. Roberts, D.Y.Curtin, *J. Am. Chem. Soc.*, 1946, **68**, 1658

21. D. A. Shirley, J. R. Johnson,Jr.,J. P. Hendrix, *J. Organomet. Chem.*, 1968, **11**, 209

22. H. Gilman, T. S. Soddy, *J. Org. Chem.*, 1957, **22**, 1915

23. Y. Kim and J.G. Verkade, *Organometallics*, 2002, **21**, 2395

24. S. D. Bull, M. G. Davidson, A. L. Johnson, D. E. J. E. Robinson and M. F. Mahon, *Chem. Commun.*, 2003, 1750

25. M. Kol, M. Shamis, I. Goldberg, Z. Goldschmidt, S. Alfi, E. Hayut-Salant, *Inorg. Chem. Commun.*, 2002, **4**, 177

26. J. Emsley, *The Elements,* Oxford University Press, Oxford, 1995

27. P. W. Atkins, *Physical Chemistry,* Oxford University Press, Oxford, 1995

28. S. Tinkler, R. J. Deeth, D. J. Duncalf, A. McCamley, *Chem. Commun.*, 1996, 2623

29. N. A. H. Male, M. Thornton-Pett, M. Bochmann, *J. Chem. Soc., Dalton Trans.*, 1997, 2487

30. See, for example: (a) D.C.Bradley, M.B.Hursthouse, I.F.Rendall, *J. Chem. Soc. D*, 1970, 368. (b) M.L. Illingsworth, A.L.Rheingold, *Inorg. Chem.*, 1987, **26**, 4312. (c) M.L. Illingsworth, B.P. Cleary, A.J. Jensen, L.J. Schwartz, A.L.Rheingold, *Inorg. Chim. Acta*, 1993, **207**, 147. (d) T. Toupance, S.R. Dubberley, N.H. Rees, B.R. Tyrrell, P.Mountford, *Organometallics*, 2002, **21**, 1367

31. E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.* , 2000, 379

32. P. Corradini, G. Guerra, *Prog. Polymer Sci.*, 1991, **16**, 239

33. J.K. Day, S. Aldridge, unpublished results

34. X. Bei, D.C. Swenson, R.F.Jordan, *Organometallics*, 1997, **16**, 3282

35. (a) P. J. Wilson, A. J. Blake, P. Mountford, M. Schroder, *Chem. Commun.* 1998, 1007. (b) P. J. Wilson, P. A. Cooke, A. J. Blake, P. Mountford, M. Schroder, *New J. Chem.*, 1999, **23**, 271. (c) P. J. Wilson, A. J. Blake, P. Mountford, M. Schroder, *J. Organomet. Chem.*, 2000, **600**, 71. (d) N. A. H. Male, M. E. G. Skinner, P. J. Wilson, P. Mountford, M. Schroder, *New J. Chem.* 2000, **24**, 575. (e) N. A. H. Male, M. E. G. Skinner, S. Y. Bylikin, P. J. Wilson, P. Mountford, M. Schroder, *Inorg. Chem.*, 2000, **39**, 5483. (f) J. D. Gardner, D. A. Robson, L. H. Rees, P. Mountford, *Inorg. Chem.*, 2001, **40**, 820

36. (a) U. Auerbach, T. Weyhermuller, K. Wieghardt, B. Nuber, E. Bill, C. Butzlaff, A. X. Trautwein, *Inorg. Chem.*, 1993, **32**, 508. (b) G. Schlager, K. Wieghardt, H. Grondey, A. Rufinska, B. Nuber, *Inorg. Chem.*, 1995, 34, 6440.

37. (a) L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes,* Cambridge University Press, Cambridge, 1989. (b) K. P. Wainright, *Coord. Chem. Rev.*, 1997, **166**, 35

38. For recent examples, see: (a) C. Cruz, S. Carvalho, R. Delgado, M. G. B. Drew, V. Felix, B. J. Goodfellow, *Dalton Trans.*, 2003, 3172. (b) K. -Y. Choi, *J. Coord. Chem.*, 2003, **56**, 41. (c) I. A. Fallis, P. C. Griffiths, P. M. Griffiths, D. E. Hibbs, M. B. Hursthouse, A. L. Winnington, *Chem. Commun.*, 1998, 665. (d) K. E. Barefield, G. M. Freeman, D. G. Van Derveer, *Inorg. Chem.*, 1986, **25**, 552

39. N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Pergamon Press, Oxford, 1986, pp1348

40. F. A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, Wiley, Fifth Edition, pp744

Chapter 5

Catalytic Studies

5.1 Introduction

For over fifty years olefin polymerisation catalysis has received a vast amount of research attention from both industry and academia.[1,2] Group 4 metal catalysed olefin polymerisation has progressed from the original Ziegler-Natta system,[3] to cyclopentadienyl complexes,[2,4] and more recently to complexes containing amide or alkoxide donors.[5,6] Previous research has identified many important characteristics that are possessed by active polymerisation catalysts.[1,2] The nature of the active species is generally accepted to be an electrophilic cationic metal alkyl with a vacant coordination site $[L_nMR]^+$;[7] furthermore, it has been shown that the symmetry of the complex can play an important role in the outcome of the stereochemistry of the polymer, with C_2 symmetric species in some cases giving material with a high degree of isotacticity.[8,9,10] Incorporation of hemi-labile donors into the complex has been shown to increase activity by reducing the extent of competing side reactions by reducing the electrophilicity of the metal.[11]

5.2 Aims of Research

The activity of the complexes $\mathbf{L^{20}}Ti(O^iPr)_2$, $(H\mathbf{L^{21}})/Ti(O^iPr)_4$, $\mathbf{L^{18}}Ti_2(O^iPr)_6$, $[Ti\mathbf{L^{19}}]^+$ and $\mathbf{L^{20}}Zr_2$ towards the polymerisation of ethylene was tested using a large excess of MAO as the activator. The activity of $\mathbf{L^{20}}Ti(O^iPr)_2$ towards hex-1-ene was also

investigated. In addition to the aforementioned complexes, the *in situ* generated mixtures $(H_2L^{12})/Zr(Bz)_4$ and $(HL^{16})/Zr(Bz)_4$ (in ratios 1:1) were tested for their activity towards ethylene polymerisation. The measured activities have then been compared to those reported in the literature for similar polymerisation catalyst systems.

5.3 Experimental

5.3.1 Reactions with Ethylene

In a typical reaction the titanium or zirconium complex (~ 0.1 mmol) was dissolved in toluene (50 cm^3) and MAO (10 wt % solution in toluene Al:M ~100:1) added by syringe. The solution was stirred for 15 min and transferred by cannula to a Fisher-Porter tube. The Fisher-Porter tube was then filled with ethylene to a pressure of 2.8 bar and stirred for 1 h. The reaction was deactivated by the addition of methanol (50 cm^3), filtered and any solid produced was washed with methanol, acidified with concentrated HCl and dried under vacuum. An aliquot of the filtrate was analysed by GC-MS spectroscopy. Any solid obtained was submitted to RAPRA for analysis by high temperature gel permeation chromatography.

5.3.2 Reactions with 1-Hexene

In a typical reaction the titanium or zirconium complex (~ 0.1 mmol) was dissolved in toluene (50 cm^3) and MAO (10wt% solution in toluene Al:M ~100:1) added by syringe. The solution was stirred for 15 min and transferred by cannula to a Fisher-

Porter tube. 1.5 mL of 1-hexene was added and the reaction then stirred for 1 h. The reaction was deactivated by the addition of methanol (50 cm^3). The reaction mixture was filtered and any solid produced was washed with methanol, acidified with concentrated HCl and dried under vacuum. An aliquot of the filtrate was analysed by GC-MS spectroscopy. Any solid obtained was submitted to RAPRA for analysis by high temperature gel permeation chromatography.

5.4 Results and Discussion

5.4.1 Catalyst Activities

The formulations of the pre-catalysts used during this research are summarised in Table 5.1.

Table 5.1: Pre-catalysts for polymerisation experiments.

Pre-catalyst	Catalytic Run Number
$\mathbf{L^{20}}Ti(O^iPr)_2$	1 and 8
$(HL^{21})/Ti(O^iPr)_4$	2
$(HL^{16})/Zr(Bz)_4$ 1:1 mixture	3
$(H_2L^{12})/Zr(Bz)_4$ 1:1 mixture	4
$\mathbf{L^{18}}Ti_2(O^iPr)_6$	5
$[\mathbf{L^{19}}Ti]^+$	6
$(\mathbf{L^{20}})_2Zr$	7

Table 5.2: Polymerisation data for selected compounds.

Run (RAPRA ref)	Amount of Catalyst (mmol)	Monomer	Pressure (bar)	Equivs of Initiator	Yield (g)	Activity ($gPmmol^{-1}h^{-1}$)	Activity ($gPmmol^{-1}h^{-1}bar^{-1}$)
1 (2ET)	0.11	Ethylene	2.8	100:1	0.365	3.318	1.185
2 (1ET)	0.14	Ethylene	2.8	100:1	0.250	1.786	0.638
3 (3ET)	0.10	Ethylene	2.8	100:1	0.074	0.740	0.268
4	0.10	Ethylene	2.8	100:1	0	0	0
5	0.07	Ethylene	2.8	100:1	0	0	0
6 (4ET)	0.10	Ethylene	2.8	100:1	0.086	0.860	0.312
7	0.07	Ethylene	2.8	100:1	0	0	0
8 (2HX)	0.11	Hex-1-ene	-	100:1	0.04	0.364	-
9	0	Ethylene	2.8	control solution	0	0	0
10	0	Hex-1-ene	2.8	control solution	0	0	0

[a] All reactions carried out in $50cm^3$ toluene at 25°C using MAO as the activator.

The results of the catalytic testing are summarised in Table 5.2. Solid material was obtained from runs 1, 2, 3, 6 and 8. No activity was observed for runs 4, 5 and 7. Runs 9 and 10 were performed as controls containing just MAO and toluene to ensure that the activator was not contributing to any solid that was produced. Addition of MAO to a toluene solution of $\mathbf{L^{20}}Ti(O^iPr)_2$ in toluene (run 1) gave rise to a colour change from colourless to brown/yellow. Polymerisation was observed on addition of the ethylene monomer, with solid polymer observed in the solution after one hour. The activity of the catalyst was calculated to be 1.185 gP $mmol^{-1}$ h^{-1} bar^{-1}. Activation of a toluene solution of $(HL^{21})/Ti(O^iPr)_4$ (run 2) with an excess of MAO gave rise to a colour change from colourless to brown/yellow. After quenching the polymerisation reaction a gel-like precipitate of polymer was observed. The activated catalyst showed

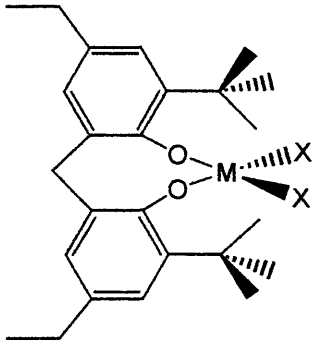
activity for the polymerisation of ethylene (0.638 gP $mmol^{-1}$ h^{-1} bar^{-1}). Addition of excess MAO to a toluene solution of (HL^{16}):$Zr(Bz)_4$ (run 3) gave an active catalyst which produced a solid from ethylene after one hour (0.268 gP $mmol^{-1}$ h^{-1} bar^{-1}). Run 6 showed a toluene solution of $[L^{19}Ti]^+$ was active towards ethylene after activation with excess MAO (0.312 gP $mmol^{-1}$ h^{-1} bar^{-1}). Addition of excess MAO to a toluene solution of $L^{20}Ti(O^iPr)_2$ (run 8) gave an active catalyst which produced a solid from hex-1-ene after one hour (0.364 gP $mmol^{-1}$ h^{-1}). In all cases the solids obtained were very insoluble in solvents such as toluene and DMSO. Table 5.3 shows ratings for catalyst effectiveness based on activity.[1]

Table 5.3: Rating of the effectiveness of a catalyst based on its activity

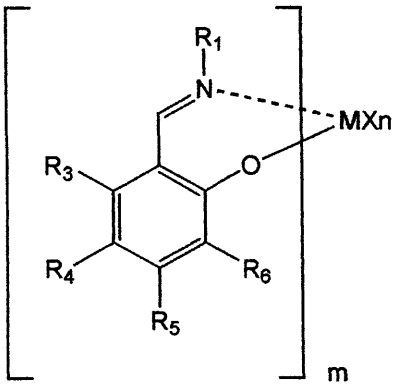
Rating	**Activity [gP $mmol^{-1}$ h^{-1}]**
Very low	<1
Low	1-10
Moderate	10-100
High	100-1000
Very high	>1000

The activities obtained for this research were compared with literature values for similar catalysts. Thus, chelating aryloxide complex **1** shows moderate activity towards ethylene (130 gP $mmol^{-1}$ h^{-1} bar^{-1});[11] high activities are observed towards ethylene for the mixed alkoxide/imine complex **2** (519000 g P $mmol^{-1}$ h^{-1} bar^{-1}).[12] Complexes **3** and **4**, reported by Goldschmidt et al.,[10] are probably the most similar to the complexes tested during this research as they contain a primary ligand with a

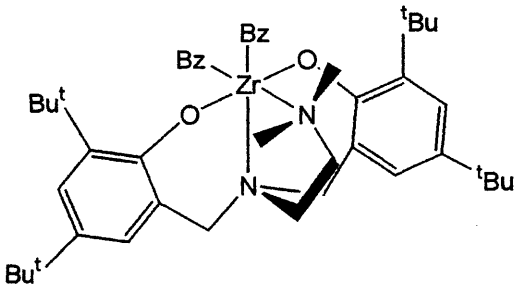
combination of two alkoxide donors and one or two amine donors. Their activity towards hex-1-ene was tested; moderate activity was observed for **3** (23 gP $mmol^{-1}$ h^{-1} bar^{-1}) in contrast to complex **4** where the addition of an extra amine donor drastically boosts the activity to 15500 gP $mmol^{-1}$ h^{-1} bar^{-1}. Comparison of the polymerisation results for this research with literature values shows that the activities obtained are very low in all cases.



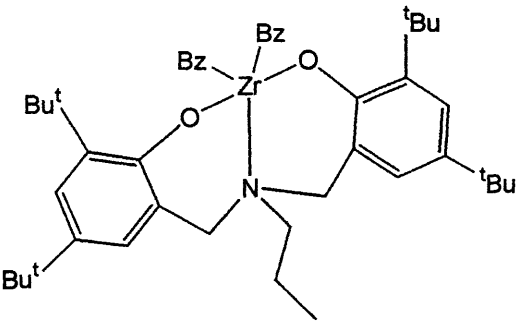
1



2



3



4

5.4.2 GPC Analysis of Polymeric Material

Each of the solids obtained from runs 1, 2, 3, 6 and 8 were sent to RAPRA for analysis by high temperature gel permeation chromatography (GPC). Problems were encountered with the solubility of some solid samples. In all cases there were significant amounts of residual inorganic material despite copious washing of the solids with methanol acidified with HCl. Insolubility of the polymer could either be due to cross-linking or very high molecular weight. No data could be determined for the solids from runs 1 and 8 because of the low solubility of the material submitted. Table 5.4 shows the molecular weight and polydispersity data measured for each sample.

Table 5.4: Molecular weight and polydispersity data

(RAPRA Ref.)	Run Number	M_w	M_n	Polydispersity
1ET	1	255000	910	280
	2	211000	1010	210
2ET	1	No response		
	2			
2HX	1	No response		
	2			
3ET	1	113000	1220	92
	2	Poor chromatogram		
4ET	1	222000	1690	130
	2	225000	1840	120

Figure 5.1 shows the differential pressure chromatograms for runs $L^{18}Ti(O^iPr)_2$ [2ET], $(HL^{21})/Ti(O^iPr)_4$ [1ET], $(H_2L^{12})/Zr(Bz)_4$ 1:1 mixture [3ET] and $[L^{19}Ti]^+$ (4ET). The chromatograms are all dominated by a large response at low retention volume that corresponds to a high molecular weight polymer. The high molecular weight material detected appears to be common to all four samples. The response for run 1 was very weak, hence the noisy chromatogram; as a result the molecular weight of this sample could not be determined.

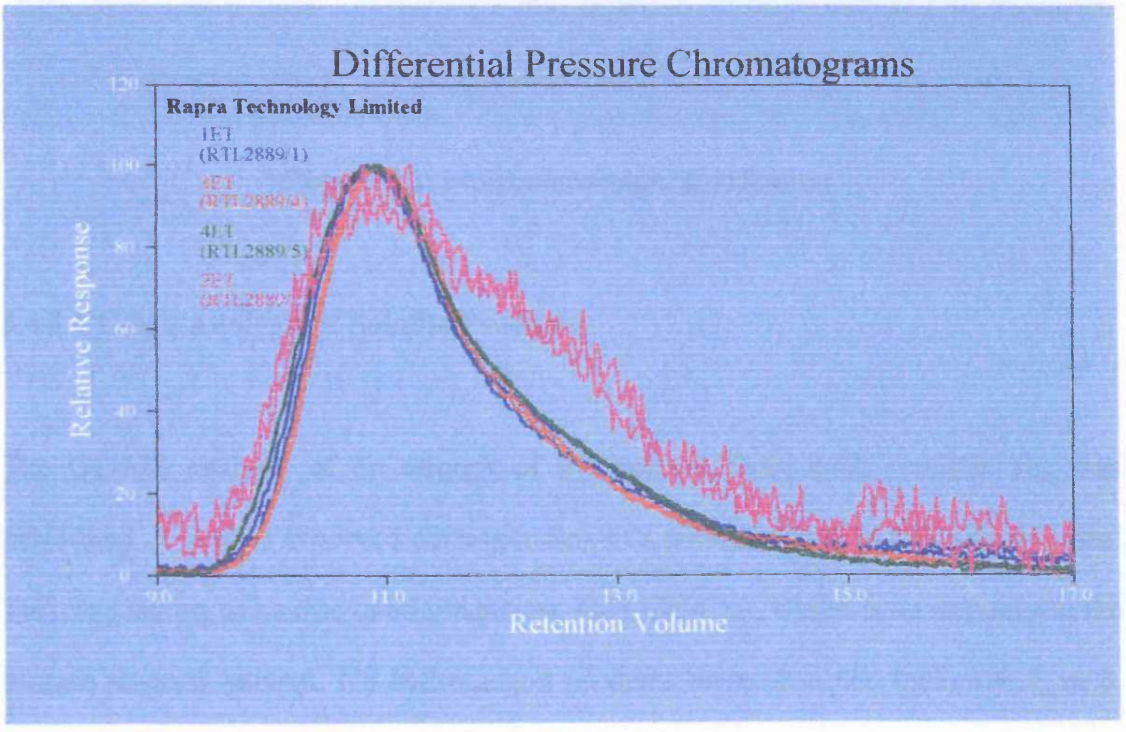


Figure 5.1: Differential pressure chromatograms.

Figure 5.2 illustrates the molecular weight distribution for the polymer obtained from catalytic runs 2 (1ET), 3 (3ET) and 6(4ET). All three samples are similar in that they have a wide molecular weight distribution showing that the materials obtained have high polydispersities.

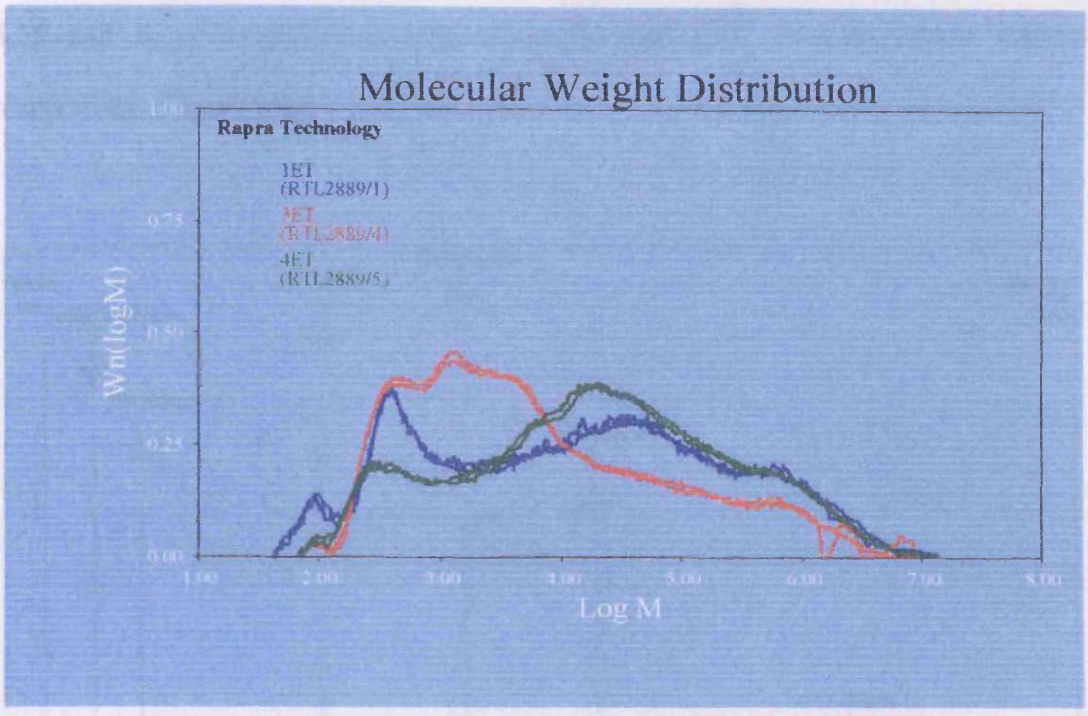


Figure 5.2: Molecular weight distribution.

5.4.3 GC-MS Analysis of Soluble Products

The GC-MS analysis of an aliquot of the solvent from each catalytic run was performed. A peak is observed corresponding to a retention time of 6.38 s in all cases. This was shown to be due to ethylbenzene, $C_6H_5CH_2CH_3$, which is an impurity in the toluene reaction solvent. No hydrocarbon products were observed for run 4, 7, or 8. The clearest set of results was obtained from run 2. The total ion current for catalytic run 2 clearly shows the presence of alkanes and alkenes (Figure 5.3). From the GC-MS results it can be seen that the odd alkanes, from C9 to C17, are by far the most prevalent toluene-soluble products of the reaction. Comparison of these mass spectra with library data (including fragmentation analysis) indicates that the alkanes in general have straight chains, with the exception of those observed at retention times of

6.25 and 11.09 s, which correspond to C9 and C11 branched chain alkanes, respectively (Figure 5.4).

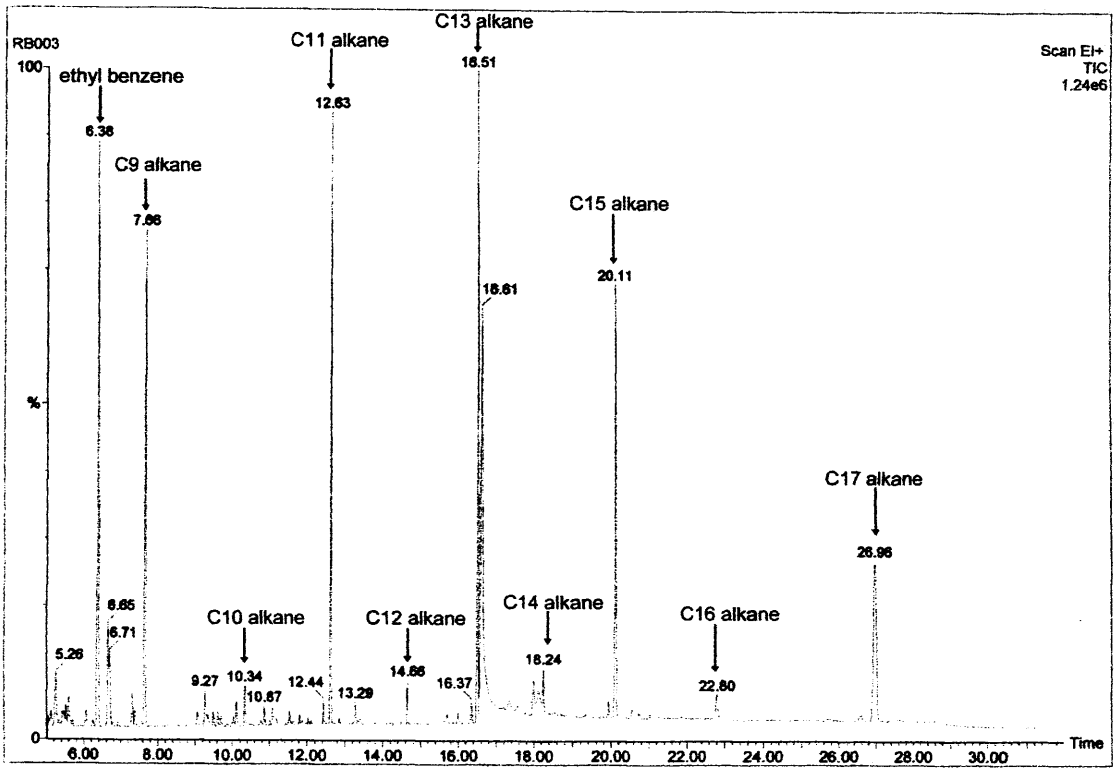


Figure 5.3: Total ion current for catalytic run 2.

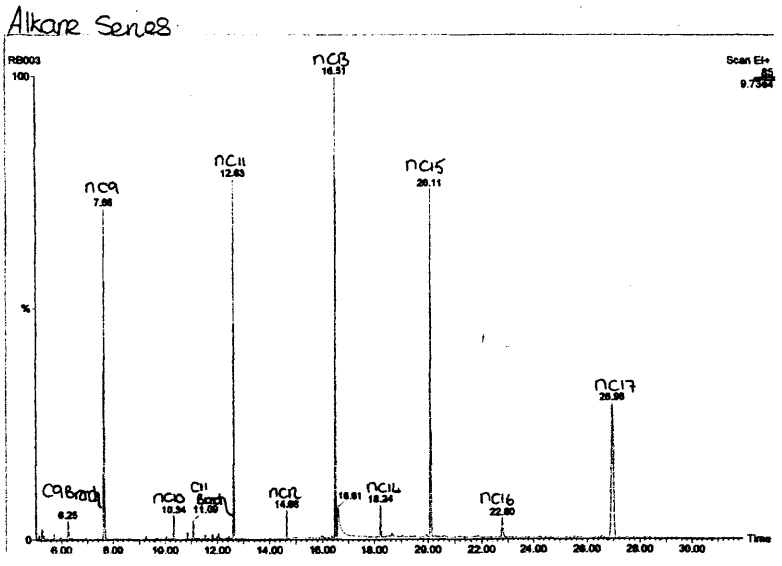


Figure 5.4: GC-MS spectrum resolved for alkanes (run 2).

Even chain length alkanes were also observed (mainly C10 to C16) but are present in much lower concentrations. Even smaller amounts of alkenes were also observed, with both even and odd chain lengths from C11 to C17 being observed (Figure 5.5).

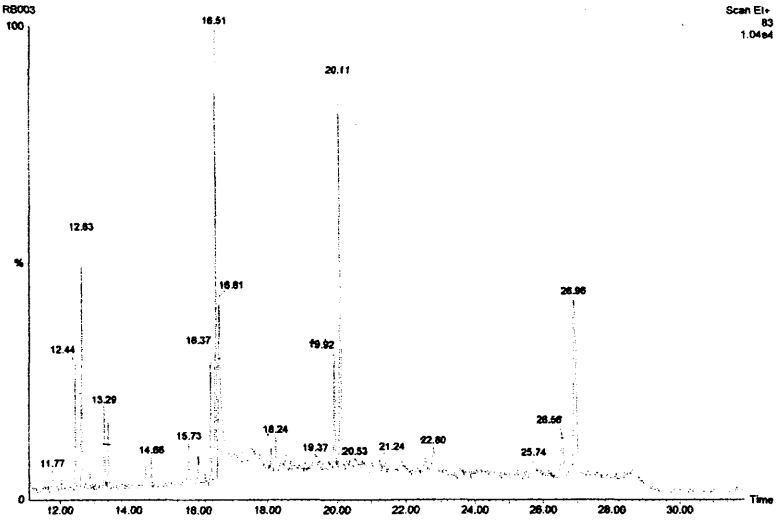


Figure 5.5: GC-MS resolved for alkenes (run 2).

The GC-MS data for run 1 (Figure5.6) shows that the products of oligomerization are predominantly odd chain length alkanes, although some even alkanes are also detected. There was also a small amount of alkene visible.

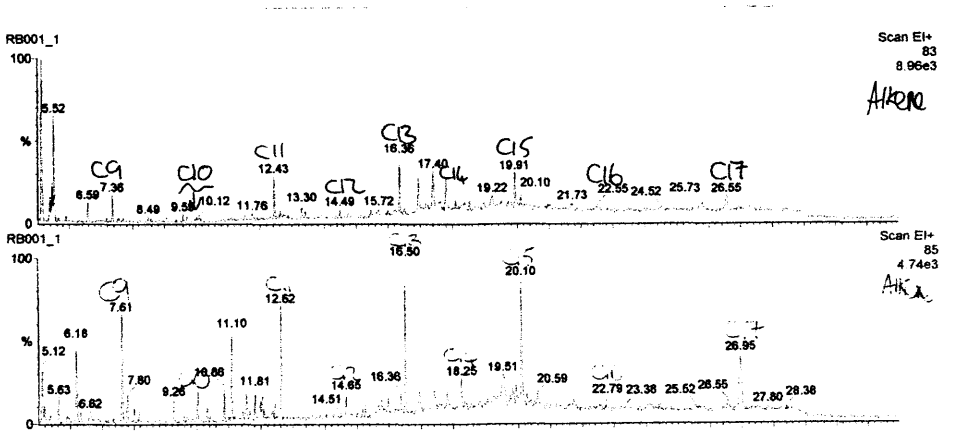


Figure 5.6: Alkene (top) and alkane(bottom) resolved GC-MS for run 1.

For run 3 the same predominantly odd chain length alkane pattern is also observed (Figure 5.7), but there is no evidence of alkene among any of the products for this reaction.

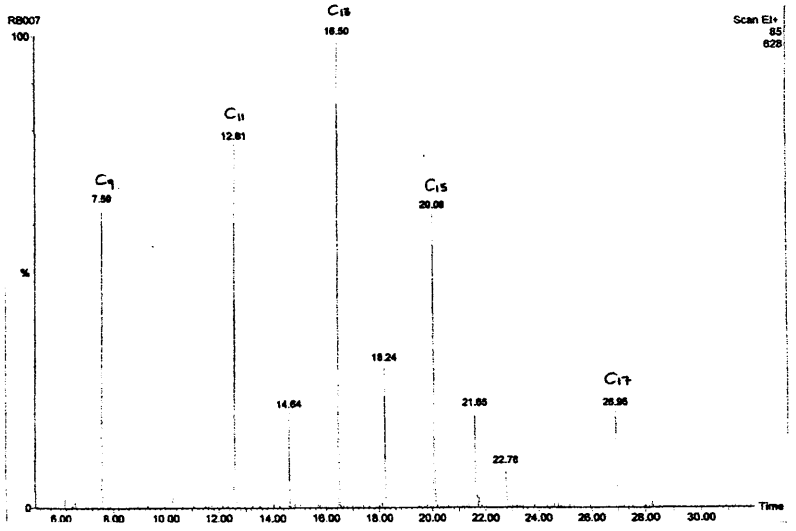


Figure 5.7: Alkane resolved GC-MS for run 3.

Run 5 also shows mainly odd chain length alkanes as the main product with some even chain length alkanes. As with run 3 there are no alkene products observed in the GC-MS (figure 5.8).

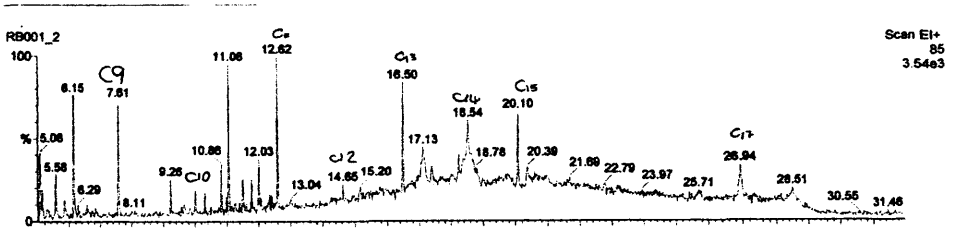


Figure 5.8: Alkane resolved GC-MS for run 5.

For run 6 the GC-MS trace is very weak but alkanes with odd chain lengths can be identified. There appear to be no alkenes amongst the products for this reaction (Figure 5.9).

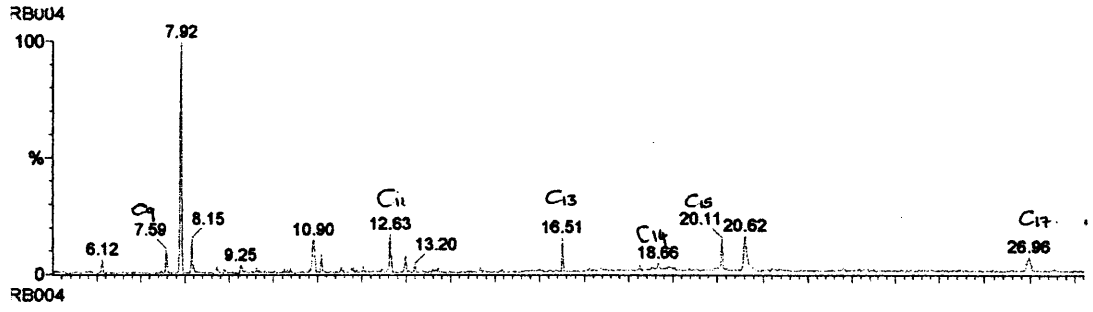
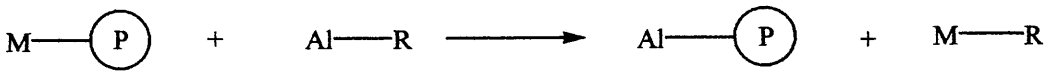


Figure 5.9: Alkane resolved GC-MS for run 6.

5.5 Discussion

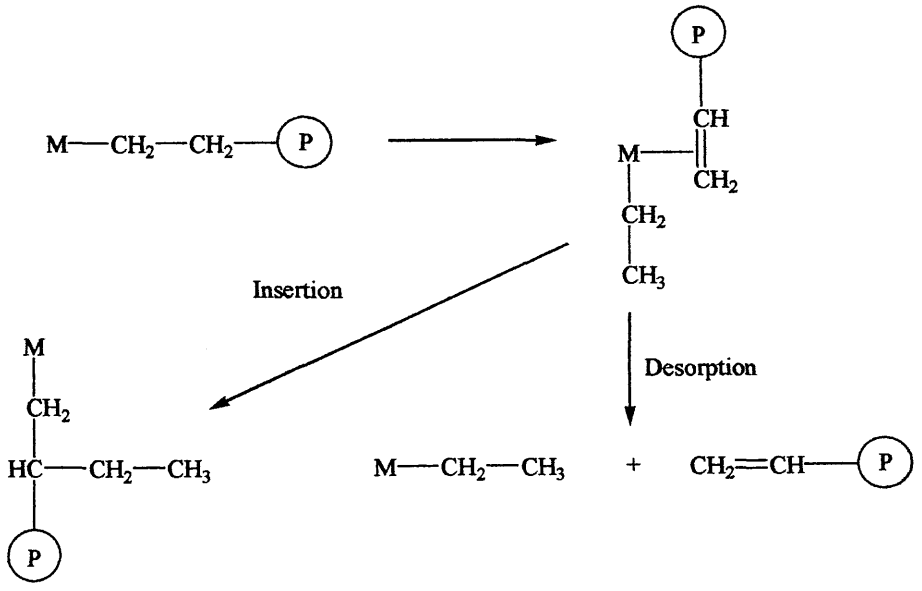
The nature and relative amounts of hydrocarbon products observed allows some speculation to be made as to the mechanisms in operation during polymerisation. It seems likely that liberation of free alkane occurs because of chain transfer to aluminium (Scheme 5.1) followed by hydrolysis during the quenching of the catalytic reaction mixture.[13,14]



Scheme 5.1: Chain transfer to aluminium (M = Ti or Zr; R = alkyl liand; P = polymer chain).

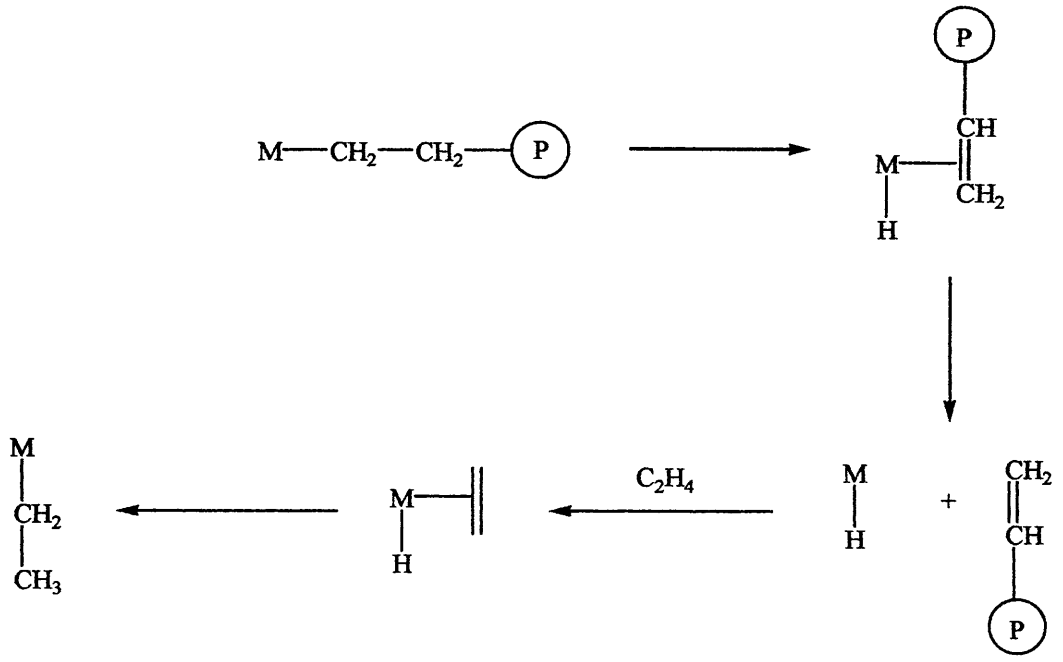
Alkanes with odd chain length would be formed by the insertion of ethylene into an odd chain length metal alkyl. In this case the alkyl in question is most likely a metal-bound methyl group which would have been formed during activation of the catalyst

with MAO. Even alkanes are observed in some cases. These could be due to insertion of ethylene into an even metal alkyl. Such even metal alkyls could be formed during side reactions occurring during the polymerisation process (vide infra). The presence of small amounts of alkene suggest that a β-hydride elimination mechanism is operating to some extent during the polymerisation reaction.[13,15,16] β-hydride elimination can occur with or without coordinated monomer. With coordinated monomer present, β-hydride elimination with subsequent insertion of monomer into the M-H bond results in the formation of an unsaturated polymer and a metal alkyl.[13] There are then two possible scenarios: (i) desorption of unsaturated polymer leaving a metal alkyl' or (ii) insertion of unsaturated polymer into the metal alkyl resulting in a branched polymer chain (Scheme 5.2) The presence of the branched C9 alkane in the GCMS spectrum suggests that this mechanism may be in operation to a small degree.



Scheme 5.2: Desorption and insertion proesses following β hydride elimination.

In the absence of coordinated monomer β-hydride elimination occurs resulting in the formation of a metal hydride and an unsaturated polymer (Scheme 5.3).[13]



Scheme 5.3: Formation of a metal hydride by β hydride elimination.

In both β-hydride elimination mechanisms, the formation of an even chain length metal alkyl occurs. This could account for the generation of the even alkanes observed in the GCMS traces.

For the runs that produced solid during the catalytic reaction it is interesting to note that although the reported activity was very low, the molecular weight of the material produced was very high. If the catalyst was very inactive (in that the insertion of monomer into the metal alkyl bond was not facile), the reaction would be expected to yield oligomers or very low molecular weight material. As the molecular weight of the solids obtained from catalytic runs 1, 2, 3, 6 and 8 was very high it seems unlikely that the catalysts, once formed, were inactive for insertion. There are two possible scenarios which could explain the observed outcome. Firstly it could be the activation

step that is responsible for the low activity results. If the activation step forming the catalyst from the precatalyst is inefficient then few active species will be formed per unit time. The activated species may show high activity towards insertion of monomer into the metal alkyl bond (compared to deactivating side reactions), and may thereby perform many insertion steps to form a high molecular weight polymer. If the active species is, however, only present in small amounts relative to the precatalyst, the overall rate will suggest a very inefficient system. Thus one possibility is that, for the catalyst systems investigated during this research, the alkylation and subsequent abstraction steps are relatively slow.

Another possibility is that if the activation step is efficient in producing active catalyst, it may be that other reactions are more predominant than insertion. For example it may be possible that the rate of β-hydride elimination for the active species is faster than that of insertion of monomer. If then the alkene product of β-hydride elimination re-enters the catalytic cycle effectively as a higher molecular weight monomer (Scheme 5.2) it can be incorporated into the growing polymer chain. Although both scenarios are feasible, given the experimental evidence from the catalytic runs it seems more reasonable to suggest that the low activity is due to the activation step. In the catalytic runs, toluene soluble alkene products were only present in small amounts compared to alkanes suggesting that the rate of β-hydride elimination probably not as fast as insertion. β-hydride elimination from a straight chain oligomer or polymer would result in a terminal alkene. The alkene would no longer be simple and symmetrical (like ethylene) but would posses an alkyl group on one carbon, making it more akin to propylene. As a result, insertion of such an alkene can result in branching in the polymer as the orientation of the monomer during

insertion now becomes important. This may explain the presence of the branched alkane in the GC-MS. The presence of branched polymer may be reflected in the high polydispersity of the solids obtained. For d^0 Ti(IV) complexes β-hydride elimination would not be expected to be facile as electrons from metal d orbitals are generally required to populate the σ* orbital of C-H for the bond to break. However, if the primary ligand of a d^0 Ti(IV) complex has π donor capabilities and can therefore transfer electron density into the d orbital which is of the correct orientation to overlap with σ* of the polymer C-H, β-hydride elimination could occur. In the case of $(HL^{21})/Ti(O^iPr)_4$, $L^{18}Ti_2(O^iPr)_6$ and $L^{20}Ti(O^iPr)_2$, the alkoxide donors of the primary ligands could conceivably act as the required π donors. The crystal structure of $L^{20}Ti(O^iPr)_2$ on the other hand (chapter 4) shows that the amine donors, rather than the alkoxides are trans to the positions that would be occupied by the growing polymer chain. Amines are not π donors and as a result population of the d orbital would be minimal and β-hydride elimination therefore would not be expected to be facile. This may explain why there are very few β-hydride elimination products observed for the alkoxide based polymerisation catalysts reported in this chapter.

The possibility that the initial pre-catalyst activation step may be the 'bottleneck' in the catalytic processes has been examined by considering the reactivity of $L^{20}Ti(O^iPr)_2$ towards the alkylating agent methyl lithium.Although this reaction was carried out with the primary intention of replacing the isopropoxide ligands to give a more conventional catalyst precursor viz $L^{20}TiMe_2$, the reaction did not proceed as predicted. Indeed the appreciable degree of decomposition of the $L^{20}Ti$ framework under alkylation conditions (as revealed by NMR data) is similar to results previously reported by Jordan et al.[17] In view of the outcome of this attempted alkylation process,

it is possible that the low activity of the complex $\mathbf{L}^{20}Ti(O^iPr)_2$ may be due to inefficient methylation of the pre-catalyst by MAO.

Finally, given the very low activities observed for all of the catalyst runs, it is difficult to make any definitive conclusions concerning the steric and electronic influences of the complexes on polymerisation activity. It is probably not surprising that runs 6 and 7 featuring effectively encapsulated titanium and zirconium centres produce negligible activity, and that the highest activity is observed for $\mathbf{L}^{20}Ti(O^iPr)_2$, which is the only system which has been shown unequivocally to contain the mutually cis vacant sites model for active catalysts. Beyond this any further structure/activity speculation is clearly not justified.

5.6 Conclusions

A few of the compounds tested during this research showed some activity towards ethylene and in one case hex-1-ene. In all cases the activity was very low (> 2 gP $mmol^{-1}$ h^{-1} bar^{-1}). The solids recovered from the successful reactions were of a very high molecular weight and broad polydispersity. Examination of the data obtained suggested that for these particular catalysts β-hydride elimination is not significant in deactivating the catalyst and the low activity due to inefficient activation to form the precatalyst. It would be interesting to investigate these catalysts further to establish whether activity could be improved by using different activators and alkylating agents.

References

1. G .J. P.Britovsek, V. C. Gibson, D. F. Wass, *Angew. Chem., Int. Ed.,* 1999, **38**, 428

2. H. H. Brintzinger, D. Fischer, R. Mullhaupt, B. Reiger, R. M. Waymouth, *Angew. Chem. Int. Ed.,* 1995, **34**, 1143

3. (a) K. Ziegler, E. Holzkamp H. Breil, H. Martin, *Angew. Chem., Int. Ed. Engl.,* 1955, **67,** 541. (b) G. Natta, *Angew. Chem., Int. Ed. Engl.,* 1956, **68**, 393

4. D. Van Leusen, D. J. Beetstra, B. Hessen, J. H.Teuben, *Organometallics*, 2000, **19**, 4084

5. (a) V.C.Gibson, B. S. Kimberley, A. J. P.White, D. J. Williams, P. Howard, *Chem. Commun.,* 1998 313. (b) L. Matilainen, M. Klinga, M. Leskela, *J. Chem. Soc. Dalton Trans.,* 1996, 219

6. A. K. Zefirova, A. E .Shilov, *Proc. Acad. Sci. USSR,* 1961, **136**, 77

7. P.Longo, A.Grassi, C. Pellecchia, A. Zambelli, *Macromolecules,* 1987, **20**, 1015

8. R.Waymouth, P.Pino, *J. Am. Chem. Soc.*, 1990,**112**,4911

9. P.Corradini, G.Guerra, *Prog. Polym. Sci.*,1991, **16**, 239

10. E. Y. Tshuva, I. Goldberg, M. Kol, H. Weitman, Z. Goldschmidt, *Chem. Commun.,* 2000, 379

11. A.van der Linden, C. J. Schaverien, N. Meijboom, C. Ganter, A. G. Orpen, *J. Am. Chem. Soc.*, 1995, **117**, 3008

13. S. Matsui, T. Fujita, *Catalysis Today*, 2001, **66**, 63

14. R. F. Jordan, *Adv. Organomet. Chem.,* 1991, **32**, 325

15. B .J .Burger, M. E. Thompson, W. D. Cotter, J. E. Bercaw *J. Am. Chem. Soc.,* 1990, **112**, 1566

16. P. L. Watson, D. C. Roe, *J. Am. Chem. Soc.,* 1982, **104**, 6471

17. X. Bei, D. C. Swenson, R. F. Jordan, *Organometallics,* 1997, **16**, 3282