Preparation of Initiators for Sustainable Polymerisation

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A thesis submitted for the degree Doctor of Philosophy

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C. Abstract

Current plastics are mostly derived from petrochemical sources, as it is a finite resource renewable replacements are sought after. Polymers derived from cyclic esters such as; lactide, valerolactone and caprolactone are of interest. An industrially viable method of producing stereocontrolled polylactide (PLA) from rac-lactide is desired. Previous work on poly(cyclic esters) is overviewed in chapter 1 with an emphasis upon PLA.

Chapter 2 reports the coordination of Ti(OiPr)₄ to homo/piperazine bridged bis(phenol) (salan) ligands. Under ambient conditions bimetallic structures were produced and a steric dependent equilibrium system is discussed. Forcing conditions resulted in monometallic homopiperazine salan complexes. Their application for the ring-opening-polymerisation (ROP) of rac-lactide is investigated. Homo/piperazine salan titanium catecholates were synthesised and their cytotoxicity investigated by collaborators.

Chapter 3 details the synthesis of monometallic homopiperazine salan zirconium/hafnium isopropoxide complexes. Their utility for the ROP of rac-lactide in solution and solvent free systems are discussed. Bimetallic or tetrametallic solid state structures from attempts to coordinate Zr(IV)/Hf(IV) metals to piperazine salan ligands are also discussed.

Chapter 4 discusses the complexation of AlMe₃ with homopiperazine salan ligands. The resulting monometallic complexes were inactive for the ROP of lactide. Benzyl alcohol derivatives were synthesised and trialled for solvent free ROP of rac-lactide, δ-valerolactone, ε-caprolactone. Co-polymerisations were investigated and a tri-block polymer of poly(ε-caprolactone/δ-valerolactone/rac-lactide) was prepared.

Chapter 5, trans-1,4-DACH salen ligands were synthesised and investigated as ligands with Al(III), Ti(IV), Zr(IV), and Zn(II) metal centres. Bimetallic Al(III) and Ti(IV) structures were characterised and trialled for the ROP of rac-lactide. Isotactic PLA was reported for aluminium complexes, dependent upon phenoxy substituents, and these polymerisations were shown to be immortal in nature.
Chapter 6 details the synthesis of *trans*-1,2-DACH salalen ligands which were complexed to AlMe₃, these initiators were investigated for the solution ROP of *rac*-lactide. The further synthesis of benzyloxy derivatives is also reported and they were utilised for solution and solvent free polymerisations of *rac*-lactide. The initiator’s behaviour is discussed with respect to varying amine and imine groups.
D. Abbreviations

BDI $\beta$-Diketiminate
CHN Carbon, Hydrogen, and Nitrogen
C$_p$ Cyclopentadienyl
DACH Diaminocyclohexane
DOSY Diffusion-Ordered Spectroscopy
EDBP 2,2'-Ethylidenebis(4,6-di-tert-butylphenol)
ESI Electrospray ionisation
GPC Gel permeation chromatography
IC$_{50}$ Half maximal inhibitory concentration
IR Infrared
$k_{app}$ Apparent rate constant
$k_{int}$ Rate constant of initiation
$k_{intra,trans}$ Rate constant of intramolecular-transesterification
$k_{inter,trans}$ Rate constant of intermolecular-transesterification
$k_{prop}$ Rate constant of propagation
MALDI Matrix-assisted laser desorption/ionization
$M_n$ Number average molecular weight
$M_w$ Weight average molecular weight
NMR Nuclear magnetic resonance
PDI Polydispersity index
PGA Poly(glycolide)
PLGA Poly(lactide-co-glycolide)
PLA Poly(lactide)
$P_m$ Probability of isotactic enchainment
$P_r$ Probability of racemic enchainment
ROP Ring-Opening-Polymerisation
RT Room temperature
t$_{1/2}$ Half life
THF Tetrahydrofuran
ToF Time of Flight
UV Ultraviolet
VT Variable tempreature
E. Publications

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PAPER

Crystallographic characterisation of Ti(IV) piperazine complexes and their exploitation for the ring opening polymerisation of rac-lactide

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In this paper a series of eight Ti(IV) piperazine based complexes have been prepared and fully characterised in the solid-state by X-ray crystallography and in solution via NMR spectroscopy. In the solid-state either Ti(IV)(OPr)₄ or Ti(IV)(OEt)₂(OPr)₂ were observed depending upon the nature of the starting ligand. For complexes with less sterically demanding ligands (H₂ and 2H₂) an equilibrium was observed: 2 Ti(IV)(OPr)₄ + Ti(IV)(OPr)₂ + Ti(IV)(OPr)₂. The thermodynamic properties (ΔG, ΔH and ΔS) have been investigated via variable temperature NMR spectroscopy. With more sterically demanding ligands (3-MePh) the Ti(IV)(OPr)₂ form was the most prevalent in the solid-state and in solution. These complexes have been tested for the production of polylactide under melt and solution conditions with high conversions being obtained.

Introduction

The preparation of homogenous Lewis acidic complexes for the ring opening polymerisation (ROP) of cyclic esters (such as rac-lactide) has received considerable attention in recent years. Examples of initiators for this process include groups 1-3, Al(Ⅲ), Ti(Ⅳ), Zn(Ⅱ) and lanthanides and pertinent to this study group 4 metal centers. The polymers themselves have found many uses from commodity plastics to high value biomedical applications. The use of amine bisphosphonate ligands in such chemistry is ubiquitous and there are numerous examples of such initiators in the literature. However, the use of the more conformationally strained piperazine derived ligands for this polymerisation remains limited. A notable example of work in this area is that by Yao and co-workers who have recently prepared a Yb–Li bimetallic piperazine-containing complex. This was shown to act as a promising initiator for the ROP of L-lactide. The same group have also very recently prepared lanthanide-containing complexes for L- and rac-lactide polymerisation based on piperazine ligands. It has been found that 4-NH₂-substituted piperazine complexes are very versatile and can bind to either one or two metal centers. Previous crystallographically characterised piperazine-phosphonate complexes include Al(Ⅲ), Pb(Ⅱ), Zn(Ⅱ) and Cu(Ⅱ). For example, a series of Al(Ⅲ) complexes with 1,4-bis(2-hydroxy-3,5-di-tert-buty1)piperazine have been prepared and in this case either mononuclear or bimetallic complexes were formed in the solid-state. With the same ligand Zn(Ⅱ) bimetallic structures have been prepared. To the best of our knowledge there are no reported examples of crystallographically characterised piperazine-phosphonate complexes with Ti(IV), although the analogous 1,4-bis2-aminobenzyl-piperazine ligand has been used by Mountford to prepare Ti(IV) imido complexes. Also to the best of our knowledge there are no crystallographically characterised complexes of piperazine substituted piperazine ring systems. Crystallographically characterised complexes with the homopiperazine ligand (7 membered ring) remain limited to Fe(Ⅱ), Cu(Ⅱ), Ni(Ⅱ) and one example of a Ti(IV) oxo complex has been previously published.

In this paper we report the preparation and characterisation of new piperazine and homopiperazine ligands. These ligands were complexed to Ti(IV) and other complexes of the form Ti(IV)(OPr)₁₂ or Ti(IV)(OEt)₂(OPr)₂ have been isolated in the solid-state. Interests in these cases a complex equilibrium was observed in solution between these two dimers and Ti(IV)(OPr)₂. The complexes have been tested for the ROP of rac-lactide with high conversions.

Results and discussion

Synthesis of ligands and complexes

The ligands were prepared via a modified Mannich reaction as shown in Scheme 1. All ligands were characterised via H and 13C NMR spectroscopy and HR-MSS. H₂ was also characterised using single crystal X-ray diffraction. The complexes were prepared by the reaction of 1 equivalent of ligand with 2 equivalents of Ti(IV)(OPr)₂ in CH₂Cl₂. It was observed that the same products were also isolated in the solid-state with 1 equivalent of Ti(IV)(OPr)₂. For complexes with ligands H₂ and 2H₂ the solid-state structures are shown in Fig. 1 and selected bond lengths and angles are in Table 1.
Homopiperazine and Piperazine Complexes of ZrIV and HfIV and Their Application to the Ring-Opening Polymerisation of Lactide


Keywords: Titanium / Zirconium / Hafnium / Ring-opening polymerization / Sustainable chemistry

In this paper we describe the preparation and characterisation, by single-crystal X-ray diffraction, of twelve ZrIV/HfIV complexes based on piperazine or homopiperazine salan ligands. With the piperazine ligands, a mixture of species was observed, and when solid-state structures were isolated, however, with homopiperazine salan ligands, 1:1 ligand-meric complexes were observed both in solution and in the solid state. Interestingly, for the homopiperazine complexes the isopropoxo ligands are trans to one another in the solid state, most likely because of the rigid nature of the homopiperazine backbone. All homopiperazine HfIV and ZrIV complexes were tested for the ring-opening polymerisation (ROP) of rac-lactide. The complexes are active and produce poly(lactide) with narrow polydispersity indices. The kinetics and living characteristics of the polymerisation have also been investigated.

Introduction

In recent years there has been an explosion of interest in the use of single-site homogeneous catalysts for the ring-opening polymerisation (ROP) of rac-lactide (rac-LA) to produce polylactide (PLA).[4] This process has been commercialised by Purac and NatureWorks, and the current catalyst used for this process is based on SnII.[4,7] There is currently a desire to replace tin in this system, and – as a consequence – a significant amount of work has been performed in catalyst development.[8] The polymers themselves have found extensive utility from biomedical to commodity polymer applications[9] due to the biodegradability and biocompatibility of PLA and the fact that the monomer can be sourced from sustainable raw materials. The catalyst can have a dramatic effect on the physical properties and degradation rates of the resultant PLA.[4] For example, catalysts based on group 13 trialkyls[10] and group 14[11] or 15[12] ZrIV[13,14] and HfIV[15] and, pertinent to this study, group 4 metals have all been shown to have significant activity.[13] We have recently shown that TiIV salan systems with a piperazine backbone are very effective catalysts for the bulk polymerisation of rac-LA.[8] Kol has shown that a ZrIV complex of a tetradentate phenyleneamidophenolate affords heterotactic PLA under melt conditions.[16] The same group has also shown that dithiololate complexes with ZrIV are active for the production of heterotactic PLA.[10] It has been shown that dimeric ZrIV and HfIV complexes of Jacobsen’s ligand are active for the controlled ROP of both rac-LA and β-butyrolactone.[10] In the case of rac-LA, atactic PLAs were formed. It has also been shown that bis(phenoxy)ethane complexes of ZrIV show high activities in the polymerisation.[10]

The chemistry of group 4 metal complexes with symmetrical amine-bis(phenoxy) ligands is rich and diverse, and many ligand-metal complexes are known with possible geometries shown in Scheme 1.[13] The use of bis(phenoxy)ligands based on 2,2’-bipyridyl, N,N’-dimethyl-2,2’-diaminobenzene, N,N’-dimethyl-1,2-ethylenediamine and N,N’-dimethyl-1,2-diaminobenzene forms the α-isomer both in the solid state and solution once reacted with Zr(OBu)4.[13] Interestingly, a search of the Cambridge Structural Database (CSD) indicates there are no crystallographically characterised complexes of the trans isomer of group 4 metal complexes with amine bis(phenoxy) ligands, where X = alkoxide, with the α-cis and β-cis forms being prevalent.[10] Intriguingly, Buschel has shown, using computational methods, that the trans geometry (mer-mer, where the ligand occupies the equatorial position) is the intermediate ion pair in olefin polymerisation.[10] The use of homopiperazine as a backbone for bis(phenoxy) ligands remains limited with the only examples characterised in the solid state involving copper, nickel and iron.[10]

Scheme 1. Possible isomers of ONNO ligands with ZrIV or HfIV.
Al(III)-homopiperazine complexes and their exploitation for the production of polyesters†

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In this paper we report the synthesis and characterisation of a series of Al(III)-homopiperazine complexes. The ortho substituent has been varied from H, Me, iBu to investigate the effect this has on the solid-state structures and on the catalytic activity. Aluminium–methyl complexes involving ligands 1H2, 2H2 and 5H2 have been characterised in the solid-state and the aluminium centres are in pseudo trigonal bipyramidal geometries. The aluminium–methyl complexes were further reacted with boronyl alcohol to generate alkoxide complexes, which have been fully characterised by multinuclear NMR spectroscopy and elemental analysis. The alkoxide complexes were tested in the ring opening polymerisation of rac-lactide, δ-valerolactone and ε-caprolactone. Furthermore, triblock polymers were also prepared with these initiators.

Introduction

Ring opening polymerisation (ROP) of lactide to produce polylactide (PLA) has received a remarkable degree of attention in recent years. This is due to the biocompatibility of the final polymer and the fact that the starting lactide can be prepared from sustainable sources.2,3c This is truly making PLA a viable alternative to crude oil based polymers for commodity applications. Furthermore, PLA and its copolymers are currently being exploited for high value biomedical applications. Initiators for ROP based on Al(III), Zn(II),31 tin(II)32 group 4 metals33 and group 2 metals34 are prevalent in the literature. One of the most studied monomers is rac-lactide (50:50 mixture of the D- and L-enantiomers). This is due to the fact that different (steric block, tacticity, heterotactic and anisotactic) stereo-forms of PLA can be prepared. The physical properties of the final polymer are directly related to its microstructure.35,36 However, the properties of the polymer can also be varied by the copolymerisation of lactide with other monomers – such as ε-caprolactone or δ-valerolactone.37,38 One of the main driving forces of this approach is to produce polymers which have desirable gas/moisture permeability and mechanical strength properties.39

A significant number of aluminium complexes that are active for the ROP of rac-LA or other cyclic esters are based on either salen or salan ligands.40–49 One such class of salan ligands are those utilising a piperazine or homopiperazine backbone. For example, Fulton and Wang have shown that binuclear Al(III) complexes of piperazine derived phosphonates show activity for the polymerisation of ε-caprolactone.49 Further more, we have previously shown that amino bis(phosphonate) ligands based on homopiperazine ligands complexed to group 4 metals are active initiators of the controlled ROP of rac-lactide.50,51

In the vast majority of aluminium examples an alkoxide initiator is generated in situ from the aluminium-alkyl and thus the resultant polymerisation is performed in solution.52–54 However, this has a significant disadvantage in the fact that the polymerisation cannot be performed under the industrially preferred melt conditions. Therefore, in this study we have chosen to prepare a series of aluminium–homopiperazine alkoxide complexes for the application in ROP with a variety of initiators for melt polymerisation studies.

Results and discussion

Synthesis of complexes

The ligands were prepared by modified Fischer reactions and complexes were prepared via standard literature procedures. Scheme 1.55–57 The choice of ortho substituent allows us to probe the effect of steric influence on catalysis and solid-state structure. All ligands were characterised via multinuclear NMR spectroscopy and HRMS.

The Al-methyl complexes were prepared by addition of 1 equivalent of AlMe3 to 1 equivalent of ligand and it was noted that products of higher purity were isolated when the reactions were conducted at 50 °C. Complexes Al(III)SMe were characterised by single crystal diffraction studies, see Fig. 1 for 4AlMe and Table 1 for selected bond distances and angles. The aluminium centres are in a highly distorted trigonal bipyramidal geometry. For complex Al(III)Me a significant degree of disorder was observed in the homopiperazine ring moiety. For complexes Al(III)Me and Al(III)SMe the methyl group bound to the
Aluminium salen complexes based on 1,2-diaminocyclohexane and their exploitation for the polymerisation of rac-lactide

Stuart L. Hancock, Mary F. Mahon and Matthew D. Jones*

In this paper nine various salen ligands have been prepared and characterised. The steric and electronic effects of both the salen and salan fragments have been varied in a systematic fashion to ascertain how this affects the selectivity for the rDP of rac-lactide. These were compared to AlMe3 to generate pseudo trigonal bipyramidal metal centered complexes. Upon addition of benzyl alcohol the active initiator can be easily prepared. The complexes were screened for the rDP of lactide in solution and melt conditions. PLA with narrow molecular weight distributions (PDIs range from 1.07–1.67) could be isolated with moderate degrees of tacticity. Significantly it was found that chloro groups on the imine fragment increased the degree of hetero tactic enchainment in the polymer. The kinetics for one series of salen-Al complexes was also investigated.

Introduction

In recent years the metal catalysed polymerisation of lactide to produce polylactide (PLA) has been a “hot-topic” and will continue to be so for many years to come. This is due to the favourable properties of the polymer; namely biodegradability and the fact that it can be sourced from renewable material. Lactide can be prepared from lactic acid which in turn is produced from fermentation of starch. PLAs have found utility in medical devices such as high value medical devices to more traditional commodity products. Furthermore, if the racemic version of the monomer is used (rac-lactide or rac-PLA) then various stereoforms of PLA can be prepared (hetero tactic, atactic and stereoblock isotaetic). Many metal centres have been employed in the production of PLAs for example groups 1–4, lanthanides, zinc(II) and Sn(II). One of the main Lewis acid metals centres that is suitable for this polymerisation is Al(n). Pioneering work by Feljen,7 Chisholm,8 Nomura,9 Spassky,10 Goate11 and Gibson12 (amongst others) have shown that initiators based on Al(n) can produce controlled molecular weight PLA and are capable of inducing strong aesthetic into the final polymer.13 Without question the two main ligands bound to the aluminium centres are based on salen or salan moieties.14 These are typically symmetrical in nature, due to their preparation.

Recently, Katsuki and co-workers have prepared a series of salen complexes for the enantioselective hydrophosphonation of aldehydes and aldmines and sulphur oxidations.15 High enantioselectivities and conversions have been reported. An advantage of such systems is that there is a high degree of synthetic variation possible in terms of the steric electronics of either phenyl ring. Koi and co-workers have recently shown that Ti(IV) salen complexes are active for the isospecific polymerisation of 1-hexene and propylene.16 We have previously reported the utility of group 4 salen complexes for the polymerisation of rac-lactide.17 Furthermore, we have recently shown that Al(III)-salen complexes can produce either isotactic or hetero tactic PLA depending on the nature of the substituent on the amine nitrogen centre.18 One of the most Al(n) complexes prepared to date was based on Jacobson’s ligand19 ([(R,R)(-)-Me,p-tolyl][(2,6-diisopropylphenyl)(salicyliden-1,2-diaminocyclohexane) with highly isotactic PLA being produced.16,20 In this paper we have prepared a range of salen ligands based on the 1,2-diaminocyclohexane backbone. These have been complexed to Al(n) and tested for the ring opening polymerisation of rac-lactide in solution and under the industrially preferred melt conditions.

Results and discussion

Ligand and complex preparation

The ligands were prepared by modified literature procedures, as shown in Scheme 1.21,22 The trans form (R,R or S,S) of 1,2-diaminocyclohexane was initially mono-protected and treated with an equivalent of an aldehyde and subsequent reduction
Chapter 1

1. Introduction
1. Introduction

1.1 Biopolymers

Over the last century interest in plastics has developed considerably with much focus on synthetic polyolefins derived from petrochemicals.\(^1\) Although polyolefins have been very successful, they do have considerable drawbacks. Petrochemical derived plastics are associated with many environmental concerns, one such current issue is that petrochemical sources are being depleted and our present use of fossil fuels for plastic production is not sustainable.\(^2\) Furthermore, petrochemical plastics are becoming a major pollutant, polyolefin plastics are not readily decomposed and when considered with our common use of disposable plastics there is an inevitable disposal problem. In recent years replacement plastic sources are becoming commercially more viable due to the rising cost of oil and public environmental concern. As a consequence of these concerns much research has been focused in the last few decades on developing biodegradable and sustainable plastics to replace petrochemical derived materials.\(^3,\,4\)

Biopolymers are polymers obtained from renewable resources which have acquired interest as replacements for petrochemical polymers, particularly within plastics. It should be noted not all biopolymers are biodegradable.\(^5\) A variety of biopolymers have been developed over the last few decades one such example is cellulose derived polymers.\(^6\) Cellulose is a major constituent of all plants therefore it is the most common naturally produced polymer, which is currently obtained from; wood pulp, algae and cotton.\(^6\) Although cellulose is mass produced by nature it is difficult to extract and obtain in a form which can be easily manipulated. A critical element of cellulose research is controlling the structure and hence the properties, such examples are the ester and ether derivatives of cellulose particularly cellulose acetates used for polymer coatings.\(^6\) Aliphatic polyesters such as polylactide (PLA) and polyglycolide (PGA) have received attention over the last few decades as suitable replacements for petrochemical polymers. Particular advantages of aliphatic polyesters include; suitable mechanical characteristics, renewable feedstocks, biodegradable, and biocompatible.\(^2\)
Degradability is another important aspect of plastic production; there are two common methods of engineering degradable polymers, introducing degradable substituents into the polymer chain or creating the polymer from inherently degradable monomers. Biodegradable monomer units can be introduced into petrochemical polymers to increase their degradability. As an example, hydrolytic degradation of poly(ethylene terephthalate) was increased by incorporation of lactide units. Introduction of metal substituents into polymers propagate its degradation to smaller polymer chains, these polymers are classified as oxo-degradable. Such oxo-degradable polymers breakdown on exposure to U.V. light and oxygen, this method only break-down polymers into shorter chain oligomers at which point biological processes may decompose the shorter chains. As stated oxo-degradation only reduces the polymers to shorter chains which still present an environmental issue. Additionally the metals incorporated in the polymer enhance the environmental issues as toxicology and metal leaching must be considered. Arguably more sought after are fully biodegradable polymers where the individual monomeric units of the polymer chain can decompose to water and carbon dioxide. Biodegradation of polymers often requires specific conditions such as; elevated heat, oxygen, and light, which are obtained in a composting facility.

As stated above polylactide and polyglycolide are biodegradable, renewable and characteristically suitable replacements, within certain applications, for petrochemical derived polymers. Polylactide and polyglycolide are derived from the base components lactic acid and glycolic acid respectively. Although the direct production of PLA and PGA by polycondensation from lactic acid and glycolic acid results in polymers of low molecular weight. As control over the aspects of the polymer is paramount within industry the dehydrated lactide and glycolide products are utilised to produce their respective polymers (Figure 1.01), consequently the dehydrated dimers have seen considerable attention.
PLA is not a new polymer being first observed by Pelouze in 1845 by dehydrating lactic acid.\textsuperscript{15, 16} Within the last decade PLA has matured from a specialist chemical into an available commodity polymer. NatureWorks part of Cargill Dow LLC chemicals are the major producer of PLA with a facility in Blair, Nebraska capable of producing 140,000 tonnes of PLA per annum.\textsuperscript{17} PLA is derived from any sugar source such as sugar beet, corn or wheat which is first introduced into a fermentation faculty to extract lactic acid. Lactic acid is partially polymerised by a condensation reaction yielding low chain length polymers due to the equilibrium nature of the direct condensation reaction and the practicalities of removing the final remnants of water (Figure 1.02).\textsuperscript{16} Via use of a catalyst the oligomers are depolymerised into selective lactide units, which are sublimed before polymerisation using an organotin catalyst, in the NatureWorks process.

Since the continuous lower cost production of PLA by NatureWorks this biodegradable polymer (PLA) has become viable as a disposable material, examples include; drinking cups, yogurt pots, and cutlery.\textsuperscript{18} Although PLA is considered as a remarkable biodegradable polymer as it is not limited to short term disposable applications, other applications include textile materials and paper coatings. Prior to large scale production of PLA its most notable use was for biomedical applications.\textsuperscript{19, 20}
An exemplary aspect of PLA is its inherent biocompatibility attained from its base component lactic acid. Under physiological conditions PLA is hydrolysed to lactic acid, which is naturally found within the human body and consequently PLA is non-toxic. Medical applications require defined physical properties and degradation rates of polymers. Within PLA these characteristics are influenced by the steric orientation and crystallinity of the material. Fortunately lactide offers two chiral centres and by controlling the orientation of the chiral centres throughout PLA, its crystallinity, rigidity, and degradation can be tuned. Alternatively characteristics of PLA are tuned by co-polymerisation with other monomers. For example PLA and PGA co-polymer’s (PLGA) are utilised for surgical sutures. Increasing the quantity of glycolide moieties reduces the resulting co-polymer’s rigidity and decreases its degradation rate. As a further example a blend of PLA and polyethylene-co-vinylacetate was investigated by Kenawy et al. as a media for drug delivery. Kenawy et al. showed the co-polymer gave a stable release of the antibiotic tetracycline hydrochloride, over a period of 5 days, compared to negligible release from pure PLA.
1.2 Ring-Opening-Polymerisation (ROP) of Lactide

ROP of lactide often gives good control over the resulting PLA properties. In the presence of a catalytic initiator the ROP of lactide proceeds via a multitude of mechanistic pathways, which are generically grouped as; anionic, cationic, or coordination insertion mechanisms.

1.2.1 Anionic mechanism

The anionic lactide mechanism is typically observed if the ROP catalyst contains a labile cationic metal such as; lithium, potassium, or magnesium. There are two mechanisms of initiation of anionic polymerisation shown in figure 1.03 and 1.04. The first initiation approach discussed is the direct nucleophilic attack of an ionic alkoxide to ring open lactide by acyl bond cleavage. This reaction yields a further lactide derived alkoxide unit and propagation ensues (Figure 1.03).

![Figure 1.03: Direct nucleophilic attack of anionic ROP mechanism.](image)

The alternative initiation method of anionic ROP begins with deprotonation of a lactide monomer. This deprotonated species can rearrange into a tautomeric metal-enol species (Figure 1.04). Both species are capable of initiating ROP by nucleophilic attack of a lactide monomer, consequently leading to acyl bond cleavage. The propagation step is less clear. One proposition is it proceeds via the direct nucleophilic attack mechanism (Figure 1.03) where the ring-opened lactide, an alkoxide, becomes the nucleophilic initiator for continued propagation. To elucidate the mechanism end-group analysis can be used, as the direct nucleophilic attack route will incorporate an alkoxide from the metal initiator or co-initiator.
1.2.2 Cationic mechanism

The cationic ROP mechanism is mostly observed for organic initiators and can also be referred to as a monomer-activated mechanism. Cationic acid catalysed ROP of caprolactone and valerolactone was established and proceeded using HCl as the acid catalyst. The polymerisation of lactide proceeds via a cationic mechanism utilising trifluoromethanesulfonic acid and methyl trifluoromethanesulfonate catalysts. The polymerisation initiates by cationic activation of lactide and then the triflate cleaves the alkyl oxygen, over the acyl oxygen bond, by a $S_N^2$ style mechanism (Figure 1.05). \(^2, 13\)

![Figure 1.05: Cationic polymerisation mechanism, R = H, Me, or a growing lactide chain.](image)

Figure 1.05: Cationic polymerisation mechanism, R = H, Me, or a growing lactide chain.  

\(^2\)
A later development by Bourissou et al. is the cationic acid catalysis of lactide utilising a trifluoromethanesulfonic acid catalyst in the presence of a protic solvent. Bourissou et al. proposed a mechanism based on the selective activation of a lactide unit over PLA (Figure 1.06), where the activated lactide is opened by acyl cleavage.

\[ \text{Figure 1.06: Acid catalysed ROP of lactide, adapted from Bourissou et al.}^{2, 27}. \]

1.2.3 Coordination insertion mechanism

Throughout the literature the coordination insertion mechanism is the prevalent ROP mechanism.\cite{2, 13, 25} The coordination insertion mechanism requires a catalytic initiator which contains an electropositive metal, where the metal does not readily dissociate as a cation. The mechanism proceeds by first coordinating the catalytic initiator, \textit{via} the electropositive metal centre, to a carbonyl oxygen of the monomer (Figure 1.07).\cite{2} Secondly, the monomer inserts into the metal alkoxide bond by attack of the alkoxide to the carbonyl carbon. This is followed by cleavage of the acyl bond to ring-open the monomer, leaving the metal coordinated to a newly formed lactide alkoxide bond. Formation of an alkoxide allows the polymerisation to propagate further by insertion of monomer into metal-lactide bonds. Finally the ROP reaction is quenched by saturation of the polymerisation with a proton source, typically methanol, hydrolysing the resulting metal-PLA linkage. This mechanism has been experimentally studied by Kricheldorf \textit{et al.} in 1988\cite{28} and further supported by Teyssié \textit{et al.} in 1991\cite{29} both by the study of Al(O\textit{Pr})\textsubscript{3} as the ROP initiator.\cite{2} Interestingly this mechanism allows the presence of a non-dissociative ligand bound to the active metal which appears to “spectate” within the reaction. This aspect of the mechanism can be exploited and the spectator ligand(s) can be used to impart control over the mechanism, inducing chirality over the metal centre. A renowned example was by Fiejen \textit{et al.} using an Al-alkoxide initiator.\cite{30}
1.2.4 Transesterification side reactions

Anionic, cationic and coordination insertion mechanism are all capable of transesterification side reactions. Transesterification is undesirable, an ester linkage within an existing polymer chain is attacked in preference to a lactide ester linkage. As a consequence transesterification reactions cause molecular weights to be lower or distributed over a larger molecular weight range. Transesterification can occur by two generic mechanisms, either intramolecular or intermolecular (Figure 1.08).\(^2\)

Intramolecular transesterification or backbiting is defined as when a growing polymer chain reacts with itself, hence reducing PLA molecular weight and forming cyclic compounds. Intermolecular transesterification is attack of one polymer to another chain thus causing wide disparity between polymer chains and high distribution of molecular weights.

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\(^2\) Figure 1.07: Coordination-insertion mechanism.\(^2\)
Figure 1.08: Schematic representations of intermolecular and intramolecular transesterification side reactions, within the ROP of lactide.²

An ideal ROP mechanistic scenario involves chain-end-control where the polymerisation proceeds by incorporating lactide monomers only at the end of a PLA chain. The chain-end control mechanism allows a tailored initiator to arrange each monomer inserted into the chain. In the circumstance that an initiator can further polymerise on addition of more monomer before quenching the polymerisation is known as “Living”.³¹ For a polymerisation to be considered living the above statement must be true but in addition the molecular weight of the polymer chain must coincide with the monomer-to-initiator ratio i.e. one polymer chain per initiation site. A living coordination-insertion polymerisation can be terminated by quenching of the reaction by hydrolysing the end group. In contrast immortal polymerisations cannot be quenched by addition of typical reagents, such as alcohols.
The concept of living polymerisations was first observed and introduced for ring-opening polymerisation by Inoue et al. Immortal polymerisations share traits with living polymerisations, predominantly each reaction will continue to polymerise on addition of further monomer. As stated immortal polymerisation cannot be terminated on addition of alcohol as the polymer chains are rearranged. This rearrangement shortens the polymer chains to a degree, where the chain length is equal to the monomer:alcohol ratio.

1.2.5 Immortal ROP mechanisms

![Diagram](https://via.placeholder.com/150)

**Figure 1.09:** Schematic representations of the coordination-insertion based immortal mechanism for the ROP of lactide.

Within the immortal ROP of lactide the polymer chains grow in a uniform manner based upon the quantity of a secondary initiator source, which is typically a protic alcohol. Two methods are discussed herein; coordination insertion with rapid chain-end exchange mechanism, the second where propagation occurs via a transesterification method and an activated monomer mechanism. The coordination insertion and rapid exchange reaction propagates through a coordination insertion mechanism (figure 1.09). During the propagation, rapid proton exchange between the terminating metal and a protic co-initiator/PLA chain occurs. The proton terminated PLA chain is still available for propagation and the $L_nM$ species continues to polymerise.
Figure 1. 10: Schematic representation of the activated monomer immortal mechanism for the ROP of lactide.33, 34

The activated monomer mechanism for the immortal ROP of lactide is depicted in figure 1.10.33, 34 A lactide carbonyl coordinates to the metal complex further polarising the carbonyl bond and activating it towards nucleophilic attack. A co-initiator, typically a protic alcohol, attacks the carbonyl carbon which is followed by acyl bond cleavage. The lactide chain is terminated by a proton and the metal complex transfers from the polymer chain to a lactide monomer activating the new monomer for propagation.

1.2.6 GPC and determining polymer molecular weights

Polymers are characterised by either their physical characteristics or chemical structures. Gel permeation chromatography (GPC) can be utilised to determine structural characteristics of linear aliphatic polyesters. Herein is discussed two measurements; number average molecular weight ($M_n$), a measure directly related to the chain lengths within the polymer, and the polydispersity index (PDI), a measure of chain length distribution. GPC is a method of size exclusion chromatography where larger polymer chains will flow through the system at a much faster rate. The polymer must first be solubilised in a compatible solvent and the solution is then passed through a series of porous beads. Smaller polymer chains permeate the beads
while larger chains flow around (Figure 1.11). As a consequence smaller chains take a much more turbulent route directly causing a higher retention time.

Figure 1.11: GPC diagram depicting polymer flow paths.

\[
\text{PDI} = \frac{M_w}{M_n} \quad \text{Equation: 1.01}
\]

\[
M_n = \frac{\sum M_i N_i}{\sum N_i} \quad \text{Equation: 1.02}
\]

\[
M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i} \quad \text{Equation: 1.03}
\]

Figure 1.12: Equations relating: polydispersity index (PDI), number average molecular weight \((M_n)\), and weight average molecular weight \((M_w)\).

The polydispersity index (PDI) is calculated by the equation 1.01 (Figure 1.12). It is dependent on the number average molecular weight \((M_n)\) calculated by equation 1.02 (Figure 1.12) and the weight average molecular weight \((M_w)\) given by equation 1.03 (Figure 1.12). \(M_n\) is a measure of the mean average molecular weight, while \(M_w\) accounts for the fact that larger individual molecules account for a higher percentage of the total weight. A direct comparison of \(M_n\) and \(M_w\) is PDI, PDI = 1 indicates uniform polymer chains, PDI > 1 indicates varied polymer chain lengths. \(M_i\) and \(N_i\) values are obtained from a GPC trace (Figure 1.13) by correlating inverse retention time and relative intensity. To determine \(M_i\) from retention time a GPC instrument is calibrated to polystyrene standards. To account for the difference in hydrodynamic volume between lactide and polystyrene standards a correction value of 0.58 can be applied.\textsuperscript{35}
$M_n$ and PDI values are related to the rates of individual mechanisms within the polymerisation. If the rate of initiation ($k_{\text{int}}$) $\gg$ rate of propagation ($k_{\text{prop}}$) the resulting polymer chains should all be uniform (PDI $\approx 1$). Alternately if the opposite is true $k_{\text{int}} << k_{\text{prop}}$ a polymer chain can grow significantly before an additional chain initiates resulting in higher chain distribution (PDI $>> 1$). The above assumes the initiator contains one initiation site or only propagates one polymer chain. If an initiator has more than one initiation site further chain distribution will result as a consequence of multiple $k_{\text{int}}$ values. For the coordination insertion mechanism where $k_{\text{int}} >> k_{\text{prop}}$ then the polymer chain length can be predicted from conversion of lactide by equation 1.04.

$$M_n = \frac{\text{Monomer ratio} \times \text{Conversion} \times 144.13}{\text{Initiator ratio}} + \text{End group} (M_w)$$  

Equation: 1.04

Figure 1.14: Equation used to calculate theoretical molecular weight from conversion of lactide for PLA.

Molecular weight control is not limited to the rate of propagation and rate of initiation as stated previously transesterification is detrimental to uniform chain length. If $k_{\text{prop}} >> k_{\text{inter,trans}}$ (rate of intermolecular transesterification) uniform chain
growth ensues. In the case that $k_{\text{prop}} \gg k_{\text{intra.trans}}$ (rate of intramolecular transesterification) controlled growth is observed, where $k_{\text{prop}} << k_{\text{intra.trans}}$ we get both high PDI and lower $M_n$.

Molecular weight can be determined by other methods, which can be used in addition to GPC. A valuable method is MALDI-TOF mass spectrometry which gives the repeat unit of the polymers and is highly regarded for end group analysis. Mass spectrometry has limitation due to difficulties in ionising polymer chains, limiting the polymer samples to lower molecular weights. Methods which detect polymer concentration and can work in-situ with GPC include; refractive index, IR, and UV absorption. Other methods which can be utilised in-situ with GPC or possible to get measurements directly include low angle light scattering, viscosity, and multi angle light scattering detectors.

1.2.7 Stereochemistry and characterisation by NMR spectroscopy

Lactic acid is present in the $L$ and $D$ forms (the $S$ and $R$ enantiomers respectively). As a result lactide can be isolated as a series of diastereomers. The commercially available lactide diastereomers are $L$-Lactide, $D$-Lactide, Meso-lactide and an mixture of $L$-lactide and $D$-lactide known as rac-lactide (Figure 1.15). Both $L$-lactide and $D$-lactide result in isotactic PLA with their respective stereochemistry throughout the polymer. rac-Lactide can yield different PLA arrangements, which are determined by the initiator and reaction conditions. The resulting PLA stereoforms from rac-lactide are; isotactic stereoblock PLA is the arrangement of $L$-lactide units as a block of PLA followed by a corresponding block of $D$-lactide units, heterotactic PLA is an alternating arrangement of $L$-lactide and $D$-lactide, and atactic PLA is the random arrangement of lactide monomers throughout the polymer chain. meso-Lactide also results in different stereo arrangements of PLA and like rac-lactide can also yield heterotactic and atactic PLA. In contrast to rac-lactide meso-lactide can produce syndiotactic PLA where each lactic acid (or each stereocentre) adopts the opposite conformation in an alternating manner.

Each stereo-arrangement of PLA has different physical properties. Isotactic PLA derived from $L$-lactide and $D$-lactide both have similar properties; they show a higher degree of crystallinity and as such are more brittle and ridged than other stereoforms of PLA. Atactic, syndiotactic and heterotactic lactide all have similar
properties due to lack of crystallinity within the respective polymers. Isotactic stereoblock PLA results in further crystallinity within the polymer displaying similar physical properties to isotactic PLA. Isotactic stereoblock PLA exhibits a higher melting temperature than isotactic PLA derived from pure L-lactide or D-lactide. This observation has been attributed to increased intermolecular interactions between L-PLA and D-PLA chains. Isotactic stereoblock PLA can be synthesised directly from rac-lactide via the use of certain initiators.\textsuperscript{30,37} Blending L-PLA and D-PLA in differing quantities has been studied with the intention of mimicking isotactic stereoblock PLA with moderate success but cannot fully yield the same properties as isotactic stereoblock PLA.\textsuperscript{18,38}
Figure 1.15: Stereoforms of lactide and resulting PLA arrangements.\textsuperscript{36}

NMR spectroscopy is used in PLA analysis to determine conversion, tacticity, and end group analysis of low molecular weight PLA. Conversion is obtained by comparing the relative integrals of lactide methines to PLA methines by $^1$H NMR.
spectroscopy. End group analysis by NMR spectroscopy is highly dependent on the end-group in question but it generally requires higher resolution and more concentrated polymer samples. Tacticity of PLA can be determined by two methods; $^1$H homonuclear decoupled NMR spectroscopy, and $^{13}$C{$^1$H} NMR spectroscopy.

$^{13}$C{$^1$H} NMR spectroscopic method for determining tacticity was developed by Kasperczyk in 1995 and focused on the carbonyl region of the spectra and implemented a hexad system to determine tacticity. PLA tacticity determination by homonuclear decoupled methine region $^1$H NMR spectroscopy was later development by Thakur et al. in 1997 and utilised a tetrad model.

A typical spectrum of a $^1$H homonuclear decoupled NMR spectrum of atactic PLA is shown in figure 1.16. By removing the coupling from the methine protons located at 1.62 ppm the methine region becomes five discrete resonances. The resonances are allocated to tetrad units, groups of four lactic acid units where; $i =$ an isotactic linkage ($R,R$ or $S,S$), and $s =$ a syndiotactic linkage ($R,S$ or $S,R$). Thus, it follows that the [iii] tetrad corresponds to an isotactic PLA tetrad with the respective lactic acid chirality of $R,R,R,R$ or $S,S,S$. See figure 1.17.

![Figure 1.16: $^1$H homonuclear decoupled NMR spectrum of the methine region from atactic PLA.](image-url)
Within the decoupled $^1$H NMR spectrum heterotactic PLA is observed as an equal combination of the $[\text{sis}]$ and $[\text{isi}]$ tetrads. Atactic PLA derived from rac-lactide yields all five tetrad possibilities (Figure 1.17). The relative integrals of the tetrad peaks within the homonuclear decoupled $^1$H NMR spectrum are; $[\text{sis}]:1[\text{isi}]:1[\text{iis}]:3[\text{iii}]:2[\text{isi}]$ for atactic PLA. The ratios for the eight possible tetrads are derived by Bernoullian statistics, which calculates the probability of each tetrad linkage occurring (Table 1.01). Out of the eight possibilities only five are possible for rac-lactide as neither $L$, or $D$-lactide units allow two adjacent syndiotactic linkages “s”. Bernoullian statistics are also applied for PLA derived from meso-lactide and disallow possibilities which contain two adjacent isotactic linkages “i”. Transesterification may cause the disallowed possibilities to occur as transesterification is not limited to lactic acid diads.

When considering rac-lactide the probability of racemic enchainment ($P_r$) is inversely proportional to the probability of isotactic enchainment ($P_m$) and can be calculated by rearrangement of equation 1.05 (Figure 1.18). To keep the calculations simplistic the $[\text{sis}]$ relative integral is chosen to calculate $P_r$ (Equation 1.06), which gives $P_m$ via equation 1.05. $P_r$ is a measure of the tacticity within PLA, when $P_r = 1$
the polymer has only racemic lactide linkages as such is heterotactic. It follows that when $P_m = 0$ there is no isotactic enchainment and the PLA is heterotactic. Therefore when $P_r = 0$ and $P_m = 1$ there is total isotactic enchainment of the PLA chains.$^{36}$

<table>
<thead>
<tr>
<th>Tetrad</th>
<th>Probabilities based on Bernoullian statistics</th>
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<tbody>
<tr>
<td></td>
<td>rac-lactide</td>
</tr>
<tr>
<td>[iii]</td>
<td>$P_m^2 + P_r P_m / 2$</td>
</tr>
<tr>
<td>[iis]</td>
<td>$P_r P_m / 2$</td>
</tr>
<tr>
<td>[sii]</td>
<td>$P_r P_m / 2$</td>
</tr>
<tr>
<td>[sis]</td>
<td>$P_r^2 / 2$</td>
</tr>
<tr>
<td>[sss]</td>
<td>0</td>
</tr>
<tr>
<td>[ssi]</td>
<td>0</td>
</tr>
<tr>
<td>[iss]</td>
<td>0</td>
</tr>
<tr>
<td>[isi]</td>
<td>$(P_r^2 + P_r P_m) / 2$</td>
</tr>
</tbody>
</table>

**Table 1.01**: Tetrad probabilities based on Bernoullian statistics.$^{36}$

$$P_r + P_m = 1$$  \text{ Equation 1.05}

$$\sqrt{2 \times [sis]} = P_r$$  \text{ Equation 1.06}

**Figure 1.18**: Equations derived from Bernoullian statistics to calculate probability of racemic enchainment ($P_r$).

Determination of tacticity is not limited to $^1$H NMR spectroscopy, differential scanning calorimetry can be used to determine tacticity in stereoregular PLA via melting points and crystallinity.$^2$ $^{13}$C{${}^1$H} NMR spectroscopy is also utilised in the determination of tacticity, the method is similar to $^1$H homonuclear decoupled NMR spectroscopy methine analysis in that the carbonyl region is separated into a series of hexads and the probability of enchainment is calculated through equations derived from pair addition Bernoullian statistics.$^{39}$
1.3 Ring-Opening-Polymerisation Initiators for Lactide

The ROP of lactide requires an initiator which can be either metal based or non-metal based. The initiator is the key variant of the ROP reaction in obtaining stereoselectivity from rac-lactide and also determines the reaction rate and resulting PLA properties. Metal initiators with simple ligands rarely impart stereoselectivity over the ROP of rac-lactide, although there are examples contrary to this.\textsuperscript{41, 42} The need to control the polymerisation of rac-lactide has led to the use of metal complexes which utilise bulky, chelating or chiral ligands. Typical metal complex PLA initiators contain at least one or any combination of these properties. Design of metal complexes and their associated ligand groups achieved improved stereo-control, molecular weight control and/or low PDI values, which is discussed throughout this chapter. A metal centre can control the tacticity of PLA resulting from the ROP of rac-lactide by chain-end-control where control over the tacticity is induced by the growing polymer chain. Another method of stereo-control involves forcing chirality over the metal centre \textit{via} the ligand(s), referred to as enantiomorphic site control.\textsuperscript{43}

Initiators for the ROP of lactide have been comprehensively reviewed before.\textsuperscript{2, 4, 13, 18, 25, 44-48} Herein, selected initiators are reported for their originality in the subject, importance to the field, stereoselectivity, activity, or relevance to the study that follows. Using these criteria groups of metal based initiators (sections 1.3.1 - 1.3.7) are discussed with a short overview of organic based initiators (section 1.3.8). Following this cyclic-ester co-polymers are briefly discussed (section 1.4).

1.3.1 Tin initiators

The current industrially favoured initiator for the ROP of lactide is Tin(II) 2-ethylhexanoate or tin(II) octoate \{Sn(Oct)\textsubscript{2}\} as it is easy to handle, commercially available, and shown to polymerise at high ratios in solvent free conditions. It was shown that Sn(Oct)\textsubscript{2} polymerises lactide at 110 °C to 98 % conversion after 24 h at very high monomer to initiator ratios.\textsuperscript{49} Furthermore, a significant increase in ROP control and rate was observed on the addition of a protic co-initiator.\textsuperscript{50} There was much speculation over the ROP mechanism but it has been shown that Sn(Oct)\textsubscript{2}
initiates by the coordination insertion mechanism with and without a purposefully added co-initiator (Figure 1.19).\textsuperscript{2,51}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1.19.png}
\caption{Computationally predicted mechanism of the ROP of lactide by Sn(Oct)\textsubscript{2} in the presence of a protic co-initiator. \textsuperscript{a} Computationally derived for R = Me.\textsuperscript{132}}
\end{figure}

Sn(Oct)\textsubscript{2} contains high degrees of impurities, mostly water and octanoic acid, which have a significant effect on the ROP reaction rate and resulting molecular weight ($M_n$) of the PLA produced. The impurities were revealed to act in a similar fashion to a protic species and form a tin-alkoxide which becomes the active initiating species.\textsuperscript{50,52} Although Sn(Oct)\textsubscript{2} is the industrially favoured initiator it shows no stereoselectivity and although Sn(Oct)\textsubscript{2} is non toxic, its related tin hydroxides are harmful, making them unsuitable for biomedical applications where conditions to produce tin hydroxides may occur.\textsuperscript{53}

Gibson \textit{et al.} has synthesised amino-phenol derived tin complexes for the polymerisation of lactide.\textsuperscript{54} The tridentate Schiff base ligands coordinate to Sn(II) then attack of the amide to the imine occurs to yield a tetra-dentate Sn(II) complex. This amide migration is a reversible process allowing access to both tetradernte and tridentate Sn(II) complex forms (Figure 1.20).\textsuperscript{54} This Sn(II) complex surprisingly...
polymerises *rac*-lactide with a high degree of control despite its fluxional nature due to the amide migration mechanism. All the derivatives show little difference in their resulting *rac*-lactide polymerisation yielding $> 90\%$ conversion at $60 \, ^\circ\text{C}$ after 2 h at $100:1$ [monomer]:[initiator] ratio. All the polymerisations show good molecular weight control with low polydispersity index values ($\text{PDI} \approx 1.2$). Interestingly NMR spectroscopy and MALDI-TOF mass spectrometry have both resolved the PLA end group as dimethylamide. It was suggested that the complex acts as a single-site initiator and further propagation proceeds *via* the lactide-Sn-ligand complex shown in figure 1.20.

![Figure 1.20: Sn(II) tridentate Schiff base complexes and amide migration to the Sn(II) tetradeinate complex. Also depicted is a hypothesised polymerisation intermediate.](image)

Further work by Gibson has shown this amide migration to be present with similar ligands such as bidentate aminophenols. Under similar conditions ($60 \, ^\circ\text{C}$, $100:1$ [monomer]:[initiator] ratio) the bidentate aminophenol Sn(II) dimer (Figure 1.21) polymerised lactide to $> 90 \%$ conversion after 1 h. It was speculated that the dimer separates on inclusion of a lactide to produce a four-coordinate active species (Figure 1.21).
Figure 1.21: Reaction of lactide with an aminophenol Sn(II) dimer showing a hypothesised propagation species.\textsuperscript{55}

Tin β-diketiminate complexes have been established as efficient initiators for the polymerisation of \textit{rac}-lactide (Figure 1.22).\textsuperscript{56,57} Initial polymerisation studies of β-diketiminate tin complex Sn(1)O\textsuperscript{i}Pr with lactide displayed polymerisation in CH\textsubscript{2}Cl\textsubscript{2} at ambient temperature to > 99 % conversion after 96 h at 100:1 [monomer]:[initiator] ratio.\textsuperscript{56} Furthermore increasing the temperature to 60 °C (toluene) afforded an enhanced rate and achieved 85 % conversion after 4 h. Notably the higher temperature reaction yielded no loss of control over the polymerisation. Both the low and high temperature polymerisation gave good molecular weight control alongside low PDI values. All the Sn(II) complexes Sn(1-4)O\textsuperscript{i}Pr produced moderately heterotactic polymer from \textit{rac}-lactide \( P_r \approx 0.65.\textsuperscript{57}\) By reducing the steric bulk of the aromatic substituent the reaction rate increased. At 60 °C (100:1 [monomer]:[initiator] ratio), Sn(4)O\textsuperscript{i}Pr attained 93 % conversion of \textit{rac}-lactide after 2 h with no loss of selectivity. Additionally the introduction of electron withdrawing substituents was shown to enhance reaction rate without selectivity loss.\textsuperscript{57}

Figure 1.22: Tin β-diketiminate alkoxide complexes.\textsuperscript{56,57}
Gibson et al. investigated 1-butyramidinate tin(II) complexes as initiators for the ROP of rac-lactide (Figure 1.23).\textsuperscript{58} As a comparison the Sn(II) complex Sn(5)O\textsuperscript{OPr} was significantly faster for the polymerisation of rac-lactide than its analogous β-diketiminate Sn(II) complexes \{Sn(1-2)O\textsuperscript{OPr}\}. Under the same conditions (60 °C, toluene, 100:1 ratio) tin(II) complex Sn(5)O\textsuperscript{OPr} afforded > 85 % conversion after 90 mins compared to 4 h for Sn(1)O\textsuperscript{OPr} and 8 h for Sn(2)O\textsuperscript{OPr}.\textsuperscript{57,58} Although 1-butyramidinate tin(II) complexes proved to be faster for the propagation of rac-lactide they yielded PLA with a similar heterotacticity to that observed by the Sn(II) β-diketiminate. Gibson et al. determined that this similar behaviour for both nitrogen binding bidentate Sn(II) ligand systems can be attributed to electronic effects of the Sn(II) metal. A 5s\textsuperscript{2} Sn(II) lone pair plays an important role in controlling the orientation of a coordinating lactide/PLA unit and furthermore influences the control over the propagation reaction.\textsuperscript{57,58}

Chisholm et al. has reported Sn(IV) initiators for the polymerisation of L-lactide.\textsuperscript{59} Tin (IV) complexes of the basic formula Ph\textsubscript{2}SnX\textsubscript{2} and Ph\textsubscript{3}SnX were synthesized and proven to be slow initiators for the polymerisation of L-lactide.\textsuperscript{53} The bis(phenyl) Sn(IV) complexes were shown to be faster initiators than their tri(phenyl) Sn(IV) counter-parts with relative reaction rates; $k_{prop} \{\text{Ph}_2\text{Sn(NMe}_2\text{)}\text{2}\} = 3.8(2) \times 10^{-5} \text{ s}^{-1}$, and $k_{prop} \{\text{Ph}_3\text{SnNMe}_2\} = 2.8(4) \times 10^{-6} \text{ s}^{-1}$ (80°C, toluene, [LA]\textsubscript{0} = 0.084 M, [Sn]\textsubscript{0} = 1.7 mM). These Sn(IV) complexes showed a very high degree of transesterification with a significant amount of cyclic esters produced during the polymerisation, to the extent that at 50 % conversion of L-lactide with Ph\textsubscript{2}Sn(NMe\textsubscript{2})\textsubscript{2} initiator the resulting product was mostly cyclic esters.\textsuperscript{59} The initiating group –X was shown to have a significant impact on the
polymerisation where $X = \text{O}$Pr the polymerisation displayed a reduced amount of intramolecular transesterification than $X = \text{NMe}_2$.

1.3.2 Group 1 initiators

Group 1 metal complexes have proven to be active for the polymerisation of lactide. A notable simple initiator initially reported by Kasperczyk was LiO\text{tBu} which polymerises \textit{rac}-lactide at room temperature in tetrahydrofuran (THF).\textsuperscript{39} LiO\text{tBu} was shown to be a highly active initiator for the polymerisation of \textit{rac}-lactide achieving 78 \% conversion after 40 mins at 20 °C in THF at the [monomer]:[initiator] ratio of 250:1.\textsuperscript{42} Interestingly LiO\text{tBu} yields heterotactic enriched lactide under the above conditions with reasonable control over the polymerisation. Further studies have indicated that lowering the temperature increases the heterotactic selectivity. It was also shown that heterotactic selectivity was much more significant at early reaction times and a $P_r = 0.94$ was reported at - 20 °C (THF) after 5 mins ([monomer]:[initiator] ratio of 250:1). The reduced selectivity after longer reaction times was attributed to an increasing degree of transesterification reactions as the propagation reaction proceeds.

Potassium \textsuperscript{1}butoxide has been demonstrated as an active initiator for \textit{L}-lactide polymerisation proving to be a fast initiator at ambient temperature.\textsuperscript{60} A significant reduction in rate is observed as the reaction approaches 80 \% conversion. The control potassium \textsuperscript{1}butoxide exhibits over the ROP of \textit{L}-lactide can be enhanced by the addition of 18-crown-6 ether decreasing the PDI from 1.42 to 1.17. While 18-crown-6 ether addition gives enhanced polymerisation control it also decreases the ROP reaction rate, $k_{\text{rop}}$ (potassium \textsuperscript{1}butoxide) = $5.9 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{rop}}$ (potassium \textsuperscript{1}butoxide + 18-crown-6 (1:1)) = $5.3 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$.

Lithium is renowned for forming aggregates but Lin \textit{et al.} synthesised a lithium dimer from the addition of \textsuperscript{9}BuLi and benzyl alcohol (BnOH) to 2,2’-ethylidenebis(4,6-di-\textit{tert}-butylphenol) (EDBP-H\textsubscript{2}).\textsuperscript{61} In the presence of THF the \{(EDBP-H)-Li(BnOH)\}_2 dimer separates into lithium monomers with the formula \{(EDBP-H)Li(BnOH)(THF)\}_2 (Figure 1.24). The \{(EDBP-H)-Li(BnOH)\}_2 dimer is a highly active initiator for the ROP of \textit{L}-lactide at room temperature yielding > 99 \% conversion after 1 h (CH\textsubscript{2}Cl\textsubscript{2}, 50:1 [monomer]:[initiator] ratio).
Experimental evidence suggested the dimeric species separated into monomers on coordination of an \( L \)-lactide moiety. The \(((\text{EDBP-H})-\text{Li(BnOH)})_2\) dimer is still highly active for \( L \)-lactide ROP at reduced temperatures albeit displaying lower activity, at 0 °C after 2 h a conversion of 91 % was obtained (\( \text{CH}_2\text{Cl}_2, 50:1 \) [monomer]:[initiator] ratio). While very active the \(((\text{EDBP-H})-\text{Li(BnOH)})_2\) dimeric complex also displays good control over the ROP of \( L \)-lactide with linear correlation between molecular weight and monomer-to-initiator ratio alongside narrow PDI values (PDI = 1.04 – 1.16). Introduction of benzyl alcohol as a co-initiator revealed a dependency of molecular weight upon the benzyl alcohol (BnOH) ratio. The monomeric species \(((\text{EDBP-H})\text{Li(BnOH)(THF)}_2\) was also proven to be a highly active initiator for \( L \)-lactide polymerisation although it was shown to be less active than its dimeric counterpart \(((\text{EDBP-H})-\text{Li(BnOH)})_2\). Furthermore, it was speculated that THF hinders the coordination of \( L \)-lactide units about the lithium metal centre.\(^{61}\)

![Diagram showing 2,2’-ethylenedibis(4,6-di-tert-butylphenol) lithium benzyl alcohol dimer \(((\text{EDBP-H})-\text{Li(BnOH)})_2\), and related THF derived lithium monomer \(((\text{EDBP-H})\text{Li(BnOH)(THF)}_2\).](image)

**Figure 1.24:** Diagram showing 2,2’-ethylenedibis(4,6-di-tert-butylphenol) lithium benzyl alcohol dimer \(((\text{EDBP-H})-\text{Li(BnOH)})_2\), and related THF derived lithium monomer \(((\text{EDBP-H})\text{Li(BnOH)(THF)}_2\).\(^{61}\)

### 1.3.3 Group 2 initiators

Magnesium \( \beta \)-diketiminate (BDI) complexes have been thoroughly studied for the ROP of lactide by Chisholm *et al.* alongside the corresponding calcium complexes.\(^{36, 62-65}\) Magnesium BDI alkoxides were obtained as dimers \( \{\text{Mg}_2(6)(O\text{Pr})_2\} \) bridged by alkoxide groups (Figure 1.25) and have been proven to
be highly active initiators for the ROP of rac-lactide, achieving complete conversion after 2 mins at 20 °C (CH₂Cl₂) with a 200:1 [monomer]:[initiator] ratio. While the magnesium BDI complex Mg₂(6)₂(iPr)₂ is one of the most active initiators within the literature it showed a limited degree of control, affording molecular weights ~ 2.5 times the predicted value and moderately broad PDI values of 1.59. Chisholm et al. speculated this reduced level of control is a consequence of a slow initiation rate compared to the rate of propagation. Interestingly the addition of a catalytic equivalent of 2-propanol significantly enhances the molecular weight control within the polymerisation giving lower PDI values of 1.29 under the same conditions. The dimeric magnesium BDI complexes do not exhibit stereocontrol over the ROP of rac-lactide.

Figure 1.25: Magnesium BDI complexes for the ROP of lactide.⁶²

Magnesium BDI complexes are still active for the ROP of rac-lactide upon variation of the aromatic groups, a notable variation is the introduction of ether groups on the aromatic ring \{Mg₂(7)₂(OiPr)₂\} (Figure 1.25).⁶² Structurally the magnesium BDI complex Mg₂(7)₂(OiPr)₂ is a dimer like Mg₂(6)₂(iPr)₂, NMR spectroscopic evidence suggests the ether groups are in a fluxional coordination state with the magnesium metal centre. Magnesium BDI complex Mg₂(7)₂(OiPr)₂ was less active than Mg₂(6)₂(iPr)₂ achieving 91 % conversion after 20 mins at 20 °C (CH₂Cl₂) with a 100:1 [monomer]:[initiator] ratio. While less active there is also a decrease in molecular weight control, yielding ~7.5 times higher molecular weight than predicted with a high PDI value (PDI = 2.23). Although poor molecular weight control was observed with Mg₂(7)₂(OiPr)₂ it displayed enhanced stereoselectivity control over the ROP of rac-lactide (\(P_s = 0.61\)). Changing the solvent has a profound
effect upon the ROP of lactide.\textsuperscript{52} Using THF as the solvent lowered the activity of the reaction (90\% conversion, 90 mins, 20 °C (THF) with a 100:1 [monomer]:[initiator] ratio), while also enhancing molecular weight control and heterotactic stereoselectivity ($P_r = 0.90$) Ether and THF affect the ROP of lactide by reversibly coordinating to the magnesium metal, this creates a competitive coordination environment for lactide monomers. Due to coordinating THF or ethers the magnesium metal is less accessible thus creating stereoselective demands for a coordinating lactide.

![Magnesium BDI complexes with coordinated THF.](image)

Figure 1.26: Magnesium BDI complexes with coordinated THF.

Chisholm also isolated monomeric magnesium BDI complexes with coordinated THF, one such is complex Mg(8)O\textsuperscript{i}Bu.THF (Figure 1.26).\textsuperscript{63, 64} The active propagation species within the ROP of rac-lactide is a dimeric species \{Mg(8)(lactide)\}_2 similar to the complex Mg_2(6)_2(O\textsuperscript{i}Pr)_2. As a result of the labile THF and the nature of the active propagation species the ROP of rac-lactide by Mg(8)O\textsuperscript{i}Bu.THF did not significantly vary from Mg_2(6)_2(O\textsuperscript{i}Pr)_2. If THF was used as the solvent a noteworthy increase in stereoselectivity was observed ($P_r = 0.93$). THF also decreased the activity of the polymerisation of rac-lactide yielding 95\% conversion after 5 mins at 20 °C at 100:1 [monomer]:[initiator] ratio.

\textbeta\text-diketiminate ligands were also complexed to calcium and trialled as rac-lactide ROP initiators. NMR spectroscopic evidence suggests the calcium BDI complex \{Ca(8)N(SiMe\textsubscript{3})\_2.THF\} (Figure 1.27) is unstable as a monomer and a plethora of species are present in solution. The complex was still shown to be highly active towards the ROP of lactide yielding atactic PLA up to 90\% conversion after 2 h at room temperature (THF) with a 200:1 [lactide]:[initiator] ratio.\textsuperscript{66}
Figure 1.27: Monometallic BDI calcium complexes with coordinated THF.

![Diagram of a complex with Ca and THF coordination]

Figure 1.28: Group 2 tris-pyrazolyl borate complexes for the ROP of lactide.

![Diagram of a tris-pyrazolyl borate complex]

A tris(3-tert-butylpyrazolyl)borate magnesium alkoxide complex \{Mg(9)OEt\} (Figure 1.28) was investigated for the ROP of lactide and has proven to be a highly active initiator, akin to other magnesium initiators.\(^6^7,^6^8\) The magnesium tris-pyrazolyl borate complex Mg(9)OEt resulted in 90% conversion of \(L\)-lactide after 1 h (20 °C, CH\(_2\)Cl\(_2\), 500:1 [monomer]:[initiator] ratio). While a highly active initiator Mg(9)OEt also displayed good molecular weight control exhibiting linear relationship of \(M_n\) with conversion, a PDI value of \(~1.2\) is maintained up to a 1000:1 [monomer]:[initiator] ratio.\(^6^7\) Mg(9)OEt showed a significant preference towards the ROP of \(meso\)-lactide over \(rac\)-lactide. A chiral tris-pyrazolyl borate magnesium complex was also synthesised and determined to give a 25% preference for syndiotactic PLA from \(meso\)-lactide.\(^6^8\)

Chisholm \textit{et al.} have utilised tris-pyrazolyl borate ligands for complexation to calcium and further investigated these complexes for the ROP of \(rac\)-lactide.\(^6^5,^6^6\) Both the tris-pyrazolyl borate calcium complexes Ca(9,10)O-2,6-Pr\(_2\)C\(_6\)H\(_3\) were isolated as five coordinate metal complexes (Figure 1.28), with THF completing the coordination sphere. With prolonged heating and reduced pressure the coordinated
THF was removed to yield the four coordinate complex Ca(9)O-2,6-iPr₂C₆H₃ (Figure 1.28). This calcium complex is highly active towards the ROP of rac-lactide achieving 90% conversion within 1 min (RT, THF, 200:1 [monomer]:[initiator] ratio). Introduction of an amide {Ca(9)N(SiMe₃)₂} as the initiating group did not have a detrimental effect on the rate of propagation for rac-lactide, under the same conditions. Initiators Ca(9)N(SiMe₃)₂, and Ca(9,10)O-2,6-iPr₂C₆H₃ are all highly active initiators for rac-lactide ROP but they exhibited moderate molecular weight control (PDI = 1.61 – 1.74). Both of these calcium initiators showed a high degree of heterotactic stereoselectivity in THF at room temperature (Pᵣ > 0.93). The stereoselectivity was influenced by the steric demands of the HB(3-tBup)₃ ligand as introduction of less sterically demanding groups, demonstrated by Ca(10)O-2,6-iPr₂C₆H₃, afforded atactic PLA under the same ROP conditions.

Figure 1.29: Magnesium Scorpionate complexes used as initiators for the ROP of lactide₆₉,₇₀

Magnesium scorpionate complexes were investigated for the ROP of rac-lactide by Sánchez-Barba et al.₆₉,₇₀ Mg(12)CH₂SiMe₃ was identified as the isomer (Figure 1.29), while the analogous complexes {Mg(14,15)CH₂SiMe₃} are isomers of each other. The less sterically bulky magnesium scorpionate complexes undergo a rearrangement at high temperature (90 °C, 4 days) to form “sandwich” complexes with two scorpionate ligands per metal.₆₉ The methyl substituted magnesium scorpionate complexes Mg(11,12)CH₂SiMe₃ are significantly less active towards the ROP of rac-lactide than other reported magnesium complexes Mg₂(6,7)₂(Pr)₂, Mg(8)O'Bu.THF, and Mg(9)OEt {Mg(11)CH₂SiMe₃, 42 %, 72 h, 70 °C, toluene, 100:1 [rac-lactide]:[initiator] ratio, PDI = 1.09} {Mg(12)CH₂SiMe₃,
Although less active for the ROP of lactide both magnesium complexes Mg(11,12)CH₂SiMe₃ gave good control over the polymerisation showing molecular weights (Mₙ) close to predicted values and low PDI values (PDI = 1.09), also an experiment with L-lactide revealed no epimerisation of the PLA chains. Addition of a catalytic equivalent of isopropanol as a co-initiator enhanced the activity of Mg(12)CH₂SiMe₃ (54 %, 48 h) under the same conditions, while slightly broadening the resulting PLA molecular weights (PDI = 1.13). These less sterically bulky magnesium scorpionate complexes {Mg(11,12)CH₂SiMe₃} afforded no stereoselectivity. It should be noted that magnesium complexes {Mg(11,12)CH₂SiMe₃} were also very active initiators for the ROP of caprolactone.⁶⁹

The more sterically bulky magnesium scorpionate complexes Mg(13-15)CH₂SiMe₃ investigated by Sánchez-Barba et al.⁷⁰ proved more stable in solution than Mg(11,12)CH₂SiMe₃ complexes,⁶⁹ with no evidence of ligand rearrangement into “sandwich” complexes. As noted above Mg(14,15)CH₂SiMe₃ are isomers with each other and were synthesised with a relative isomeric ratio of 3:7, where the magnesium isomer Mg(15)CH₂SiMe₃ was the dominant product. Isomers Mg(14,15)CH₂SiMe₃ were individually isolated before investigation for the ROP of lactide and alongside magnesium complex Mg(15)CH₂SiMe₃ were revealed as highly active initiators for the ROP of rac-lactide. Magnesium complexes Mg(13,15)CH₂SiMe₃ achieved 49 % - 51 % conversion after 2 minutes (0 °C, THF, 100:1 [rac-lactide]:[initiator] ratio) with excellent molecular weight distributions (PDI < 1.03), additionally polymerisation of L-lactide showed no epimerisation was. The sterically bulky magnesium scorpionate complexes {Mg(13-15)CH₂SiMe₃} yielded heterotactic PLA from rac-lactide (Pᵣ = 0.70 – 0.79). Reducing the temperature slightly increased the selectivity, the isomer Mg(14)CH₂SiMe₃ afforded the highest selectivity with Pᵣ = 0.79 at 0 °C.

The hybrid scorpionate/cyclopentadienyl magnesium complex shown in figure 1.30 was trialled for the ROP of L-lactide and rac-lactide.⁷¹ This hybrid scorpionate/cyclopentadienyl magnesium complex was an active initiator for the ROP of L-lactide affording 97 % conversion after 2.5 h (90 °C, toluene, 200:1 [monomer]:[initiator] ratio), with good molecular weight control and low PDI values.
(PDI = 1.05), and no epimerisation occurs. The ROP of rac-lactide was revealed to be less active under the same conditions yielding 59 % conversion after 8 h for the ROP of rac-lactide. Similar molecular weight control (PDI = 1.12) and a very slight heterotactic bias was reported. The hybrid scorpionate/cyclopentadienyl magnesium complex was tested for the “bulk” ROP of rac-lactide and a 41 % conversion was observed after 2 h, alongside a decrease in molecular weight control (PDI = 1.41). The hybrid scorpionate/cyclopentadienyl magnesium complex is comparable to the less sterically bulky magnesium scorpionate complexes Mg(11,12)CH2SiMe3 but far less active than the bulky magnesium scorpionates Mg(13-15)CH2SiMe3.

Figure 1.30: Hybrid scorpionate/cyclopentadienyl magnesium complex utilised as an initiator for the ROP of lactide.

Lin et al. studied NNO-tridentate ketiminate magnesium complexes and demonstrated that they initiate the ROP of rac-lactide and L-lactide with high activities (Figure 1.31). Magnesium complex {Mg(16)OBn}2 afforded 90 % conversion of rac-lactide after 12 h, whereas the less active derivative {Mg(17)OBn}2 afforded 96 % conversion after 25 h under the same conditions (30 °C, THF, 100:1 [monomer]:[initiator] ratio). Both initiators displayed good molecular weight control with average chain lengths consistent with each dimeric initiator propagating two PLA chains. Small variance of chain length was also observed with PDI values of 1.10 and 1.13 for {Mg(16,17)OBn}2 respectively, under the conditions stated above. Magnesium NNO-tridentate ketiminate complexes displayed heterotactic selectivity, {Mg(16)OBn}2 gave a $P_r$ of 0.85 (30 °C in THF), complex {Mg(17)OBn}2 gave a reduced $P_r$ of 0.54 (30 °C in THF). Further ROP studies on {Mg(16)OBn}2 have shown stereoselectivity is reduced upon changing the solvent to CH2Cl2 ($P_r = 0.64$). Stereoselectivity of {Mg(16)OBn}2 was further
enhanced \((P_r = 0.87)\) by reducing the temperature at the expense of activity (61 %, 0 °C, THF, 100:1 [monomer]:[initiator] ratio).

![Mg(16)OBn]_2 and Mg(17)OBn]_2 complexes](image)

**Figure 1.31**: NNO-tridentate ketiminate magnesium complexes investigated as initiators for the ROP of lactide.72

### 1.3.4 Group 3 and lanthanide initiators

Group 3 and lanthanide metal complexes have been shown to initiate the ring opening polymerisation of lactide.73, 74 Early investigation of yttrium alkoxides revealed them as highly active potential initiators. The commercially available \(\text{Y}_5(\mu-\text{O})(\text{OiPr})_{13}\) cluster species was trialled for the ROP of lactide but it took days to obtain appreciable conversion.73, 75 The monometallic tris(2,6-di-tert-butylphenoxy)yttrium species was shown to ring-open \(L\)-lactide, albeit comparatively slowly reaching full conversion after 10 h.74 End group analysis of PLA resulting from tris(2,6-di-tert-butylphenoxy)yttrium initiation was indeterminate and no single end-group was detected, it was further speculated that impurities and solvents are mechanismically important for the ROP of lactide.74 Tris(2,6-di-tert-butylphenoxy)yttrium activity towards the polymerisation of \(L\)-lactide is significantly enhanced in the presence of a less sterically hindered alcohol co-initiator, with an isopropanol co-initiator 100 % conversion was obtained after 2 mins at 22 °C at 50:1:0.3 [monomer]:[alcohol]:[initiator] ratio. The resulting PLA revealed well defined molecular weights (PDI = 1.24) alongside identification of isopropoxide end-groups. It was deduced that tris(2,6-di-tert-butylphenoxy)yttrium with isopropanol as a co-initiator proceeds \textit{via} a fast exchanging yttrium isopropoxide
intermediate (Figure 1.32),\textsuperscript{73,74} which is not readily accessible to the bridging oxide yttrium cluster compound $Y_5(\mu-O)(O^{\prime}\text{Pr})_{13}$.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{reaction_scheme.png}
\caption{Reaction scheme depicting the ROP mechanism of lactide by tris(2,6-di-tert-butylphenoxy)yttrium with isopropanol as a co-initiator.\textsuperscript{73,74}}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{bis initiator.png}
\caption{Bis(thiophosphinic amido)yttrium initiators investigated for the ring-opening polymerisation of lactide.\textsuperscript{76}}
\end{figure}
Williams et al. reported bis(thiophosphinic amido)yttrium initiators as active candidates for the ROP of rac-lactide. It was shown that the backbone (X group) had little effect on the ROP polymerisation of rac-lactide, whereas the phosphorus moieties (R groups) had a profound influence (Figure 1.33). Steric influence had a minimal effect on the activity of the yttrium initiator. Sterically iso-propyl and phenyl are similar but a significant difference in activity was observed (R = iso-propyl, > 90% conversion, 3.7-6.8 mins, 25 °C, CH₂Cl₂, 200:1 [monomer]:[initiator] ratio) (R = phenyl, > 90% conversion, 25-90 mins, 25 °C, CH₂Cl₂, 200:1 [monomer]:[initiator] ratio). It was deduced that the polymerisation reaction proceeds by a coordination insertion mechanism where the insertion step is rate limiting. An electron withdrawing phosphorus substituent increases the Lewis acidity of the yttrium metal and consequently increases the metal alkoxide bond strength, therefore hindering the insertion of a new lactide molecule. This justifies the experimental ROP activity for this series of yttrium initiators where iso-propyl > phenyl > ethoxy. ROP reactions revealed a linear relationship between molecular weight and conversion for all the bis(thiophosphinic amido)yttrium derivatives. From MALDI-TOF mass spectrometry it was determined that significant transesterification was occurring resulting in high PDI values (PDI > 1.5). A heterotactic bias was observed for bis(thiophosphinic amido)yttrium complexes with ethoxy phosphorus groups (X = ethylene, R = ethoxy, \( P_r = 0.68 \))(X = trans-1,2-cyclohexylene, R = ethoxy, \( P_r = 0.79 \)). This stereoselectivity was attributed to the hemilabile ethoxy exerting coordination geometry control over the active yttrium metal.

![Figure 1.34](image)

**Figure 1.34**: Group 3 and lanthanide diaminobis(phenoxide) borohydride complexes trialled for the ROP of L-lactide and rac-lactide.
Group 3 and lanthanide borohydride complexes utilising dianinobis(phenoxide) ligands \{Y(18)BH_4\}_2, \{Sm(18)BH_4\}_2, and \{Nd(18)BH_4\}_2 were investigated by Mountford et. al. for the ROP of L-lactide and rac-lactide.\(^7\)

The complexes were identified as dimers (Figure 1.34), the Sm complex \{Sm(18)BH_4\}_2 has the structure depicted, the Y dimer \{Y(18)BH_4\}_2 contained an additional coordinated THF, and the Nd dimeric complex \{Nd(18)BH_4\}_2 contained two coordinated THF moieties (one THF per metal). Complexes (\{Y(18)BH_4\}_2, \{Sm(18)BH_4\}_2, and \{Nd(18)BH_4\}_2 were active at room temperature for the ROP of L-lactide and rac-lactide. Kinetic experiments revealed a first order dependence on rac-lactide concentration where the order of activity is \{Sm(18)BH_4\}_2 > \{Y(18)BH_4\}_2 > \{Nd(18)BH_4\}_2. Complexes \{Y(18)BH_4\}_2 and \{Sm(18)BH_4\}_2 typically polymerised rac-lactide to \~70\% conversion after 1 h (25 °C, THF, 200:1 [rac-lactide]:[initiator] ratio), whereas the neodymium complex \{Nd(18)BH_4\}_2 achieved 33 \% conversion after 2 h under the same conditions. THF promotes the activity of these complexes, as a result using toluene at elevated temperature (70 °C) revealed a significant reduction in initiator activity for the ROP of rac-lactide. PLA resulting from these dianinobis(phenoxide) lanthanide complexes displayed a significant degree of transesterification with lower molecular weights than expected and broader molecular weight distributions (PDI = 1.41 – 1.59). The samarium bimetallic complex \{Sm(18)BH_4\}_2 displayed the greater molecular weight control.

PLA resulting from initiation of rac-lactide by yttrium and samarium complexes (\{Y(18)BH_4\}_2 and \{Sm(18)BH_4\}_2) revealed a heterotactic bias \{P_r \{Y(18)BH_4\}_2 = 0.87, P_r \{Sm(18)BH_4\}_2 = 0.72\}. A significant decrease in activity of initiators \{Y(18)BH_4\}_2 and \{Sm(18)BH_4\}_2 was reported when utilised for the ROP of L-lactide, which is consistent with their preference in producing heterotactic PLA. The heterotactic selectivity of complexes \{Y(18)BH_4\}_2 and \{Sm(18)BH_4\}_2 was shown to be dependent on either the solvent and temperature of the polymerisation.\(^7\)
Carpentier et al. synthesised a series of group 3 and lanthanide complexes derived from alkoxy-amino-bis(phenol) ligands (Figure 1.35). Furthermore these alkoxy-amino-bis(phenol) lanthanide complexes were investigated for the ROP of rac-lactide under various conditions. Initially the complexes Y(19)N(SiHMe₂)₂·THF and La(19)N(SiHMe₂)₂·THF were reported as highly active initiators for the ROP of rac-lactide, where the yttrium initiator achieved full conversion within 1 h at room temperature at a 500:1 [monomer]:[initiator] ratio. The synthesised yttrium, lanthanum, and neodymium amides based on ligands (19-22)H₂ ROP rac-lactide in THF to 100 % conversion within 20 mins at 200:1 [rac-lactide]:[initiator] ratio. Lanthanide complexes of these alkoxy-amino-bis(phenol) ligands polymerise lactide in a living manner with molecular weights consistent with one PLA chain per metal centre and narrow molecular weights (PDI = 1.19 – 1.34). The molecular weight distribution was slightly higher than expected for a truly living polymerisation, which was attributed to transesterification side reactions. Initially PLA derived from initiators Y(19)N(SiHMe₂)₂·THF and La(19)N(SiHMe₂)₂·THF revealed a heterotactic bias giving $P_r = 0.80$ for Y(19)N(SiHMe₂)₂·THF, and $P_r = 0.65$ for La(19)N(SiHMe₂)₂·THF. A solvent comparison between toluene and THF proved that THF is necessary to obtain heterotactic PLA. Substituting the methoxy group for an amide {Y(20)N(SiHMe₂)₂·THF} has minimal effect on the activity but a profound effect on the stereoselectivity yielding PLA with a reduced $P_r = 0.60$. This is to be expected as the structure of Y(20)N(SiHMe₂)₂·THF is ambiguous.
Y(21)N(SiHMe₂)₂·THF initiated the ROP of rac-lactide to yield PLA with a $P_r = 0.56$. One suggested reason for this decrease in heterotactic selectivity, was the structural ambiguity due to a formation of aggregates. Secondly, the reduction in steric bulk about the active metal centre imparts less coordination geometry control over the active metal-lactide propagating species. The highest heterotactic stereoselectivity ($P_r = 0.90$) for this series of complexes was achieved by the complex Y(22)N(SiHMe₂)₂·THF. By the same principle the bulky −Me₂Ph group imparts additional steric control over the yttrium metal centre enhancing coordination geometry control over the active metal-lactide propagating species. The larger metals La and Nd result in less heterotactic stereoselectivity due to less steric control, $P_r \{\text{La(19)N(SiHMe}_2\}_2\cdot\text{THF}\} = 0.65$, $P_r \{\text{Nd(19)N(SiMe}_3\}_2\cdot\text{THF}\} = 0.49$. The addition of isopropanol as a co-initiator to the ROP of rac-lactide by yttrium initiators {Y(19)N(SiHMe₂)₂·THF, Y(22)N(SiHMe₂)₂·THF} was shown to yield narrower PLA chain distribution (PDI = 1.06 – 1.24). Stereoselectivity was retained upon addition of isopropanol. Addition of excess isopropanol is directly proportional to the PLA average chain length. Furthermore isopropanol is an effective chain transfer agent within the polymerisation reactions as the presence of cyclic esters was not detected.

![Figure 1.36: Further group 3 and lanthanide diamino-bis(phenox) complexes utilised for the ROP of rac-lactide.](image)

Following on from Mountford’s⁷⁷ and Carpentier’s⁷⁸, ⁷⁹ work, Cui et al.⁸⁰ investigated further diamino-bis(phenox) derivatives complexed to group 3 and lanthanide metal alkys and investigated these for the ROP of lactide (Figure 1.36).
Y/Lu(23)CH₂SiMe₃·THF and Y(24)CH₂SiMe₃·THF were very active initiators for the ROP rac-lactide achieving > 90 % conversion after 1 h (20 °C, THF, 300:1 [monomer]:[initiator] ratio). Y(23)CH₂SiMe₃·THF and Lu(23)CH₂SiMe₃·THF displayed similar activities although by increasing the amide alkyl chain tether (n = 3) the yttrium complex became inactive for the ROP of rac-lactide at 20°C, showing no conversion after 6 h under the same conditions. Molecular weights showed some variance from the predicted values and moderate PDI values were obtained (PDI = 1.32 – 1.59). The yttrium and lutetium complexes {Y/Lu(23)CH₂SiMe₃·THF} (excluding when n = 3) yielded elevated heterotacticity, \( P_r > 0.94 \), from the ROP of rac-lactide. Y(23)CH₂SiMe₃·THF also yielded heterotactic PLA under the same conditions giving a \( P_r = 0.90 \). It was shown that THF as the ROP solvent enhances the heterotactic stereoselectivity. X-ray determined complexes Y/Lu(23)CH₂SiMe₃·THF (for n = 2) adopted a twisted octahedral geometry about the metal. Y(24)CH₂SiMe₃·THF adopted a less twisted octahedral geometry. A trend was revealed where a more twisted octahedral geometry about the metal resulted in higher activity and stereoselectivity.

Figure 1.37: Group 3 and lanthanide salan¹⁰ and piperazine salan¹¹ complexes investigated for the polymerisation of lactide.

The yttrium salan complex \{Y(25)CH₂SiMe₃·THF\} (Figure 1.37) was synthesised and investigated for the ROP of rac-lactide it was shown to be highly active resulting in > 100 % conversion after 1 h (20 °C, THF, 300:1 [monomer]:[initiator] ratio).¹⁰ Unlike the analogous aluminium salan (see figure 1.63, Al(90)Me)²¹ Y(25)CH₂SiMe₃·THF gave little polymerisation control (PDI = 1.64) and a small degree of heterotactic stereoselectivity was observed (\( P_r = 0.65 \)).
Group 3 and lanthanide metals were complexed to piperazine salan ligands (Figure 1.37) and investigated for the ROP of L-lactide and rac-lactide. For all the listed metals (Figure 1.37) a monometallic complex was obtained with the piperazine salan ligand (26H₂), where the piperazine ring adopted a boat configuration. The lanthanide complexes M(26)CH₂SiMe₃·THF displayed very high activity for the ROP of L-lactide achieving 97% conversion within 4 minutes (70 °C, toluene, 700:1 [monomer]:[initiator] ratio). Molecular weights were consistent with one chain per metal although some deviation was reported, PDI was dependent upon the metal {PDI (Yb) = 1.12 – 1.15, PDI (Y) = 1.12 – 1.25, PDI (Lu) = 1.27 – 1.41, PDI (Gd) = 1.21 – 1.40}. Only the yttrium complex Y(26)CH₂SiMe₃·THF was reported for the ROP of rac-lactide, it was shown to ROP rac-lactide to 100% conversion within 2 h (20 °C, THF, 700:1 [monomer]:[initiator] ratio). Although an active initiator towards the ROP of rac-lactide Y(26)CH₂SiMe₃·THF yielded much broader molecular weight distribution than reported for L-lactide, with a PDI = 1.61 for rac-lactide under the above conditions. Alongside broader PDI values little stereocontrol was observed, $P_r = 0.48 – 0.61$.

![Figure 1.38: Group 3 complexes bound to phosphido-diphosphine pincer ligands used as initiators for the ROP of lactide](image)

Complexes of group 3 metals utilising phosphido-diphosphine pincer ligands have been reported as initiators for the ROP of lactide (Figure 1.38). The yttrium initiator displayed a high activity towards the ROP of lactide at room temperature. The yttrium initiator Y(27)(CH₂SiMe₃)₂·THF achieved 65% conversion after 15 mins (THF) at 20 °C with a 200:1 [monomer]:[initiator] ratio. By introducing less electron donating substituents to the phenyl ring {Y(28)(CH₂SiMe₃)₂·THF} the yttrium metal becomes more Lewis acidic. This caused an enhancement in activity where initiator Y(28)(CH₂SiMe₃)₂·THF gave a conversion of 92% after 15 mins
under the same conditions. The scandium initiators were much slower with Sc(27)(CH2SiMe3)2.THF achieving 38% conversion after 20 h under the same conditions, this was attributed to scandium being a smaller metal hindering lactide coordination and further lactide insertion. Despite two possible initiation sites per metal it was revealed that at room temperature phosphido-diphosphine complexes of group 3 metals propagate one PLA chain per metal centre. They displayed good control over molecular weight being almost a controlled living polymerisation. Molecular weight distributions of the resulting polymers were relatively low with PDI values between 1.20 - 1.28 for initiators Y(27,28)(CH2SiMe3)2.THF and Sc(27)(CH2SiMe3)2.THF under the above conditions. The deviation from a controlled living polymerisation (PDI < 1.10) was acknowledged as transesterification side reactions. PLA resulting from the ROP of rac-lactide by the yttrium initiators Y(27,28)(CH2SiMe3)2.THF was identified as having a heterotactic bias, with respective $P_r^{Y(27)(CH2SiMe3)2.THF}$ = 0.63, $P_r^{Y(28)(CH2SiMe3)2.THF}$ = 0.64. Scandium initiators {Sc(27)(CH2SiMe3)2.THF and Sc(28)(CH2SiMe3)2.THF2} revealed a heterotactic bias, with respective $P_r^{Sc(27)(CH2SiMe3)2.THF}$ = 0.60 and $P_r^{Sc(28)(CH2SiMe3)2.THF2}$ = 0.62. Solvent free conditions (130 °C) complicated the ROP of lactide, typically showing broader PDI values and as each yttrium metal propagated two PLA chains at the highly elevated temperature.
Dicationic and zwitterionic yttrium complexes were synthesised by Mountford et al.\textsuperscript{84} who investigated their properties as initiators for the ROP of rac-lactide (Figure 1.39). The dicationic yttrium complex \{[Y(29)O^iPr.THF$_3$]$^{2+}$ 2[BPh]$^-$\} was moderately active towards the ROP of rac-lactide yielding high conversions after 12 h (70 °C, 100:1:5 [monomer]:[initiator]:[co-initiator]). The direct polymerisation of rac-lactide by [Y(29)O$^i$Pr.THF$_3$]$^{2+}$ was shown as a living polymerisation system. Furthermore addition of 5 eq. of co-initiator (iPrOH or BnNH$_2$) resulted in proportionally lower molecular weights, consistent with an immortal polymerisation system. Analysis of the resulting PLA revealed an atactic microstructure. The zwitterionic yttrium complex Y(30)$_2$H was shown as highly active for the ROP of rac-lactide resulting in high conversion after 20 mins (RT, THF, 100:1:5 [monomer]:[initiator]:[BnOH]). While Y(30)$_2$H is a neutral complex it possesses a Lewis acid yttrium centre and a Brønsted acidic proton, both are capable of coordinating or enhancing the coordination of lactide. The zwitterionic yttrium complex was also identified as an immortal initiator for the ROP of lactide resulting in very controlled molecular weights and low PLA chain distribution (PDI = 1.17, for the above conditions). Additionally the resulting PLA was highly heterotactic ($P_r = 0.93$) and negligible transesterification was observed.
Figure 1.40: Iminophosphorane neodymium(III) Complexes investigated as initiators for the ROP of lactide.\(^{85}\)

Monometallic iminophosphorane neodymium(III) amide complexes Nd(31,32)(N(SiMe\(_3\))\(_2\))\(_2\) were shown to be highly active initiators for the ROP of lactide (Figure 1.40).\(^{85}\) The monometallic neodymium(III) complexes \{Nd(31,32)(N(SiMe\(_3\))\(_2\))\(_2\}\) both yielded > 95 % conversion of rac-lactide within 5 mins (25 °C, THF, 200:1 [monomer]:[initiator] ratio). A linear molecular weight increase proportional to conversion was observed with moderate chain length distribution (PDI ~1.3), although molecular weights were about 10 times the expected value implying only 10 % of initiators were active. Furthermore, intermolecular transesterification was indentified by MALDI-TOF, alongside amido and hydroxyl end groups. An analogous bis(alkoxide) of Nd(32)(N(SiMe\(_3\))\(_2\))\(_2\) was synthesised from the neodymium(III) bis(phosphorus-amide) and further shown to decompose after 2h, following this polymerisation experiments were conducted by adding \(^{t}\)PrOH in-situ as a co-initiator. The in-situ generated alkoxide derivatives of Nd(31,32)(N(SiMe\(_3\))\(_2\))\(_2\) achieved > 95 % conversion after 6 mins (25 °C, THF, 200:1:2 [monomer]:[initiator]:[\(^{t}\)PrOH] ratio). The in-situ polymerisation displayed molecular weights consistent with 2 PLA chains from each metal, also very low
molecular weight distributions were observed (PDI = 1.05 – 1.07). Furthermore, the resulting polymer displayed a slight heterotactic bias (P, = 0.57 – 0.60). Treatment of iminophosphorane potassium complex with 0.5 Eq. of neodymium (III) iodide resulted in a bis(iminophosphorane) neodymium (III) iodide complex, further addition of a base produced the neodymium (III) carbene complex Nd(31)2I (Figure 1.40). Formation of bis(iminophosphorane) neodymium (III) iodide was dependent on steric bulk of the nitrogen substituents. The Nd (III) carbene complex Nd(31)2I was investigated for the ROP of rac-lactide but it was proven to be inactive. Addition of iPrOH to Nd(31)2I resulted in the decomposition into neodymium (III) alkoxydes and free ligand, which consequently produced PLA, albeit with a lack of control. Interestingly addition of iPrOH or KOEt to a mixture of Nd(31)2I and rac-lactide resulted in the moderately fast polymerisation (iPrOH = 81 %, KOEt = 0.85 %, 60 mins, RT, THF, 200:1:1 [monomer]:[initiator]:[iPrOH/KOEt]), molecular weights were consistent with one polymer chain per neodymium and low chain length distributions (PDI = 1.05 – 1.11) were observed. A monomer activated mechanism was proposed, where neodymium activates the monomer for alcohol/alkoxide attack. After the polymerisation reaction reaches completion the alcohol/alkoxide terminated polymer chains proceed to attack the neodymium complex to yield free ligand. Chain length could not be controlled by addition of excess iPrOH as the additional alcohol decomposed the neodymium initiator.

1.3.5 Group 4 initiators

Group 4 metal complexes are successful initiators for the ROP of lactide, of particular note due to their relevance to this study are the salen, salan, and salalen (-ONNO-) group 4 complexes. Tris-phenolates and other C3 symmetric group 4 complexes have been investigated for the ROP of lactide and yielded a high degree of stereo-selectivity. Although titanium is the most prominent throughout the literature zirconium and hafnium initiators are often more active, or more stereoselective than their titanium counterparts.
Figure 1.41: Scheme depicting chiral Schiff bases complexed to Ti(IV) and Zr(IV) alkoxides investigated for the ROP of rac-lactide.  

Chiral Schiff base ligands (33-36)H$_2$ were complexed with Ti(IV) and Zr(IV) isopropoxides by Davidson et al. and investigated as initiators for the ROP of rac-lactide (Figure 1.41). Pure chiral $R,R$ and $S,S$ complexes were synthesised alongside racemic mixtures ($S,R$ and $R,S$), NMR spectroscopic analysis showed the complexes were fluxional in solution at room temperature. All the Ti(IV) Schiff base complexes $\{Ti(33-36)_2(O^\text{iPr})_2\}$ were inactive in solution at 80 °C, whereas the Zr($33-36)_2(O^\text{iPr})_2$ initiators ring opened rac-lactide with moderate activities achieving 45 – 69 % conversion after 24 h (20 °C, 100:1, [rac-lactide]:[initiator] ratio). Under these conditions Zr(IV) Schiff base complexes $\{Zr(33-36)_2(O^\text{iPr})_2\}$ displayed good chain length control (PDI < 1.12) and resulted in heterotactic biased PLA ($P_r = 0.68 – 0.76$). Ti(IV) Schiff base complexes $\{Ti(33-36)_2(O^\text{iPr})_2\}$ were active for the ROP of rac-lactide in solvent free conditions (130 °C, 30 mins, 300:1 [rac-lactide]:[initiator] ratio) and afforded good molecular weight control but yielded atactic PLA. Utilising melt conditions the Zr(IV) Schiff base initiators gave a reduced degree of chain length control (PDI = 1.39 – 2.49) but retained their heterotactic bias ($P_r = 0.68 – 0.73$). These Schiff base initiators were shown to have a degree of tolerance to water and impurities, and were capable of the polymerisation of lactide under such conditions.
Salen supported titanium(IV) bis(alkoxide) complexes \{Ti(37)(O^{i}Pr)_{2}\} (Figure 1.42) were shown to be moderately active initiators for the ROP of rac-lactide.\textsuperscript{87} The salen complexes \{Ti(37)(O^{i}Pr)_{2}\} adopted a solution stable \textit{trans} octahedral geometry. As initiators for the ROP of \textit{rac}-lactide they achieved between 66 - 97 \% conversion after 24 h (70 °C, toluene, 100:1 [\textit{rac}-lactide]:[initiator] ratio). The variance in activity was dependent upon the \textit{para}-substituent, where the more electron withdrawing substituents resulted in lower activities. A significant induction period before the propagation stage of the polymerisation was observed and the authors speculated that the initial metal-lactide coordinated species is relatively stable towards propagation. Although two likely alkoxide initiation sites are present in the titanium salen complexes \{Ti(37)(O^{i}Pr)_{2}\}, only one PLA chain per metal was observed alongside well defined molecular weights (PDI = 1.15 – 1.21), the resulting PLA was atactic.

Further 1,2-diaminocyclohexane (1,2-DACH) salens were complexed to titanium, yielding a monomeric species \{Ti(38)(O^{i}Pr)_{2}\}, and zirconium/hafnium resulted in bimetallic complexes \{Zr\textsubscript{2}(38)(O^{i}Pr)\textsubscript{6}, Hf\textsubscript{2}(38)(O^{i}Pr)\textsubscript{6}\} (Figure 1.43).\textsuperscript{87,88} Unlike the related Ti(37)(O^{i}Pr)\textsubscript{2} structures the titanium DACH salen \{Ti(38)(O^{i}Pr)_{2}\} adopted an \textit{a-cis} octahedral structure. Titanium DACH salen \{Ti(38)(O^{i}Pr)_{2}\} was less active than its analogous Ti(IV) salen \{Ti(37)(O^{i}Pr)_{2}\} achieving 57 \% conversion after 24 h (70 °C, toluene, 100:1 [\textit{rac}-lactide]:[initiator] ratio). Although slightly less active towards the ROP of \textit{rac}-lactide, slightly lower molecular weight distribution was observed (PDI = 1.11) whilst atactic PLA was obtained.

**Figure 1.42:** Salen supported titanium (IV) bis(alkoxide) complexes trialled for the ROP of \textit{rac}-lactide.\textsuperscript{87}
Figure 1.43: Group 4 alkoxide complexes supported by \( R,R \)-DACH salen ligands trialled for the ROP of \( \text{rac} \)-lactide and cyclic esters.\(^{87,88}\)

The bimetallic Zr(IV)/Hf(IV) \( R,R \)-DACH salens \( \{ \text{Zr}_2(38)(\text{OiPr})_6, \text{Hf}_2(38)(\text{OiPr})_6 \} \) were trialled for the ROP of \( \text{rac} \)-lactide in solvent free conditions, reaching completion after 48 mins \( \{ \text{Zr}_2(38)(\text{OiPr})_6 \} \), and 66 mins \( \{ \text{Hf}_2(38)(\text{OiPr})_6 \} \) (140 °C, 200:1 [\( \text{rac}\)-lactide]:[initiator] ratio).\(^{88}\) Very good molecular weight control was observed for both Zr(IV) and Hf(IV) initiators \( \{ \text{Zr}_2(38)(\text{OiPr})_6, \text{Hf}_2(38)(\text{OiPr})_6 \} \) resulting in PDI = 1.02 and molecular weights consistent with one PLA chain per bimetallic complex. Although atactic PLA was obtained the ROP of \( \text{rac} \)-lactide proceed by a living mechanism and retained molecular weight control upon addition of further monomer. Other cyclic esters including; caprolactone, valerolactone, and \( \text{rac} \)-butyrolactone were investigated for ROP using \( \text{Zr}_2(38)(\text{OiPr})_6 \) and \( \text{Hf}_2(38)(\text{OiPr})_6 \) as solvent free ROP initiators. The ROP of caprolactone, valerolactone, and \( \text{rac} \)-butyrolactone proceeded at 80 °C and retained the good molecular weight control (PDI < 1.08) observed for \( \text{rac} \)-lactide.

Figure 1.44: Diamine-bis(phenol) (salan) ligands complexed to group 4 metal alkoxides and utilised for the ROP of \( L \)-lactide and \( \text{rac} \)-lactide.\(^{89,90}\) *Not all combinations of complexes were synthesised.
Group 4 metal alkoxides have been complexed to diamine-bis(phenol) (salam) ligands and investigated for the ROP of L-lactide and rac-lactide by Davidson et al. and Kol et al. (Figure 1.44). Titanium and zirconium salan complexes \{Ti(39-42)(O’Pr)\_2, Zr(39-42)(O’Pr)\_2\} adopt chiral (Δ, Λ) α-cis pseudo octahedral isomers with pseudo C\_2 symmetry. Kol et al. synthesised chloro and tBu derivatives Ti(39,42)(O’Pr)\_2 and Ti(39,42)(O’Pr)\_2 and reported moderate activity for the ROP of L-lactide under solvent free conditions. Davidson et al. showed Zr(40)(O’Pr)\_2 was the only initiator in the series to ROP rac-lactide in solution (> 99 %, 110 °C, toluene, 100:1 [monomer]:[initiator] ratio). Titanium initiators polymerise rac-lactide to yield atactic lactide with 62 – 74 % conversion after 2 h under solvent free conditions (130 °C, 300:1 [monomer]:[initiator] ratio). Zr(IV) and Hf(IV) salan initiators \{Zr(39-42)(O’Pr)\_2, Hf(39-42)(O’Pr)\_2\} resulted in isotactic biased PLA under the same conditions (P\_r = 0.25 – 0.30), the most selective salan derivative in this initiator series was Zr(40)(O’Pr)\_2. The origin of stereoselectivity was attributed to the induced Δ, Λ chirality about the metal centre. Furthermore, back-chelation of PLA lactate units was considered to influence stereoselectivity of following lactide units. The lack of stereoselectivity observed for Ti(39-42)(O’Pr)\_2 initiators was attributed to the inability of titanium to increase it coordination sphere to allow chelation of a lactate unit.

![Figure 1.45: Group 4 alkoxide complexes supported by amine–bis(phenolate) ligands utilised for the ROP of L-lactide and rac-lactide.](image-url)
Kol et al. synthesised amine-bis(phenoxo) titanium and zirconium complexes with a coordinated dimethylamine side arm \{Ti(43,44)(O'Pr)₂, Zr(43,44)(O'Pr)₂\} (Figure 1.45), where Ti(43,44)(O'Pr)₂ and Zr(43,44)(O'Pr)₂ adopted Cs symmetry. The Ti(IV) alkoxide complexes initiated the ROP of \(L\)-lactide to low conversions after an extended reaction time under solvent free conditions (130 °C, 300:1 [monomer]:[initiator] ratio). The Ti(43)(O'Pr)₂ derivative was more active than Ti(44)(O'Pr)₂ and both resulted in well defined PLA chain distributions (PDI = 1.21 - 1.28). Zr(43,44)(O'Pr)₂ complexes both initiated the ROP of \(L\)-lactide under the same conditions but revealed enhanced reactivity. The phenoxy substituents had the reverse effect upon activity where Zr(44)(O'Pr)₂ displayed a 10 fold activity increase over the related Zr(43)(O'Pr)₂ complex. Similar control over the ROP of \(L\)-lactide was observed for the initiator Zr(43)(O'Pr)₂ whereas initiator Zr(44)(O'Pr)₂ resulted in higher PDI = 1.56.

Davidson et al. synthesised amine-bis(phenol) ligands with a pyridine derived side arm and complexed them to Ti(IV), Zr(IV), and Hf(IV) alkoxides \{Ti(45-47)(O'Pr)₂, Zr(45-47)(O'Pr)₂, and Hf(45-47)(O'Pr)₂\} (Figure 1.45). Solution ROP of \(L\)-lactide were attempted with these complexes and only Zr(45)(O'Pr)₂ was active, good activity was revealed achieving > 99 % conversion after 2 h with narrow PDI values (PDI = 1.13) (110 °C, toluene, 100:1 [monomer]:[initiator] ratio). Investigations into the solvent free ROP of rac-lactide were reported, Ti(45)(O'Pr)₂ was shown to be active achieving 75 % conversion after 2 h (130 °C, 300:1 [monomer]:[initiator] ratio). The Zr(45-47)(O'Pr)₂, and Hf(45-47)(O'Pr)₂ initiators were also moderately active revealing 10 – 45 % conversion under the same conditions, although the sterically bulky \(R = \) \(^1\)Bu phenol substituents displayed a reduced activity requiring 24 h reaction time for low conversion. The Zr(IV) initiators Zr(45,47)(O'Pr)₂ resulted in PLA with an isotactic bias (\(P_c = 0.35 – 0.45\)) whereas the bulky \(^1\)Bu substituents \{Zr(46)(O'Pr)₂\} yielded atactic PLA alongside Ti(45-47)(O'Pr)₂ initiators. Although PLA with an isotactic bias was observed it is less than the related Zr(IV) bis(phenoxo) complexes Zr(39-42)(O'Pr)₂,\(^89,90\) this was attributed to the non-chiral symmetry of Zr(45-47)(O'iPr)₂. The unsymmetrical complexes Zr(47)(O'Pr)₂/Hf(47)(O'Pr)₂ revealed no stereoselectivity enhancement over Zr(45)(O'Pr)₂/Hf(45)(O'Pr)₂ complexes with -Me phenoxy substituents.
Salalen ligands were complexed to group 4 metal alkoxides by Jones et al. and utilised for the ROP of rac-lactide (Figure 1.46). The group 4 salalen complexes were shown to adopt a pseudo octahedral fac-mer geometry by X-ray diffraction and was confirmed in solution by NMR spectroscopy, with the exception of Hf(50)(OiPr)2 which was shown as two isomers in solution both present in equal proportions. The salalen group 4 complexes initiated the ROP of rac-lactide in solution and revealed good activities achieving > 96 % conversion after 24 h (80 °C, toluene, 100:1 [monomer]:[initiator] ratio). The Zr(IV) and Hf(IV) salalen complexes typically displayed better molecular weight control over the solution ROP of rac-lactide (PDI = 1.07 - 1.13), while Ti(48,49)(OiPr)2 and Hf(50)(OiPr)2 yielded broader PDI values (PDI = 1.42 - 1.62). Ti(48,49)(OiPr)2 and Hf(50)(OiPr)2 resulted in atactic PLA, Zr(48)(OiPr)2 and Zr(49)(OiPr)2 resulted in a slightly heterotactic biased PLA ($P_r = 0.56 - 0.60$), Hf(48)(OiPr)2 and Hf(50)(OiPr)2 resulted in an isotactic biased PLA ($P_r = 0.30$) using the above conditions. Studies were also conducted without the presence of solvent, it was shown that Ti(IV) and Zr(IV) salalen initiators gave atactic lactide with good conversions (52 – 98 %) after 15 mins (130 °C, 300:1 [monomer]:[initiator] ratio). Hafnium initiators were slower for the ROP of rac-lactide in solvent free conditions with high conversion obtained after 2 days {Hf(48)(OiPr)2}, 1 day {Hf(49)(OiPr)2} and 15 mins {Hf(50)(OiPr)2}. Hf(48)(OiPr)2 and Hf(50)(OiPr)2 still retain their isotactic selectivity at elevated temperature in solvent free conditions. Although isotactic stereoselectivity was
observed Hf(50)(O^tBu)_2 displayed a lack of molecular weight control with lower \( M_n \) values than expected. This was attributed to the lower steric bulk about the metal allowing propagation of multiple PLA chains, also transesterification was thought to be more prevalent as a consequence of its higher activity. The ROP of \( \text{rac-lactide} \) using Hf(50)(O^tBu)_2 was also conducted at a lower temperature which resulted in an enhanced isotactic bias \( (P_r = 0.25) \) and 99 % conversion within 6 h \( (20 \, ^\circ\text{C}, \text{CH}_2\text{Cl}_2, 100:1 \, [\text{monomer}]:[\text{initiator}] \) ratio). Additionally more molecular weight control was observed \( (\text{PDI} = 1.25) \) consistent with one PLA chain per metal.

Group 4 complexes supported by dithiodiolate ligands \{((51,52)H_2)\} (Figure 1.47) were trialled for the ROP of \( \text{L-lactide} \) and \( \text{rac-lactide} \) in toluene and solvent free conditions.\(^{92}\) The titanium structure Ti(51)(O^tBu)_2 was isolated and characterised by X-ray diffraction and showed the complex adopts a pseudo \( \alpha\)-cis octahedral geometry. It was reported that the complexes Ti(51,52)(O^tBu)_2, Zr(51,52)(O^tBu)_2, and Hf(51,52)(O^tBu)_2 are fluxional in solution inter-converting between two isomers, where the M(52)X_2 complexes gave greater fluxionality. The group 4 dithiodiolate complexes are very active initiators for the ROP of \( \text{rac-lactide} \). The activity was more dependent upon the metal than the sulphur bridging group which, displayed minimal effect upon activity. Titanium complexes Ti(51,52)(O^tBu)_2 were very active initiators for the ROP of \( \text{rac-lactide} \) under solvent free conditions achieving high conversion within 35 and 17 mins respectively \( (130 \, ^\circ\text{C}, 300:1 \, [\text{monomer}]:[\text{initiator}] \) ratio). Zirconium initiators Zr(51,52)(O^tBu)_2 were more active reaching high conversion in \( < 4 \) mins under the same condition. Hafnium initiators Hf(51,52)(O^tBu)_2 were reported to have slightly higher activities than their zirconium analogues obtaining high conversion in \( < 2 \) mins. Furthermore the hafnium initiator Hf(52)(O^tBu)_2 was shown to polymerise \( \text{rac-lactide} \) to high conversion within 5 minutes at 3000:1 \( [\text{monomer}]:[\text{initiator}] \) ratio. Moderate molecular weight control was observed with a range of PDI values \( (\text{PDI} = 1.17 - 1.75) \) and molecular weights were significantly lower than expected, attributed to more than one PLA chain being propagated per metal and transesterification side reactions. Additionally under melt conditions initiators, Zr(51,52)(O^tBu)_2 and Hf(51,52)(O^tBu)_2 yielded PLA with a heterotactic bias \( (P_r \approx 0.70) \). By using toluene as a solvent and lowering the reaction temperature \( (75 \, ^\circ\text{C}) \) the stereoselectivity was enhanced, the highest heterotactic bias was obtained by Zr(52)(O^tBu)_2 \( (P_r = 0.89) \).
Titanium tetra-isopropoxide was investigated for the ROP of \textit{L-}lactide and \textit{rac-}lactide. Furthermore the isopropoxide moieties were substituted by chloride ligands to varying degrees \([\text{Ti(O}^\text{iPr})_4]_{4-x}\text{Cl}_x\).\(^93,\,94\) All these complexes from \(X = 3\) though to \(X = 0\) were active for the ROP of \textit{rac-}lactide in solvent free conditions (130 °C) and in toluene (70 °C). Activity decreased with increasing degrees of chloride substitution although increasing chloride substitution resulted in narrower molecular weight distributions. With larger degrees of chloride substitution (\(X = 2, 3\)) the ROP of \textit{rac-}lactide resulted in PLA with a heterotactic bias.

Bimetallic \(\{\text{Ti}(53)\text{(O}^\text{iPr})\}_2\), trimetallic \(\text{Ti}_3(54)_{2}(\text{O}^\text{iPr})_6\), and tetrametallic \(\text{Ti}_4(55)_{2}(\text{O}^\text{iPr})_{10}\) titanium complexes were investigated as initiators for the ROP of \textit{rac-}lactide and \textit{L-}lactide in both solution and solvent free conditions (Figure 1.48).\(^93,\,94\) The dimeric complex \(\{\text{Ti}(53)\text{(O}^\text{iPr})\}_2\) utilises triethanolamine ligands and is an active initiator for the ROP \textit{L-}lactide and \textit{rac-}lactide. Moderate activities were achieved 70 % conversion after 1.5 days (70 °C, toluene, 300:1 [monomer]:[metal] ratio).\(^94\) Under these conditions \(\{\text{Ti}(53)\text{(O}^\text{iPr})\}_2\) yields PLA with very narrow molecular weight distributions with PDI values < 1.15 and molecular weights consistent with one polymer chain per-metal centre. Elevated temperature (130 °C) resulted in a higher activity but also a slight increase of molecular weight distribution (PDI = 1.35). Under solvent free conditions at the same elevated temperature (130 °C) a significant increase in molecular weight distribution was observed.

\textbf{Figure 1.47}: Group 4 alkoxide complexes bearing dithiodiolate ligands which were investigated as initiators for the ROP of \textit{rac-}lactide.\(^92\)
(PDI = 1.69 - 1.70), although at above 90% conversion transesterification reactions are thought to further increase PDI = 2.55 – 3.68.\textsuperscript{93}

The triphenoxy supported titanium complex Ti\textsubscript{3}(54)\textsubscript{2}(O\textsubscript{i}Pr)\textsubscript{6} was synthesised as the kinetic and thermodynamic product. The solid state structure shown in figure 1.48 deviates slightly in solution, where the phenoxy groups do not bridge between titanium metals. The initiators were moderately active for the ROP of lactide.\textsuperscript{93, 94}
lactide in toluene, achieving 95 % conversion after 12 h (130 °C, toluene, 200:1 [monomer]:[metal] ratio). The ROP reaction also revealed good molecular weight control with one PLA chain being propagated per-metal and low molecular weight distributions (PDI = 1.12 – 1.36).

The tetrametallic titanium alkoxide complex \{Ti_4(55)_2(OiPr)_{10}\} was studied as an initiator the ROP of lactide alongside \{Ti(53)(OiPr)\}_2 and Ti_3(54)_2(OiPr)_6. Ti_4(55)_2(OiPr)_{10} was shown to be relatively stable at ambient temperature although at elevated temperature it was demonstrated as slightly unstable. As an initiator for the ROP of lactide it achieved 99 % PLA yield after 24 h (70 °C, toluene 400:1 [monomer]:[metal] ratio). Ti_4(55)_2(OiPr)_{10} revealed good control over molecular weight with a linear increase of \(M_n\) with increasing monomer concentration, although as molecular weight increased the PDI increased in a linear relationship (PDI = 1.33 - 1.52). Unlike titanium complex Ti_3(54)_2(OiPr)_6 which propagated one PLA chain per metal despite the presence of six potentially initiating isopropoxides. The ROP of lactide by Ti_4(55)_2(OiPr)_{10} resulted in PLA molecular weights consistent with a PLA chain being propagated per isopropoxide. While most of the study focused on the ROP of \textit{L}- lactide, the ROP of \textit{rac}-lactide by Ti_4(55)_2(OiPr)_{10} yielded atactic PLA.

Figure 1.49: Scheme over-viewing the synthesis of group 4 trisphenolates which were investigated for the ROP of lactide.\textsuperscript{90, 95}
Group 4 trisphenolates were first investigated by Kol et al. for the ROP of L-lactide. The trisphenolate group 4 complexes adopted a chiral C3 symmetric penta-coordinate structure (Figure 1.49). The titanium complexes Ti(56-58)OiPr were shown to polymerise L-lactide. Increasing the steric bulk of the phenoxy substituents was detrimental to the titanium initiators activity. Furthermore, investigation of Ti(56)OiPr for the ROP of rac-lactide resulted in atactic PLA under solvent free conditions (130 °C). While Kol et al. demonstrated Zr(56)OiPr as an active initiator for the ROP of L-lactide, Davidson et al. reported Zr(56)OiPr to be seven times faster for the ROP of rac-lactide. The Zr(IV) trisphenolate \{Zr(56)OiPr\} yields strongly heterotactic PLA from the ROP of rac-lactide hence the ROP of L-lactide is slower due to the inability to insert alternating enantiomers of the monomer. Both Zr(56)OiPr, and Hf(56)OiPr polymerised lactide to high conversion within 30 mins (130 °C, solvent free, 300:1 [monomer]:[initiator] ratio) and maintain control over the molecular weight (PDI = 1.19 – 1.22). The Hafnium trisphenolate Hf(56)OiPr also results in heterotactic PLA under melt conditions \(P_r\{Hf(56)OiPr\} = 0.88, P_r\{Zr(56)OiPr\} = 0.96\). It was suggested that zirconium and hafnium trisphenolates control the geometric orientation of a propagating lactide by inversion of the axial chirality about the metal centre during propagation. Although it is currently unclear if the heterotactic selectivity is induced from the ligand steric bulk, via a chain-end control mechanism.

![Zr(59)OiPr2 and Zr(60)OiPr2](image)

*Figure 1.50:* Group 4 metal alkoxide complexes supported by tetradentate bis(sulfonamide)amine ligands investigated for the ROP of rac-lactide.

Group 4 metal tetradeionate bis(sulfonamide) complexes were trialled for the ROP of rac-lactide by Mountford et al (Figure 1.50). Forcing conditions were used in the coordination synthesis of the tetradeionate bis(sulfonamide) ligands to group 4
metal alkoxides, requiring either elevated temperature or alcohol removal by vacuum in solvent free conditions. The resulting zirconium complexes initiated the ROP of rac-lactide with good activities for group 4 metals, although initiator Zr(59)(O^iPr)_2 was less active than initiator Zr(60)(O^iPr)_2. The zirconium initiator Zr(60)(O^iPr)_2 was further studied and achieved 95 % conversion within 5.5 h (70 °C, toluene, 100:1 [monomer]:[initiator] ratio). The ROP reaction was well controlled in solution and molecular weights were linear with conversion and molecular weight distributions were consistently low (PDI = 1.12 - 1.14). Conversely MALDI-TOF mass spectrometry revealed transesterification reactions were also present and NMR spectroscopy showed the resulting PLA was atactic. Studies using solvent free conditions proved initiator Zr(60)(O^iPr)_2 was very active and gave comparable reaction rates to group 4 trisphenolates {Zr/Hf(56)O^iPr}.95 Titanium derivatives of tetradeutate bis(sulfonamide) complexes Zr(59,60)(O^iPr)_2 were synthesised and also trialled for the ROP of caprolactone alongside the zirconium initiators Zr(59,60)(O^iPr)_2.96

Further sulphonamide group 4 initiators were synthesised by Mountford et al. and trialled for the ROP of caprolactone and rac-lactide (Figure 1.51).97 The titanium complexes Ti(61,62)(O^iPr)_2 proved unstable for prolonged ROP of rac-lactide and the reaction was halted before full conversion was obtained. While limited conversion was obtained the titanium initiators revealed low PDI values (PDI = 1.13 - 1.22). The four coordinate sulphonamide complex Ti(61)(O^iPr)_2 exhibited little variation upon rates between R = toluene and R = Mes. The five coordinate titanium sulphonamide complex Ti(62)(O^iPr)_2 displayed higher activity for R = Me over R = Tol. Zirconium tris(sulphonamide) complexes {Zr(63)CH_2SiMe_3} were also investigated for the ROP of rac-lactide and it was found that alkoxides generated in-situ gave a significant activation enhancement. The five coordinate zirconium complex Zr(63)CH_2SiMe_3 was less active than its previously investigated six coordinate sulphonamide relative Zr(60)(O^iPr)_2. Unlike the titanium sulphonamides {Ti(61,62)(O^iPr)_2} the zirconium sulphonamides Zr(63)CH_2SiMe_3 achieved high conversion 89 - 95 % within 24 h (70 °C, toluene, 100:1 [monomer]:[initiator] ratio). Increasing the steric demands of the sulphonamide groups within Zr(63)CH_2SiMe_3 decreased the rate of the reaction in
the order R = Me > toluene > ArF. All the group 4 sulphonamides complexes reported here have resulted in atactic lactide.

Figure 1.51: Further group 4 sulphonamide-supported complexes trialled for the ROP of cyclic esters.97

Figure 1.52: Group 4 complexes supported by sulphur and tellurium bridged bis(phenol) ligands, which were utilised for the ROP of L-lactide.98,99

Harda et al. investigated titanium complexes, bridged by bis(phenol) ligands which contain a sulphur or tellurium bridging atom \{Ti(64)(NEt)2 and (Ti(65)Cl)2\}, for the ROP of L-lactide.98,99 Other titanium bis(phenoxo) complexes of this type were synthesised but were mainly trialled for the ROP of caprolactone and other cyclic esters. The sulphur bridged bis(phenoxo) titanium amide complex \{Ti(64)(NEt)2\} (Figure 1.52) was an active initiator for the ROP of L-lactide although it was slow affording 96% yield after 120 h (100 °C, toluene, 200:1 [monomer]:[initiator] ratio).99 Ti(64)(NEt)2 exhibited linear molecular weight growth
with conversion but a slightly linear increase in PDI was also observed, which led to speculation about the presence of transesterification/back-biting reactions.

The dimeric titanium chloride complex \{(\text{Ti}(65)\text{Cl})_2\} containing a bis(phenol) ligand bridged by tellurium was active for the ROP of \(L\)-lactide without the addition of a co-initiator.\(^9\) \((\text{Ti}(65)\text{Cl})_2\) (Figure 1.52) achieved 98% conversion of \(L\)-lactide after 48 h (100 °C, anisole, 200:1 [monomer]:[metal] ratio) with good molecular weight control (PDI = 1.04 – 1.13) throughout the polymerisation reaction. Linear growth of PLA molecular weight was observed alongside conversion and further addition of lactide to a completed ROP reaction indicating a living polymerisation. Further experiments were conducted into co-polymerisation of lactide with caprolactone.\(^9\)

1.3.6 Zinc initiators

![Figure 1.53: β-Diketiminate zinc complexes utilized for the ROP of rac-lactide.\(^{36}\)](image)

Zinc complexes have been tested for the ROP of lactide and many zinc complexes are coordinated to analogous ligands as group 2 metals. Some β-diketiminate (BDI) ligands which have been complexed to group 2 metals \{(\text{Mg}(6)^{\text{iPr}})_2,\}, \((\text{Mg}(7)^{(\text{O}^\text{Pr})})_2,\}, \((\text{Mg}(8)^{\text{O}^\text{Bu}.\text{THF}},\), \((\text{Ca}(8)^{(\text{N}^{\text{SiMe}_3})_2.\text{THF}})^{66}\) were discussed earlier in this report. The BDI zinc complexes \{(\text{Zn}(66-68)^{\text{iPr}})_2\} were isolated as dimers in the solid state and shown to retain their dimeric structure in solution (Figure 1.53).\(^{36}\) BDI zinc complexes \{(\text{Zn}(66-68)^{\text{O}^\text{Pr}})_2\} are active initiators for the ROP of rac-lactide. Substitution of the -\text{O}^\text{Pr} initiating groups for -N^{\text{SiMe}_3}, \text{-Et}, and \text{-OAc resulted in a decrease in polymerisation control. The zinc BDI complexes achieved high conversion (97 %)
within 20 mins when R = \textsuperscript{t}Pr (20 °C, CH\textsubscript{2}Cl\textsubscript{2}, 200:1 [monomer]:[zinc] ratio). The reaction activities were dependent upon the “R” substituents where the ROP activities order follows R = \textsuperscript{t}Pr > Et > \textsuperscript{b}Pr, to the extent that when R = \textsuperscript{t}Pr the ROP is \sim 33 times faster than R = \textsuperscript{b}Pr. (Zn(66-68)O\textsuperscript{t}Pr)\textsubscript{2} complexes exhibited good molecular weight control over the ROP of rac-lactide (PDI = 1.09 – 1.18), furthermore the ROP has living polymerisation characteristics. The resulting PLA was revealed as heterotactic with a $P_r = 0.90$ for initiator (Zn(66)O\textsuperscript{t}Pr)\textsubscript{2}. When substituting the aromatic substituents for -Et, or -\textsuperscript{b}Pr a significant decrease in selectivity was observed ($P_r = 0.76 – 0.79$) although the PLA was still highly biased towards heterotactic PLA.

![Zn complexes](image)

**Figure 1.54:** Monometallic BDI zinc complexes investigated for the ROP of lactide.\textsuperscript{63, 64, 100}

Chisholm *et al.* isolated monometallic BDI zinc complexes \{Zn(69)X\} with bulky initiating alkoxydes and amides (Figure 1.54).\textsuperscript{63, 64} The complex Zn(69)O\textsuperscript{t}Bu resulted in 95 % conversion within 10 mins (20 °C, CH\textsubscript{2}Cl\textsubscript{2}, 100:1 [monomer]:[zinc] ratio) and displayed good control over the molecular weight distributions (PDI = 1.15). The mono-coordinate ligand “X” has a large effect upon the initiators activity and the degree of control the complex exhibits upon the ROP reaction. Substitution of X = O\textsuperscript{t}Bu to N\textsuperscript{t}Pr\textsubscript{2} or OSiPh\textsubscript{3} significantly decreased the activity and molecular weight control of complex Zn(69)X, for example when X = OSiPh\textsubscript{3} the
91 % conversion was obtained after 70 h under the same conditions. Zinc BDI complex \{Zn(69)X\} resulted in heterotactic PLA to a similar degree as the closely related zinc BDI complexes \(\text{Zn(66-68)OiPr}_2\). Interestingly the ROP of \textit{rac}-lactide proceeded slower in THF but the stereoselectivity observed was not affected, unlike the analogous magnesium complexes.\textsuperscript{62-64}

Gibson \textit{et al.} studied the zinc BDI complex \textit{Zn(71)OiPr}, which contains two \textit{ortho}-methoxyphenyl substituents, for the ROP of lactide.\textsuperscript{100} Additionally Chisholm \textit{et al.} investigated analogous zinc complexes \{\textit{Zn(70)X}\} containing one \textit{ortho}-methoxyphenyl substituent for the ROP of lactide.\textsuperscript{62} \textit{Zn(69)OSiPh}_3 achieved high conversion for the ROP of lactide in 30 h, whereas zinc complex \textit{Zn(70)OSiPh}_3 reached high conversion in 30 mins under similar conditions.\textsuperscript{64, 100} The zinc BDI initiators become more active with a higher degree of \textit{ortho}-methoxyphenyl substitution thus the general zinc BDI initiator activity order follows \textit{Zn(71)OiPr} > \textit{Zn(70)X} > \textit{Zn(69)X}. While more active \textit{Zn(70)X} gave a much lower degree of molecular weight control with molecular weights over four times higher than expected, although PDI remained low for \textit{Zn(70)X} and \textit{Zn(71)OiPr}. The resulting PLA was predominantly atactic with a slight heterotactic bias \((P_r = 0.59 – 0.67)\).\textsuperscript{62} While it was speculated that zinc BDI complexes \textit{Zn(69)X} initiated the ROP of lactide by first reacting with impurities within the lactide. Analogous complexes \textit{Zn(70)X} were shown to polymerise lactide without such impurities, furthermore \(-\text{OSiPh}_3\) and \(-\text{N(SiMe}_3)_2\) PLA end groups were identified \textit{via} \textit{^1H} NMR spectroscopy. It was concluded that the \textit{ortho}-methoxyphenyl substitutes did not coordinate to the zinc metal centre. Decreasing molecular weight control could be attributed to the reduced steric demands of \textit{ortho}-methoxyphenyl substituents over isopropylphenyl substituents.\textsuperscript{62}

A zinc (NNO-tridentate diaminophenolate) alkoxide complex \{(\textit{Zn(72)OEt})_2\} was investigated for the ROP of \textit{rac}-lactide by Hillmyer and Tolman \textit{et al.}\textsuperscript{101} Zinc complexed to NNO-tridentate diaminophenolate ligand \(\textit{72H}_2\) formed a dimeric structure in the solid state (Figure 1.55), while the solution structure was identified as a monometallic species. \(\textit{Zn(72)OEt}_2\) is a highly active initiator for the solution polymerisation of \textit{rac}-lactide achieving 93 % conversion after 18 mins at high monomer to initiator ratios (25 °C, \textit{CH}_2\textit{Cl}_2, 1500:1 [monomer]:[metal] ratio). A linear molecular weight increase with conversion was established, although the
molecular weight was lower than anticipated. This was attributed to impurities which deactivate the initiators or act as propagating chain exchange agents. Chain exchange agents were experimentally shown to reduce molecular weights by the addition of benzyl alcohol to the ROP reaction.

![DIAGRAM](image-url)

**Figure 1.55:** Dimeric zinc alkoxide complexes supported by a NNO-tridentate dianiminophenolate ligand (72H$_2$) and NNO-tridentate Schiff base ligands (73-77)$_2$.

Similar NNO-tridentate Schiff base ligands were coordinated to zinc alkyls and further reacted with benzyl alcohol to yield the zinc alkoxide complexes (Zn(73-77)OBn)$_2$ (Figure 1.55). The zinc complexes {(Zn(73-77)OBn)$_2$} were demonstrated to be dimeric species in the solid state as shown in figure 1.55. The dimeric structures adopted an equilibrium in solution between three zinc complex species. Zinc complexes {(Zn(73-77)OBn)$_2$} were active initiators for the ROP of L-lactide and rac-lactide and all the phenyl substituents resulted in well controlled molecular weights with low PDI values (PDI = 1.06 – 1.26). The initiators {(Zn(73-77)OBn)$_2$} activity increased when electron donating substituents are present upon the phenoxy ring. Although the presence of steric bulk hinders lactide monomer units approach to the zinc metal and hence has a negative influence on the ROP reaction rate. A first order dependence on both lactide and the initiator was
shown and from this the authors proposed a monometallic structure as the active propagating species. The NNO-tridentate Schiff base zinc complexes (Zn(73-77)OBn)₂ resulted in PLA with a heterotactic bias in CH₂Cl₂ at 25 °C, the highest selectivity was obtained by the bulky 4,6-di-⁵Bu phenyl substituents \{(Zn(77)OBn)₂\} \(P_r = 0.74\). The selectivity was increased further \{\(P_r (Zn(73-77)OBn)₂ = 0.91\}\) by cooling the reaction to -55 °C although at the expense of initiator activity.

\[ \text{Figure 1.56: Reaction scheme depicting the synthesis of a dimeric zinc guanidinate investigated for the ROP of lactide.}^{103} \]

A dimeric zinc acyclic guanidinate complex \{(Zn(78)N(SiMe₃)₂)₂\} (Figure 1.56) was investigated for the ROP of rac-lactide by Hitchcock and Coles.\(^{103}\) The polymerisation was shown to proceed at room temperature with moderate activities achieving 95 \% conversion within 2 h (CDCl₃, 85:1 [monomer]:[initiator] ratio). While the initiation time for –N(SiMe₃)₂ groups is often slow for the ROP of lactide, initiation for zinc complex (Zn(78)N(SiMe₃)₂)₂ proceeded rapidly. The ROP was proven as a living reaction and proceeded to further polymerise lactide after completion. Atactic PLA was obtained and linear molecular weight control was demonstrated with respect to conversion.
The hybrid scorpionate/cyclopentadienyl ligands discussed earlier for magnesium (Figure 1.30) were also coordinated to zinc \( \{Zn(79)R\} \) (Figure 1.57) and trialled for the ROP of lactide. The solid-state structure is given in figure 1.57, and the solution studies have shown the \( \eta^1 \)-cyclopentadienyl to undergo fast haptotropic exchange. The zinc complexes \( Zn(79)R \) were active for the ROP of \( L \)-lactide (92 \%, 18 h, toluene, 200:1 [monomer]:[initiator] ratio, \( R = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{O} \)) albeit less active than its related magnesium initiator (Figure 1.30) (97 \%, 2.5 h, toluene, 200:1 [monomer]:[initiator] ratio). The zinc initiators \( Zn(79)R \) gave good control over the polymerisation reaction yielding one PLA chain per metal and low PDI values (PDI = 1.07 – 1.19).

Further chiral scorpionate zinc complexes were synthesised and investigated for the ROP of both \( L \)-lactide and \( rac \)-lactide. The zinc initiators...
(Zn\(\text{80-82}\)CH\(_2\)SiMe\(_3\))\(_2\) were moderately active and were shown to achieve 85 % conversion after 3.5 h (50 °C, THF, 100:1 [monomer]:[metal] ratio). The dimeric zinc structure shown in figure 1.58 was confirmed as the solid state structure for (Zn\(\text{80-82}\)CH\(_2\)SiMe\(_3\))\(_2\) complexes. The solution state structure was ambiguous and a possible equilibrium process is present between monomeric and dimeric structures. Despite the ambiguity the initiators (Zn\(\text{80-82}\)CH\(_2\)SiMe\(_3\))\(_2\) exhibited good control over the ROP of lactide (PDI = 1.08 – 1.12). The resulting PLA was moderately heterotactic \(P_r = 0.67 – 0.77\) additionally increasing the reaction temperature reduced the selectivity \{\(P_r\) (50 °C) = 0.77, \(P_r\) (65 °C) = 0.70\}. Also the tacticity was enhanced when THF was used as the solvent over toluene \{\(P_r\) (THF) = 0.72, \(P_r\) (toluene) = 0.64\}. The ROP is initiated by nucleophilic alkyl attack upon the monomer, which was proven by mass spectrometry and NMR spectroscopy identification of a \((\text{CH}_3)\text{C(O)}\)– end group.

1.3.7 Group 13 initiators

![Figure 1.59: Aluminium porphyrin initiators for the ROP of D-lactide.](image)

Aluminium complexes were some of the earliest initiators investigated for the ROP of lactide. One of the first reported aluminium complexes investigated for the ROP of lactide were aluminium porphyrin complexes Al\(\text{83}\)R (Figure 1.59) investigated by Inoue \textit{et al.}\(^\text{105}\) The ROP of \(D\)-lactide by the complexes of basic form Al\(\text{83}\)R were similar in ROP activity and control, their activity was relativity slow achieving 94 % conversion after 96 h \{R = (OCH(CH\(_3\))CH\(_2\))\(_n\)Cl (n = 20), CH\(_2\)Cl\(_2\), 100 °C, 100:1 [monomer]:[initiator] ratio \}. While slow these aluminium porphyrin
initiators revealed living character and well defined molecular weight control (PDI \approx 1.12). The initiator $\text{Al}(83)\text{R}$ ($\text{R} = \text{Cl}$) was also trialled for the ROP of $D$-lactide but showed no activity.

The relatively simple aluminium complex $\text{Al}(\text{O}^\text{Pr})_3$ proved an effective initiator for lactide polymerisation. Furthermore $\text{Al}(\text{O}^\text{Pr})_3$ exists as two aggregates; a trimer ($\text{Al}(\text{O}^\text{Pr})_3)_3$, and a tetramer ($\text{Al}(\text{O}^\text{Pr})_3)_4$. The two aggregates were investigated independently and the trimer was found to initiate the ROP of lactide faster than the tetramer. Although, as the polymerisation proceeds, the propagation rates become equal and the propagating species for both aggregates is believed to be a monomeric compound.

![Aluminium complex](image)

**Figure 1.60:** Aluminium complex supported by $R- (+)-1,1'-\text{binaphthyl}-2,2'-\text{diamine linked bis(phenol) ligand reported for the ROP of lactide.}^{37}$

Imine bis(phenol) ligands have been prominent throughout the ROP of lactide by aluminium complexes. Spassky *et al.* developed a $R- (+)-1,1'-\text{binaphthyl}-2,2'-\text{diamine linked bis(phenol) ligand coordinated to aluminium \{Al(84)OMe\}}$ (Figure 1.60) for the ROP of lactide. The aluminium complex was slow for the ROP of rac-lactide at 70 °C reaching 90 % conversion after 113 h (toluene 75:1 [monomer]:[initiator] ratio). Although slow the resulting PLA was isotactic with well defined molecular weight distributions (PDI = 1.10 – 1.15). A preference for the ROP of $D$-lactide was demonstrated with significant conversion up to 38 % within a relatively short time period (3.5 h). After the preferential conversion of $D$-lactide (~ 40 %) from rac-lactide, $L$-lactide is then polymerised as it is the prevalent
monomer remaining. Investigation of the racemic complex Al(84)OMe for the ROP of *rac*-lactide has shown the formation of stereoblock PLA polymer chains, where each chiral *R* or *S* binaphthyl derived aluminium initiator \{Al(84)OMe\} individually propagates a *D*-PLA or *L*-PLA chain. During the ROP process an exchange process transfers the PLA chains between chiral initiators allowing the formation of stereoblock PLA chains. Additional *in-situ* investigations where chiral “*S*” binaphthyl linked bisphenol ligand and Al(O’Pr)₃ were used to ROP *rac*-lactide resulted in ~50 % conversion of lactide to *L*-PLA, upon which addition of the “*R*” binaphthyl linked bisphenol ligand resulted the formation of a *D*-PLA stereoblock, with an enhanced melting temperature of 210 °C. Thus, demonstrating an exchange mechanism is determining the formation of stereoblock PLA.

![Figure 1.61: Aluminium alkyl/alkoxide complexes supported by salen ligands investigated for the ROP of Lactide.](image)

Salen aluminium alkyl/alkoxide complexes Al(85)R³ (Figure 1.61) were studied by Nomura *et al.* for the ROP of lactide. These aluminium salen complexes yielded PLA with an isotactic bias to varying degrees. The highest stereo-selectivity \( (P_r = 0.02) \) from this series of complexes was obtained from the initiator Al(85)R³ \( (R^1 = ^t\text{BuMe}_2\text{Si}, R^2 = H, R^3 = \text{OBn}, X = \text{CH}_2\text{CMe}_2\text{CH}_2) \) which resulted in 96 % conversion after 14 h \( (70 \, ^o\text{C}, \text{toluene}, 100:1 \, [\text{monomer}]:[\text{initiator}] \, \text{ratio}) \). While the above binaphthyl linked bis(phenoxy) aluminium complexes \{Al(84)R³\} exhibited stereo-control through enantiomorphic site control the salen aluminium complexes \{Al(85)R³\} control selectivity via a chain end control
mechanism. Further solvent free polymerisation studies were performed using the same initiator, 97 % conversion was obtained after 1 h (130 °C, 300:1 [monomer]:[initiator] ratio). Aluminium initiator Al(85)R³ still displayed isotactic selectivity to a lesser extent (Pr = 0.08 – 0.10) under solvent free conditions.

Chiral R,R-, S,S-, rac- diaminocyclohexane (DACH) linked salen aluminium complexes {Al(86)OiPr} were trialled for the ROP of rac-lactide by Feijen et al. (Figure 1.62).³⁰ ¹¹¹ Rac-Al(86)OiPr is a slow initiator for the ROP of rac-lactide requiring 12 days to achieve 85 % conversion (70 °C, toluene, 62:1 [monomer]:[initiator] ratio).³⁰ Although slow the polymerisation was highly selective yielding isotactic PLA (Pr = 0.07) and low molecular weight distributions (PDI = 1.06). Stereoselectivity was also retained under solvent free conditions to a lesser degree (Pr = 0.12), while activity was significantly enhanced reaching 95 % conversion after 2 days (130 °C, 200:1 [monomer]:[initiator] ratio). R,R-Al(86)OiPr displayed a strong preference towards the ROP of L-lactide over D-lactide with respective rate constants k_app = 0.902 day⁻¹ and k_app = 0.067 day⁻¹.¹¹¹ Furthermore the rate constant for the ROP of L-lactide (k_app = 0.509 day⁻¹) by racemic complex rac-Al(86)OiPr, as expected, was approximately half of the R,R-Al(86)OiPr L-lactide ROP rate constant. Stereoselectivity is controlled by an enantiomorphic site control mechanism, and similar to aluminium complexes Al(84)OMe a polymer exchange mechanism ensures the formation of isotactic stereoblock PLA from the ROP of rac-lactide by rac-{Al(86)OiPr}.¹¹¹
Later work by Feijen et al. included the investigation of a similar reduced form \(\{\text{Al}(87-89)\text{Et}\}\) (imine to amine) of their previous DACH salen aluminium complex \(\text{Al}(86)\text{O}^\text{Pr}\) (Figure 1.62) for the ROP of lactide.\(^{112}\) The alkyl aluminium salan complexes \(\text{Al}(87-89)\text{Et}\) contained a further two chiral centres upon the nitrogen atoms, thus the proceeding complexes were present as stereoisomers. The complexes \(\text{Al}(87-89)\text{Et}\) were active initiators for the ROP of lactide with the addition of isopropoxide as a co-initiator. The activity for the ROP of rac-lactide was dependent upon the phenyl ring substituents, the order of activity follows; \(\text{H} > \text{Cl} > \text{Me}\). Although slow initiators, rac-Al(87)Et achieved 89 % conversion in 9 h (toluene, 70 °C, 50:1 [monomer]:[initiator] ratio), and the polymerisation was well defined (PDI = 1.09 - 1.12). Tacticity was also dependent upon the phenyl ring substituents, isotactic biased PLA was obtained when \(R = \text{H}\) \((P_r = 0.34 - 0.38)\), and heterotactic biased PLA was obtained when \(R = \text{Cl, Me}\) \((P_r = 0.55 - 0.73)\). Furthermore it was demonstrated that the \(R.R-(\text{DACH})-\text{Al}(87)\text{Et}\) initiator was 10.1 times more active towards the ROP of \(L\)-lactide over \(D\)-lactide. Evidence suggested these initiators proceed \(via\) a combination of chain exchange mechanisms and site control mechanisms.
Further salan ligand systems have been coordinated with aluminium and their resulting complexes \{\text{Al(90)Me}\} investigated for the ROP of \textit{rac}-lactide (Figure 1.63).\textsuperscript{82} These aluminium complexes \{\text{Al(90)Me}\} were active, albeit slow initiators, for the ROP of \textit{rac}-lactide in the presence of benzyl alcohol co-initiator. The reaction activity increased with decreasing steric influence from the phenyl ring substituents, interestingly the presence of chloro-phenyl substituents showed an enhanced rate over the methyl-phenyl substituents indicating possible electronic effects. Good molecular weight control was observed (PDI = 1.04 - 1.11), along with a varying stereocontrol. A strong isotactic bias was observed when \(R^2 = H\) (\(P_r = 0.21 - 0.32\)), when \(R^2 = \text{Me}, \text{tBu}, \text{or Cl}\) heterotactic biased PLA was obtained (\(P_r = 0.61 - 0.96\)). The chloro-phenyl substituents yielded the highest degree of heterotactic selectivity indicating stereocontrol is not entirely sterically dependent. The amino nitrogen groups amplified any observed tacticity when the benzyl amine substituent was present (\(R^1 = \text{CH}_2\text{Ph}\)).

\[ \text{Figure 1.64: Salalen aluminium alkyl investigated for the ROP of rac-lactide in solution.} \textsuperscript{113} \]
Monometallic salalen aluminium \( \{ \text{Al}(91)\text{Me} \} \) (Figure 1.64) complexes were investigated by Jones et al. for the ROP of rac-lactide in solution.\(^{113}\) While active in the presence of a catalytic equivalence of benzyl alcohol the ROP reaction was slow. Well defined PLA chains were produced with molecular weights consistent with one propagating chain per metal and limited evidence of transesterification reactions occurring. In contrast to the related salan and salen aluminium initiators \( \{ \text{Al}(85)\text{R}^3, \text{Al}(90)\text{Me} \} \) only minor-moderate stereocontrol was reported, additionally the stereocontrol exhibited was more dependent upon the amine substituents than the phenyl substituents. When \( \text{R}^1 = \text{Me} \) (except for \( \text{Al}(91)\text{Me} \), \( \text{R}^2 = \text{R}^3 = \text{tBu} \)) the resulting PLA was biased towards heterotactic stereoselectivity (\( P_r = 0.59 - 0.75 \)), and a slight isotactic bias was observed when \( \text{R}^1 = \text{Ph} \) (\( P_r = 0.40 - 0.50 \)).

In more recent years indium has been investigated for the ROP of lactide and the homoleptic complex \( \text{InCl}_3 \) was shown as a moderately active initiator for the ROP of rac-lactide achieving 96% conversion in 5 h (25 °C, \( \text{CH}_2\text{Cl}_2 \), 203:1:1:2 monomer:initiator:BnOH:NEt\(_3 \)).\(^{41,114}\) All three initiating components are required as exclusion of the \( \text{InCl}_3 \), BnOH, or NEt\(_3 \) renders the ROP reaction inactive. Excellent molecular weight control was reported with a linear relationship of molecular weight with varying rac-lactide, or varying BnOH ratio with respect to all other components. \( \text{InCl}_3 \) yields highly heterotactic PLA from the ROP of rac-lactide, this stereoselectivity was observed upon variation of initiator ratios and exposure to air. Although a very robust system an increase in temperature was detrimental to stereoselectivity and so is excess \( \text{InCl}_3 \) with respect to BnOH and NEt\(_3 \). The formation of an in-situ indium lactate complex as the active initiating/propagating species was speculated upon.

![Figure 1.65: A dimeric indium complex supported by (NNO) asymmetrically substituted trans-diaminocyclohexane ligands.]

\(^{115}\)
A dimeric indium complex bearing (NNO) asymmetrically substituted \textit{trans}-diaminocyclohexane (DACH) ligands (92H$_2$) (Figure 1.65) was the first reported example of the ROP of lactide by an indium complex.\textsuperscript{115} The indium complex \{(In(92)Cl)$_2$(μ-OEt)(μ-Cl)\} is a dimeric structure in solution and the solid state. Moreover, the chiral DACH groups are exclusively \textit{RR,RR} or \textit{SS,SS} pairs within the dimer, no evidence was present to suggest an \textit{RR,SS} or \textit{SS,RR} dimer. The indium complex \{(In(92)Cl)$_2$(μ-OEt)(μ-Cl)\} is active for the ROP of lactide achieving 90\% in 30 mins (25 °C, CH$_2$Cl$_2$, 200:1 [monomer]:[initiator] ratio). The following ROP was living in character until high conversion was reached yielding low molecular weight distributions (PDI = 1.09 – 1.20). The resulting PLA was revealed as slightly isotactic ($P_r = 0.38 – 0.47$). While not dissociative at room temperature the indium complex \{(In(92)Cl)$_2$(μ-OEt)(μ-Cl)\} separates in the presence of a coordinating species, such as lactide, into the active species In(NNO)ClOEt and an inactive species In(NNO)Cl$_2$. There was a marked difference in the ROP activities towards \textit{rac}-lactide between the racemic and enantiopure resolved indium structures, with respect to the DACH groups. Consequently enantiomorphich site control is thought to be significant for these indium initiators.

1.3.8 Non-metal initiators

4-Dimethylaminopyridine (DMAP) (93) was amongst the first non-metal based initiators reported for the ROP of lactide (Figure 1.66).\textsuperscript{116} A protic alcohol was required as a co-initiator for the polymerisation to proceed. Furthermore the degree of polymerisation was dependent on the stoichiometric amount of alcohol utilised. Complete conversion was obtained after 50 h at 35 °C in CH$_2$Cl$_2$ at 120:1:2 [lactide]:[initiator]:[alcohol] ratio. These organic based initiators resulted in well defined molecular weight distributions (PDI = 1.08 – 1.13) and no indication of transesterification side reactions. The nucleophilic DMAP (93) is thought to activate the lactide monomer which allows the protic alcohol in initiate the polymerisation \textit{via} attack of the activated DMAP-lactide species.
Hillmyer and Tolman et al. reported the use of carbenes for the ROP of rac-lactide. The carbene 94 (Figure 1.66) was investigated at reduced temperature (-20 °C, CH₂Cl₂) and obtained good conversion (71%) within 20 mins at 150:1 [rac-lactide]:[initiator] ratio in the presence of benzyl alcohol. A moderate isotactic bias ($P_r = 0.25$) was observed for the reduced temperature polymerisation of rac-lactide by 94. Upon increasing the polymerisation temperature (25 °C) a reduction in selectivity was observed ($P_r = 0.41$). Further work on carbenes was conducted by Waymouth and Hedrick et al. for the ROP of rac-lactide and meso-lactide. The carbene 95 (Figure 1.66) was investigated at variable temperatures and resulted in a similar degree of isotacticity ($P_r = 0.28$) at -15 °C. The polymerisation proceeded at -70 °C achieving 91% conversion after 2 h at 100:1 [rac-lactide]:[initiator] ratio, under these condition a high isotactic ($P_r = 0.10$) bias was reported.

A dimeric phosphazene base 96 (Figure 1.66) was reported for the ROP of rac-lactide and was demonstrated to be highly active resulting in high conversion (85%) after 3 mins with a catalytic equivalence of 1-pyrenebutanol co-initiator (25 °C, toluene, at 100:1 [rac-lactide]:[initiator] ratio). At reduced temperature (-75 °C) the reaction required 3 h to achieve full conversion (> 99%) and the resulting PLA was highly isotactic ($P_r = 0.05$). The polymerisation was controlled with no evidence of transesterification side reactions occurring at -75 °C and a low PDI value was obtained (PDI = 1.11). From experimental evidence it was postulated...
that the ROP initially proceeded via activation of the alcohol by the phosphazene base (96).

1.4 Co-Polymers

1.4.1 Poly(lactide-co-glycolide)

The physical properties of polylactide can be tuned through co-polymerisation of lactide and glycolide. Adjusting the glycolide to lactide ratio within poly(lactide-co-glycolide) (Figure 1.67) co-polymer adjusts the physical properties, in particular the biodegradability. Both lactide and glycolide are biocompatible along with their resulting polymers as they degrade into lactic acid and glycolic acid respectively under biological conditions. Poly(lactide-co-glycolide) co-polymers have seen use within the medical industry for sutures and backbone pins. Surgical applications of poly(lactide-co-glycolide) co-polymers contain higher proportions of glycolide (70 % – 92 %). Co-polymer blends containing lower proportions of glycolide (20 % - 50 %) have seen use within drug delivery systems typically in the form of polymer implants. The polycondensation reaction of glycolic acid and lactic acid yields low molecular weight polymers. As a consequence the dehydrated cyclic starting reagents (lactide and glycolide) procured interest. As high molecular weight polymers could be produced together with potential control over the monomer sequence. A large degree of variation is possible of the co-polymers as not only can glycolide be varied the stoichiometry of L-, D-lactide isomers can tuned.
1.4.2 Poly(lactide-co-ε-caprolactone)

Co-polymers of lactide with ε-caprolactone have been reported through the literature, each polymer has been investigated individually for medical and pharmaceutical applications. The co-polymerisation of ε-caprolactone and lactide allows physical aspects of each polymer to be varied in the resulting co-polymer (Figure 1.6). Poly(lactide-co-ε-caprolactone) combines the good degradation in physiological media of PLA with the high permeability towards drug molecules that poly(ε-caprolactone) displays. PLA has good mechanical properties and poor elasticity while poly(ε-caprolactone) has poor mechanical properties, good elasticity, and enhanced thermal properties. The co-polymer properties can be adjusted by the; stoichiometry of the incorporated cyclic esters, molecular weight, and monomer sequence (block and random polymer). Block co-polymers of poly(lactide-co-caprolactone) have been reported, Davidson et al. reported that the order of addition was critical to prepare a block-co-polymer. For example, caprolactone must be polymerised first, if lactide is polymerised first only a homopolymer was isolated. A random co-polymer microstructure in a 1:1 ratio of lactide and caprolactone where equal proportions of each were introduced into the polymer chains was reported by Nomura et. al.
1.4.3 Poly(lactide-co-δ-valerolactone)

Polymeric material formed from cyclic esters have been used for pharmaceutical and medical purposes for the biocompatibility and biodegradable properties of these polymers, including poly(δ-valerolactone). Poly(δ-valerolactone) has similar properties to poly(ε-caprolactone) and co-polymerisation with lactide monomers can selectively vary the physical properties of the polymers. The melting point ($T_m$) of poly(δ-valerolactone) is 62 °C and co-polymer blends with lactide reduce the $T_m$ of the co-polymer dependent upon the quantity of lactide introduced into the polymer, to widen the application of both polymers. The microstructure of the co-polymerisation of δ-valerolactone and lactide is dependent upon the initiator. Where the initiator preferred the incorporation of the one monomer over the other a tapered co-polymer can be formed. The degree of polymerisation of a block of a single monomer within random poly(lactide-co-δ-valerolactone) (Figure 1.69) was dependent upon the stoichiometry of the valerolactone and lactide. The co-polymerisation of δ-valerolactone has been conducted using $L$-lactide and $rac$-lactide.
1.5 Aims and Objectives

The development of initiators for the ROP of lactide and investigation of their behaviour is reported herein. The aim is to develop stereoselective initiators which preferably produce highly isotactic stereoblock PLA from rac-lactide for its enhanced thermal properties and crystallinity. High activity and polymer molecular weight control is desired for applicability within industry. Meeting these requirement under relatively environmentally favoured solvent free conditions is desired. The initiators should use non-toxic and bio-compatible materials to fully exploit the uses of PLA. Where possible abundant and cheap materials should be investigated to enhance the initiators industrial appeal.

This thesis focuses upon metal based initiators around group 4 and aluminium. Piperazine/homopiperazine amine bis(phenol) ligands were complexed with group 4 and aluminium metals. Their relation to group 4 salan complexes \( \{M(39-42)(O\text{Pr})_2\} \), which have previously reported moderate isotacticity led to our interest. Also aluminium salan complexes \( \{\text{Al}(90)\text{Me}\} \) have reported interesting stereoselectivity, which is dependent upon the phenoxy substituents. Furthermore, 1,4-DACH based salen ligands were investigated, which are a derivative of the 1,2-DACH salen ligands that previously resulted in highly isotactic selective aluminium initiator.

Figure 1.69: Scheme depicting the formation of poly(lactide-co-δ-valerolactone).
Further work was conducted with 1,2-DACH salalen aluminium initiators, as stated above, 1,2-DACH salalen aluminium complexes previously resulted in high stereoselectivity. The salalen ligand system allows the systematic study of the amine and imine influence upon the ROP of lactide. Additionally aluminium salalen complexes \{Al(\text{O}i\text{Pr})\} have previously shown promise as initiators for the ROP of lactide.\textsuperscript{113}

1.6 References

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Chapter 2

2. Titanium (IV) Homo/Piperazine Salan Complexes and Their Application for the ROP of rac-Lactide
2. Titanium (IV) Homo/Piperazine Salan Complexes and Their Application for the ROP of \textit{rac}-Lactide

2.1 Introduction

Metal complexes derived from tetradeionate amine bis(phenol) ligands (Figure 2.01) have been extensively utilised for the ROP of lactide.\textsuperscript{1-7} Aluminium tetradeionate imine bis(phenoxy) complexes containing flexible backbones have been used to produce highly isotactic enriched PLA from \textit{rac}-lactide.\textsuperscript{8, 9} Related aluminium tetradeionate amine bis(phenoxy) complexes have also been reported for the ROP of \textit{rac}-lactide, the stereoselectivity obtained was shown to be reliant upon the phenoxy substituents.\textsuperscript{2} Although they were all slow, moderately isotactic biased PLA was reported ranging to highly heterotactic PLA.

![Figure 2.01](image_url)

\textbf{Figure 2.01}: Examples of flexible tetradeionate amine bis(phenol) ligands and ridged piperazine and homopiperazine bis(phenol) ligands.

Group 4 metals complexed to tetradeionate imine bis(phenol) ligands have been reported for the polymerisation of lactide, these initiators produced atactic PLA from the ROP of \textit{rac}-lactide.\textsuperscript{10, 11} Although no stereoselectivity was obtained the initiators proved moderately active and resulted in well defined molecular weight PLA. The related group 4 tetradeionate amine bis(phenoxy) complexes investigated by Davidson \textit{et al.}\textsuperscript{5} and Kol \textit{et al.}\textsuperscript{4} proved to be more stereoselective for the ROP of
rac-lactide. Limited activity was observed in the solution state but all the initiators proved to be moderately active initiators for the solvent free polymerisation of lactide. Moderate isotacticity was reported for these bis(phenoxo) complexes that contain a flexible bridging diamine.\textsuperscript{5} Herein is reported the synthesis and polymerisation activity of related compounds where the flexible bridging diamine has been substituted with a ridged piperazine and homopiperazine diamines.

Piperazine salan ligands complexed to aluminium have previously been utilised for the ROP of rac-lactide with little success (Figure 2.01).\textsuperscript{12} Bimetallic\textsuperscript{13} and monometallic\textsuperscript{14} complex coordination geometries have been reported and shown to be highly active initiators for the ROP of \(\varepsilon\)-caprolactone. Yao \textit{et al.}\textsuperscript{15, 16} have reported the synthesis of piperazine salan ligands for the coordination to lanthanides with various monometallic and bimetallic configurations being adopted. The formation of lanthanide-lithium multi-metallic piperazine salan complexes were also developed by Yao \textit{et al.}\textsuperscript{15, 16} The lanthanide metal complexes were shown to be highly active initiators for the ROP of lactide at > 1000:1 [monomer]:[initiator] ratios. Furthermore, the resulting PLA form rac-lactide exhibited moderate heterotactic selectivity. Mountford \textit{et al.}\textsuperscript{17} previously reported the coordination of similar piperazine bridged bis(phenylamino) ligands to titanium resulting in monometallic titanium imido structures.
2.2 Homo/Piperazine Salan Ligands

2.2.1 Synthesis of homo/piperazine salan ligands

![Reaction pathway](image)

The piperazine salan ligands were synthesised according to literature methods.\(^{18}\) With the exception of 11H\(_2\), which was adapted from the synthesis procedure reported by Balakrishna \textit{et al.}\(^{19}\) The reaction is a one pot synthesis which requires heating (Figure 2.02), the pure ligands are obtained in good yields by filtration and washing with methanol. Specifically for 11H\(_2\) the reactive iminium ion is first produced then the phenol is introduced under less thermodynamic conditions. This method limits the probability of attack upon both \textit{ortho}-positions of the 4-\text{'}Bu-phenol.

2.2.2 Characterisation of homo/piperazine salan ligands

All the ligands isolated were fully characterised by \(^1\text{H}\) and \(^{13}\text{C}(^1\text{H})\) NMR spectroscopy and high resolution ESI-TOF mass spectrometry. 1H\(_2\) (Figure 2.03) 3H\(_2\) and 8H\(_2\) (Figure 2.04) were characterised by X-ray crystallography. In all cases the solid-state structure showed the ligands adopt the chair configuration. A hydrogen bond exists between the phenol and the amine nitrogen, in all cases the hydrogen bond length was found to be between 1.8204 and 1.9954 Å.
**Figure 2.03**: Solid-state structure for \(1H_2\). Ellipsoids are shown at the 30 % probability level, hydrogens have been omitted for clarity.

**Figure 2.04**: Solid-state structure for \(8H_2\). Ellipsoids are shown at the 30 % probability level, hydrogens have been omitted for clarity.
The $^1$H and $^{13}$C-$^1$H NMR spectra for (1-15)H$_2$ were consistent with the solid-state structures. The $^1$H NMR spectra for piperazine bridged salan 3H$_2$ is shown in figure 2.05a. The aromatic proton region shows two proton resonances and a singlet for the N-CH$_2$-Ar protons at 3.72 ppm, these observations are consistent across ligands (1-5)H$_2$. The piperazine ring is fluxional on the NMR timescale where the equatorial and axial protons are interconverting, this is represented by the corresponding broad region between 2.20 – 3.10 ppm (Figure 2.05a).

The homopiperazine bridged salan ligands {(6-11)H$_2$} revealed similar trends, a representative $^1$H NMR spectrum of 8H$_2$ is given in figure 2.05b. The aromatic protons (6.70 – 7.30 ppm), N-CH$_2$-Ar (3.70 – 3.90 ppm), and the phenoxy substituent regions (~ 1.00 – 2.00 ppm) were well defined throughout compounds (6-11)H$_2$ (Figure 2.05b). For compounds (6-11)H$_2$ the homopiperazine ring proton region showed three resonances (2.87, 2.81, 1.95 ppm), this was attributed to a fast homopiperazine ring-flipping process on the $^1$H NMR timescale. The fast
homopiperazine ring-flipping process causes the axial and equatorial ring protons to be observed as equivalent.

The $^1$H NMR spectra for compounds (12-15)H$_2$ were more complex due to their unsymmetrical nature. Two phenol O-H environments were observed clearly indicating the two phenyl rings are not chemically equivalent. The N-CH$_2$-Ar protons were observed as a multiplet and a broad region, indicative of inequivalent proton environments alongside the influence of fluxionality. A broad region was observed for the methyl substituted piperazine ring –CH$_2$ protons. In contrast to the single broad resonance for 3H$_2$ (Figure 2.05a), broad regions were observed at 2.10 - 2.60 ppm, and 2.60 - 3.00 ppm.

2.3 Synthesis of Titanium Piperazine Salan complexes

![Reaction scheme](image)

**Figure 2.06:** Reaction scheme detailing the synthesis of piperazine and homopiperazine titanium monometallic and bimetallic complexes.
2.4 Titanium Bimetallic Complexes

2.4.1 Synthesis

The room temperature complexation of Ti(O\textsuperscript{i}Pr\textsubscript{4}} to piperazine salan ligands resulted in an incomplete reaction when a 1:1 ratio of ligand and metal was utilised. The species produced were not identified although it was clearly observed that unreacted ligands were still present in solution. Further attempts to isolate a pure complex were fruitful when two equivalents of Ti(O\textsuperscript{i}Pr\textsubscript{4}} were introduced. The titanium metal centres were bound to each phenoxy resulting in the 2:1 metal to ligand complexes {Ti\textsubscript{2}(1-5,8,9,12-13)(O\textsuperscript{i}Pr\textsubscript{6})} depicted in figure 2.06. These LM\textsubscript{2} style complexes have been previously reported for piperazine salan ligands by Fulton \textit{et al.}\textsuperscript{12} who complexed them to aluminium and reported X-ray crystallographically determined structures. Attempts to isolate LM\textsubscript{2} complexes containing less steric bulk in the \textit{ortho} phenoxy position and a homopiperazine ring {Ti\textsubscript{2}(6,7,11)(O\textsuperscript{i}Pr\textsubscript{6})} or a methyl substituted piperazine ring {Ti\textsubscript{2}(15)(O\textsuperscript{i}Pr\textsubscript{6})} were unsuccessful, the resulting complexes proved very soluble in all common organic solvents and purification was problematic. Ligands containing amyl phenol substituents with a homopiperazine ring and methylated piperazine ring (10,14H\textsubscript{2}) were complexed to Ti(O\textsuperscript{i}Pr\textsubscript{4}} under ambient conditions, NMR spectroscopy evidence suggests the formation of the LM\textsubscript{2} structural geometry but the enhanced solubility of said complexes caused difficulties in the separation from significant Ti(O\textsuperscript{i}Pr\textsubscript{4}} impurities. All of the titanium complexes produced at room temperature in CH\textsubscript{2}Cl\textsubscript{2} at a 2:1 ratio were recrystallised from hexane to yield a complex of the general formula, LTi\textsubscript{2}(O\textsuperscript{i}Pr\textsubscript{6})\textsubscript{2}, in the solid state. The solid-state structure was confirmed by X-ray crystallography or supported by CHN analysis. Structures were determined for Ti\textsubscript{2}(2-5,8,12-13)(O\textsuperscript{i}Pr\textsubscript{6}) via X-ray diffraction studies. Additionally an isolated titanium 2:2 species {Ti\textsubscript{2}(1)\textsubscript{2}(O\textsuperscript{i}Pr\textsubscript{4})} was determined by X-ray crystallography, although further analysis showed this L\textsubscript{2}M\textsubscript{2} structure was not consistent with the bulk material. The Ti\textsubscript{2}(1)(O\textsuperscript{i}Pr\textsubscript{6}) complex was isolated in a repeated reaction, as determined by CHN analysis. \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectroscopy was consistent with the stated LM\textsubscript{2} titanium complexes when the \textit{ortho} phenoxy group substituents were sterically bulky \textsuperscript{1}Bu or amyl groups. Where the \textit{ortho} substituents were methyl groups the \textsuperscript{1}H and \textsuperscript{13}C{\textsuperscript{1}H} NMR spectra revealed
the presence of an equilibrium, which is later discussed in more depth (see section 2.4.3).

### 2.4.2 Solid-state characterisation by X-ray crystallography

At room temperature the titanium salan complexes synthesised primarily resulted in crystals of the LM$_2$ form, which were characterised by X-ray diffraction. Figure 2.07 displays a representative structure for the LM$_2$ titanium piperazine salan complexes that contain a 6 membered bridging piperazine ring \{Ti$_2$(2-5)(O'Pr)$_6$\}. These structures contain an inversion centre situated within the molecule as such the local environments around individual titanium metal centres are crystallographically equivalent. Selected bond lengths (Å) and angles (°) about the titanium metal centre are given in table 2.01. The piperazine ring adopts the favoured chair configuration. Each titanium metal centre resides in a distorted trigonal bipyramidal structure, with three isopropoxide groups, an amine nitrogen, and a phenoxy coordinating to the titanium. The axial-isopropoxide (1.7758 - 1.7838 Å) is shorter than the equatorial-isopropoxide groups (1.8003 - 1.8360 Å). The cis-phenoxy titanium bonds (Ti1-O4, 1.8649 - 1.8883 Å) are longer than the isopropoxide groups and as expected the axial nitrogen titanium bonds (2.3499 - 2.3567 Å) are longer than the alkoxide bonds. The angle between the two axial moieties (N1-Ti1-O1 = 173.06 - 177.20 °) deviates from the ideal trigonal bipyramidal value of 180 °. Additionally the angle between equatorial oxygens and the axial nitrogen (79.86 - 84.62 °) deviates from the idealistic value of 90 °, this is consistent with the axial nitrogen titanium bond being longer than the axial isopropoxide causing all the equatorial oxygens to converge towards the nitrogen. An analogous LM$_2$ aluminium alkyl complex reported by Fulton et al.$^{12}$ has a shorter phenoxy-metal bond length \{1.7586(12) Å\} and a shorter nitrogen-metal bond length \{2.0631(14) Å\}. 

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Figure 2.07: Solid-state structure for Ti$_2$(O'Pr)$_6$. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and isopropoxide –CH$_3$ moieties have been removed for clarity.

<table>
<thead>
<tr>
<th></th>
<th>Ti$_2$(2)(O'Pr)$_6$</th>
<th>Ti$_2$(3)(O'Pr)$_6$</th>
<th>Ti$_2$(4)(O'Pr)$_6$</th>
<th>Ti$_2$(5)(O'Pr)$_6$</th>
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<td>Ti1-O1</td>
<td>1.7813(18)</td>
<td>1.7758(17)</td>
<td>1.7838(17)</td>
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<tr>
<td>Ti1-O2</td>
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<td>1.8131(17)</td>
<td>1.8003(16)</td>
<td>1.8127(17)</td>
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<tr>
<td>Ti1-O3</td>
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<td>1.8340(17)</td>
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<td>Ti1-N1</td>
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<td>81.07(7)</td>
<td>79.29(6)</td>
<td>80.49(6)</td>
</tr>
</tbody>
</table>

Table 2.01: Selected bond lengths (Å) and angles (°) for LM$_2$ titanium salan complexes, as determined by X-ray crystallography.
Figure 2.08: Solid-state structure for Ti₂(8)(OPr)₆. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and isopropoxide –CH₃ moieties have been removed for clarity.

Figure 2.09: Solid-state structure for Ti₂(12)(OPr)₆. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and isopropoxide –CH₃ moieties have been removed for clarity.
Selected bond lengths (Å) and angles (°) for titanium salan complexes of the general structure \( \text{LM}_2 \) containing an unsymmetrical bridging piperazine ring is shown in table 2.02. A single homopiperazine based salan titanium complex was characterised by X-ray crystallography \( \{ \text{Ti}_2(8)\text{(O}^\text{Pr})_6 \} \) (Figure 2.08). Both titanium salan complexes bridged by a methyl substituted piperazine ring were modelled with a degree of disorder. For \( \text{Ti}_2(12)\text{(O}^\text{Pr})_6 \) (Figure 2.09) the piperazine methyl group was disordered over three positions in a 60:20:20 ratio, additionally the isopropoxide and \textit{tert}-butyl substituents were disordered. \( \text{Ti}_2(13)\text{(O}^\text{Pr})_6 \) was modelled with an inversion centre, although the piperazine methyl substituent was disordered over two positions in a 50:50 ratio, furthermore the isopropoxide groups were disordered. Akin to the symmetrical piperazine salan \( \text{LM}_2 \) titanium complexes (table 2.01) the

Table 2.02: Selected bond lengths (Å) and angles (°) for \( \text{LM}_2 \) titanium salan complexes, as determined by X-ray crystallography. a The piperazine ring methyl was located in the inverse symmetry position in a 50:50 ratio, values are the same due to an inversion centre.

<table>
<thead>
<tr>
<th></th>
<th>( \text{Ti}_2(8)\text{(O}^\text{Pr})_6 )</th>
<th>( \text{Ti}_2(12)\text{(O}^\text{Pr})_6 )</th>
<th>( \text{Ti}_2(13)\text{(O}^\text{Pr})_6 )</th>
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<td>1.817(3)</td>
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</tr>
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<td>1.869(3)</td>
<td>1.8691(19)</td>
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</tr>
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<td>1.8396(18)</td>
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<td></td>
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<td>165.3(8)</td>
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<td>81.73(11)</td>
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<td>N2-Ti2-O8</td>
<td>81.28(7)</td>
<td>80.78(12)</td>
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</table>

Akin to the symmetrical piperazine salan \( \text{LM}_2 \) titanium complexes (table 2.01) the
bridging homo/piperazine ring adopts a chair configuration and the titanium metal centres adopt a distorted trigonal bipyramidal structure. The titanium bond lengths and angles for unsymmetrical homo/piperazine salan titanium complexes (table 2.02) are similar to their analogous bond lengths and angles for symmetrical piperazine salan titanium complexes (table 2.01).

The titanium centres within the homopiperazine salan LM$_2$ titanium complex \{Ti$_2$(8)(O’Pr)$_6$\} (Figure 2.08) are not in crystallography equivalent environments, albeit the differences are inconsequential. Notably, the titanium amine bonds are different, Ti1-N1 = 2.3775(19) Å, Ti2-N2 = 2.3525(19) Å. Also the phenoxy bonds are significantly different, Ti1-O4 = 1.8622(17) Å, Ti2-O8 = 1.8823(17) Å. Furthermore, there is a difference in the chelating phenoxy-titanium-nitrogen angle, N1-Ti1-O4 = 80.26(7) °, N2-Ti2-O8 = 81.28(7) °. The two titanium metal centres are not in equivalent environments for the methyl substituted piperazine ring derivative \{Ti$_2$(12)(O’Pr)$_6$\}. Markedly the chelating phenoxy-titanium-nitrogen angles \{N1-Ti1-O4 = 81.73(11) °, N2-Ti2-O8 = 80.78(12) °\} are also different.

Figure 2.10: Solid-state structure for Ti$_2$(1(1)(O’Pr)$_3$). Ellipsoids are shown at the 30 % probability level, hydrogen atoms and isopropoxide –CH$_3$ moieties have been removed for clarity.
An isolated Ti₂(1)₂(O'iPr)₄ crystal was characterised by X-ray diffraction (Figure 2.10) and selected bond length (Å) and angles (°) are given in table 2.03. This structure contains two titanium metal centres and two ligands, where each ligand coordinates to two titanium metals via independent phenols. Both ligands adopt a chair configuration and the ligands are significantly twisted in comparison to the ligands in the LM₂ structures, as a consequence of geometric strain. Each titanium metal adopts a distorted trigonal bipyramidal structure with two coordinating phenoxy groups, two coordinating isopropoxide groups, and one coordinating amine, also one amine per ligand is un-coordinated. The Ti-O isopropoxide bond lengths (1.8500 - 1.8624 Å) are similar to the bond lengths reported for LM₂ Ti-O isopropoxide (1.8003 - 1.8810 Å). When considering a single titanium metal centre the chelating phenoxy exhibited longer bond lengths (Ti1-O2 = 1.8173(5) Å, Ti2-O6 = 1.7950(5) Å) than the non-chelating phenoxy (Ti1-O1 = 1.7749(4) Å, Ti2-O5 = 1.7715(4) Å). The equatorial oxygen atoms are deviated towards the axial nitrogen with an angle below 90 ° {O4-Ti1-N1 = 81.29 (9), O8-Ti2-N2 = 81.29 (9)}. No evidence of this structure has been observed in further analysis when a more sterically bulky tBu groups were present in the ortho-position of the phenol. It was proposed that the increased steric demands of tBu groups make the L₂M₂ type structure geometrically unfavourable.
2.4.3 Characterisation by solution NMR spectroscopy

The titanium complexes \{Ti_2(1-5,8-9,12-13)(OiPr)_6\} reported herein were characterised by $^1$H NMR and $^{13}$C\{$^1$H\} NMR spectroscopy. The solution state characterisation for Ti_2(3-5,8-9,12-13)(OiPr)_6 was consistent with the solid state structures being maintained in solution. For Ti_2(1-2)(OiPr)_6 the NMR spectroscopic characterisation was contradictory to a LM_2 or L_2M_2 structures being solely present.

![Figure 2.11: $^1$H NMR spectrum for Ti_2(3)(OiPr)_6 in CDCl_3.](image)

A representative $^1$H NMR spectrum for Ti_2(3-5)(OiPr)_6 is given in figure 2.11. Only two aromatic proton environments are present, as two doublets (6.95, 7.19 ppm), showing the two phenoxy rings are in equivalent environments. The septet at 4.91 ppm corresponds to six methine isopropoxide protons, the fact only one environment is present is indicative of the isopropoxide groups being highly fluxional. The N-CH_2-Ar protons are associated with a singlet at 4.15 ppm, a slight broadening of this resonance indicates the presence of a fluxional process on the NMR timescale. The axial and equatorial protons of the piperazine ring are observed as two very broad regions between 2.00 – 4.00 ppm, further supporting a fluxional process on the NMR timescale.
Upon cooling of the complexes in solution the fluxional processes become slower, the $^1$H NMR spectrum for Ti$_2$(3)(OiPr)$_6$ at 233 K is shown in figure 2.12 as a representative example for Ti$_2$(3-5)(OiPr)$_6$ complexes. The aromatic region separates into four environments, it should be noted that in the example given an Ar resonance is located under the solvent. The single resonance assigned to the isopropoxide methine region (figure 2.11) separates into three broad methine resonances {5.04, 4.92, 4.75 ppm (figure 2.12)}. These observations show the complexes undergo conformational locking and reduced fluxionality at 233 K on the NMR timescale. The CH$_2$ ring protons display distinct resonances at lower temperature demonstrating a slower ring flipping mechanism on the NMR timescale.

The $^1$H NMR spectra (CDCl$_3$) for titanium isopropoxide complexes supported by homopiperazine salan ligands {Ti$_2$(8-9)(OiPr)$_6$} were consistent with the characterised solid-state structures. The solution NMR spectra revealed similar trends to those observed for Ti$_2$(3)(OiPr)$_6$, a truncated representative $^1$H NMR spectra (CDCl$_3$) for Ti$_2$(8-9)(OiPr)$_6$ is given in figure 2.13a. The methine isopropoxide region septet, upon cooling (213 K, in d$_8$-toluene) this region separates into three broad resonances, demonstrating a similar fluxional process. The homopiperazine ring CH$_2$ protons are represented by three broad resonances, the resonances are more defined than the piperazine ring CH$_2$ protons of the Ti$_2$(3)(OiPr)$_6$ complex (Figure 2.11). The homopiperazine based salan titanium complexes are more fluxional than the piperazine based salan titanium complexes, where the 7 membered
ring undergoes a faster ring inversion mechanism. The fluxional nature of the ring is reduced, upon cooling the ring CH$_2$ region of the $^1$H NMR spectrum became more complex. The resonances were still less defined than analogous piperazine based LM$_2$ complexes, even under less thermodynamic conditions.

![Figure 2.13: $^1$H NMR spectrum showing the isopropoxide methine and N-CH$_2$-Ar regions for; a) Ti$_2$(8)(OPr)$_6$, b) Ti$_2$(12)(OPr)$_6$ in CDCl$_3$.](https://example.com/figure2.13)

The methyl substituted piperazine ring salan ligands (12-13)H$_2$ are asymmetric, which is represented in their NMR spectra (previously discussed 2.1.2). The asymmetric nature is retained for the titanium complexes Ti$_2$(12-13)(OPr)$_6$, part of a representative $^1$H NMR spectrum is given in figure 2.13b. The methine isopropoxide region contains two resonances, presumably three protons from each titanium centre. A quartet and a singlet were observed for the N-CH$_2$-Ar region, both visual representations demonstrating asymmetry. Furthermore, four singlets are identifiable in the aromatic region of the $^1$H NMR spectrum. As expected low temperature studies resulted in more complex spectra. The isopropoxide methine broadened and presumably the isopropoxide groups are fluxional on the $^1$H NMR timescale.
When ortho methyl groups are present on the phenol ring (1-2)H₂ the resulting titanium complexes form an equilibrium system in solution. The Ti₂(1-2)(OiPr)₆ structural motif was predominantly formed and isolated after a room temperature reaction, this was confirmed by CHN analysis and the structure demonstrated by X-ray diffraction {Ti₂(2)(OiPr)₆}. An isolated crystal was obtained for the L₂M₂ motif but the structure was not consistent with the bulk solid material obtained from room temperature synthetic conditions. Equilibrium systems with titanium alkoxides have been previously reported by Sharpless\(^{20}\) {titanium tartrate complexes} and Boyle\(^{21}\) {titanium binaphtholate complexes}.

\[ 2 \text{LTi}_2(O_i\text{Pr})_6 \rightleftharpoons 2 \text{Ti}(O_i\text{Pr})_4 + \text{L}_2\text{Ti}_2(O_i\text{Pr})_4 \]

Figure 2.14: \(^1\)H NMR spectrum showing the isopropoxide methine and aromatic regions for Ti₂(1)(OiPr)₆ in CDCl₃ at a) 298 K, b) 233 K.

Figure 2.15: Proposed equilibrium scheme for Ti₂(1-2)(OiPr)₆ in solution.
The $^1$H NMR spectrum for Ti$_2$(1)(O$^i$Pr)$_6$ in CDCl$_3$ at 298 K is given in figure 2.14, the aromatic region shows two dominant singlets which correspond to the LM$_2$ structural motif. The aromatic region also shows a significant amount of broad/multiplets resonances, these were assigned to the L$_2$M$_2$ structural motif. The isopropoxide methine region shows a significant amount of free Ti(O$^i$Pr)$_4$ (4.45 ppm) and titanium isopropoxide groups coordinated to the LM$_2$ complex. Upon cooling the isopropoxide methine region shows a clear shift in concentration of free Ti(O$^i$Pr)$_4$ and ligand coordinated titanium isopropoxide groups, with the equilibrium shifted towards LTi$_2$(O$^i$Pr)$_6$. At room temperature the complexed isopropoxide groups:titanium tetra-isopropoxide groups ratio is approximately 1:1 which changes to 3:1 when cooled to 233 K. Additionally the relative integral of the aromatic regions changed by a comparable degree when low temperature $^1$H NMR spectroscopy was performed. Alongside a ratio change in relative integrals the resonances related to L$_2$M$_2$ structural motif became more defined at lower temperatures. From analysis of the NMR spectra under varying conditions the equilibrium given in figure 2.15 was proposed. Equilibrium constants of Ti$_2$(1-2)(O$^i$Pr)$_6$ in CDCl$_3$ were calculated from $^1$H NMR spectroscopy at different temperature intervals. The Van’t Hoff equation (Figure 2.16) was used to quantitatively determine thermodynamic values (Table 2.04), from a plot of lnK against 1/T (Figure 2.17). The thermodynamic values are comparable to those reported for previous titanium equilibria. Higher temperatures favour the formation of multiple products, thus lower temperature entropically favour the Ti$_2$(1-2)(O$^i$Pr)$_6$ structural motif.

$$
lnK = -\frac{\Delta H^\theta}{RT} + \frac{\Delta S^\theta}{R}
$$

Figure 2.16: Van’t Hoff equation.
Table 2.04: Thermodynamic values determined by the Van’t Hoff equation, $\Delta G$ calculated at 298 K

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<tr>
<th></th>
<th>$\Delta G$ (kJ mol$^{-1}$)</th>
<th>$\Delta H$ (kJ mol$^{-1}$)</th>
<th>$\Delta S$ (J K$^{-1}$ mol$^{-1}$)</th>
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<td>11.0(3)</td>
<td>30.7(19)</td>
<td>66.2(7)</td>
</tr>
</tbody>
</table>

![Van’t Hoff plot](image)

Figure 2.17: Van’t Hoff plot for; Ti$_2$(O'Pr)$_6$ and Ti$_2$(2)(O'Pr)$_6$ an NMR scale sample was used of concentration 0.022 mmol/ml in CDCl$_3$.

The addition of excess Ti(O'Pr)$_4$ to the equilibrium resulted in the almost exclusive formation of the LM$_2$ structural motif and Ti(O'Pr)$_4$ in the solution, in accordance with Le Chatelier's Principle. The location of the equilibrium was affected by changing the solvent with a preference for LM$_2$ structural motif in d$_8$-THF. The presence of Ti(O'Pr)$_4$ and ligand complexed species in solution was further confirmed by diffusion ordered spectroscopy (DOSY) NMR spectroscopic investigations.
The synthesis of homopiperazine and methyl piperazine salan titanium complexes was attempted at room temperature, where the ortho phenoxy substituents were methyl groups. The $^1$H NMR spectra for these complexes suggested the presence of an equilibrium system but the complexes could not be isolated to a degree of purity where conclusive characterisation could be conducted.

### 2.5 Elevated Temperature Synthesis of Titanium Piperazine Salan Compounds

#### 2.5.1 Synthesis

![Reaction scheme depicting the synthesis of Ti$_2$(I)$_2$(O$^\text{Pr}$)$_4$](image)

**Figure 2.19:** Reaction scheme depicting the synthesis of Ti$_2$(I)$_2$(O$^\text{Pr}$)$_4$
Further synthetic methods were trialled in an attempt to isolate 1:1 titanium piperazine salan complexes. Most reactions using a 1:1 titanium to ligand ratio yielded partially reacted products or mixtures, which often contained free ligands. Prolonged heating (80 °C) of Ti(O\text{Pr})\text{4} and 1H\text{2} under a dynamic inert gas flow resulted in the exclusive formation and isolation of the L\text{2}M\text{2} structural motif (Figure 2.19). Under these conditions any liberated isopropanol was gradually removed, therefore kinetically forcing the equilibrium. It was speculated that isopropanol groups dissociate the phenoxy groups from the titanium permitting the coordination of other phenoxy groups, allowing a dynamic system. This species was confirmed by CHN elemental analysis, \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectroscopy. Attempts to replicate this method for 2H\text{2} proved unsuccessful and a mixture of products were still obtained, including Ti\textsubscript{2}(2)(O\text{Pr})\textsubscript{6}.

The same reaction method was utilised for homopiperazine salan ligands, (6-11)H\textsubscript{2}. The removal of isopropanol from the reaction formed products with a 1:1 metal to ligand ratio. The additional heating (80 °C) allowed the homopiperazine ring backbone to adopt a boat type configuration and furthermore coordinate both phenols to a single titanium metal centre (Figure 2.20). These complexes were characterised by CHN elemental analysis, \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectroscopy. DOSY NMR spectroscopy was used to confirm the presence of the L\text{2}M\text{2} and LM structural motifs in solution.

![Figure 2.20: Reaction scheme depicting the synthesis of titanium monometallic complexes supported by homopiperazine salan ligands](image-url)
2.5.2 Solid-state characterisation by X-ray crystallography

**Figure 2.21**: Solid-state structure for Ti(7)(O'Pr)$_2$ in the $\beta$-cis configuration. Ellipsoids are shown at the 30% probability level, hydrogen atoms and isopropoxide $-$CH$_3$ moieties have been removed for clarity.

**Figure 2.22**: Solid-state structure for Ti(11)(O'Pr)$_2$ in the trans-configuration. Ellipsoids are shown at the 30% probability level, hydrogen atoms and isopropoxide $-$CH$_3$ moieties have been removed for clarity.

X-ray crystallography was used to determine the structure of monometallic complexes Ti(7,9-11)(O'Pr)$_2$, while the Ti$_2$(I)$_2$(O'Pr)$_4$ structure is discussed previously (Figure 2.10). The titanium metal centres of complexes containing Me, 'Bu, or Amyl ortho-phenol substituents were shown to adopt a pseudo octahedral configuration, contrasting to the prior determined titanium piperazine salan structures in this chapter. The structure obtained for Ti(7)(O'Pr)$_2$ is given as a representative example (Figure 2.21), these solid-state structures adopted a $\beta$-cis configuration.
(Figure 2.23). Less steric bulk in the ortho-phenol position resulted in the isolation of a pseudo trans-octahedral titanium complex supported by a homopiperazine salan ligand, Ti(11)(O’Pr)₂ (figure 2.22).

![Figure 2.23: Binding modes of piperazine salan ligands](image)

Selected bond length (Å) and angles (°) are given in table 2.05 for the crystallographically characterised titanium homopiperazine complexes. Those complexes which adopted a β-cis configuration {Ti(7,9-11)(O’Pr)₂} revealed similar bond length and angles. There was no significant difference in the isopropoxide metal (Ti1-O1, Ti1-O2) bond lengths, but phenoxy-metal bond lengths (Ti1-O3, Ti1-O4) were significantly different where the phenoxy trans to an isopropoxide exhibited a longer bond length. The two Ti-N bonds have different lengths; the nitrogen which is trans to an isopropoxide is longer. The amine bond length can be compared to the trans Ti-O bond, a longer phenoxy titanium bond (Ti1-O4) results in a shorter bond for the trans titanium nitrogen (Ti1-N1). The complexes adopted a distorted octahedral conformation, which is demonstrated by the deviation of the titanium angles from 90° or 180°, for cis or trans angles respectively. A high degree of variation from the idealistic 90° angle was observed between N1-Ti1-N2, giving angles between 67.90(13) - 68.08(7) ° (Table 2.05).
The less sterically hindered salan with a hydrogen at the ortho position adopted a distorted trans-octahedral structural configuration \{Ti(11)(O^iPr)_2\} (Figure 2.22). The two phenoxy-titanium bonds (Ti1-O1, Ti1-O2) are equivalent in length, additionally the two nitrogen-titanium bonds (Ti1-N1, Ti1-N2) are equivalent in length. This is indicative of the structures symmetrical nature. Similar to β-cis configurations the trans-octahedral structure deviates from an ideal octahedral environment.

<table>
<thead>
<tr>
<th></th>
<th>Ti(7)(O^iPr)₂</th>
<th>Ti(9)(O^iPr)₂</th>
<th>Ti(10)(O^iPr)₂</th>
<th>Ti(11)(O^iPr)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1-O1</td>
<td>1.8310(17)</td>
<td>1.836(4)</td>
<td>1.812(3)</td>
<td>1.8490(18)</td>
</tr>
<tr>
<td>Ti1-O2</td>
<td>1.8375(16)</td>
<td>1.833(3)</td>
<td>1.838(3)</td>
<td>1.8323(17)</td>
</tr>
<tr>
<td>Ti1-O3</td>
<td>1.9568(16)</td>
<td>1.931(3)</td>
<td>1.939(3)</td>
<td>1.9175(19)</td>
</tr>
<tr>
<td>Ti1-O4</td>
<td>1.8834(17)</td>
<td>1.873(3)</td>
<td>1.892(3)</td>
<td>1.9106(18)</td>
</tr>
<tr>
<td>Ti1-N1</td>
<td>2.285(2)</td>
<td>2.293(4)</td>
<td>2.298(4)</td>
<td>2.255(2)</td>
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<tr>
<td>Ti1-N2</td>
<td>2.349(2)</td>
<td>2.346(4)</td>
<td>2.334(4)</td>
<td>2.268(2)</td>
</tr>
<tr>
<td>N1-Ti1-O1</td>
<td>101.94(7)</td>
<td>102.78(16)</td>
<td>103.54(15)</td>
<td>86.18(8)</td>
</tr>
<tr>
<td>N1-Ti1-O2</td>
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<td>89.46(16)</td>
<td>89.09(14)</td>
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<tr>
<td>N2-Ti1-O1</td>
<td>168.57(8)</td>
<td>170.35(16)</td>
<td>171.26(14)</td>
<td>88.51(8)</td>
</tr>
<tr>
<td>N2-Ti1-O2</td>
<td>84.54(7)</td>
<td>86.07(15)</td>
<td>86.41(14)</td>
<td>87.99(8)</td>
</tr>
<tr>
<td>N1-Ti1-N2</td>
<td>68.08(7)</td>
<td>67.91(15)</td>
<td>67.90(13)</td>
<td>70.09(8)</td>
</tr>
</tbody>
</table>

Table 2.05: Selected bond lengths (Å) and angles (°) for Ti(7,9-11)(O^iPr)_2, as determined by X-ray crystallography.

2.5.3 Characterisation by solution NMR spectroscopy

Under these more thermodynamic forcing conditions Ti₂(I)_2(O^iPr)_4 was isolated as the bulk product. The \(^1H\) NMR spectrum of this complex is given in figure 2.25b, a comparative \(^1H\) NMR spectrum of Ti₂(I)(O^iPr)_6 and the resulting solution equilibrium is shown again in figure 2.25a. The isopropoxide -CH₃ resonances of Ti₂(I)_2(O^iPr)_4 are present in each spectrum as sets of doublets at 0.93 ppm, 0.96 ppm and 1.14 ppm respectively. It was assumed the doublet at
1.28 ppm (Figure 2.25b) is located under the broad resonance at a similar chemical shift in the equilibrium spectra (Figure 2.25a). Similarly the –CH isopropoxide septet resonances \(4.47 \text{ ppm}, 4.92 \text{ ppm}\) (Figure 2.25b) coincide almost directly with the isopropoxide –CH \(^1\text{H}\) NMR resonances from both Ti\(_2\)\(\text{I}\)(O\(^\text{iPr}\))\(_6\) and Ti(O\(^\text{iPr}\))\(_4\) within the equilibrium spectra \(4.47 \text{ ppm}, 4.89 \text{ ppm}\) (Figure 2.14b), a subtle shoulder upon the broad resonance at 4.89 ppm supports this observation. It is difficult to distinguish resonances at 2.25 - 4.25 ppm as the -CH2- region is inherently complex, due to ring flipping and fluxionality mechanisms. The aromatic region shows four singlets in both spectra, it should be noted a slight shoulder upon the resonance at 6.83 ppm is indicative of two overlapping resonances. Parallel observations are observed in variable temperature \(^1\text{H}\) NMR spectra. The NMR spectrum of Ti\(_2\)\(\text{I}\)(O\(^\text{iPr}\))\(_6\) afforded two diffusion rates for the piperazine salan titanium complexes (Figure 2.18), the larger Ti\(_2\)\(\text{I}\)_2(O\(^\text{iPr}\))\(_4\) diffuses more slowly. The DOSY spectra for the isolated Ti\(_2\)\(\text{I}\)_2(O\(^\text{iPr}\))\(_4\) complex diffused at a rate of \(5.09 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}\) and comparison to the determined diffusion rates for Ti\(_2\)\(\text{I}\)(O\(^\text{iPr}\))\(_6\) confirmed the presence of Ti\(_2\)\(\text{I}\)_2(O\(^\text{iPr}\))\(_4\) in each solution spectra. The Stokes-Einstein equation (Figure 2.24)\(^{22}\) was used to obtain predicted radii of the molecules within solution (Table 2.06), although these complexes significantly deviate from the ideal spherical shape which is assumed for the Stokes-Einstein equation. While a perfect comparisons to the solid-state structures were difficult the radii shows the Ti\(_2\)\(\text{I}\)_2(O\(^\text{iPr}\))\(_4\) species is larger than the Ti\(_2\)\(\text{I}\)(O\(^\text{iPr}\))\(_6\) species in solution, therefore further supporting the formation of Ti\(_2\)\(\text{I}\)_2(O\(^\text{iPr}\))\(_4\) over Ti\(\text{I}\)(O\(^\text{iPr}\))\(_2\).

\[
\text{Radius of the molecule} = \frac{kT}{6\pi\eta D}
\]

**Figure 2.24:** Stokes-Einstein equation.\(^{22}\)
Figure 2.25: a) $^1$H NMR spectrum of Ti$_2$($^1$OPr)$_6$, and resulting equilibrium in CDCl$_3$ (233 K). b) $^1$H NMR spectrum of Ti$_2$($^1$OPr)$_4$ in CDCl$_3$ (233 K).

<table>
<thead>
<tr>
<th>Diffusion Rate ($10^{-10}$ m$^2$ s$^{-1}$)</th>
<th>Calculated spherical radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$($^1$I)($^1$OPr)$_6$ $^a$</td>
<td>5.11</td>
</tr>
<tr>
<td>Ti$_2$($^1$I)($^1$OPr)$_4$ $^a$</td>
<td>5.65</td>
</tr>
<tr>
<td>Ti$_2$($^1$I)($^1$OPr)$_4$</td>
<td>5.09</td>
</tr>
</tbody>
</table>

Table 2.06: Diffusion rates obtained from DOSY spectra for titanium isopropoxide ($^1$I) complexes and spherical radii calculated from by the Stokes-Einstein equation$^{22}$ from the diffusion rates. $^a$ Data obtained from the solution $^1$H NMR spectrum of Ti$_2$(I)(OPr)$_6$. Data obtained in CDCl$_3$ at 294 K.
The NMR spectra for the monometallic titanium piperazine salan complexes Ti(6-10)(O\text{Pr})\textsubscript{2} show that the complexes adopt multiple conformations, unlike the X-ray crystal structures where a single β-cis conformation was present. Representative \textsuperscript{1}H NMR spectra for complexes Ti(6-7)(O\text{Pr})\textsubscript{2} are given in figure 2.26a, these ortho methyl containing complexes show two conformations in solution. One of the two species in solution is comparatively well defined where as the other is fluxional. For example isopropoxide –CH\textsubscript{3} resonances were located at 0.42 ppm and 1.16 ppm and a proportional quantity was identified as a broad region between 0.50 - 1.50 ppm (Figure 2.26a). The fluxional nature is supported by VT NMR spectroscopy (233 K) where the resonances become more defined at lower temperatures. These complexes can adopt the α-cis, β-cis, and trans octahedral conformations. Although the Δ and Λ forms of α-cis and β-cis conformations are possible they are indistinguishable by conventional NMR spectroscopy (Figure 2.23).

It should be noted that although three octahedral conformations are present the orientation of the homopiperazine ring can further complicate the NMR spectra.

The more sterically hindered complexes Ti(8-10)(O\text{Pr})\textsubscript{2}, with respect to the ortho-phenoxy positions, primarily adopted two conformations. The two conformations can be observed in their NMR spectra, a representative \textsuperscript{1}H NMR spectrum example is given in figure 2.26b. The isopropoxide -CH\textsubscript{3} region shows two doublets at 0.39 ppm and 1.01 ppm which are related to one conformation. The analogous doublets resonances are present from different conformations at 0.55 ppm, 0.73 ppm, 0.94 ppm, and 0.97 ppm. The two species were present in an approximate 1:0.9 ratio. The same can be observed in the aromatic region where resonances at 6.88 ppm, and 7.25 ppm were attributed to the slightly dominant conformation. The \textsuperscript{1}H NMR resonances are relatively well defined for each conformation at room temperature, it was speculated that the increased steric demands of the ligands reduce fluxionality within the complex when compared to Ti(6-7)(O\text{Pr})\textsubscript{2}. The same conformations can be adopted as discussed above for Ti(6-7)(O\text{Pr})\textsubscript{2} (Figure 2.23).
The less sterically hindered Ti(11)(O\textit{i}Pr)_2 exclusively formed the \textit{trans} octahedral conformation in solution and the solid-state, as determined by $^1$H/$^{13}$C{$^1$H} NMR spectroscopy and X-ray crystallography. A truncated $^1$H NMR spectrum for Ti(11)(O\textit{i}Pr)_2 is given in figure 2.27, specifically concentrating on the –CH$_3$ isopropoxide region, and the -CH$_2$/CH region. The isopropoxide –CH$_3$ protons afforded only two resonances at 0.63 ppm and 1.15 ppm thus consistent with a \textit{trans} octahedral geometry being formed exclusively. This is further supported by the presence of two isopropoxide septets at 3.84 ppm and 4.82 ppm.

DOSY spectra mostly showed one diffusion rate, or 2 similar diffusion rates for Ti(7-11)(O\textit{i}Pr)$_2$. When considered alongside the X-ray crystallography evidence for these complexes it was concluded that the structures in solution adopt varying monometallic octahedral structures in preference to a dimeric (L$_2$M$_2$) structural motif.
2.6 Ring-Opening-Polymerisation of rac-lactide

The titanium homo/piperazine based salan complexes \{Ti_{2}(1-5,8,9,12-13)(O’Pr)_{6}\} were trialled for the ROP of rac-lactide in solvent and solvent free conditions. Conversion (%) was calculated by $^1$H NMR spectroscopy from which the theoretical molecular weight was derived by equation shown in figure 2.28, which assumes the linear growth of one PLA chain per metal. Number average molecular weight ($M_n$) and polydispersity index (PDI) was determined by GPC in THF which was referenced to polystyrene standards. The probability of racemic enchainment ($P_r$) was calculated from the methine region of a methyl decoupled $^1$H NMR spectra by Bernoullian statistics.\textsuperscript{24}

\[
M_{n(\text{Theo.})} = \text{Conv.}(\%) \times 144.13 \times \frac{[\text{Lactide}]}{[\text{Metal}]} + 60.10
\]

Figure 2.28: Equation showing the calculation of theoretical PLA molecular weight for titanium isopropoxide complexes.
2.6.1 Bimetallic titanium initiators for the solution ROP of \textit{rac}-lactide

The ROP of \textit{rac}-lactide was performed in toluene (10 ml) at 80 °C using 1.0 g of lactide. A 100:1 \textit{rac}-lactide to initiator ratio was used, which equated to 50:1 \textit{rac}-lactide to metal ratio. The mass of catalyst required was determined by the solid state LM$_2$ structure for consistency reasons, although the preservation of the LM$_2$ structure within solution at 80 °C was not assumed. The solution polymerisation data is given in table 2.07.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Conv. (%)$^a$</th>
<th>$M_n^{b}$ (theo)</th>
<th>$M_n^{c}$</th>
<th>PDI$^c$</th>
<th>$P_r^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$(1)(OPr)$_6$</td>
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<td>1750</td>
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<td>6900</td>
<td>5550</td>
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</tr>
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<td>Ti$_2$(3)(OPr)$_6$</td>
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<td>6900</td>
<td>5850</td>
<td>1.37</td>
</tr>
<tr>
<td>Ti$_2$(5)(OPr)$_6$</td>
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<td>20800</td>
<td>11300</td>
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</tr>
<tr>
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<td>7000</td>
<td>1500</td>
<td>1.51</td>
</tr>
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<td>Ti$_2$(7)(OPr)$_6$</td>
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<td>94</td>
<td>6850</td>
<td>4200</td>
<td>1.34</td>
</tr>
<tr>
<td>Ti$_2$(8)(OPr)$_6$</td>
<td>24</td>
<td>94</td>
<td>6850</td>
<td>1200</td>
<td>2.31</td>
</tr>
<tr>
<td>Ti$_2$(9)(OPr)$_6$</td>
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<td>95</td>
<td>6900</td>
<td>1400</td>
<td>1.36</td>
</tr>
<tr>
<td>Ti$_2$(10)(OPr)$_6$</td>
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<td>91</td>
<td>6600</td>
<td>1200</td>
<td>2.21</td>
</tr>
<tr>
<td>Ti$_2$(11)(OPr)$_6$</td>
<td>24</td>
<td>96</td>
<td>7000</td>
<td>3750</td>
<td>1.28</td>
</tr>
</tbody>
</table>

Table 2.07: Solution ROP of \textit{rac}-lactide for Ti$_2$(1-5,8,10,12,14)(OPr)$_6$ in 10 ml of toluene at 80 °C in a 100:1 \textit{rac}-lactide]:[initiator]. $^a$ Conversion ascertained by $^1$H NMR spectroscopy. $^b$ Theoretical molecular weight calculated from conversion (Conv. × 100/2 × 144.13 + 60.10) (rounded to the nearest 50). $^c$ Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. $^d$ $P_r$ as calculated from $^1$H NMR homonuclear decoupled spectroscopy in CDCl$_3$. $^e$ 300:1 \textit{rac}-lactide]:[initiator].

High conversions were obtained after 24 h under solution conditions at 100:1 \textit{rac}-lactide]:[initiator] ratio for all initiators tested. The initiators Ti$_2$(1,3)(OPr)$_6$ were trialled at a 300:1 \textit{rac}-lactide]:[Initiator] ratio under the same conditions and resulted in high conversion. Generally the average molecular weight determined by GPC was lower than the theoretical molecular weight $M_n$(theo). The reduced $M_n$ values were attributed to the presence of more than one potentially initiating isopropoxide.
group present on each metal centre, with a total of six possible initiating isopropoxide groups per complex. The large degree of possible polymerisation sites contributes to the high distribution of molecular chain lengths (PDI = 1.28 – 2.31). It was previously established that these complexes are not fixed in one geometric structure, notably Ti$_2$(1-2)(OiPr)$_6$ forms an equilibrium system in solution. Furthermore Ti$_2$(8-10)(OiPr)$_6$ were shown to form a monometallic structural motif under similar conditions. High temperature $^1$H NMR spectroscopy scale analysis of the complexes showed these initiators in a contained system formed, to a small degree, the LM structural motif. Both the equilibrium and new structure formation contributes to the high PDI values observed. The initiators were shown to be highly fluxional complexes and there is evidence indicating high liability between titanium metals and ligands. As such a small degree of stereo-selectivity was observed with a very slight heterotactic bias being observed for the majority of initiators (see $P_r$ in table 2.07).

**2.6.2 Bimetallic titanium initiators for the solvent free ROP of rac-lactide**

The ROP of rac-lactide was attempted in solvent free conditions using 1.0 g of lactide in a 300:1 [rac-lactide]:[initiator] ratio at 130 °C. As there are two metals per initiator the ratio of [rac-lactide]:[metal] is 150:1. The solvent free polymerisation data for Ti$_2$(1-5,8-9,12-13)(OiPr)$_6$ is given in table 2.08.

At 130 °C high conversion was obtained after 30 mins for all of the titanium homo/piperazine salan complexes. The initiators Ti$_2$(1,3)(OiPr)$_6$ also attained high conversion at a 300:1 [rac-lactide]:[Initiator] ratio under the same conditions. The molecular weights were more consistent with one PLA chain per metal centre than the analogous solvent polymerisation (Table 2.07). However, there was some reduction in number average molecular weights ($M_n$) when compared to the theoretical $M_n$ values. This observation is similar to the solution polymerisations where the lower molecular weight were attributed to the presence of multiple isopropoxide groups on each metal, which are all potential PLA initiation sites. The PDI values were higher, and the $P_r$ values were closer to atactic ($P_r = 0.5$) than observed for the solution polymerisations. These multiple possible initiating isopropoxide groups contribute to high PDI values. The true behaviour of these
initiators under these conditions is difficult to monitor, and it was further assumed that the initiating species was the LM$_2$ structural motif, although the possibility of other structures was also considered.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Conv. (%)$^a$</th>
<th>$M_n$ $^b$ (theo)</th>
<th>$M_n$ $^c$</th>
<th>PDI$^c$</th>
<th>$P_r$ $^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$(1)(O’Pr)$_6$</td>
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<td>15950</td>
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</tr>
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</tr>
<tr>
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<td>23900</td>
<td>1.53</td>
</tr>
<tr>
<td>Ti$_2$(3)(O’Pr)$_6$</td>
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<td>95</td>
<td>20600</td>
<td>20900</td>
<td>2.01</td>
</tr>
<tr>
<td>Ti$_2$(3)(O’Pr)$_6$</td>
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<td>62900</td>
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<tr>
<td>Ti$_2$(4)(O’Pr)$_6$</td>
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<td>21450</td>
<td>23650</td>
<td>2.01</td>
</tr>
<tr>
<td>Ti$_2$(5)(O’Pr)$_6$</td>
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<tr>
<td>Ti$_2$(6)(O’Pr)$_6$</td>
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<td>20400</td>
<td>1.63</td>
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</tbody>
</table>

Table 2.08: Solvent free ROP of rac-lactide for Ti$_2$(1-5,8-10,12-14)(O’Pr)$_6$ at 130 °C in a 300:1 \([rac\text{-}lactide] : \text{[initiator]}\).$^a$ Conversion ascertained by $^1$H NMR spectroscopy. $^b$ Theoretical molecular weight calculated from conversion (Conv. × 300/2 × 144.13 + 60.10) (rounded to the nearest 50). $^c$ Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. $^d$ $P_r$ as calculated from $^1$H NMR homonuclear decoupled spectroscopy in CDCl$_3$. $^e$ 900:1 \([rac\text{-}lactide] : \text{[initiator]}\).

### 2.6.3 Monometallic titanium initiators for the solution ROP of rac-lactide

The isolated Ti$_2$(1)$_2$(O’Pr)$_4$ and Ti(6-11)(O’Pr)$_2$ complexes were trialled for the ROP of rac-lactide in toluene (10 ml) at 80 °C at a 100:1 \([rac\text{-}lactide] : \text{[Initiator]}\) ratio (Table 2.09). Limited activity was observed for this initiator series under these conditions typically achieving low conversions after 24 h. The molecular weights were consistent with one PLA chain per metal; additionally PDI values were lower indicating a more controlled polymerisation system than the LM$_2$ counterparts. The monometallic system is stable at 80 °C therefore it was assumed the monometallic species were initiating the polymerisation reaction. Due to the low activity of the
monometallic initiators it was concluded that the monometallic species potential contribution to the Ti$_2$(1-5,8,10,12-14)(O’Pr)$_6$ solution polymerisations (Table 2.07) was minor. Where the initiators were active enough to obtain reliable $P_r$ values a slight isotactic bias was observed.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Conv. (%) $^a$</th>
<th>$M_n^b$ (theo)</th>
<th>$M_n^c$</th>
<th>PDI $^c$</th>
<th>$P_r^d$</th>
</tr>
</thead>
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<td>Ti$_2$(1)(O’Pr)$_4$</td>
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<td>-</td>
<td>-</td>
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<td>7250</td>
<td>8200</td>
<td>1.06</td>
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<td>32</td>
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<td>6950</td>
<td>1.11</td>
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</tbody>
</table>

Table 2.09: Solution ROP of rac-lactide for Ti$_2$(1)(O’Pr)$_4$, Ti(6-11)(O’Pr)$_2$ in 10 ml of toluene at 80 °C in a 100:1 [rac-lactide]:[initiator] *200:1 [rac-lactide]:[initiator]. $^a$ Conversion ascertained by $^1$H NMR spectroscopy. $^b$ Theoretical molecular weight calculated from conversion (Conv. $\times$ 100 $\times$ 144.13 $+$ 60.10) (rounded to the nearest 50). $^c$ Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. $^d$ $P_r$ as calculated from $^1$H NMR homonuclear decoupled spectroscopy in CDCl$_3$. $^e$ $P_r$ could not be accurately determined, strong tacticity was not observed.

2.6.4 Monometallic titanium initiators for the solvent free ROP of rac-lactide

Ti$_2$(1)(O’Pr)$_4$ and Ti(6-11)(O’Pr)$_2$ titanium salan complexes were trialled for the ROP of rac-lactide without solvent at 130 °C at a 300:1 [rac-lactide]:[Initiator] ratio (Table 2.10). Under solvent free conditions these initiators were comparatively slow, typically achieving 41 - 60 % conversion after 24 h, when compared to the Ti$_2$(1-5,8,9,12-13)(O’Pr)$_6$, which achieved > 94 % conversion after 30 mins. Molecular weights were consistent with two PLA chains propagating per metal centre. Despite the presence of two potentially initiating isopropoxide groups per metal the PDI values remained low (PDI < 1.25) at the elevated temperature. The more resolved structure permits the formation of controlled PLA chains but the lack of flexibility within the molecules causes the initiators to be more hindered thus leading to reduced activity. The Ti$_2$(1)(O’Pr)$_4$ and Ti(6-11)(O’Pr)$_2$ titanium
piperazine salan complexes produced PLA with a slight heterotactic bias ($P_r = 0.51 - 0.63$).

<table>
<thead>
<tr>
<th></th>
<th>Time (hours)</th>
<th>Conv. (%)</th>
<th>$M_n^b$ (theo)</th>
<th>$M_n^c$</th>
<th>PDI$^c$</th>
<th>$P_r^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$_2$(1)$_2$(O'Pr)$_4$</td>
<td>24</td>
<td>74</td>
<td>32050</td>
<td>21250</td>
<td>1.25</td>
<td>0.51</td>
</tr>
<tr>
<td>Ti(6)(O'Pr)$_2$</td>
<td>24</td>
<td>54</td>
<td>23400</td>
<td>12050</td>
<td>1.07</td>
<td>0.56</td>
</tr>
<tr>
<td>Ti(7)(O'Pr)$_2$</td>
<td>24</td>
<td>50</td>
<td>21700</td>
<td>7900</td>
<td>1.19</td>
<td>0.63</td>
</tr>
<tr>
<td>Ti(8)(O'Pr)$_2$</td>
<td>24</td>
<td>42</td>
<td>18200</td>
<td>7050</td>
<td>1.14</td>
<td>0.53</td>
</tr>
<tr>
<td>Ti(9)(O'Pr)$_2$</td>
<td>24</td>
<td>41</td>
<td>17800</td>
<td>6750</td>
<td>1.10</td>
<td>0.63</td>
</tr>
<tr>
<td>Ti(10)(O'Pr)$_2$</td>
<td>24</td>
<td>60</td>
<td>26000</td>
<td>10900</td>
<td>1.14</td>
<td>0.61</td>
</tr>
<tr>
<td>Ti(11)(O'Pr)$_2$</td>
<td>24</td>
<td>51</td>
<td>22100</td>
<td>6850</td>
<td>1.23</td>
<td>0.55</td>
</tr>
</tbody>
</table>

Table 2.10: Solvent free ROP of rac-lactide for Ti$_2$(1)(O'Pr)$_4$, Ti(6-11)(O'Pr)$_2$ at 130 °C in a 300:1 [rac-lactide]:[initiator] *600:1 [rac-lactide]:[initiator]. a Conversion ascertained by $^1$H NMR spectroscopy. b Theoretical molecular weight calculated from conversion (Conv. $\times$ 100/2 $\times$ 144.13 + 60.10) (rounded to the nearest 50). c Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. d $P_r$ as calculated from $^1$H NMR homonuclear decoupled spectroscopy in CDCl$_3$.

2.7 Titanium Homo/Piperazine Salan Catecholates

2.7.1 Introduction

Catechol is a bidentate, chelating ligand; the initial proposal was to observe the effect of a chelating agent upon the titanium piperazine salan equilibrium system. A series of monometallic piperazine salan catecholates complexes were isolated and characterised. Prior titanium catechol complexes were reported by Davidson et al.\textsuperscript{25} the catecholate complexes form bimetallic structures {Ti(catechol)$_2$(HOiPr)$_2$}$_2$ where the catecholates both chelate to a single titanium and bridge two titanium metals. The titanium homo/piperazine catecholates reported herein proved ineffective for the ROP of rac-lactide this is presumably due to the lack of labile ligand to initiate the polymerisation.

Although inactive for the ROP of rac-lactide these titanium homo/piperazine catecholates were investigated for their cytotoxicity towards tumour cells. Cisplatin was the first metal compound to be utilised as an anticancer reagent, following this
derivatives have also been commercially used as anticancer treatments over the last decade. While Cisplatin is an effective cancer treatment compound its effectiveness is limited to a small range of cancer types, particularly ovarian and testicular cancers. Additionally Cisplatin is a highly toxic compound, as such the dosage is limited to minimise adverse effects. Titanium compounds have been investigated for cytotoxicity with some promise towards different tumour cell lines which are either susceptible or resistant to treatment by Cisplatin (Figure 2.29, left) and its derivatives. Budotitane \(\{\text{cis}-\text{diethoxybis(1-phenylbutane-1,3-dionato)titanium(IV)}\}\) (Figure 2.29, centre) showed good toxicity towards tumour cells but the complex was proven to be unstable, as a consequence of the labile ligands, also the unsymmetrical ligands give rise to multiple geometric configurations.\(^{27,28}\) Titanocene dichloride (\(\text{Cp}_2\text{TiCl}_2\)) (Figure 2.29, right) was also investigated as an anticancer compound but it was deemed inefficient due to its high toxicity.\(^{27,28}\) Titanium compounds have a promising range of toxicity towards different cell lines but active compounds typically decompose quickly making it difficult to analyse and indentify the active species, or study the compound in mechanistic manner.\(^{27,28}\)

\[
\begin{align*}
\text{H}_3\text{N} & \quad \text{PtCl}_2 \\
\text{H}_3\text{N} & \quad \text{Cl}
\end{align*}
\]

Cisplatin

\[
\begin{align*}
\text{Me} & \quad \text{O} \\
\text{Me} & \quad \text{O} \\
\text{Ph} & \quad \text{Ti} \\
\text{OEt} & \quad \text{OEt}
\end{align*}
\]

Budotitane

\[
\begin{align*}
\text{Ti} & \quad \text{Cl} \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

Titanocene dichloride

Figure 2.29: Notable anticancer compounds. left – Cisplatin, Centre – Butotitane, Right – Titanocene dichloride.\(^{27,28}\)

Cytotoxic salan titanium (IV) complexes have been investigated by Tshuva et al.\(^{29}\) for their applicability as anticancer compounds (Figure 2.30a). These complexes proved to be more cytotoxic towards colon HT-29 and ovarian OVCAR-1 cell lines than Cisplatin and other reported titanium (IV) compounds (Budotitane / Titanocene dichloride) (Figure 2.29). The salan titanium complexes proved to be resilient
towards hydrolysis with a maximum half life of hydrolysis ($t_{1/2}$) of 32 h. The hydrolysis product, a trimer, was shown to be inactive by conventional \textit{in-vitro} cell treatment. More recent studies revealed the trimeric hydrolysis product as active; the limiting factor is reported as cell penetration effects which were overcome by nano-particulate encapsulation of the complex. Ligand lability is not essential, even detrimental, for titanium complexes to be cytotoxic towards tumour cells advocating the use of the relatively non-labile catecholates ligands. A titanium salan catecholate was synthesised and reported as cytotoxic for HT-29 and OVCAR-1 cell lines, albeit with slightly reduced activity than the isopropoxide containing analogue (Figure 2.30a). The titanium salan catecholate was more stable towards hydrolytic degradation. Furthermore, a titanium salen catecholate has been investigated for the same cell lines (Figure 2.30b), negligible hydrolytic decomposition was observed, and the complex proved active towards the investigated cell lines, although the titanium salen isopropoxide analogue was more effective.

\begin{figure}
\begin{center}
\includegraphics[width=\textwidth]{figure_2.30.png}
\end{center}
\caption{Titanium bis(phenoxo) complexes investigated as anti-tumour compounds a) Titanium salan isopropoxide/catecholate, b) Titanium salen isopropoxide/catecholates.}
\end{figure}
2.7.2 Synthesis

Figure 2.31: Reaction scheme detailing the initially desired homo/piperazine salan titanium catecholates.

The initial premise was the introduction of catechol to the titanium piperazine salan complexes would reduce the number of titanium coordinated isopropoxide groups. The ideal product would have resulted in one catechol per titanium thus leaving one lactide ROP initiating isopropoxide group per metal (Figure 2.31). It was anticipated that this would dictate the PLA chain growth leading to well defined molecular weights and PDI values. Additionally the effect of the chelating catechol upon the L₂M₂ titanium complexes and the equilibrium was an area of interest.

Figure 2.32: Reaction scheme detailing the synthesis of piperazine and homopiperazine salan titanium catecholates.
At room temperature the introduction of catechol, homo/piperazine salan ligand and Ti(O\textit{t}Pr)\textsubscript{4} in a 1:1:1 ratio yielded monometallic complexes (Figure 2.32). The formation of a monometallic complex at lower temperature is presumably a consequence of the reduced steric demands of catechol when compared to two isopropoxide moieties. The investigation of this complex series was limited to methyl substituents as the presence of large alkyl groups is normally detrimental to water solubility, which is a consideration particularly in administration of a potential drug.\textsuperscript{34} For comparison reasons a single complex was synthesised which contained \textit{t}Bu groups in the \textit{para} position of the phenoxy rings \{Ti(2)\textit{Catechol}\}. Due to the limitations upon the piperazine salan phenoxy moieties a variety of readily available catechols with varying substituents were utilised for the synthesis. Additionally homopiperazine and piperazine complexes were investigated. Excess Ti(O\textit{t}Pr)\textsubscript{4} or catechol still resulted in the formation of monometallic homo/piperazine salan titanium catecholates. The room temperature synthesis of piperazine salan titanium catecholates resulted in pure products and high yields which were characterised by \textsuperscript{1}H NMR spectroscopy, \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectroscopy, and CHN analysis. Recrystallisation from hot toluene or CH\textsubscript{2}Cl\textsubscript{2} resulted in crystals suitable for X-ray crystallography, for Ti(1)Catechol, Ti(1)-3,5-di-\textit{t}ert-butylcatechol, Ti(1)-4-NO\textsubscript{2}-catechol, and Ti(6)-4-NO\textsubscript{2}-catechol. The isolation of Ti(6)-3,5-di-\textit{t}ert-butylcatechol was attempted but the complex could not be supported by NMR spectroscopy although the formation of multiple isomers was a possibility.

2.7.3 Solid-state characterisation by X-ray crystallography

A representative example \{Ti(1)\textit{Catechol}\} of a modelled X-ray crystallography structure for the 6 membered piperazine bridged salan titanium catecholates \{Ti(1)\textit{Catechol}, Ti(1)-3,5-di-\textit{t}ert-butylcatechol, Ti(1)-4-NO\textsubscript{2}-catechol\} is given in figure 2.33. The solid-state structure for Ti(6)-4-NO\textsubscript{2}-catechol is displayed in figure 2.34. All the structures were determined as six coordinate \textit{pseudo} octahedral geometries, specifically $\beta$-\textit{cis} geometric configurations are adopted (Figure 2.23). Both $\Lambda$ and $\Delta$ forms are present according to the X-ray crystallography data as all the crystal structures contain centres of inversion.
Figure 2.33: Solid-state structure for Ti(1)Catechol. Hydrogen atoms have been removed for clarity ellipsoids are shown at the 50 % probability.

Figure 2.34: Solid-state structure for Ti(6)-4-NO$_2$-catechol. Hydrogen atoms have been removed for clarity ellipsoids are shown at the 50 % probability. The NO$_2$ group was found in the 4 and 5 positions of the catechol ring at a 50:50 ratio.
Selected bond lengths and angles for the homo/piperazine titanium catecholates are given in table 2.11. Typically the catechol Ti-O bonds (Ti-O1, Ti-O2) are longer than titanium phenoxy Ti-O bonds (Ti-O3, Ti-O4) with respective bond ranges of 1.920 – 1.991 Å and 1.854 – 1.888 Å. There is little effect upon bond length from the trans component, which is contrasting to the observation made for Ti(6-11)(OPr)2 complexes. The N1-Ti1-O4 angle deviates from the idealist value of 180 ° giving angles between 146.30 - 153.41 °, the N1-Ti1-O3 angle deviates from the idealist value of 90 ° giving angles between 78.84 – 79.56 °. The homopiperazine complex allows for a larger bite angle between the two nitrogen groups where the N1-Ti1-N2 angles were 66.04 ° and 69.92 ° for Ti(1)-4-NO2-catechol and Ti(6)-4-NO2-catechol respectively.

Table 2.11: Selected bond lengths (Å) and angles (°) for Ti2(1)2(OPr)4, as determined by X-ray crystallography.

<table>
<thead>
<tr>
<th></th>
<th>Ti(1)Catechol</th>
<th>Ti(1)-3,5-di-tert-butylcatechol</th>
<th>Ti(1)-4-NO2-catechol</th>
<th>Ti(6)-4-NO2-catechol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti1-O1</td>
<td>1.934(3)</td>
<td>1.920(3)</td>
<td>1.939(2)</td>
<td>1.9607(15)</td>
</tr>
<tr>
<td>Ti1-O2</td>
<td>1.975(3)</td>
<td>1.944(3)</td>
<td>1.991(2)</td>
<td>1.9583(15)</td>
</tr>
<tr>
<td>Ti1-O3</td>
<td>1.864(3)</td>
<td>1.888(3)</td>
<td>1.8589(19)</td>
<td>1.8486(14)</td>
</tr>
<tr>
<td>Ti1-O4</td>
<td>1.855(3)</td>
<td>1.861(3)</td>
<td>1.8395(19)</td>
<td>1.8539(14)</td>
</tr>
<tr>
<td>Ti1-N1</td>
<td>2.207(3)</td>
<td>2.219(3)</td>
<td>2.206(2)</td>
<td>2.2514(17)</td>
</tr>
<tr>
<td>Ti1-N2</td>
<td>2.230(3)</td>
<td>2.232(3)</td>
<td>2.211(2)</td>
<td>2.2677(18)</td>
</tr>
<tr>
<td>N1-Ti1-O1</td>
<td>93.05(12)</td>
<td>95.63(12)</td>
<td>95.86(9)</td>
<td>94.00(6)</td>
</tr>
<tr>
<td>N1-Ti1-O2</td>
<td>98.47(12)</td>
<td>94.40(12)</td>
<td>97.49(9)</td>
<td>94.55(6)</td>
</tr>
<tr>
<td>N1-Ti1-O3</td>
<td>79.56(12)</td>
<td>78.84(12)</td>
<td>79.35(8)</td>
<td>80.55(6)</td>
</tr>
<tr>
<td>N1-Ti1-O4</td>
<td>146.30(12)</td>
<td>147.81(13)</td>
<td>146.54(9)</td>
<td>153.41(7)</td>
</tr>
<tr>
<td>N1-Ti1-N2</td>
<td>65.87(12)</td>
<td>65.32(13)</td>
<td>66.04(8)</td>
<td>69.92(6)</td>
</tr>
</tbody>
</table>
2.7.4 Characterisation by solution NMR spectroscopy

Without utilising forcing conditions the monometallic titanium catechols were isolated and the $^1$H/$^{13}$C/$^1$H} NMR spectroscopy characterisation was consistent with the structures identified by X-ray crystallography and CHN analysis. A representative $^1$H NMR spectrum for Ti(1)Catechol is given (Figure 2.35) for the piperazine salan catechols {Ti(1)Catechol, Ti(1)-3,5-di-tert-butylcatechol, Ti(1)-3-Methoxycatechol, Ti(1)-4-NO$_2$-catechol}. The ring –CH$_2$ protons were observed as discrete multiplets at 2.18, 2.63, 3.22, and 3.80 ppm. Two distinct doublets at 3.38 and 4.52 ppm were assigned to the N-CH$_2$-Ar protons. Although the aromatic region of the spectra is sharp the region was complicated by overlapping of the four proton resonances at 6.62 ppm.
A representative $^1$H NMR spectrum $\{\text{Ti(6)Catechol}\}$ is shown in figure 2.36 for the homopiperazine based salan titanium catechols $\{\text{Ti(6)Catechol, Ti(6)-3-Methoxycatechol, Ti(6)-4-NO}_2\text{-catechol}\}$. The spectrum is consistent with the X-ray crystallography determined solid state structure (Figure 31). The $^1$H NMR spectra for the homopiperazine salan titanium catecholates shows a distinct broadening of resonances when compared to their analogous piperazine complexes. The N-CH$_2$-Ar protons resulted in distinctive doublets at 3.22 and 4.38 ppm. The homopiperazine ring-CH$_2$ protons displayed a significant degree of complication (2.02, 2.39, 2.56, 3.15, and 4.14 ppm) including a noteworthy broadening of the resonance at 4.14 ppm. The aromatic region shows three resonances (6.40, 6.65, and 6.93 ppm) where four protons (two equivalent environments) are overlapping at 6.65 ppm. It was deduced that the broadening of the spectra is related to the higher degree of fluxionally typically observed for the homopiperazine compounds in comparison to the piperazine compounds.

### 2.7.5 Stability and cytotoxicity

Stability and cytotoxicity studies were performed by Dr. Edit Tshuva at The Hebrew University of Jerusalem, the investigation is currently ongoing at the date of writing. Preliminary cytotoxicity data was investigated with HT-29 and OVCAR-1 tumour cells lines, IC$_{50}$ values are outlined in table 2.12. Stability of complexes towards hydrolysis was also investigated and the half lives ($t_{1/2}$) are given in
The titanium isopropoxide complex Ti₂(1)(OPr)₆ was investigated and the compound proved non-toxic towards the cell lines, additionally the equilibrium complicated half life studies. Ti(1)Catechol was evidently toxic towards the investigated cell line with IC₅₀ values rivalling other titanium compounds and enhanced toxicity compared to Cisplatin, the stability was lower than previously investigated catecholates. The nitro subsistent upon the catechol ring enhanced the stability. The low stability of the compounds was attributed to the strained piperazine ring, as a boat configuration is less favourable. Upon introducing a homopiperazine ring the stability was significantly enhanced presumably due to the reduced steric strain of the 7 membered homopiperazine ring. Additionally Ti(6)-4-NO₂-catechol gave an increase toxicity towards the investigated cell lines.

<table>
<thead>
<tr>
<th></th>
<th>IC₅₀ value for HT-29 (µM)</th>
<th>IC₅₀ value for OVCAR-1 (µM)</th>
<th>t₁/₂(min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₂(1)(OPr)₆</td>
<td>Inactive</td>
<td>Inactive</td>
<td>*</td>
</tr>
<tr>
<td>Ti(1)Catechol</td>
<td>21.9±4.6</td>
<td>27.8±4.6</td>
<td>16</td>
</tr>
<tr>
<td>Ti(1)-4-NO₂-catechol</td>
<td>20.7±7.3</td>
<td>25.6±3.0</td>
<td>25</td>
</tr>
<tr>
<td>Ti(6)-4-NO₂-catechol</td>
<td>11.5±4.3</td>
<td>7.2±3.4</td>
<td>92</td>
</tr>
</tbody>
</table>

Table 2.12: Preliminary IC₅₀ values for HT-29 and OVCAR-1 cell lines, and half life stability of the complexes towards hydrolysis.

2.8 Conclusion

Tetradentate salan ligands containing homo/piperazine backbones were coordinated to titanium (IV) tetra-isopropoxide resulting in Ti₂(1-5,8-9,12-13)(OPr)₆ complexes. Their reliance upon backbone rigidity, reaction conditions, and steric requirements are discussed and their relevance in determining the structural motif obtained. Ti₂(2-5,8,12,13)(OPr)₆ were isolated as crystals and characterised as LM₂ structures by X-ray crystallography. From the same conditions a Ti₂(1)₂(OPr)₄ crystal was obtained and characterised by X-ray crystallography, although a bulk solid compound of Ti₂(1)(OPr)₆ was obtained in further synthesis. A titanium piperazine salan equilibrium based upon steric requirements was investigated for Ti₂(1,2)(OPr)₆. The equilibrium position was shown to vary upon temperature changes, solvent, and excess reagents. The more flexible homopiperazine structures
were complexed to Ti(O\textsuperscript{3}Pr\textsubscript{4})\textsubscript{4} produce monometallic structures \{Ti(6-11)(O\textsuperscript{3}Pr)\textsubscript{2}\} after exposure to extended thermal conditions. X-ray crystallography characterisation was successfully conducted for Ti(7,9-11)(O\textsuperscript{3}Pr)\textsubscript{2}. \textsuperscript{1}H NMR spectroscopy revealed titanium metal centres were present in solution as multiple pseudo octahedral conformations.

The titanium LM\textsubscript{2} complexes \{Ti\textsubscript{2}(1-5,8,12-13)(O\textsuperscript{3}Pr)\textsubscript{6}\} were trialled for the ROP of rac-lactide and were shown to be active in both solvent and solvent free conditions. Ti\textsubscript{2}(1-5,8,12-13)(O\textsuperscript{3}Pr)\textsubscript{6} initiators achieved high conversion of rac-lactide to PLA within 24 h at 80 °C in toluene at 100:1 [rac-lactide]:[initiator] ratio. The solvent free polymerisation obtained high conversion within 30 mins at 130 °C at 300:1 [rac-lactide]:[initiator] ratio. The resulting PLA typically had lower molecular weights than expected and high PDI values were generally exhibited, it was speculated that more than one isopropoxide per metal was initiating the propagation of a PLA chain. The resulting PLA was generally atactic with slight variations of \(P_r\) about 0.5. The LM complexes \{Ti(6-11)(O\textsuperscript{3}Pr)\textsubscript{2}\} were poorly active under the same conditions for the ROP of rac-lactide. The solution ROP of rac-lactide required 24 h for low conversion to be obtained, the solvent free ROP required 24 h for moderate conversions to be obtained. The resulting PLA was predominantly atactic where slight deviations were observed towards isotactic or heterotactic lactide.

The favourable formation of monometallic catecholates is discussed along with their characterisation. The ligands (1,2,6)\textsubscript{2}H\textsubscript{2} were investigated and four variants of catecholate were complexed to Ti(O\textsuperscript{3}Pr)\textsubscript{4}. Ti(1)Catechol, Ti(1) 3,5-di-tert-butylcatechol, Ti(1)-4-NO\textsubscript{2}-catechol, and Ti(6)-4-NO\textsubscript{2}-catechol solid-state structures were determined by X-ray crystallography. These catecholates did not display any activity towards the ROP of rac-lactide. These titanium piperazine salan catecholates have been preliminarily revealed as moderately promising compounds as anti tumour reagents by Dr. Edit Tshuva.
2.9 Future Work

The equilibrium observed for Ti$_2$(1,2)(O'Pr)$_6$ poses on interesting area, thus further investigation into the nature of the equilibrium under various conditions would be of interest. Other derivatives of these ligands could be investigated to better constitute the requirements for an equilibrium system. The mechanistic details of these titanium complexes could be investigated further, beginning with kinetic experiments at low monomer:initiator ratio. Further work is being conducted on the anti-tumour properties of the titanium piperazine salan catecholates. Depending upon the trends observed other derivatives of these complexes could be investigated.

2.10 References

Chapter 3

3. Zirconium/Hafnium (IV) Homo/Piperazine Salan Complexes and Their Application for the ROP of rac-Lactide
3. Zirconium/Hafnium (IV) Homo/Piperazine Salan Complexes and Their Application for the ROP of \( \text{rac}-\text{Lactide} \)

3.1 Introduction

Group 4 tetradeutate amine bis(phenoxy) complexes have been previously reported for the ROP of \( \text{rac}-\text{lactide} \).\(^1\)\(^-\)\(^4\) Zirconium and hafnium metals can form complexes in different manners with tetradeutate -(ONNO)- ligands compared to titanium. For example, zirconium and hafnium metals have a stronger preference towards bridging to form dimers.\(^5\)\(^,\)\(^6\) Zirconium and hafnium complexes typically exhibit an enhancement for the ROP of lactide in terms of activity,\(^1\)\(^,\)\(^7\) and/or molecular weight control.\(^2\)\(^,\)\(^7\) Also stereoselectivity is often observed with zirconium and hafnium initiators over titanium initiators, due to the ability of lactide to chelate to the larger zirconium/hafnium metal. For example, isotactic enriched PLA was produced from \( \text{rac}-\text{lactide} \) by Davidson \textit{et al.} with the -(ONNO)- initiators given in figure 3.01.\(^2\) Furthermore, hafnium and zirconium trisphenolate initiators have resulted in strong heterotactic stereoselectivities (Figure 3.02).\(^1\)\(^,\)\(^8\) Reported herein is the synthesis of zirconium and hafnium piperazine and homopiperazine based salan complexes and their use as initiators for the ROP of \( \text{rac}-\text{lactide} \). This follows prior titanium piperazine salan work (Chapter 2).\(^9\)

\[ \text{Figure 3.01: Zirconium and hafnium -\{ONNO\}- based bis(phenoxy) initiators.}^2 \]

\[ \text{Figure 3.02: Heterotactic stereoselectivity with zirconium and hafnium trisphenolate initiators.}^1\)\(^,\)\(^8\) \]
3.2 Synthesis of Zirconium/Hafnium (IV) Homopiperazine Salan complexes

The homo/piperazine salan ligands (1-15)H₂ discussed in chapter 2 (Figure 2.02) were complexed to Zr(O\(^{i}\)Pr)_4.HO\(^{i}\)Pr and Hf(O\(^{i}\)Pr)_4.HO\(^{i}\)Pr. The complexation of zirconium and hafnium isopropoxide to the piperazine based salan ligands (1-5,12-15)H₂ was conducted with limited success (Figure 3.03).
complexation of zirconium with (1-5.12-15)H$_2$ at elevated or ambient temperature, resulted in a plethora of species being observed; furthermore purification by recrystallisation either yielded mixed zirconium species and/or ligand. In two cases recrystallisation of zirconium piperazine salan complexes from hot hexane afforded crystals suitable for X-ray diffraction studies. A complex with a 4:1 metal to ligand ratio was isolated \{[Zr$_4$(1)(O$^i$Pr)$_{14}$](HO$^i$Pr)$_2}\}. A 2:1 metal to ligand ratio complex was also observed \{[Zr$_2$(15)(O$^i$Pr)$_6}\}, with a differing structural motif than the previously discussed titanium complexes. The solution NMR spectroscopic analysis for these structures was not consistent with the structure being maintained in solution.

The complexation of Hf(O$^i$Pr)$_4$.HO$^i$Pr with (1-5.12-15)H$_2$ at room temperature also resulted in the production of a mixture of species (Figure 3.03). Recrystallisation attempts from small amounts of hexane yielded crystals for \{[Hf$_2$(1,3)(O$^i$Pr)$_6}\}, these complexes displayed the same structural motif. The bimetallic structure was observed in the solution state NMR spectra as the major product, but the high solubility of all the products made purification difficult and any isolated material contained significant degrees of impurities. The synthesis of zirconium and hafnium six membered piperazine salan complexes lacked the repeatability required for systematic study.

The complexation of Zr/Hf(O$^i$Pr)$_4$.HO$^i$Pr to the homopiperazine salan ligands \{(6-10)H$_2}\} proved fruitful (Figure 3.03). Monometallic complexes were obtained at room temperature and furthermore recrystallisation from hexane resulted in crystals suitable for X-ray diffraction studies for Zr(6-7,10)(O$^i$Pr)$_2$, and Hf(6-8,10)(O$^i$Pr)$_2$. The synthetic methodology was repeatable and a pure product was consistently obtained, which was characterised by $^1$H/$^{13}$C{$^1$H} NMR spectroscopy and CHN analysis. Analysis by $^1$H/$^{13}$C{$^1$H} NMR spectroscopy and CHN analysis was consistent with the solid-state structure remaining in solution. Utilising heat and longer reaction times enhanced the obtained yields, presumably assisting to overcome the energy barrier between the chair and boat configurations of the bridging homopiperazine ring. The introduction of THF to the synthesis of Zr(6)(O$^i$Pr)$_2$ lead to the determination of a crystal structure with a partially coordinated THF bound to the zirconium metal centre \{[Zr(6)(O$^i$Pr)$_2$.0.5THF.0.5IPA}.
3.3 Characterisation by X-ray Crystallography

Figure 3.04: Solid-state structures of a) Zr₄(1)(OⁱPr)₁₄.(HOⁱPr)₂ b) Zr₂(15)(OⁱPr)₆. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and ᵄPr–CH₃ groups have been omitted for clarity.

Two structural motifs were obtained by X-ray crystallography for the zirconium piperazine salan complexes; Zr₄(1)(OⁱPr)₁₄.(HOⁱPr)₂ (Figure 3.04a), Zr₂(15)(OⁱPr)₆ (Figure 3.04b). The tetramer Zr₄(1)(OⁱPr)₁₄.(HOⁱPr)₂ has two unique zirconium environments (Figure 3.04a), the complex has an inversion centre hence there are two pairs of equivalent zirconium centres. Both zirconium metals adopt a pseudo octahedral environment where both are bound to a bridging phenoxy group {Zr₁-O₁ = 2.168(3) Å, Zr₂-O₁ = 2.257(3) Å}, and a bridging isopropoxide moiety {Zr₁-O₁ = 2.184(3) Å, Zr₂-O₁ = 2.223(3) Å}. Zr₁ is bound to three isopropoxide
groups with bond lengths ranging between 1.939(3) - 2.034(3) Å, and one chelating nitrogen \{Zr1-N1 = 2.523(3) Å\}. Zr2 also coordinated to three terminal isopropoxide groups with bond lengths ranging between 1.944(3) - 1.953(3) Å. An isopropanol was bound to Zr2 \{Zr2-O6 = 2.287(3) Å\}, the isopropanol hydrogen bonds to an isopropoxide oxygen (O6). The bridging groups favour binding to Zr1, which is an artefact from the stronger coordination of a neutral isopropoxide ligand to Zr2 over the coordination of a neutral nitrogen to Zr1. The bridging phenoxy oxygen (O1) is trans to two terminal isopropoxide groups of each Zr metal giving angles; O1-Zr1-O3 = 159.43(11) °, O1-Zr2-O7 = 160.89(12) °, both cases significantly deviate from the idealistic trans octahedral angle. D(amine/imine) bridged bis(phenol) ligands have previously resulted in bimetallic zirconium complexes although examples typically include two ligands and two zirconium metals unlike Zr2(15)(OPr)6.10, 11 No previous tetrametallic bis(phenoxo) complexes have been reported as a bulk material or crystallographically determined.

The bimetallic Zr2(15)(OPr)6 has two zirconium metal centres, the piperazine salan ligands adopt the boat configuration and coordinate as a tetradentate ligand to Zr2 (Figure 3.04b). The pipazine methyl substituents are disordered over two positions in a 50:50 ratio, which are shown in figure 3.04b. Zr1 adopt a six coordinate pseudo octahedral structure and is only directly bonded to the piperazine salan ligand by a single bridging phenoxy group \{Zr1-O2 = 2.286(4) Å\}. Three terminal isopropoxide groups are coordinated to Zr1 with bond lengths ranging between 1.931(6) – 1.959(4) Å. The two zirconium metals are bridged by two isopropoxide groups with bond lengths between 2.153(4) - 2.327(5) Å, with the bridging oxygen bonds to Zr2 being shorter. Zr2 coordinates to the pipazine salan ligand through two phenoxy groups \{Zr2-O1 = 2.043(4) Å, Zr2-O2 = 2.199(4) Å\} and two amine groups \{Zr2-N1 = 2.481(5) Å, Zr2-N2 = 2.450(6) Å\}. Zr2 is coordinated to a single terminal isopropoxide moiety to give a final seven coordinate metal centre which adopts a pseudo pentagonal bipyramidal structure. Seven coordinate zirconium complexes have been previously reported to adopt pseudo pentagonal bipyramidal conformations.12, 13
Figure 3.05: Solid-state structure of Hf$_2$(1)(OPr)$_6$. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and Pr –CH$_3$ groups have been omitted for clarity.

Two hafnium piperazine salan structures \{Hf$_2$(1,3)(OPr)$_6$\} were characterised by X-ray crystallography and a representative structure for Hf$_2$(1,3)(OPr)$_6$ is given in figure 3.05. The piperazine ring adopts the boat configuration and each hafnium metal centre is bridged by two isopropoxide groups, selected bonds length are shown in table 3.01. Each hafnium metal adopts a *pseudo* octahedral structure chelating to one half of the piperazine salan ligand (a phenoxy and an amine) along with two terminal isopropoxide groups. The terminal isopropoxide Zr-O bonds are typically shorter, 1.891(11) – 1.964(9) Å, than the bridging isopropoxide Zr-O bonds, with bond lengths ranging between 2.122(9) -2.204(10) Å. A slight deviation from an idealistic octahedral structure was observed where the *trans* angles (N1-Hf1-O1), and *cis* angles (N1-Hf1-O2, N1-Hf1-O4) revealed deviations from 180 ° and 90 ° respectively. Bimetallic hafnium structures coordinated to diamine linked bis(phenol) ligands have been previously reported, although they are not prevalent in the literature. Further bimetallic hafnium structures have been reported with -ON(N)O- based bis(phenol) ligands.
Table 3.01: Selected bond lengths (Å) and angles (°) for piperazine salan hafnium complexes \( \{ \text{Hf}_2(1,3)(O^\text{Pr})_6 \} \), as determined by X-ray crystallography.

<table>
<thead>
<tr>
<th></th>
<th>Hf(_2)(O^\text{Pr})_6</th>
<th>Hf(_2)(3)(O^\text{Pr})_6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf1-O1</td>
<td>1.908(9)</td>
<td>1.917(7)</td>
</tr>
<tr>
<td>Hf1-O2</td>
<td>1.913(10)</td>
<td>1.929(9)</td>
</tr>
<tr>
<td>Hf1-O3</td>
<td>1.995(9)</td>
<td>2.009(6)</td>
</tr>
<tr>
<td>Hf1-O4</td>
<td>2.204(10)</td>
<td>2.152(10)</td>
</tr>
<tr>
<td>Hf1-O5</td>
<td>2.122(9)</td>
<td>2.180(11)</td>
</tr>
<tr>
<td>Hf1-N1</td>
<td>2.548(12)</td>
<td>2.534(9)</td>
</tr>
<tr>
<td>N1-Hf1-O1</td>
<td>173.9(4)</td>
<td>169.6(3)</td>
</tr>
<tr>
<td>N1-Hf1-O2</td>
<td>80.1(4)</td>
<td>87.1(3)</td>
</tr>
<tr>
<td>N1-Hf1-O4</td>
<td>80.9(4)</td>
<td>84.4(3)</td>
</tr>
</tbody>
</table>

The homopiperazine salan ligands \( \{ (6\text{-}10)\text{H}_2 \} \) were complexed to zirconium which resulted in monometallic structures, a representative solid-state structure is displayed in figure 3.06a. Selected bond lengths (Å) and angles (°) for Zr(6)(O^\text{Pr})\(_2\), Zr(7)(O^\text{Pr})\(_2\), Zr(10)(O^\text{Pr})\(_2\), and Zr(6)(O^\text{Pr})\(_2\).0.5THF.0.5IPA are given in table 3.02. The zirconium metal centre adopts a pseudo trans-octahedral structure (Chapter 2.5.2, figure 2.23) where the homopiperazine salan ligand chelates equatorially, the phenoxy groups were orientated cis to each other, and the amines are also cis orientated. The two terminal isopropoxide ligands are trans to each other in the axial position with no significant difference in bond length between the two axial moieties. The axial isopropoxide groups revealed a slight deviation from 180 °, with O1-Zr-O2 angles between 173.5(2) - 175.9(2) °. A large deviation (from 90 °) between the two cis phenoxy groups was observed with the O3-Zr-O4 angles being ~120 °. The two phenyl rings are orientated towards the same isopropoxide, the angle between the planes of the phenyl rings ranges between 73.7 – 81.2 °.

A solid-state structure of Zr(6)(O^\text{Pr})\(_2\) with a coordinated THF/isopropanol group was determined by X-ray crystallography. The resulting structure is given in
The zirconium metal centre is seven coordinate and adopts a *pseudo* pentagonal bipyramidal structure, where the THF was found in a 50:50 ratio with an isopropanol moiety. The isopropoxide groups remain in the axial position of the complex although the *trans* isopropoxide angle was more acute \(\{O1-Zr1-O2 = 169.18(7) \, ^\circ\}\). The introduction of the neutral coordinating oxygen group elongates the amine zirconium bonds \((Zr1-N1 \text{ and } Zr1-N2)\). The angle between the two phenoxy groups becomes more obtuse \(\{O3-Zr1-O4 = 137.96(6)\}\) to allow the introduction of an extra coordinating group.

**Figure 3.06**: Solid-state structures of a) Zr(6)(O’Pr)\(_2\) b) Zr(6)(O’Pr)\(_2\)0.5THF.0.5IPA. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and iPr –CH\(_3\) groups have been omitted for clarity.
Table 3.02: Selected bond lengths (Å) and angles (°) for monometallic zirconium complexes, as determined by X-ray crystallography. a The molecule contains a mirror plane; Zr1-O3 = Zr1-O4, Zr1-N1 = Zr1-N2.

<table>
<thead>
<tr>
<th></th>
<th>Zr(6)(O’Pr)₂</th>
<th>Zr(7)(O’Pr)₂</th>
<th>Zr(10)(O’Pr)₂</th>
<th>Zr(6)(O’Pr)₂.0.5 THF.0.5IPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr1-O1</td>
<td>1.9689(14)</td>
<td>1.968(4)</td>
<td>1.962(6)</td>
<td>1.9708(17)</td>
</tr>
<tr>
<td>Zr1-O2</td>
<td>1.9665(14)</td>
<td>1.964(4)</td>
<td>1.966(5)</td>
<td>1.9652(16)</td>
</tr>
<tr>
<td>Zr1-O3</td>
<td>2.0476(15)</td>
<td>2.041(2)</td>
<td>2.047(6)</td>
<td>2.0950(17)</td>
</tr>
<tr>
<td>Zr1-O4</td>
<td>2.0567(14)</td>
<td>-ₐ</td>
<td>2.027(6)</td>
<td>2.1292(15)</td>
</tr>
<tr>
<td>Zr1-O5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.469(10) b</td>
</tr>
<tr>
<td>Zr1-N1</td>
<td>2.3958(18)</td>
<td>2.387(3)</td>
<td>2.391(8)</td>
<td>2.4831(19)</td>
</tr>
<tr>
<td>Zr1-N2</td>
<td>2.3876(18)</td>
<td>-ₐ</td>
<td>2.381(8)</td>
<td>2.4945(18)</td>
</tr>
<tr>
<td>N1-Zr1-O1</td>
<td>87.20(6)</td>
<td>86.25(14)</td>
<td>87.8(3)</td>
<td>84.05(7)</td>
</tr>
<tr>
<td>N1-Zr1-O4</td>
<td>152.67(6)</td>
<td>153.50(8)ₐ</td>
<td>152.8(3)</td>
<td>142.89(6)</td>
</tr>
<tr>
<td>O1-Zr1-O2</td>
<td>174.71(6)</td>
<td>173.5(2)</td>
<td>175.9(2)</td>
<td>169.18(7)</td>
</tr>
<tr>
<td>O3-Zr1-O4</td>
<td>121.40(6)</td>
<td>119.57(13)</td>
<td>120.6(2)</td>
<td>137.96(6)</td>
</tr>
</tbody>
</table>

Figure 3.07: Solid-state structure of Hf(6)(O’Pr)₂. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and Pr – CH₃ groups have been omitted for clarity.

Similar monometallic structures were identified by X-ray crystallography for the hafnium isopropoxide homopiperazine salan complexes {Hf(6-8,10)(O’Pr)₂}. The structures for Hf(6)(O’Pr)₂, Hf(7)(O’Pr)₂, Hf(8)(O’Pr)₂, and Hf(10)(O’Pr)₂ were obtained. The structure of Hf(6)(O’Pr)₂ is given in figure 3.07 as a representative example. Selected bond lengths (Å) and angles (°) determined by X-ray
Crystallography can be found in Table 3.03. These structures all adopt a pseudo trans-octahedral geometry (Chapter 2.5.2, figure 2.23) where the homopiperazine ligand coordinates via two amines and two phenoxy groups to the equatorial positions of the hafnium metal centre. The isopropoxide groups coordinates in the axial positions, while trans to each other a slight deviation from 180° was observed \( \{O1-Hf1-O2 = 172.7(4) - 176.36(13)°\} \). Similarly the phenyl rings are both orientated towards the -(CH\(_2\))\(_3\)- group of the homopiperazine ring, where the angle between planes of the two phenyl rings ranged between 71.8 – 81.1°. The trans octahedral geometry is not prevalent in the literature for Zr(IV) or Hf(IV) \{-ONNO\} bis(phenoxy) isopropoxide complexes. Titanium has been reported to adopt the trans octahedral configuration in solution.\(^{16}\) However, the trans octahedral geometry is favourable in the presence of metal coordinated chloride moieties.\(^{12,17}\)

<table>
<thead>
<tr>
<th></th>
<th>Hf(6)(O'Pr)(_2)</th>
<th>Hf(7)(O'Pr)(_2)</th>
<th>Hf(8)(O'Pr)(_2)</th>
<th>Hf(10)(O'Pr)(_2)</th>
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<tr>
<td>Hf1-O1</td>
<td>1.960(4)</td>
<td>1.957(7)</td>
<td>1.982(3)</td>
<td>1.969(2)</td>
</tr>
<tr>
<td>Hf1-O2</td>
<td>1.955(4)</td>
<td>1.993(6)</td>
<td>1.966(3)</td>
<td>1.964(2)</td>
</tr>
<tr>
<td>Hf1-O3</td>
<td>2.030(4)</td>
<td>2.040(2)</td>
<td>2.037(3)</td>
<td>2.040(3)</td>
</tr>
<tr>
<td>Hf1-O4</td>
<td>2.041(4)</td>
<td>-a</td>
<td>2.037(3)</td>
<td>2.035(3)</td>
</tr>
<tr>
<td>Hf1-N1</td>
<td>2.364(5)</td>
<td>2.363(3)</td>
<td>2.340(4)</td>
<td>2.355(4)</td>
</tr>
<tr>
<td>Hf1-N2</td>
<td>2.357(5)</td>
<td>-a</td>
<td>2.349(3)</td>
<td>2.359(3)</td>
</tr>
<tr>
<td>N1-Hf1-O1</td>
<td>87.14(16)</td>
<td>88.06(17)</td>
<td>87.95(12)</td>
<td>88.09(11)</td>
</tr>
<tr>
<td>N1-Hf1-O4</td>
<td>153.63(16)</td>
<td>155.00(9)(^a)</td>
<td>153.88(12)</td>
<td>154.66(13)</td>
</tr>
<tr>
<td>O1-Hf1-O2</td>
<td>174.83(16)</td>
<td>172.7(4)</td>
<td>176.36(13)</td>
<td>175.55(11)</td>
</tr>
<tr>
<td>O3-Hf1-O4</td>
<td>119.17(15)</td>
<td>117.34(13)</td>
<td>119.36(12)</td>
<td>118.82(11)</td>
</tr>
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</table>

Table 3.03: Selected bond lengths (Å) and angles (°) for homopiperazine salan hafnium complexes, as determined by X-ray crystallography. \(^a\) The molecule contains a mirror plane; Zr1-O3 = Zr1-O4, Zr1-N1 = Zr1-N2.
3.4 Characterisation by NMR Spectroscopy

$^1$H NMR spectroscopy was utilised to analyse the products from the complexation reaction of zirconium and hafnium isopropoxide to piperazine salan ligands (1-5,12-15)H$_2$. The $^1$H NMR spectra were typically indeterminable and acidic phenol protons were often observed indicating incomplete reactions. The isolated hafnium piperazine salan \{Hf$_2$(1,3)(O$i$Pr)$_6$\} product contained several impurities. These $^1$H NMR spectra indicated the formation of structures with a metal-to-ligand ratio of 2:1, as determined by X-ray crystallography, but significant degrees of impurities were observed in the recrystallised product.

![Figure 3.08: 1H NMR spectra for Zr(7)(O$i$Pr)$_2$, top 298 K, bottom 233 K.](image)

The solution NMR spectra for Zr(6-10)(O$i$Pr)$_2$ were consistent with the X-ray crystallographically determined structures being maintained in solution. A representative room temperature $^1$H NMR spectrum for Zr(7)(O$i$Pr)$_2$ is given in figure 3.08 alongside a low temperature $^1$H NMR spectrum. The room temperature $^1$H NMR spectra are typically broad around the CH$_2$ regions and the CH isopropoxide region (2.00 - 4.50 ppm). There are two broad isopropoxide CH$_3$
resonances at ~ 0.38 ppm and ~ 1.10 ppm, the broad regions are indicative of fluxionality in the isopropoxide moieties and the backbone of the homopiperazine salan ligand. Upon cooling (233 K) the aromatic region remains defined with two doublets at 6.83 ppm, and 7.11 ppm, whereas the lower chemical shift regions become more distinct. The homopiperazine ring system displays a significant sharpening of resonances at 3.53 ppm, 3.27 ppm, 2.88 ppm, 2.25 ppm, 2.18 ppm (partial overlap with the CH₃ resonances), and 1.73 ppm. A pronounced enhancement is observed for the isopropoxide moieties; both CH isopropoxide groups were located at 3.28 ppm and 4.43 ppm, although in this specific example (Figure 3.08) both resonances are located in the same region as the CH₂ group resonances. The CH₃ isopropoxide resonances are present at 0.15 ppm and 1.22 ppm, the resonance at 1.22 ppm coincides with resonances attributed to tBu groups. The resonance at 0.15 ppm is significantly shifted upfield than typical zirconium bound isopropoxide CH₃ groups. It was deduced that this isopropoxide orientated towards the -(CH₂)₃- homopiperazine region and is profoundly shielded by the phenoxy aromatic rings orientated in the same direction.

Subsequent NMR spectroscopy investigations of the homopiperazine salan hafnium complexes \{Hf(6-10)(O'Pr)₂\} evidently proved the solution state structures were of the same pseudo trans-octahedral geometry as determined by X-ray crystallography (Figure 3.07). A representative ¹H NMR spectrum of Hf(7)(O'Pr)₂ under ambient conditions is provided, accompanied by a low temperature ¹H NMR spectrum of the same complex (Figure 3.09). Similar to the analogous zirconium complex \{Zr(7)(O'Pr)₂\} the ¹H NMR spectrum for Hf(7)(O'Pr)₂ revealed a broadening of the homopiperazine salan CH₂ resonances and the CH/CH₃ isopropoxide resonances. Upon cooling the phenoxy substituent resonances (1.21 ppm, 2.17 ppm) and aromatic resonances remain relatively unchanged. The CH₂ piperazine ring protons results in defined resonances, 1.17 ppm, 2.15 ppm (partial overlap with the CH₃ resonance), 2.35 ppm, 2.95 ppm, 3.35 ppm, and 3.54 ppm. The isopropoxide CH resonances become defined, 4.51 ppm and 3.35 ppm, although the latter resonance coincides with a CH₂ resonance. Similar to the Zr(7)(O'Pr)₂ ¹H NMR spectrum a single isopropoxide moiety reveals a significant upfield shift, as a consequence of the proximity of two phenoxy groups orientated towards a particular isopropoxide moiety.
3.5 Ring-Opening-Polymerisation of rac-Lactide

The zirconium and hafnium homopiperazine salan complexes were trialled for the ring opening polymerisation (ROP) of rac-lactide in both solution and solvent free conditions. Furthermore no co-initiator was required and selected complexes were investigated at different monomer to initiator ratios.

3.5.1 Solution ROP of rac-lactide

The ROP of rac-lactide was investigated in toluene (10 ml) at 80 °C typically allowing 24 h reaction time. In all cases 1.0 g of rac-lactide was used and the initiator was added in a 100:1 [rac-lactide]:[initiator] ratio, no co-initiator was required for the ROP reaction to proceed. The polymerisation typically achieved high conversion after 24 h at which point the reaction was quenched with methanol (Table 3.04). Lower conversions were obtained for initiators that contain an ortho-Bu ring substituent {Zr(8-9)(O’Pr)₂, Hf(8-9)(O’Pr)₂}. This is presumably a
steric effect of the bulkier t-Bu substituents hindering access to the zirconium or hafnium metal centre. The hafnium complexes containing t-Bu groups on the ortho-position of the phenoxy ring \{Hf(8-9)(O'iPr)\_2\} gave lower conversions than their zirconium counterparts. Complexes containing amyl phenoxy ring substituents did not show same degree of reduction in activity, it was speculated that the bulky amyl groups may destabilise the complex during the ROP reaction. Hence, higher conversions were observed despite the increased steric demands of amyl groups compared to t-Bu moieties. It should be noted that erroneous CHN analysis of Zr/Hf\{(10)(O'iPr)\_2\} were obtained, although solution state and X-ray diffraction analysis supports the proposed structure.

Polylactide (PLA) molecular weights ($M_n$) were determined by GPC in THF (Table 3.04), the molecular weights were relatively consistent with the theoretical molecular weights, calculated from conversion, for the propagation of one PLA chain per metal centre. The majority of complexes investigated revealed narrow PDI values (PDI = 1.05 – 1.69). The zirconium complexes displayed increased molecular weight distributions in comparison to their hafnium analogues. ortho-Methyl substituents upon the phenoxy ring \{Zr(6-7)(O'iPr)\_2, Hf(6-7)(O'iPr)\_2\} resulted in higher PDI values, which was presumably a consequence of reduced steric hindrance, the effect was even more pronounced for the zirconium complexes.

The complexes \{Zr(6-10)(O'iPr)\_2\} propagated rac-lactide to produce PLA, which revealed a slight to moderate isotactic bias ($P_r = 0.38 – 0.45$) (Table 3.04) as determined by homonuclear decoupled $^1$H NMR spectroscopy. The zirconium complexes containing ortho-methyl phenoxy ring substituents \{Zr(6-7)(O'iPr)\_2\} displayed the stronger isotactic selectivity. The hafnium homopiperazine salan complexes \{Hf(6-10)(O'iPr)\_2\} also resulted in PLA with a slight to moderate isotactic bias ($P_r = 0.35 – 0.5$). Likewise the hafnium initiators with ortho-methyl phenoxy ring substituents \{Hf(6-7)(O'iPr)\_2\} revealed slightly enhanced isotactic selectivity ($P_r = 0.35 – 0.37$).
| Zr(6)(O'Pr)₂ | 24  | 96  | 13900 | 10000 | 1.69 | 0.38 |
| Zr(6)(O'Pr)₂ | 24  | 97  | 42000 | 45700 | 1.59 | 0.38 |
| Zr(7)(O'Pr)₂ | 24  | 93  | 13450 | 10550 | 1.55 | 0.42 |
| Zr(8)(O'Pr)₂ | 24  | 77  | 11450 | 7975  | 1.21 | 0.45 |
| Zr(9)(O'Pr)₂ | 24  | 26  | 3800  | 4400  | 1.22 |    |
| Zr(10)(O'Pr)₂ | 24  | 87  | 12600 | 10400 | 1.15 | 0.45 |
| Hf(6)(O'Pr)₂ | 24  | 95  | 13750 | 12850 | 1.68 | 0.37 |
| Hf(6)(O'Pr)₂ | 24  | 95  | 41150 | 52100 | 1.20 | 0.35 |
| Hf(7)(O'Pr)₂ | 6   | 83  | 12000 | 9250  | 1.11 | 0.37 |
| Hf(8)(O'Pr)₂ | 24  | 12  | 1800  | 1650  | 1.05 |    |
| Hf(9)(O'Pr)₂ | 24  | 26  | 3250  | 2550  | 1.26 | 0.52 |
| Hf(10)(O'Pr)₂ | 24  | 89  | 12900 | 9500  | 1.12 | 0.43 |

Table 3.04: Solution ROP of rac-lactide for Zr(6-10)(O'Pr)₂ and Hf(6-10)(O'Pr)₂ in 10 ml of toluene at 80 °C in a 100:1 [rac-lactide]:[initiator] ratio. a Conversion ascertained by ¹H NMR spectroscopy. b Theoretical molecular weight calculated from conversion (Conv. × 100 × 144.13 + 60.10) (rounded to the nearest 50). c Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. d Pᵣ as calculated from ¹H NMR homonuclear decoupled spectroscopy in CDCl₃. e 300:1 [rac-lactide]:[initiator] ratio.

The homonuclear decoupled ¹H NMR spectrum of PLA synthesised from rac-lactide initiated by Hf(6)(O'Pr)₂ in a 300:1 [rac-lactide]:[Initiator] ratio after 24 h, in toluene, at 80 °C is displayed in figure 3.10. There is an enhancement of the [iii] tetrad resonance at 5.16 ppm. Alongside this is a decrease in intensity of the [sis] and [isi] tetrads resonances, at 5.22 ppm and 5.15 ppm respectively. The probability of racemic enchainment (Pᵣ) was calculated using Bernoullian statistics¹⁸ using the relative integrals fraction of the [sis] resonance against all the methine resonances, 1/15.99, gives a $Pᵣ = 0.35$ from equation 1.06 (Figure 1.16). The homonuclear ¹H NMR spectrum given in figure 3.10 is a representative example for the isotactic bias determined for initiators given in table 3.04.
Figure 3.10: $^1$H NMR homonuclear decoupled spectrum showing tetrad resonances for the ROP of \textit{rac}-lactide by Hf(6)(O\textit{i}Pr)$_2$ in a 100:1 \textit{rac}-lactide:\textit{Initiator} ratio, after 24 h in toluene at 80 °C (Table 3.04).

Figure 3.11: MALDI-TOF mass spectra of PLA produced using initiator Zr(8)(O\textit{i}Pr)$_2$, at 80 °C after 24 h.
The MALDI-TOF mass spectrum of polymer resulting from PLA produced by initiator Zr(8)(OiPr)₂ is given in figure 3.11 for the major series of peaks. The spacing between signals was ~ 72 g mol⁻¹, this value is typical of half a lactide unit indicative of a degree of transesterification occurring during the ROP reaction. Analysis of peaks and splitting patterns allowed the identification of -H and -isopropoxide ends groups. The peak pattern at 4262.3 Mᵢ (Figure 3.11) corresponded to the enchainment of 29 lactide units, a terminal hydrogen, a terminal isopropoxide and ionised with a sodium ion.

3.5.2 Solvent free ROP of rac-lactide

The homopiperazine salan zirconium \{Zr(6-10)(OiPr)₂\} and hafnium \{Hf(6-10)(OiPr)₂\} complexes were trialled as initiators for the ROP of rac-lactide in solvent free conditions using 1.0 g of lactide at 130 °C. All initiators were used without a co-initiator at a 300:1 [rac-lactide]:[initiator] ratio, with selected trials at 900:1 [rac-lactide]:[initiator] ratio. High conversions were obtained for initiators containing ortho methyl or amyl phenoxy substituents \{Zr(6-7.10)(OiPr)₂, Hf(6-7.10)(OiPr)₂\} after 0.5 hours, whereas initiators with ortho-tBu phenoxy substituents \{Zr(8-9)(OiPr)₂, Hf(8-9)(OiPr)₂\} required 3 h to obtain high conversion (Table 3.04). At the higher rac-lactide to initiator ratios (900:1) the longer reaction time of 6 h resulted in partial conversion.

The Hf(6-10)(OiPr)₂ initiators were relatively consistent with one PLA chain per metal. There was some deviation in molecular weight (Mᵢ) from the conversion calculated theoretical molecular weights. Moderately low PDI (PDI = 1.12 – 1.39) values were obtained with little noted difference between initiators containing ortho-methyl and ortho-tBu phenoxy substituents, which is contrasting to the related solution ROP observations. The solvent free ROP of rac-lactide by Zr(6-10)(OiPr)₂ and Hf(8-10)(OiPr)₂ resulted in the production of predominantly atactic PLA (Pᵣ = 0.44 – 0.56) (Table 3.05). Akin to the solution ROP reactions the ortho-methyl phenoxy substituted hafnium complexes \{Hf(6-7)(OiPr)₂\} yielded PLA with a moderate isotactic bias (Pᵣ = 0.37 – 0.39), to a similar degree to the lower temperature solution ROP of rac-lactide (Pᵣ = 0.35 – 0.37) (Table 3.04).
Independent ROP reactions were performed with Zr(8)(O’Pr)₂ and Hf(8)(O’Pr)₂ initiators in solvent free conditions. The individual polymerisations were allowed to achieve varying conversions, a dual plot of $M_n$ against conversion and PDI against conversion is displayed in figure 3.12. The molecular weight growth shows a linear increase with conversion as expected for the controlled propagation of PLA chains. PDI was plotted against conversion, for the entire range the PDI values were low but a slight increase is present as conversion increases. The linear trend of molecular weight is indicative of a living polymerisation reaction, although transesterification and slowly increasing PDI values with conversion signify deviation from an idealistic living polymerisation.
3.5.3 Kinetic investigation of the solution ROP of rac-lactide

NMR spectroscopy scale kinetic experiments were performed to investigate the apparent rate of propagation ($k_{app}$) for the ROP of rac-lactide using the homopiperazine salan initiators {Zr(6)(O’Pr)$_2$, Hf(6)(O’Pr)$_2$}. The NMR spectroscopy scale experiments were performed using 50 mg of rac-lactide in d$_8$-toluene (0.6 ml) at 80 °C, in both cases a 100:1 [rac-lactide]:[initiator] ratio was used. The kinetic experiments were allowed to run until high conversion was obtained. Spectra were recorded at 15 min intervals with the initiator Zr(6)(O’Pr)$_2$, and at 30 min intervals with the initiator Hf(6)(O’Pr)$_2$, both cases are truncated due to diffusion rate limitations at high conversions. $\ln([LA]_0/[LA]_t)$ was plotted against time (Figure 3.13) to present linear plots where the slope relates to the apparent pseudo first order rate constant ($k_{app}$) (Table 3.06). The zirconium catalyst was ~3 times more active towards the ROP of rac-lactide than the related hafnium complex. Zirconium
catalysts have been previously reported as more active than corresponding hafnium complexes for the ROP of rac-lactide.6, 8, 19, 20

![Figure 3.13: Pseudo first order plots for the ROP of rac-lactide by Zr(6)(O’Pr)2 (Blue), and Hf(6)(O’Pr)2 (Red), 50 mg of rac-lactide in 0.6 ml of d8-toluene at 80 °C at 100:1 [rac-lactide]:[initiator] ratio.](image)

<table>
<thead>
<tr>
<th>k_{app} \times 10^{-3} (min^{-1})</th>
<th>R^2</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
<td>Hf(6)(O’Pr)2</td>
<td>8.00(2)</td>
</tr>
</tbody>
</table>

Table 3.06: k_{app} values and R^2 values for ROP of rac-lactide by Zr(6)(O’Pr)2 and Hf(6)(O’Pr)2 initiators.

### 3.6 Conclusion

The synthesis and characterisation of zirconium and hafnium complexes bearing strained homopiperazine based salan ligands \{Zr(6-10)(O’Pr)2, Hf(6-10)(O’Pr)2\} is reported herein. Zr(6-7,10)(O’Pr)2 and Hf(6-8,10)(O’Pr)2 were isolated as crystals and characterised by X-ray crystallography, each structure was monometallic and adopted a pseudo octahedral trans configuration. An informative Zr(6)(O’Pr)2.0.5THF.0.5IPA complex was characterised by X-ray crystallography.
where this seven coordinate variant of Zr(6)(OPr)$_2$ demonstrated a possible coordination site a lactide unit could adopt. The synthesis of piperazine salan (1-5,12-15)H$_2$ Zr(IV) and Hf(IV) complexes was attempted but generally a plethora of species was obtained and purification of a bulk material was unsuccessful. Isolated crystals of Zr$_4$(1)(OPr)$_{14}$(HOPr)$_2$ and Zr$_2$(15)(OPr)$_6$ were characterised by crystallography showing a tetrametallic structure and an interesting bimetallic structure where the ligand chelates to one metal. Consistent bimetallic structures were observed for the X-ray determination of Hf$_2$(1,3)(OPr)$_6$ complexes. The difficulty in isolating a monometallic piperazine salan Zr(IV) or Hf(IV) structure was attributed to the increased conformational ring strain associated with the piperazine backbone in comparison to a homopiperazine backbone.

Zr(6-10)(OPr)$_2$ and Hf(6-10)(OPr)$_2$ were investigated as initiators for the ROP of rac-lactide in solvent free and solution conditions. High conversion was typically obtained after 24 h at 80 °C in toluene at a 100:1 [rac-lactide]:[initiator] ratio. Higher activity was observed for complexes containing ortho-methyl phenoxy substituents over the sterically bulky ortho-^t^Bu phenoxy substituents. An isopropoxide moiety was identified by MALDI-TOF mass spectrometry as the chain end group, which supports a coordination insertion mechanism. Good molecular weight control was observed but a degree of transesterification was identified via MALDI-TOF mass spectrometry. An isotactic bias ($P_r = 0.35 – 0.5$) was generally observed for these complexes which was enhanced for complexes bearing ortho-methyl phenoxy substituents ($P_r = 0.35 – 0.42$). Hf(6,7)(OPr)$_2$ resulted in a small increase in stereoselectivity over Zr(6,7)(OPr)$_2$ complexes. The solvent free ROP was conducted at 130 °C at a 300:1 [rac-lactide]:[initiator] ratio. Zr(6,7,10)(OPr)$_2$ and Hf(6,7,10)(OPr)$_2$ achieved high conversion after 0.5 h, where as the ortho-^t^Bu phenoxy containing complexes {Zr(8,9)(OPr)$_2$, Hf(8,9)(OPr)$_2$} required 3 h to obtain appreciable conversion. Lower molecular weights were obtained for the solvent free ROP of rac-lactide experiments where the increased thermal conditions activate both isopropoxides for the initiation of PLA chain growth. Controlled molecular weight growth was demonstrated with increasing conversion with minimal increase in PDI, this supports a chain-end control mechanism. NMR spectroscopy scale kinetic investigations resulted in pseudo first order apparent rate constants for Zr(6)(OPr)$_2$ and Hf(6)(OPr)$_2$ from which the zirconium complex was
demonstrated as approximately three times more active than its direct hafnium analogue for the ROP of rac-lactide.

### 3.7 Future Work

The piperazine hafnium solid-state structures \{Hf\(_2(1,3)(O\text{Pr})_6\}\} show promise and further-work could be conducted into isolating these as pure materials, although extensive efforts were made. Variation of the homopiperazine salan ligands could be conducted particularly in the area of halide phenoxy substituents (Cl, Br) to ascertain their effect upon complexes and consequently the ROP of rac-lactide. Further-work into unsymmetrical homo/piperazine salan ligand sets could be attempted where substituents on each phenol are different. The effect of conformational hindered (6/7 membered ring backbones) diamine bridging groups upon salan complexes was conducted and future work could include 8 membered bridging ring groups (Figure 3.14).

![Figure 3.14: 8 membered ring diamines.](image)

### 3.8 References

Chapter 4

4. Aluminium (III) Homopiperazine Salan Complexes and Their Application for the ROP of Cyclic Esters.
4. Aluminium (III) Homopiperazine Salan Complexes and Their Application for the ROP of Cyclic Esters.

4.1 Introduction

Aluminium tetradentate -(ONNO)- bis(phenoxo) complexes have been previously investigated as ROP initiators for lactide.¹ Specifically aluminium diimine bis(phenoxo) (salen) complexes have seen much use for the ROP of lactide throughout the past few decades,²⁻⁶ many of which produce isotactic PLA or isotactic biased PLA. These stereoselective initiators typically required a time scale of days for appreciable conversion to be obtained. Whereas good control over molecular weight and stereoselectivity was observed in solution, a strong degree of isotactic stereoselectivity was retained in solvent free conditions for aluminium complexes supported by bis(phenol) ligands containing 1,2-diaminocyclohexane (1,2-DACH) and (NCH₂Me₂CH₂N) linkers.⁵

Aluminium diamine bis(phenoxo) (salan) complexes have also been previously investigated as initiators for the ROP of lactide (Figure 4.01).⁷,⁸ Many aluminium salan complexes contain alkyl initiating groups and hence a co-initiator (typically an alcohol) is often introduced to the polymerisation. The aluminium salan complexes (Figure 4.01) gave varying stereoselectivities ranging between a strong isotactic bias to heterotactic ($P_r = 0.21 - 0.96$).⁷ An isotactic bias was reported when $R_2 = H$ and a heterotactic bias was reported when $R_2 = Me, tBu, or Cl$, where the Cl subsistent resulted in the strongest heterotactic selectivity.

![Figure 4.01: Aluminium diamine bis(phenoxo) (aluminium salan) complexes investigated for the ROP of lactide.⁷](image-url)
Piperazine salan group 4 complexes for the ROP of rac-lactide have been previously reported and are discussed in chapters 3 and 4 of this thesis.9, 10 Furthermore aluminium piperazine salan complexes were initially synthesised by Fulton et al.11 who reported the synthesis of bimetallic and monometallic structures. The same piperazine ligand was utilised throughout the study and the monodentate aluminium substituents were varied.11 The complexes were trialled as initiators for the ROP of lactide under solution conditions and were reported as inactive, although these complexes were reported as active initiators for the ROP of ε-caprolactone (Figure 4.02).11 Yao et al.12 reported similar bimetallic aluminium salan complexes and their high activity towards the ROP of ε-caprolactone at high monomer to initiator ratios. Molecular weights were shown to be dependent upon benzyl alcohol co-initiator concentration, whilst high molecular weights were obtained a range of PDI (distribution of molecular weights) values were also reported (PDI = 1.19 - 2.01). The ROP of ε-caprolactone was also investigated using monometallic aluminium piperazine salan derivatives developed by Yao et al.13 While active initiators for the ROP of ε-caprolactone the monometallic aluminium initiators were significantly less active than their bimetallic counterparts. The monometallic aluminium piperazine salan initiators gave greater control over the ROP of ε-caprolactone resulting in lower PDI values (PDI = 1.17 - 1.52).

Prior investigations of piperazine salan and homopiperazine salan ligands complexed to group 4 metals (Chapter 2, and 3) revealed the two ligand sets can coordinate in differing manners.9, 10 Herein the benzyloxy derivatives of aluminium methyl homopiperazine salan complexes were synthesised and their ROP activity for lactide, ε-caprolactone and δ-valerolactone is reported.
4.2 Synthesis of Aluminium Homopiperazine Salan Complexes

The homopiperazine ligands synthesised and discussed in chapter 2 (Figure 2.02) were complexed to AlMe$_3$, Conrad Langridge is acknowledged for his contribution to the development of these complexes.$^{14}$ The addition of aluminium was conducted at elevated temperature (50 °C) until the initial effervescence had slowed, at which point the temperature was increased (80 °C) to ensure complete reaction (Figure 4.03). The thermally energetic conditions were required to kinetically facilitate the homopiperazine ring formation of the boat type configuration. The aluminium complexes were recrystallised from toluene and hexane solvent mixtures, using thermal and diffusion based recrystallisation methods. Crystals suitable for X-ray diffraction were obtained for Al(7,8,11)Me. Attempts to synthesise aluminium complexes using 10H$_2$ were unsuccessful presumably an artefact of the increased steric demands of the ortho-phenoxy ring amyl substituents. The complexes Al(6-9,11)Me were characterised by $^1$H/$^13$C{$^1$H} NMR spectroscopy and CHN analysis, in all cases the complexes were consistent with the solid-sate structures.
Aluminium methyl complexes typically require a co-initiator, normally an alkoxide, to enhance their properties as initiators for the ROP of cyclic esters. The direct incorporation of a co-initiating benzyl alcohol (BnOH) was attempted and the presumably active initiating species containing benzyl oxy aluminium bound substituents were isolated. Firstly, the synthesis of a homopiperazine complex \{Al(6-9,11)Me\} was conducted and the complex rapidly purified by addition of hexane to a toluene solution. An excess of benzyl alcohol (3-5 equivalents) was required to fully substitute the aluminium bound methyl groups (Figure 4.04). Despite the use of excess benzyl alcohol at elevated temperature (70-80 °C) prolonged reaction times were required to ensure complete conversion of Al(6-9,11)Me to Al(6-9,11)OBn (Figure 4.04). High conversion was required as purification of Al(6-9,11)OBn in the presence of Al(6-9,11)Me impurities was difficult. The complexes were purified by recrystallisation from toluene and hexane mixes but no crystals suitable for X-ray diffraction were obtained. Hexane washes and toluene/hexane crystallisation was conducted to ensure the complete removal of benzyl alcohol. The complexes were isolated and characterised by \(^1\)H/\(^13\)C{\(^1\)H} NMR spectroscopy and CHN analysis.

**Figure 4.04**: Reaction scheme detailing the synthesis of homopiperazine salan benzyl oxy aluminium complexes.
4.3 Solid-state characterisation by X-ray crystallography

Aluminium homopiperazine salan complexes Al(7)Me, Al(8)Me, and Al(11)Me were characterised by X-ray crystallography; Al(8)Me crystals were initially obtained by Conrad Langridge as part of the Jones group. Similar aluminium piperazine-based salan structures determined by X-ray crystallography were reported by Fulton et al. and Yao et al. The crystallographic determined structures are specifically compared with the literature structures; Al(3)Me (R₁ = R₂ = tBu) and Al(4)Et (R₁ = tBu, R₂ = Me).

![Solid-state structures for a single disordered crystal where two structures were obtained; a) Al(8)Me cis-(CH₂CH₂)₆, b) Al(8)Me cis-(CH₂CH₃CH₂)₆. Ellipsoids are shown at the 30% probability level, hydrogen atoms have been removed for clarity.](image)

**Figure 4.05**: Solid-state structures for a single disordered crystal where two structures were obtained; a) Al(8)Me cis-(CH₂CH₂)₆, b) Al(8)Me cis-(CH₂CH₃CH₂)₆. Ellipsoids are shown at the 30% probability level, hydrogen atoms have been removed for clarity.
The crystal structure for Al(8)Me was solved with a significant degree of disorder about the homopiperazine ring. The homopiperazine ring disorder could be extrapolated to generate two isomers which were present in the unit cell in a 50:50 ratio. One structure has the aluminium bound methyl orientated cis to the -(CH₂CH₂)- moiety of the homopiperazine ring (Figure 4.05a), the alternative structure has the aluminium bound methyl cis to the -(CH₂CH₂CH₂)- homopiperazine ring moiety (Figure 4.05b). Selected bond lengths (Å) and angles (°) for both Al(8)Me structures alongside other aluminium homopiperazine salan structures are given in table 4.01.

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<th>Al(8)Me&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Al(8)Me&lt;sup&gt;b&lt;/sup&gt;</th>
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Table 4.01: Selected bond lengths (Å) and angles (°) for piperazine salan aluminium complexes, as determined by X-ray crystallography. <sup>a</sup>methyl orientated cis to -(CH₂)₂- homopiperazine ring group, <sup>b</sup>methyl orientated cis to -(CH₂)₃- homopiperazine ring group.
Al(8)Me the Al1-C1 bonds (1.960 – 1.980 Å) are of a similar distance to the analogous bonds lengths reported for Al(3)Me (1.974(3) Å)\textsuperscript{11} and Al(4)Et (2.004(4) Å).\textsuperscript{13} A significant difference in bond length can be observed between the two aluminium phenoxy bonds (Al1-O1, Al1-O2) of the Al(8)Me structures, additionally a distinct difference was observed between the aluminium amine bonds lengths (Al1-N1, Al1-N2). Similarly a significant difference between analogous bond lengths was reported for the literature structures Al(3)Me\textsuperscript{11} and Al(4)Et.\textsuperscript{13} This inherent asymmetry is supported through the bond angles between C1-Al1-O1/C1-Al1-O2 and C1-Al1-N1/C1-Al1-N2 (Table 4.01).

Figure 4.06: Solid-state structures a) Al(7)Me, and b) Al(11)Me Ellipsoids are shown at the 30 % probability level, hydrogen atoms have been removed for clarity.
The X-ray crystallographically determined structures for Al(7)Me and Al(11)Me are depicted in figure 4.06, selected bond lengths and angles are given in table 4.01. Both structures adopted the geometry where the aluminium bound methyl was orientated cis to the -((CH₂)₂-) homopiperazine moiety. The complexes are five coordinate and adopt a distorted square pyramidal geometry {Al(7)Me; τ = 0.18, Al(11)Me; τ = 0.09}. The Al(11)Me structure was less distorted from the idealistic square pyramidal structure, presumably an artefact of the less sterically bulky ortho-phenoxy hydrogen substituents. The aluminium phenoxy bonds (Al1-O1, Al1-O2) and aluminium amine bonds (Al1-N1, Al1-N2) were significantly different for Al(7)Me, contrastingly the analogous bonds of Al(11)Me are statistically the same length. Both structures displayed significant variation between the C1-Al1-O1/C1-Al1-O2 and C1-Al1-N1/C1-Al1-N2 angles.

Figure 4.07: Solid-state space-filling structures showing van der Waals radii, a) Al(7)Me b) Al(8)Me (cis -((CH₂)₂-) c) Al(11)Me.
The two phenyl rings of Al(7,11)Me structures are both orientated away from the aluminium bound methyl moieties to a similar degree (Figure 4.07a,c). Whilst the Al(8)Me complex demonstrates a puckered orientation of the phenyl rings. This configuration is presumably a consequence of the sterically bulky ortho-t-Bu substituents, the puckered and steric nature is demonstrated by space filling diagrams based on van der Waals radii in figure 4.07. The aluminium metal centre is also appreciably contained by the coordinated substituents.

4.4 Computational Investigation

To investigate the two isomers for Al(8)Me, quantum mechanical calculations were performed using the ORCA electronic structure program. The crystallographically determined structures for Al(8)Me cis-(CH$_2$CH$_2$)-, and Al(8)Me cis-(CH$_2$CH$_2$CH$_2$)- were initially optimised via TightSCF conversion calculations. Initial calculations utilised the BP86 functional with RI approximation using the def2-svp basis set. The structures were further refined iteratively by the B3LYP functional with the RIJCOSX algorithm; firstly using the def2-svp basis set and finally the def2-TZVPP basis set. Empirical van der Waals corrections (VDW) were applied alongside COSMO solvent effects at infinite dielectric constant to more closely emulate solvated conditions. A 1.3 kcal mol$^{-1}$ energy difference between the structurally optimised final single point energies was observed, at this degree of computational accuracy this energy disparity is not considered significant. The Al(8)Me (cis -(CH$_2$CH$_2$)-) complex was the favourable conformation although it is possible to isolate both structures in a crystal environment, which is consistent with a small energy disparity.

4.5 Characterisation by NMR Spectroscopy

The aluminium homopiperazine salan complexes Al(6-9,11)Me, and Al(6-9,11)OBn were characterised by $^1$H and $^{13}$C{$_^1$H} NMR spectroscopy. Room temperature spectroscopy resulted in broad resonances in the CH$_2$ region of the Al(6-9,11)Me $^1$H NMR spectra. A $^1$H NMR spectrum for Al(8)Me is given in figure 4.08. The majority of CH$_2$ related resonances are shown in the truncated spectra of Al(8)Me where a distinctive sharpening of the resonances is observed.
upon cooling of the complex in solution (d-toluene). At high temperature it is not possible to distinguish between axial and equatorial protons for the CH$_2$ ring groups, due to the highly fluxional nature on the NMR timescale. Axial and equatorial CH$_2$ proton resonances become independent signals upon cooling (Figure 4.08), an artefact of conformation locking of the complexes under less thermally energetic conditions. Al(8)Me was characterised by X-ray crystallography as two geometric configurations, where the aluminium bound methyl was either cis to the -CH$_2$CH$_2$- or -CH$_2$CH$_2$CH$_2$- homopiperazine ring groups (Figure 4.05). The isomers isolated are dependent upon the crystallisation conditions. The presence of two conformations in the solution-state was an isolated case for the Al(8)Me crystals. Further synthetic attempts of Al(8)Me synthesis resulted in the formation of a single isomer, best represented by a single Al-Me proton resonance. The two isomers do not appear to interconvert upon heating in solution. A single isomer was characterised by NMR spectroscopy for complexes Al(7-9)Me, however Al(6)Me was isolated as both isomers due to two Al-Me resonances being observed.

![Figure 4.08: Variable temperature 1H NMR spectra showing the methylene region for Al(8)Me](image)

Benzyl alcohol derivatives Al(6-9,11)OBn of Al(6-9,11)Me were characterised by NMR spectroscopic methods. The complete disappearance of the aluminium bound methyl proton resonances required prolonged elevated temperature conditions and excess benzyl alcohol. Ambient conditions or stoichiometric
quantities of BnOH yielded mixtures of Al(6-9,11)OBn and Al(6-9,11)Me, unusual considering the high reactivity of aluminium methyl groups and the entropically favourable evolution of methane. A distinctive resonance at ~5 ppm was attributed to the CH₂ protons of an aluminium bound benzyloxy ligand. Stringent purification was required to ensure uncoordinated BnOH was removed from the compound. The complex Al(8)OBn (Figure 4.09) was significantly less fluxional at room temperature than the Al(8)Me complex. The aromatic region becomes more defined at reduced temperatures, overlap with solvent peaks complicated the analysis of this region.

Figure 4.09: ¹H NMR spectra for Al(8)OBn, Top 298 K, Bottom 233 K.

4.6 Investigation of the ROP of Cyclic-Esters

Prior aluminium piperazine salan complexes have been investigated for solution ROP of rac-lactide and were shown to be unsuccessful initiators.¹¹ Further solution ROP reactions of ε-caprolactone have been conducted and aluminium piperazine salan complexes were proven to be active initiators.¹¹-¹³ The ROP of the cyclic esters; rac-lactide, ε-caprolactone, and δ-valerolactone (Figure 4.10) by
aluminium homopiperazine salan initiators Al\(\text{6-9,11}\)OBn is herein reported. A focus upon the environmentally favourable solvent free ROP conditions was conducted to complement the prior literature solution ROP reported for similar structures.\(^{11-13}\) The initiators with coordinated benzyloxy derivatives \{Al\(\text{6-9,11}\)OBn\} were utilised in preference to the aluminium methyl analogues \{Al\(\text{6-9,11}\)Me\} to remove \textit{in-situ} co-initiator complications. The synthesis of the benzyloxy aluminium complexes Al\(\text{6-9,11}\)OBn from Al\(\text{6-9,11}\)Me was challenging, hence the assumption of rapid coordination and generation of the active alkoxide species \textit{in-situ} was not possible. Additionally these initiators were trialled for co-polymerisation reactions with the aforementioned cyclic-ester monomers.

\[
\begin{align*}
\text{ROP} & \quad \text{Polylactide} \\
\text{ROP} & \quad \text{Poly}(\varepsilon\text{-caprolactone}) \\
\text{ROP} & \quad \text{Poly}(\delta\text{-valerolactone})
\end{align*}
\]

\textbf{Figure 4.10}: Synthetic schemes depicting the ROP of lactide, \(\varepsilon\)-caprolactone, and \(\delta\)-valerolactone including their resulting polymers.

\subsection*{4.6.1 Investigation of the ROP of rac-lactide}

The aluminium alkyl initiators Al\(\text{6-9,11}\)Me were initially trialled in solution (toluene) at 80 °C, with benzyl alcohol as a co-initiator, for the ROP of \textit{rac}-lactide but no signs of the formation of polymer were observed. The low activity in solvent at 80 °C was thought to be linked to the difficulty of substituting a benzyl alcohol group into the aluminium coordination sphere, thus the formation the \textit{in-situ} initiator is restricted. This observation was extrapolated as an indication of the difficult coordination of a \textit{rac}-lactide monomer to the aluminium centre. The benzyloxy
aluminium complexes Al(6-9,11)OBn were investigated as initiators for the ROP of \textit{rac}-lactide in solvent free conditions at 130 °C. Respectable conversions were obtained under these conditions after 2 h, although Al(11)OBn resulted in a reduced conversion (Table 4.02). Molecular weights ($M_n$) were typically higher than expected for the formation of one PLA chain per metal centre; this is supposedly a product of low rate of initiation relative to the rate of propagation. The exception is Al(11)OBn which resulted in lower molecular weight PLA than expected, a consequence of reduced steric demands about the metal centre. Only moderate control over the PLA molecular weights ($M_n$) was observed with PDI values ranging between 1.08 – 1.42. The resulting PLA was slightly heterotactic ($P_r = 0.53 – 0.57$) with a stronger bias observed for initiators with \textit{ortho}-tBu substituents ($P_r = 0.57$).

<table>
<thead>
<tr>
<th></th>
<th>Time (hours)</th>
<th>Conv. (%)$^a$</th>
<th>$M_n^b$ (theo)</th>
<th>$M_n^c$</th>
<th>PDI$^c$</th>
<th>$P_r^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(6)OBn</td>
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<td>37750</td>
<td>42100</td>
<td>1.42</td>
<td>0.54</td>
</tr>
<tr>
<td>Al(7)OBn</td>
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<td>35150</td>
<td>56400</td>
<td>1.40</td>
<td>0.55</td>
</tr>
<tr>
<td>Al(8)OBn</td>
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<td>54400</td>
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<td>0.57</td>
</tr>
<tr>
<td>Al(9)OBn</td>
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<td>38150</td>
<td>58200</td>
<td>1.40</td>
<td>0.57</td>
</tr>
<tr>
<td>Al(11)OBn</td>
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<td>56</td>
<td>24300</td>
<td>16800</td>
<td>1.08</td>
<td>0.53</td>
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</table>

\textit{Table 4.02:} Solvent free ROP of \textit{rac}-lactide for Al(6-9,11)OBn at 130 °C in a 300:1 \textit{[rac-lactide]:[initiator]} ratio. $^a$ Conversion ascertained by $^1$H NMR spectroscopy. $^b$ Theoretical molecular weight calculated from conversion (Conv. $\times$ 300 $\times$ 144.13 + 108.14) (rounded to the nearest 50). $^c$ Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. $^d$ $P_r$ as calculated from $^1$H NMR homonuclear decoupled spectroscopy in CDCl$_3$.

### 4.6.2 Investigation of the ROP of $\varepsilon$-caprolactone

The ROP of $\varepsilon$-caprolactone was conducted in solvent free conditions at 130 °C, in a 300:1 $[\varepsilon$-caprolactone]:[initiator] ratio using the benzyloxy aluminium initiators \{Al(6-9,11)OBn\}. High conversions were obtained after 30 mins, with the exception of Al(9)OBn (Table 4.03). Conversion was calculated from the $^1$H NMR spectra methylene proton resonances H$_a$ (monomer) and H$_b$ (polymer) at 4.20 and 4.03 ppm respectively (Figure 4.11). The high relative activity when compared to \textit{rac}-lactide is consistent with literature which reported inactivity of similar piperazine
aluminium complexes towards lactide and high activity towards ε-caprolactone.\textsuperscript{11} The molecular weights ($M_n$) were consistent for high conversion polymers (Conv. > 90%), albeit higher then expected. This is indicative of a slow initiation step compared to the rate of propagation or not all of the aluminium centres initiate PCL chain growth. Al(11)OBn resulted in a lower molecular weight polymer, which was similarly observed for the ROP of rac-lactide investigation (See section 4.6.1). Similarly moderate molecular chain length control was observed with PDI values ranging from 1.15 – 1.63.

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Conv. (%)\textsuperscript{a}</th>
<th>$M_n^b$ (theo)</th>
<th>$M_n^c$</th>
<th>PDI\textsuperscript{c}</th>
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</thead>
<tbody>
<tr>
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<td>54100</td>
</tr>
<tr>
<td>Al(7)OBn</td>
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<td>32300</td>
<td>71900</td>
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<tr>
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<td>33300</td>
<td>73100</td>
</tr>
<tr>
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<td>10400</td>
<td>11400</td>
</tr>
<tr>
<td>Al(11)OBn</td>
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<td>83</td>
<td>28550</td>
<td>25800</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conversion ascertained by $^1$H NMR spectroscopy. \textsuperscript{b}Theoretical molecular weight calculated from conversion (Conv. × 300 × 114.14 + 108.14) (rounded to the nearest 50). \textsuperscript{c}Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor.

**Table 4.03:** Solvent free ROP of ε-caprolactone for Al(6-9,11)OBn at 130 °C in a 300:1 [ε-caprolactone]:[initiator] ratio.

**Figure 4.11:** $^1$H NMR spectra (CDCl$_3$) for the ROP conversion of ε-caprolactone to poly(ε-caprolactone) using the initiator Al(11)OBn.
4.6.3 Investigation of the ROP of δ-valerolactone

Homopiperazine salan aluminium benzylxy initiators were utilised for the ROP of δ-valerolactone in solvent free conditions at 130 °C, at a 300:1 [δ-valerolactone]:[initiator] ratio (Table 4.04). High conversion was obtained for the majority of initiators after 1 h with Al(9)OBn yielding lower conversion, similarly observed with caprolactone. Also Al(11)OBn resulted in a slightly lower conversion, an observation consistent with the ROP of rac-lactide and caprolactone. The conversions are calculated from the $^1$H NMR spectra methylene proton resonances H$_a$ (monomer) and H$_b$ (polymer) (Figure 4.12), 4.31 and 4.05 ppm respectively. The determined molecular weights ($M_n$) were consistent across Al(6-9)OBn initiators, the obtained molecular weight were somewhat consistent with one polymer chain being propagated by each metal centre. Similarly previously discussed ROP investigations of Al(11)OBn also resulted in lower than expected molecular weights. It was speculated that the lower steric demands of Al(11)OBn was allowing the propagation of more than one valerolactone chain. The molecular chain length distributions were moderately high with PDI values ranging between 1.12 – 1.77.

<table>
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<tr>
<th>Time (hours)</th>
<th>Conv. (%)$^a$</th>
<th>$M_n^b$ (theo)</th>
<th>$M_n^c$</th>
<th>PDI$^c$</th>
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<td>33000</td>
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<tr>
<td>Al(8)OBn</td>
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<td>88</td>
<td>26550</td>
<td>24800</td>
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<td>81</td>
<td>24450</td>
<td>16000</td>
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</table>

Table 4.04: Solvent free ROP of δ-valerolactone for Al(6-9,11)OBn at 130 °C in a 300:1 [δ-valerolactone]:[initiator] ratio. $^a$ Conversion ascertained by $^1$H NMR spectroscopy. $^b$ Theoretical molecular weight calculated from conversion (Conv. $\times$ 300 $\times$ 100.12 + 108.14) (rounded to the nearest 50). $^c$ Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor.
4.6.4 Investigation of co-polymerisations of cyclic-esters

Co-polymer investigations were trialled using these aluminium benzyloxy homopiperazine salan complexes as initiators Al(6-9,11)OBn. All ROP reactions were conducted in an inert atmosphere environment at 130 °C in solvent free conditions. Direct ROP attempts of rac-lactide/\(\varepsilon\)-caprolactone or rac-lactide/\(\delta\)-valerolactone mixes were not successful with no polymerisation being observed. The sequential addition of monomers to complete reactions led to high conversion of each sequential monomer given time for each monomer to polymerise. The insertion of a \(\varepsilon\)-caprolactone/\(\delta\)-valerolactone monomer into an Al-PLA linkage did not occur hence the sequential polymerisations starting with rac-lactide were not successful. It should be noted that the presence of un-reacted monomer from the prior step has a detrimental effect upon the subsequent ROP steps.

Sequential tri-block poly-esters were synthesised using Al(7-9)OBn initiators, the polymer sequence followed \(\varepsilon\)-caprolactone/\(\delta\)-valerolactone/rac-lactide. Each monomer was present in 100:1 ratio of [monomer]:[initiator] and the time allowed for each addition was 0.5 h/1 h/2 h to obtain high conversion for each subsequent step (Table 4.05). Al(8)OBn gave high conversion of each subsequent monomer, conversion was calculated from the \(^1\)H NMR spectra (CDCl\(_3\)). The conversion of
rac-lactide was calculated by direct comparison of the monomer/polymer methine resonances. The poly(ε-caprolactone), and poly(δ valerolactone) resonances (4.03 ppm and 4.05 ppm respectively) used for calculation of conversion overlap, the conversion was calculated from the monomer and polymer integrals with the assumption that the total amount of methylene (H_a/H_b) protons of each monomer were in a 50:50 ratio. Al(7)OBn resulted in good conversion of both ε-caprolactone and δ-valerolactone but not rac-lactide. Al(9)OBn was comparatively poorly active towards caprolactone and valerolactone this is followed within the tri-block polymerisation results. The ROP of rac-lactide still proceeded with Al(9)OBn initiator with no detrimental effect observed for the presence of ε-caprolactone and δ-valerolactone monomer. The tri-block polyester molecular weights (M_n) were consistent with the expected values through comparison with homopolymer ROP data (table 4.02, 4.03, 4.04). The molecular weight values are much higher than expected for 100:1 homopolymer conversions indicative of the formation of co-polymers. The GPC traces were also unimodal demonstrating the formation of co-polymers over multiple homopolymers.

<table>
<thead>
<tr>
<th></th>
<th>Time (hours)</th>
<th>Conv. (%)^a</th>
<th>M_n^b</th>
<th>PDI^b</th>
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<tr>
<td>Al(9)OBn</td>
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<td>88/43/64</td>
<td>29500</td>
<td>1.63</td>
</tr>
</tbody>
</table>

Table 4.05: Sequential solvent free ROP of ε-caprolactone/δ-valerolactone/rac-lactide for Al(7-9)OBn at 130 °C in a 100:100:1 [ε-caprolactone]:[δ-valerolactone]:[rac-lactide]:[initiator] ratio. ^a Conversion ascertained by 1H NMR spectroscopy. ^b Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor.

4.7 Conclusion

Aluminium methyl homopiperazine salan complexes Al(6-9,11)Me have been synthesised and characterised by NMR spectroscopy, X-ray crystallography, and CHN elemental analysis. X-ray crystallography indentified pseudo square based pyramidal monometallic structures for Al(7,8,11)Me. Two configurations were
identified for Al(8)Me one where the aluminium bound methyl was cis to the -(CH₂CH₂)- homopiperazine group, and one where the aluminium bound methyl was cis to the -(CH₂CH₂CH₂)- homopiperazine ring group. The majority of complexes were isolated where methyl was cis to the -(CH₂CH₂)- homopiperazine ring segment. Structural optimisation calculations were performed and revealed a slight preference for the Al(8)Me cis -(CH₂CH₂)- structure, with a final point energy difference of 1.3 kCal mol⁻¹. The complexes were typically identified in solution as a single isomer and were found to be structurally stable at higher temperatures.

Direct isolation of the commonly assumed in-situ aluminium benzyloxy complexes Al(6-9,11)OBn was achieved and their characterisation by NMR spectroscopy discussed. The Al(6-9,11)OBn complexes were shown to be highly active initiators for the production of homopolymers by a ROP mechanism for rac-lactide, ε-caprolactone, and δ-valerolactone. The ROP of the cyclic esters was conducted at 130 °C at a 300:1 [monomer]:[initiator] ratio in solvent free conditions. The ROP of rac-lactide achieved 56-88 % conversion after 2 h and resulted in predominantly atactic PLA. ε-Caprolactone attained 30-97 % conversion after 30 mins and δ-valerolactone attained 31-94 % conversion after 1 h. The molecular weights determined by GPC (THF) were typically higher than expected, presumably not all of the aluminium initiators were initiating a polymerisation. Investigations into co-polymer synthesis were conducted and the formation of sequential co-block polyesters was achieved, up to tri-block polyesters of poly(ε-caprolactone/δ-valerolactone/rac-lactide).

4.8 Future Work

Further derivatives of homopiperazine salan ligands could be synthesised with an emphasis of varying the electronic effect of the phenol rings using halide substituents. Investigating an 8 membered diamine ring bridging group is another interesting variation upon this ligand set. Further investigations into solution polymerisations could be conducted to elucidate the ROP mechanism. Indium has proved a promising candidate for the ROP of lactide. Indium is a promising metal for coordination to homo/piperazine salan ligands due to its relation to
aluminium. It would be interesting to compare the reactivity of indium piperazine salan complexes.

4.9 References

Chapter 5

5. Titanium (IV) and Aluminium (III) \textit{trans}-1,4-DACH Salen Complexes and Their Application for the ROP of Lactide.
5. Titanium (IV) and Aluminium (III) \textit{trans-1,4-DACH} Salen Complexes and Their Application for the ROP of Lactide.

5.1 Introduction

Aluminium imine bis(phenoxy) complexes have been investigated for the ring-opening-polymerisation (ROP) of lactide. Although active these initiators typically displayed low activity (see section 1.3.6).\textsuperscript{1-3} These ROP investigations resulted in a high degree of molecular weight control alongside the production of highly isotactic PLA from the ROP of \textit{rac}-lactide. Stereoselectivity observed for these complexes was retained under solvent free conditions for various aluminium imine bis(phenoxy) initiators. Imine mono(phenol) ligands have been coordinated to aluminium in monometallic structural motifs (Figure 5.01).\textsuperscript{4, 5} Solution polymerisations using these monometallic aluminium imine mono(phenoxy) initiators required forcing conditions to attain high conversion (70 °C/14 h, 100 °C/48 h). Only moderate molecular weight control was observed (PDI = 1.12 - 1.69) and predominately atactic lactide was reported from the ROP of \textit{rac}-lactide.\textsuperscript{4, 5} Depending upon the substituents isotactic enriched PLA was obtained, although a direct probability of racemic enchainment ($P_r$) was not reported a $^1$H NMR example was given showing slightly isotactic enriched PLA.\textsuperscript{5}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5_01.png}
\caption{Monometallic aluminium imine mono(phenoxy) complexes trialled for the ROP of lactide.\textsuperscript{4, 5}}
\end{figure}
Titanium imine bis(phenoxy) complexes (Figure 1.40, 1.41) have been utilised for the ROP of rac-lactide, they were proven to be active initiators and resulted in a high degree molecular weight control. In comparison to the aluminium analogues atactic PLA was produced with perhaps a slight heterotactic bias. Imine mono(phenol) ligands have been coordinated to group 4 metals resulting in monometallic complexes with two chelating ligands (Figure 1.39). These initiators resulted in a moderate heterotactic bias for zirconium based catalysts from rac-lactide. Similar monometallic titanium imine mono(phenoxy) complexes, containing coordinating chloride ligands have been reported as initiators for the ROP of lactide. Despite the lack of an alkoxide initiator group these titanium imine mono(phenoxy) complexes gave moderate molecular weight control and yielded predominately atactic lactide.

1,2-Diaminocyclohexane (1,2-DACH) bridged bis(phenol) ligands have been complexed to group 4 metals and aluminium, these complexes have been utilised for the ROP of lactide (Figure 5.02). Titanium 1,2-DACH bis(phenoxy) complexes were active for the ROP of rac-lactide albeit these initiators revealed low activity. They gave a good degree of molecular weight control but no significant stereoselectivity was reported. Aluminium 1,2-DACH bis(phenoxy) complexes were reported as poorly active initiators for the ROP of lactide. In contrast to their titanium analogues they resulted in the production of highly isotactic PLA. While 1,2-DACH bis(phenoxy) complexes have been synthesised and investigated as initiators for the ROP of lactide 1,4-DACH bis(phenoxy) complexes have not been previously synthesised. The following chapter discusses the synthesis and reactivity of various 1,4-DACH bis(phenoxy) complexes.

Figure 5.02: Previous DACH based complexes used for the ROP of lactide, Left - 1,2-DACH salen titanium complex, Right - 1,2-DACH salen aluminium complex.
5.2 Synthesis of *trans*-1,4-DACH Salen Ligands

*trans*-1,4-Diaminocyclohexane (1,4-DACH) salen ligands \{((16-18)H_2)\} were synthesised *via* a condensation reaction of *trans*-1,4-DACH and two equivalents of 3,5-substituted salicylaldehyde (Figure 5.03). The ligands \{((16-18)H_2)\} were isolated as pure solid compounds from the reaction solvent (MeOH), at which point they were filtered and further washed (MeOH). The resulting ligands were characterised by $^1$H/$^{13}$C\{$^1$H\} NMR spectroscopy and high resolution ESI-TOF mass spectrometry. *trans*-1,4-DACH and 3,5-$^1$Bu-salicylaldehyde were commercially obtained while 3-$^1$Bu-5-Me-salicylaldehyde and 3-trityl-5-Me-salicylaldehyde were synthesised before use. 3-$^1$Bu-5-Me-salicylaldehyde was synthesised by a less moisture sensitive deviation than reported in the literature.\(^{12}\) 3-trityl-5-Me-phenol was first synthesised by literature methods and then converted to 3-trityl-5-Me-salicylaldehyde *via* a deviation of the Duff formylation reaction.\(^{13}\)

![Diagram of synthetic preparation of *trans*-1,4-DACH salen ligands](image)

**Figure 5.03:** Scheme for the synthetic preparation of *trans*-1,4-DACH salen ligands.
5.3 *trans*-1,4-DACH Titanium Isopropoxide Complexes

5.3.1 Synthesis

Initial attempts to synthesise *trans*-1,4-DACH salen complexes using (16-18)H₂ ligands and Ti(OiPr)₄ yielded different products dependent upon the ortho-phenol substituents. Following prior titanium work with hindered salan ligands (Chapter 2), the (16-18)H₂ ligands were reacted with two equivalents of Ti(OiPr)₄ to yield a bimetallic complex (Figure 5.04). The complexation of less sterically hindered *ortho*-phenol substituted ligands (R₁ = Me, H) was attempted but these ligands resulted in insoluble titanium complexes. It was speculated the formation of polymeric material was occurring. Recrystallisation attempts from hexane or hexane/toluene mixes yielded crystals of Ti₂(16-18)(OiPr)₆ suitable for X-ray crystallographic studies. Ti₂(16-18)(OiPr)₆ were all obtained as pure products after recrystallisation and they were characterised by $¹H$/¹³C{¹H} NMR spectroscopy and CHN analysis.
5.3.2 Solid-state characterisation by X-ray crystallography

Crystals suitable for X-ray diffraction were obtained for Ti$_2$(16-18)(O$^\text{t}$Pr)$_6$, a solid-state structure is given for Ti$_2$(16)(O$^\text{t}$Pr)$_6$ in figure 5.05. These Ti$_2$(16-18)(O$^\text{t}$Pr)$_6$ structures contained an inversion centre hence both titanium metal centres are in equivalent crystallographic environments. The DACH backbone adopts the favourable chair configuration. The titanium metals are five coordinate with three isopropoxide groups, and a chelating amine/phenoxy ligand. The titanium centres adopt distorted trigonal bipyramidal geometries where the imine and a single isopropoxide moiety assume axial positions.

![Figure 5.05: Solid-state structure for Ti$_2$(16)(O$^\text{t}$Pr)$_6$. Ellipsoids are shown at the 30 % probability level, hydrogen atoms and isopropoxide –CH$_3$ moieties have been removed for clarity.](image)

Selected bond lengths and angles for Ti$_2$(16-18)(O$^\text{t}$Pr)$_6$ are given in table 5.01. The phenoxy-titanium (Ti1-O2) bond lengths are slightly longer \{1.8932(17) - 1.901(2) Å\} than previously reported Ti$_2$(2-5,8,12,13)(O$^\text{t}$Pr)$_6$ complexes \{1.8622(17) - 1.8883(17) Å\} (see section 2.4.2).$^{14}$ The imine N1-Ti1 bond \{2.224(2) - 2.239(2) Å\} presented shorter lengths than similar amine N1-Ti1 bonds \{2.3499(18) - 2.3567(18) Å\}.$^{14}$ The shorter bond lengths are indicative of the stronger coordination of the imine justifying the formation of polymeric complexes when the ortho position is less sterically hindered. The equatorial substituents are distorted towards the axial nitrogen \{80.76(9) - 84.33(8) °\}. The bulky trityl (-CPh$_3$)
group in the ortho-phenoxy position causes the axial isopropoxide to converge towards 180° (179.48(8)°) in comparison to the same angle with t-Bu ortho-phenoxy groups {174.29(8) - 174.63(10)°}. The equatorial isopropoxide groups of trityl substituted complexes are further slightly distorted towards the axial nitrogen {81.43(8) - 81.74(8)°} in comparison to complexes containing t-Bu ortho-phenoxy groups {83.58(8) - 84.33(8)°}.

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<tr>
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<th>Ti$_2$(16)(O$\text{Pr}$)$_6$</th>
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</table>

Table 5.01: Selected bond lengths (Å) and angles (°) for LM$_2$ titanium salen complexes {Ti$_2$(16-18)(O$\text{Pr}$)$_6$}, as determined by X-ray crystallography.

5.3.3 Solution characterisation by NMR spectroscopy

Ti$_2$(16-18)(O$\text{Pr}$)$_6$ were characterised by $^1$H and $^{13}$C{$^1$H} NMR spectroscopy. The $^1$H NMR spectrum for Ti$_2$(17)(O$\text{Pr}$)$_6$ is given in figure 5.06. This spectrum is consistent with the $^1$H NMR spectra obtained for Ti$_2$(16,18)(O$\text{Pr}$)$_6$ and the solid-state structures. The fact that no uncoordinated ligand resonances were observed indicated full coordination of the ligands to titanium. The presence of six isopropoxide methine resonances (4.91 ppm) and corresponding CH$_3$ isopropoxide resonances (1.27 ppm) confirms the coordination of two -Ti(O$\text{Pr}$)$_3$ groups to a single ligand, when integrated relative to one 17H$_2$ ligand. The CH$_2$ groups are in equivalent environments which is best demonstrated by a single resonance (32.5 ppm) in the
$^{13}$C-$^1$H NMR spectra. Axial and equatorial CH$_2$ protons gave rise to two separate resonances (1.58, 2.25 ppm) indicating a locked chair configuration where ring flipping is significantly hindered.

![Figure 5.06: $^1$H NMR spectrum for Ti$_2$(17)(O'Pr)$_6$ in CDCl$_3$ at 298 K.](image)

5.4 *trans*-1,4-DACH Aluminium Methyl Complexes

5.4.1 Synthesis

![Figure 5.07: Scheme depicting the synthesis of aluminium methyl *trans*-1,4-DACH salen complexes $\{Al_2(16-18)Me_4\}$](image)
Similarly *trans*-1,4-DACH salen ligands \{((16-18)H_2)\} were reacted with a 2M AlMe_3 solution in a 2:1 ratio of metal to ligand (Figure 5.07). The product was isolated by recrystallisation to yield pure Al_2(16-18)Me_4 complexes. The isolated Al_2(16-18)Me_4 complexes contained two aluminium metal centres where each was coordinated to a single ligand phenoxy group. Similar synthetic attempts under varying conditions were conducted with ligands containing less steric bulk about the ortho-phenol position but attempts resulted in undeterminable compounds. These complexes with less sterically hindered ligands yielded insoluble materials, additionally in some cases temperature and time caused more insoluble material to be produced. It was speculated that the possible formation of polymeric conglomerates of complexes and ligands was occurring. The Al_2(16-18)Me_4 complexes were characterised by ^1H/^13C{^1H} NMR spectroscopy and CHN analysis. Recrystallisation attempts resulted in crystals of Al_2(16)Me_4 and Al_2(17)Me_4 which were suitable for X-ray diffraction characterisation.

5.4.2 Solid-state characterisation by X-ray crystallography

![Image](image.png)

**Figure 5.08**: Solid-state structure for Al_2(16)Me_4. Ellipsoids are shown at the 30 % probability level, hydrogen atoms have been removed for clarity.

Recrystallisation of the aluminium *trans*-1,4-DACH salen complexes resulted in suitable crystals of Al_2(16,17)Me_4 for X-ray diffraction studies. The structure for Al_2(16)Me_4 is given in figure 5.08. The aluminium metal centres are four coordinate and only bound to a single phenoxy and a single imine of the *trans*-1,4-DACH salen
ligand, the other two coordination sites are occupied by methyl groups. The carbon aluminium bonds are similar in length to each other and are also of similar lengths to prior aluminium carbon bonds (see section 4.3) (Table 5.02).\textsuperscript{15-17} Aluminium nitrogen imine bonds \{Al1-N1 = 1.979(4) - 1.9783(12) Å\} are shorter, as expected, than previously discussed aluminium nitrogen amine bonds \{2.07(2) - 2.188(7) Å\} (see 4.3).\textsuperscript{15} The aluminium metal centres adopt pseudo tetrahedral geometries. Interestingly the nitrogen-aluminium-carbon angles \{N1-Al1-C1/C2\} are inequivalent within each structure despite their presumed similarity. The N1-Al1-C1 and N1-Al-C2 angles are also significantly different between the crystal structures of Al\textsubscript{2}(16)Me\textsubscript{4} and Al\textsubscript{2}(17)Me\textsubscript{4}. The N1-Al1-O1 chelate angle \{94.39(5) - 94.69(14) °\} significantly deviates from the ideal tetrahedral angle of 109 °.

\begin{table}[h]
\centering
\begin{tabular}{lcc}
 & Al\textsubscript{2}(16)Me\textsubscript{4} & Al\textsubscript{2}(17)Me\textsubscript{4} \\
Al1-C1 & 1.946(5) & 1.9497(17) \\
Al1-C2 & 1.952(5) & 1.9637(17) \\
Al1-O1 & 1.763(3) & 1.7684(11) \\
Al1-N1 & 1.979(4) & 1.9783(12) \\
N1-Al1-C1 & 108.73(18) & 109.05(7) \\
N1-Al1-C2 & 115.00(18) & 113.43(7) \\
N1-Al1-O1 & 94.69(14) & 94.39(5) \\
\end{tabular}
\caption{Selected bond lengths (Å) and angles (°) for LM\textsubscript{2} aluminium salen complexes \{Al\textsubscript{2}(16-17)Me\textsubscript{4}\}, as determined by X-ray crystallography.}
\end{table}

5.4.3 Solution characterisation by NMR spectroscopy

Al\textsubscript{2}(16-18)Me\textsubscript{4} were characterised by \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectroscopy. The \textsuperscript{1}H and \textsuperscript{13}C\{\textsuperscript{1}H\} NMR spectra were consistent with the solid-state structures determined by X-ray diffraction. The \textsuperscript{1}H NMR spectrum for Al\textsubscript{2}(17)Me\textsubscript{4} is given in figure 5.09, the NMR spectra were consistent throughout the Al\textsubscript{2}(16-18)Me\textsubscript{4} complexes. No ligand resonances were observed, confirming the full coordination of the (16-18)H\textsubscript{2} ligands. Twelve shielded aluminium bound methyl resonances (-0.19 ppm) were present, relative to a single ligand (17H\textsubscript{2}), confirming four
aluminium bound methyl groups (Figure 5.09). The DACH ring CH$_2$ protons were located in a slightly broad resonance region at ~1.6 ppm, this region coincided with the 1Bu-phenoxy substituent resonance at 1.65 ppm. The imine CH resonance and two phenoxy protons resonances also coincided at 7.40 ppm.

**Figure 5.09:** $^1$H NMR spectrum for [Al$_2$(17)Me$_4$] in d$_8$-toluene at 298 K
5.5 Attempts to Coordinate trans-1,4-DACH Salen Ligands to Zirconium and Zinc.

5.5.1 Synthesis

The complexation of \((16-18)\text{H}_2\) to diethyl zinc was attempted and coordination occurred and various stoichiometries were investigated. Partial success was achieved with the complexation of \((16-18)\text{H}_2\) with a two equivalence of dimethyl zinc. The reaction of \(17\text{H}_2\) with dimethyl zinc and purification by recrystallisation resulted in a mixture of zinc complexes. Exposure of the dimethyl zinc and \(17\text{H}_2\) ligand products to THF prior to recrystallisation attempts from toluene and hexane yielded crystals of \(\text{Zn}_2(17)\text{Me}_2(\text{THF})_2\) suitable for X-ray diffraction studies (Figure 5.10). Although isolated as individual crystals the \(^1\text{H}\) NMR spectrum revealed broad resonances at 298 K. \(^1\text{H}\) NMR spectroscopy was inconclusive and CHN elemental analysis significantly deviated from the calculated values. Further attempts to synthesise \(\text{Zn}_2(16,18)\text{Me}_4\) complexes either resulted in the production of a plethora of species identified by \(^1\text{H}\) NMR spectroscopy or highly soluble products which could not be purified from common solvents. Attempts at the formation of zinc complexes using less sterically bulky ligands about the ortho-phenol position (\(R_1 = \text{Me, H}\)) were troublesome, typically resulting in insoluble material.
Attempts to synthesise LM$_2$ type structures using Zr(O'Pr)$_4$.HO'Pr and (16-18)H$_2$ were unsuccessful. The resulting complexes were typically insoluble, a few cases of soluble complexes were isolated but the solubility of the complexes changed with time or heating. The zirconium products were indeterminate and any soluble product was presumed unstable in solution making analysis difficult. We speculated that formation of multiple products, where the increased size of the zirconium metal centre compared to titanium allows the coordination of more than one ligand. Furthermore zirconium complexes have been shown to bridge via phenoxy or isoproploxide groups (See section 3.2).

5.5.2 Solid-state characterisation by X-ray crystallography

![Solid-state structure for Zn$_2$(17)Me$_2$(THF)$_2$. Ellipsoids are shown at the 30 % probability level, hydrogen atoms have been removed for clarity.](image)

Zn$_2$(17)Me$_2$(THF)$_2$ was isolated as crystals and determined by X-ray diffraction (Figure 5.11), selected bond lengths (Å) and angles (°) are given in table 5.03. Similar zinc complexes containing one phenoxy and one imine have been characterised by X-ray crystallography.$^{18-20}$ Comparison to the earliest reported imine phenoxy zinc complex showed similar Zn-C bonds {1.965(2) Å} and Zn-N$_{\text{imine}}$ bonds {2.051(2) Å}$^{20}$ The zinc centres within Zn$_2$(17)Me$_2$(THF)$_2$ are four coordinate; bound to an alkyl, phenoxy oxygen, imine nitrogen and a THF oxygen. As expected the THF Zn1-O2 bond {2.2029(15) Å} is significantly longer then the phenoxy Zn1-O1 bond {1.9312(13) Å}. The zinc centres adopt a pseudo tetrahedral
structure, where the degree of distortion is represented by the N1-Zn1-C1 angle \{131.14(9)°\}.

<table>
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<th>Zn2(17)Me₂,(THF)₂</th>
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<td>N1-Zn1-O2</td>
<td>93.11(6)</td>
</tr>
</tbody>
</table>

Table 5.02: Selected bond lengths (Å) and angles (°) for the zinc salen complex \{Zn2(17)Me₂,(THF)₂\}, as determined by X-ray crystallography.

5.6 Ring-Opening-Polymerisation of Lactide

Ti₂(16-18)OPr₆ and Al₂(16-18)Me₄ were trialled as initiators for the ROP of rac-lactide. The titanium initiators \{Ti₂(16-18)OPr₆\} were investigated for the ROP of rac-lactide in toluene and solvent free conditions. The aluminium initiators were investigated for the solvent ROP of rac-lactide, benzyl alcohol was added as a co-initiator and its effect at different ratios was studied. Conversions were calculated by ¹H NMR spectroscopy by comparison of the monomer and polymer methine regions. Molecular weights \(M_n\) and PDI values were obtained from gel permeation chromatography (GPC). Stereoselectivity was calculated from homonuclear decoupled ¹H NMR spectroscopy and the probability of racemic enchainment was calculated by Bernoullian statistics.²¹

5.6.1 Titanium and aluminium initiators for the solution ROP of rac-lactide

Titanium and aluminium 1,4-DACH salen complexes \{Ti₂(16-18)OPr₆, Al₂(16-18)Me₄\} were trialled for the ROP of rac-lactide. The ROP using Ti₂(16-18)OPr₆ complexes was investigated at 80 °C in toluene at 100:1 [rac-lactide]:[initiator] ratio. The aluminium initiators utilised conditions of 80 °C in toluene, benzyl alcohol was added in-situ to promote the ROP reaction. The polymerisation data is given in table 5.04.
<table>
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<tr>
<th>Ratio&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>Conv. (%)&lt;sup&gt;b&lt;/sup&gt;</th>
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<th></th>
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<td>6750</td>
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Table 5.04: Solution ROP of rac-lactide for Ti<sub>2</sub>(16-18)(O<sub>3</sub>Pr)₆ in 10 ml of toluene at 80 °.<sup>a</sup> Ratio of [rac-lactide]:[initiator]:[benzyl alcohol].<sup>b</sup> Conversion ascertained by <sup>1</sup>H NMR spectroscopy. Theoretical molecular weight calculated from conversion (Ti = Conv. × 100/2 × 144.13 + 60.10) (Al = Conv. × 100/[co-initiator ratio] × 144.13 + 108.14) (rounded to the nearest 50).<sup>c</sup> Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor.<sup>d</sup> <sup>1</sup>H NMR homonuclear decoupled spectroscopy in CDCl₃.<sup>e</sup> P<sub>r</sub> as calculated from <sup>1</sup>H NMR homonuclear decoupled spectroscopy in CDCl₃.<sup>f</sup>

The titanium initiators Ti<sub>2</sub>(16-18)(O<sub>3</sub>Pr)₆ resulted in high conversion after 24 h. Slightly lower molecular weights than expected were obtained which was attributed to multiple initiating isopropoxide groups per metal centre. Moderate chain length distributions were observed (PDI = 1.32 -1.50), this was also attributed to the potential to initiate multiple PLA chains per metal centre.

High conversions were obtained after 24 h when the aluminium initiators {Al<sub>2</sub>(16-18)Me<sub>4</sub>} were utilised. Molecular weight distributions were typically low (PDI = 1.08 – 1.27) and the molecular weights were dependent upon the ratio of benzyl alcohol utilised, this observation is indicative of an immortal polymerisation system. All the aluminium initiators {Al<sub>2</sub>(16-18)Me<sub>4</sub>} resulted in isotactically biased PLA (P<sub>r</sub> = 0.35 – 0.43), a stronger degree of stereocontrol was found for Al<sub>2</sub>(17)Me<sub>4</sub> (P<sub>r</sub> = 0.35) independent of the amount of benzyl alcohol co-initiator. MALDI-TOF mass spectrometry of PLA initiated by Al<sub>2</sub>(16)Me<sub>4</sub> with eight equivalents of benzyl alcohol was performed (Figure 5.12). The unit spacing between peaks is ~72 g mol⁻¹.
indicating transesterification reactions. Benzyl alcohol was identified as the end group supporting a chain exchange mechanism.

Figure 5.12: MALDI-TOF mass spectra (ionised with Na⁺) of PLA produced using initiator Al₂(16)Me₄, at 80°C after 24 h at 100:1:8 [rac-lactide]:[initiator]:[benzyl alcohol] ratio.

### 5.6.2 Titanium initiators for the solvent free ROP of rac-lactide

Ti₂(16-18)OιPr₆ were trialled for the ROP of rac-lactide in solvent free conditions of 130 °C at a 300:1 [rac-lactide]:[Initiator] ratio. The aluminium analogues {Al₂(16-18)Me₄} were not investigated under these condition due to complexities involved with co-initiator addition. High conversion of rac-lactide to PLA was achieved for Ti₂(16-18)OιPr₆ initiators before methanol quenching after 1 h (Table 5.05). The molecular weights ($M_n$) were lower than the theoretical derived molecular weights ($M_n$ (theo)), higher PDI values (PDI = 1.34 - 1.74) than the analogous solvated polymerisations were obtained. The high PDI and low $M_n$ values were credited to multiple initiating isopropoxide groups per metal centre.
Table 5.05: Solvent free ROP of rac-lactide for Ti_{2}(16-18)OPr\textsubscript{6} at 130 °C in a 300:1 [rac-lactide]:[initiator] ratio. \(^a\) Conversion ascertained by \(^1\)H NMR spectroscopy. \(^b\) Theoretical molecular weight calculated from conversion (Conv. \times 300/2 \times 144.13 + 60.10) (rounded to the nearest 50). \(^c\) Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. \(^d\) \(P_r\) as calculated from \(^1\)H NMR homonuclear decoupled spectroscopy in CDCl\(_3\).

5.7 Kinetic Studies of the Ring-Opening-Polymerisation of Lactide

The apparent rate of propagation (\(k_{app}\)) was determined by NMR spectroscopy scale ROP of lactide experiments using Al\(_2\)(16,17)Me\(_4\) initiators with two equivalence of benzyl alcohol as a co-initiator. Both rac-lactide and L-lactide were investigated to quantitatively indentify any rate enhancement and stereoselective preferences of these isotactic biased initiators. The ROP reactions were performed in an NMR tube using 50 mg of lactide in 0.6 ml of d\(_8\)-toluene at 80 °C, the initiators \{Al\(_2\)(16,17)Me\(_4\)\} were in a 100:1:2 ratio of [lactide]:[initiator]:[benzyl alcohol]. By plotting pseudo first order graphs of ln([LA]\(_0\)/[LA]\(_t\)) against time the slope of the graph is equal to the apparent first order rate constant (\(k_{app}\)) \{Figure 5.13 = Al\(_2\)(16)Me\(_4\), Figure 5.14 = Al\(_2\)(17)Me\(_4\)\}.

Table 5.06: \(k_{app}\) values and \(R^2\) values for ROP of rac-lactide and L-lactide by Al\(_2\)(16-17)Me\(_4\) initiators.
Figure 5.13 Pseudo first order plots for the ROP of rac-lactide (Red) and L-lactide (Blue) by Al$_2$(16)Me$_4$. For each case 50 mg of lactide was dissolved in 0.6 ml of d$_8$-touene at 80 °C at 100:1:2 [rac-lactide]:[initiator]:[benzyl alcohol] ratio.

The pseudo first order plots for the ROP of rac-lactide and L-lactide data were truncated as the rate did not equilibrate until ~200 mins (Figure 5.13, figure 5.14). Table 5.06 gives the $k_{app}$ rates for rac-lactide and L-lactide using Al$_2$(16,17)Me$_4$ as the initiators. No significant difference between the $k_{app}$ values for L-lactide and rac-lactide was observed using Al$_2$(16)Me$_4$ initiator. Al$_2$(17)Me$_4$ revealed an approximate 70 % increase in apparent rate ($k_{app}$) towards L-lactide over rac-lactide. Al$_2$(17)Me$_4$ resulted in a much larger $k_{app}$ difference between the ROP of L-lactide and rac-lactide than Al$_2$(16)Me$_4$ (Table 5.06). This is consistent with the greater stereoselectivity observed for Al$_2$(17)Me$_4$ ($P_r = 0.35$) over Al$_2$(16)Me$_4$ ($P_r = 0.42$) (Table 5.04). The cause of the enhanced stereoselectivity upon substitution of the para-phenoxy subsistent is unresolved but the para-positioning is indicative of an electronic effect. It should be noted the N1-Al1-C1/C2 angles showed variance between the two structures Al$_2$(16,17)Me$_4$ indicating the likely lactide coordination sites upon the aluminium metal are not equivalent between the structures (Table 5.02).
**Figure 5.14:** Pseudo first order plots for the ROP of rac-lactide (Red) and L-lactide (Blue) by Al$_2$(17)Me$_4$. For each case 50 mg of lactide was dissolved in 0.6 ml of d$_8$-toluene at 80 °C at 100:1:2 [rac-lactide]:[initiator]:[benzyl alcohol] ratio.

### 5.8 Conclusion

The synthesis of novel *trans*-1,4-DACH salen complexes \{Ti$_2$(16-18)(O^Pr)$_6$, Al$_2$(16-18)Me$_4$\} is reported herein with supporting characterisation by $^1$H/$^1$H/$^1$C{$^1$H} NMR spectroscopy and CHN analysis. Ti$_2$(16-18)(O^Pr)$_6$ and Al$_2$(16,17)Me$_4$ were isolated as crystals and their structures determined by X-ray diffraction studies. Both metals were shown to coordinate to the ligands in a 2:1 metal-to-ligand ratio. The attempted synthesis of derivatives with ligands containing less sterically bulky groups (H, Me, or Cl) in the *ortho* position of the phenol rings resulted in highly insoluble complexes. The synthesis of various zirconium *trans*-1,4-DACH salen complexes was unsuccessful. The complexation of 17H$_2$ to ZnMe$_2$ resulted in the formation of Zn$_2$(17)Me$_4$(THF)$_2$ as determined by X-ray crystallography, further analysis did not confirm this species as a pure bulk material. Attempts to synthesise further Zn(II) *trans*-1,4-DACH salen complexes with (16,18)H$_2$ were unsuccessful.

The titanium complexes \{Ti$_2$(16-18)(O^Pr)$_6$\} were investigated for the ROP of rac-lactide under solvent free conditions at 130 °C in a 300:1 [rac-lactide]:[initiator] ratio. Ti$_2$(16-18)(O^Pr)$_6$ and Al$_2$(16,17)Me$_4$ were trialled for the ROP of rac-lactide at 80 °C in toluene at a 100:1 [rac-lactide]:[initiator] ratio.
Two equivalents of benzyl alcohol were added to initiate the ROP of *rac*-lactide using \( \text{Al}_2(16-18)\text{Me}_4 \). Both aluminium \( \{\text{Al}_2(16-18)\text{Me}_4\} \) and titanium \( \{\text{Ti}_2(16-18)(\text{O}^\text{Pr})_6\} \) initiators attained high conversion after 24 h. Moderate chain length control is observed for these initiators with lower molecular weight PLA being obtained due to multiple initiation sites per titanium metal centre. The aluminium initiators \( \text{Al}_2(16-18)\text{Me}_4 \) display some isotactic stereoselectivity for the ROP of *rac*-lactide, where \( \text{Al}_2(17)\text{Me}_4 \) is the most selective \( (P_r = 0.35) \). Comparative apparent rate constants \( (k_{\text{app}}) \) for the ROP of *rac*-lactide and *L*-lactide are determined by \(^1\)H NMR spectroscopy and \( \text{Al}_2(17)\text{Me}_4 \) is 70 % more active towards *L*-lactide than *rac*-lactide, which is consistent with a chain-end control mechanism. The isotactic bias observed is dependent upon the *ortho/para*-phenoxy substituents. Altering the *para* substitent to a \(^t\)Bu has a detrimental effect on the isotactic stereoselectivity observed, this was speculatively attributed to electronic variations. The addition of excess benzyl alcohol to the ROP of *rac*-lactide by \( \text{Al}_2(16,17)\text{Me}_4 \) proportionally reduces the resulting PLA molecular weights without loss of stereoselectivity. This is indicative of an immortal polymerisation system where a chain-end exchange mechanism is in operation.\(^{22}\)

**5.9 Future Work**

Smaller *ortho*-phenol substituents upon the *trans*-1,4-DACH salen ligands resulted in insoluble material after complexation to titanium or aluminium. Further work could be conducted to ascertain the structure of these complexes through further synthetic attempts and solution trails, such as monitoring the reaction via NMR spectroscopy. Solid-state characterisation techniques could also be used to identify the compounds. Further work preparing zinc complexes could be conducted in an attempt to isolate more complexes as pure material and investigate these for the ROP of cyclic esters. Attempts with other metals such as zirconium, hafnium and indium could be conducted to expand the library of this series of initiators.
5.10 References

Chapter 6

6. Aluminium *trans*-1,2-DACH Salalen Complexes and Their Application for the ROP of *rac*-Lactide
6. Aluminium *trans*-1,2-DACH Salalen Complexes and Their Application for the ROP of *rac*-Lactide

6.1 Introduction

As discussed in chapter 1.3.6 imine and amine linked bis(phenoxy) aluminium complexes have been widely investigated for the ROP of lactide.\textsuperscript{1-3} Aluminium imine bis(phenoxy) complexes are some of the most selective initiators for isotactic PLA. The aluminium \textit{R}-(+)-1,1’-binaphthyl-2,2’-diamine linked bis(phenoxy) complex was reported by Spassky \textit{et al}. and is one of the earliest examples of an aluminium imine bis(phenoxy) complex which resulted in isotactic stereoselectivity for the ROP of \textit{rac}-lactide.\textsuperscript{4} This was preceded by further aluminium salen bis(phenoxy) initiators, notably; alkane linked salen bis(phenoxy) complexes by Nomura \textit{et al}.\textsuperscript{5, 6} and 1,2-diaminocyclohexane (1,2-DACH) linked salen bis(phenoxy) complexes by Fiejen \textit{et al}.\textsuperscript{7, 8}, which both result in isotactic PLA from \textit{rac}-lactide.

Related amine bis(phenoxy) aluminium (aluminium salan) complexes were synthesised by Gibson \textit{et al}.\textsuperscript{9} who showed the stereoselectivity of such complexes could be inverted by changing the phenoxy substituents, where Me substituents gave isotactic biased PLA and Cl substituents resulted in heterotactic PLA. DACH linked salan bisphenoxy aluminium complexes were also synthesised by Fiejen \textit{et al}.\textsuperscript{10} and demonstrated high isotactic control. This has led to interest in salalen systems which contain both an imine phenol linked to an amine phenol.\textsuperscript{11} The most pertinent study of an aluminium system of this type utilised for the ROP of \textit{rac}-lactide was reported by Jones \textit{et al}.\textsuperscript{11} Only the imine phenol substituents were varied in the previous study and PLA stereoselectivity was predominately heterotactic biased. Investigation into varying the alkyl group on the nitrogen was conducted to reveal that the stereoselectivity bias could be inverted. Herein similar salalen aluminium complexes are reported using a \textit{trans}-1,2-DACH linking group. The \textit{trans}-1,2-DACH linked salen bis(phenoxy) complexes by Fiejen \textit{et al} produced highly isotactic PLA.\textsuperscript{7, 8} It was anticipated that the more ridged and chiral DACH would form strongly defined initiator structures and induce stereocontrol. Additionally, investigation into the effect of phenol substituents of both the imine phenol and amine phenol groups was
conducted with respect to steric bulk and electronic effects. Kol et al. reported the use of salalen titanium complexes for the selective polymerization of 1-hexene and propylene. Prior aluminium DACH salalen complexes have been reported in the literature for the enantioselective hydrophosphonylation of aldehydes and aldihmes. Katsuki et al. was the first to report the enantioselective oxidation of sulphides by aluminium salalen complexes and has demonstrated high enantioselectivity in various systems. The same complexes were shown to be active for the oxidation of cyclic dithioacetals and afforded high enantioselectivity alongside high diastereoselectivity. Although their catalytic activity was studied in detail the aluminium salalen structural aspects and coordinated N-methyl chirality are discussed to a lesser degree by Katsuki and Saito.

6.2 Synthesis of trans-1,2-DACH Salalen Ligands

The ligand synthesis shown in figure 6.01 is an adaptation of the procedures used by Katsuki et al. The ligands were synthesised from rac-1,2-trans-DACH which was first protected with a Boc group and the mono-boc-protected rac-1,2-trans-DACH was isolated by acid/base extractions. The mono-boc-1,2-trans-DACH was reacted with a selected salicylaldehyde by an imine condensation reaction, which was then reduced. The boc-protected half salans \{(19-21)HBoc\} were then synthesised by reductive methylation and the crude mixture was analysed by NMR spectroscopy. The compound was then deprotected with acid and reacted with a second substituted salicylaldehyde via an imine condensation to produce the pure trans-1,2-DACH salalen ligands \{(22-30)H2\}. All of the salalen ligands shown in figure 6.01 \{(22-30)H2\} were isolated and characterised by ^1H/^{13}C\{^1H\} NMR spectroscopy, and high resolution ESI-TOF mass spectrometry. This method allows independent variation of the salan phenol substituents and the salen phenol substituents. Chirally resolved \((R,R)-1,2\)-DACH was used for the synthesis of a chiral salalen ligand \((R,R-22)H2\), by the same methodology. The steric and electronic effects of the phenol substituents were upon the salan and salen sections were investigated and consequently their effect upon the ROP of rac-lactide can be probed in detail.
Figure 6.01: Reaction pathway detailing the synthesis of \textit{trans}-1,2-DACH-salalen ligands.

6.3 Aluminium \textit{trans}-1,2-DACH Salalen Complexes

6.3.1 Synthesis of aluminium \textit{trans}-1,2-DACH salalen complexes

The aluminium methyl 1,2-DACH-salalen complexes \{Al(22-30)Me\} were isolated by reacting the ligands (22-30)H$_2$ with AlMe$_3$ (2M in hexanes) in a 1:1 ratio in toluene. The crude product was recrystallised from toluene/hexane mixes. The aluminium complexes Al(22-25,28)Me were characterised by $^1$H/$^13$C/$^1$H NMR spectrometry, and CHN analysis. While the Al(22-30)Me complexes can be isolated as solids Al(26-27)Me and Al(29-30)Me were insoluble in all suitable solvents for characterisation. As shown in previously discussed work (Chapter 4) Al(6-9,11)OBn
complexes can be isolated promoting solvent free and co-initiator free polymerisation studies. Aluminium complexes Al(22-30)Me were further reacted with 1.1 equivalence of benzyl alcohol (BnOH) in toluene (Figure 6.02), which were purified by recrystallisation in toluene/hexane mixes. The benzyl alcohol complexes Al(22-30)OBn are notably more soluble in organic solvents, and as such complexes Al(22-28)OBn and Al(30)OBn were characterised by $^1$H/$^{13}$C{${^1}$H} NMR spectroscopy, and CHN analysis. After multiple attempts Al(29)OBn could not be isolated in acceptable purity although the analysis revealed the major product as the desired Al(29)OBn complex.

![Reaction scheme for the synthesis of aluminium methyl and benzyloxy 1,2-DACH-salalen complexes.](image)

**Figure 6.02:** Reaction scheme for the synthesis of aluminium methyl and benzyloxy 1,2-DACH-salalen complexes.

**6.3.2 Solid-state characterisation of aluminium trans-1,2-DACH salalen complexes**

Few structures of aluminium salalen complexes have been characterised by X-ray crystallography. A chloro-aluminium 1,2-DACH-salalen complex was reported by Saito and Katsuki, the aluminium coordinated tertiary amine was shown
to be exclusively in the $S$ configuration.\textsuperscript{13} Jones et al. reported aluminium salalen structures which contained varying phenoxy substituents upon the salan and salen segments.\textsuperscript{11} Suitable crystals for X-ray diffraction were obtained for Al(22)Me (Figure 6.03), Al($R,R$-22)Me (Figure 6.04), and Al(25)OBn (Figure 6.05).

Figure 6.03: Solid-state structure for Al(22)Me. Ellipsoids are shown at the 30 % probability level, hydrogen atoms have been removed for clarity.

Figure 6.04: Solid-state structure for Al($R,R$-22)Me. Ellipsoids are shown at the 30 % probability level, hydrogen atoms have been removed for clarity.
Figure 6.05: Solid-state structure for Al(25)OBn. Ellipsoids are shown at the 30 % probability level, hydrogen atoms have been removed for clarity.

All the aluminium 1,2-DACH salalen crystal structures obtained adopt pseudo trigonal bipyramidal geometries (Figure 6.03, 6.04, and 6.05). The N\text{amine} and the O-Ph\text{amine} adopt axial positions, which is consistent with prior literature Al salalen structures.\textsuperscript{11,13} Within the Al(22)Me structure the N\text{amine} centre (N1) is illustrated in the R configuration, and the carbon centres of the 1,2-DACH in the S,S configuration. The crystal contains a centre of inversion which allows inversion of the structure to obtain the diastereomers configuration Al-(S)-N\text{amine}, (R,R)-1,2-DACH. Conversely, the literature solid-state structure for Al(R,R-22)Cl exclusively adopted the Al-(S)-N\text{amine}, (R,R)-1,2-DACH diastereomer,\textsuperscript{13} due to chirality limitations within the synthetic procedure. Additionally the solid-state structure for the chirally resolved Al(R,R-22)Me was modelled as the exclusive Al-(R)-N\text{amine}, (R,R)-1,2-DACH diastereomers (Figure 6.04). The identification of multiple stereo-isomers is pertinent to further characterisation. A benzylkoxy aluminium salalen complex \{Al(25)OBn\} was structurally determined by X-ray crystallography and identified as the Al-(R)-N\text{amine}, (R,R)-1,2-DACH diastereomers (Figure 6.05), a centre of inversion allows the Al-(S)-N\text{amine}, (S,S)-1,2-DACH diastereomer. To our knowledge no solid-state structures of aluminium salalen complexes containing non-\textsuperscript{4}Bu phenoxy substituents upon the salan segment, or aluminium bound alkoxy groups have been previously reported.
The solid-state structures for all the salalen complexes discussed in table 6.01 show the same trends in bond lengths (Å) and angles (°). Al(22)Me and Al(R,R-22)Me show very similar bond lengths and angles. However, there is a clear twist of the amine phenoxy ring between the diastereomers, which is demonstrated through a torsion angle measured between C1-DACH-N1-Camine-Cphenoxy (Table 6.02). Similar torsion angles are observed between Al(22)Me and Al(R,R-22)Cl as they can both be the Al-(S)-Namine, (R,R)-1,2-DACH diastereomer. Therefore, Al(R,R-22)Me and Al(25)OBn have comparable torsion angles as they can both be represented as the Al-(R)-Namine, (R,R)-1,2-DACH diastereomer.

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**Table 6.01:** Selected bond lengths (Å) and angles (°) for aluminium salalen compounds and comparative literature complexes, Al(R,R-22)Cl, Al(Salen)Et, Al(Salan)Et. O3 was substituted for C(1). Cl was substituted for C(1).
As expected there is a clear difference in imine and amine bond lengths. Imine bond lengths (C=N) in these complexes \{Al(22)Me, Al(R,R-22)Me, Al(25)OBn\} are between 1.298(2) - 1.306(2) Å, which are consistent with the literature solid-state salen complex \{Al(Salen)Et\} (Figure 6.06).20 Moreover, amine-benzyl bond lengths \{1.478(8) – 1.492(3) Å\} are consistent with previously reported DACH salan complexes.10 The Al-N_amine bonds are longer \{2.1192(12) - 2.2083(16) Å\} than Al-N_imine bonds \{1.9652(12) - 1.9801(17) Å\}. Furthermore, the Al-N_imine bonds in aluminium salalen complexes are similar to equivalent bonds within 1,2-DACH salen species \{Al(Salen)Et\} (Figure 6.06). Within the Al(salan)Et structure the Al-N_amine bonds are not equal indicating a bias to coordinate more strongly to one N_amine over the other.10 The angles between equatorial and axial groups within the benzyloxy salalen complex Al(25)OBn converge towards 90 ° when compared to Al(22)Me or Al(R,R-22)Me. The reduced
steric demands of the amine phenoxy substituents possibly allow the ligands to orientate towards a less distorted trigonal bipyramidal structure.

### 6.3.3 Solution characterisation of aluminium trans-1,2-DACH salalen complexes

There are three chiral centres in the ligands when coordinated, with the *trans*-1,2-DACH ring locked in either *R*,*R* or *S*,*S* configurations, the amine becomes chiral once coordinated. The aluminium metal is also a chiral centre. There are four possible diastereomers configurations \{Al-(R)-N\textsubscript{amine}, (S,S)-1,2-DACH\}, \{Al-(S)-N\textsubscript{amine}, (S,S)-1,2-DACH\}, \{Al-(S)-N\textsubscript{amine}, (R,R)-1,2-DACH\}, \{Al-(R)-N\textsubscript{amine}, (R,R)-1,2-DACH\} (Figure 6.07). Due to the locked configurations (R,R, S,S) of the DACH ring the system can be considered as a diastereomer system. As discussed before two possible diastereomers are present in the solid-state structure for Al(22)Me, in this scenario the diastereomers are enantiomers. The solid-state structure was also supported by solution NMR spectroscopy.

![Depiction of the possible diastereomers and enantiomers that aluminium salalen complexes can adopt.](image)
A single pair of enantiomers, as opposed to diastereomers, is demonstrated by the $^1$H NMR spectrum (Figure 6.08) of the X-ray crystallographically determined compound Al(22)Me. The two enantiomers present in the solution state are not distinguishable by conventional $^1$H NMR spectroscopy. A single Al-Me resonance was identified at low chemical shift (-0.48 ppm), alongside a single N$_{amine}$-Me resonance, indicating a single diastereomer. Doublets at 2.92 ppm and 4.07 ppm are identified as inequivalent N$_{amine}$-C-H protons. Therefore, demonstrating structural rigidity around the N$_{amine}$ region and reinforcing the presence of a single pair of enantiomers.

**Figure 6.08:** Al(22)Me $^1$H NMR spectrum for the isolated enantiomers {Al-(S)-N$_{amine}$, (R,R)-1,2-DACH} and {Al-(R)-N$_{amine}$, (S,S)-1,2-DACH}.
Figure 6.09: Al(R,R-22)Me \(^1\)H NMR spectrum depicting the diastereomers \{Al-(S)-N\textsubscript{amine}, (R,R)-1,2-DACH\} and \{Al-(R)-N\textsubscript{amine}, (R,R)-1,2-DACH\}.

The \(^1\)H NMR spectrum for Al(R,R-22)Me suggests the presence of two diastereomers in solution (Figure 6.09). This observation is not consistent with a single diastereomers in the solid-state as characterised by X-ray crystallography. Two Al-Me resonances are present in the \(^1\)H NMR spectrum. The Al-Me resonance at -0.48 ppm is consistent with the previously discussed Al(22)Me structure and is attributed to the \{Al-(S)-N\textsubscript{amine}, (R,R)-1,2-DACH\} isomer exclusively, due to (R,R)-1,2-DACH being used as the staring material disallowing its enantiomer \{Al-(R)-N\textsubscript{amine}, (S,S)-1,2-DACH\}. Under the same principle the resonance at -0.42 ppm is attributed to the X-ray crystallography determined diastereomers \{Al-(R)-N\textsubscript{amine}, (R,R)-1,2-DACH\}. The N-Me resonances at 1.76 and 1.84 ppm were assigned to the \{Al-(S)-N\textsubscript{amine}, (R,R)-1,2-DACH\} and \{Al-(R)-N\textsubscript{amine}, (R,R)-1,2-DACH\} respectively. The N\textsubscript{amine}-C-H\textsubscript{2} doublets at 2.94 ppm and 4.08 ppm confirm the presence of the \{Al-(S)-N\textsubscript{amine}, (R,R)-1,2-DACH\} diastereomer. Two doublets at 2.80 ppm and 3.72 ppm were assigned to N\textsubscript{amine}-CH\textsubscript{2} protons from the \{Al-(R)-N\textsubscript{amine}, (R,R)-1,2-DACH\}, the 4.08 ppm resonance is significantly shifted upfield from its analogous 3.72 ppm N\textsubscript{amine}-C-H\textsubscript{2} resonance.
Figure 6.10: a) The $^1$H NMR spectrum of the crystallised product of Al(22)Me showing a bias towards the {Al-(S)-N$_{amine}$, (R,R)-1,2-DACH} and {Al-(R)-N$_{amine}$, (S,S)-1,2-DACH} enantiomer pairing. b) The $^1$H NMR spectrum for the further crystallised product from the same solution, resulting in a bias towards the {Al-(R)-N$_{amine}$, (R,R)-1,2-DACH} and {Al-(S)-N$_{amine}$, (S,S)-1,2-DACH} enantiomer pairing.

The exact diastereomers isolated is dependent upon the crystallisation conditions. A further attempt at synthesising Al(22)Me resulted in a mixture of diastereomers (Figure 6.10a), in this specific example the {Al-(R)-N$_{amine}$, (R,R)-1,2-DACH}/ {Al-(S)-N$_{amine}$, (S,S)-1,2-DACH} enantiomer pairing was isolated in a 2:1 majority. Further crystallisation of the resulting solution resulted in the opposite enantiomer pairing ({Al-(S)-N$_{amine}$, (R,R)-1,2-DACH}/ {Al-(R)-N$_{amine}$, (S,S)-1,2-DACH}) as the major product in a 2:1 ratio (Figure 6.10b). This dependence on crystallisation conditions is not a unique phenomenon and the other aluminium complexes discussed here have also been isolated as mixtures of diastereomers or specific enantiomer pairs. All of the aluminium methyl salalen complexes {Al(23-25,28)Me} were isolated as the {Al-(R)-N$_{amine}$, (R,R)-1,2-DACH}/ {Al-(S)-N$_{amine}$, (S,S)-1,2-DACH} enantiomer pairings with the exception of Al(22)Me (Figure 6.11).
Figure 6.11: Truncated $^1$H NMR spectrum showing aluminium methyl salalen complexes isolated enantiomer pairs.

Figure 6.12: $^1$H NMR spectrum for Al(25)OBn
The aluminium benzyloxy salalen complexes displayed similar characteristic to their aluminium methyl counterparts. The solid-state structure for the Al(25)OBn complex was identified as the \( \{ \text{Al-(}R\text{)-N}_{\text{amine}}, \ (R,R)-1,2\text{-DACH}\}/\{ \text{Al-(}S\text{-N}_{\text{amine}}, \ (S,S)-1,2\text{-DACH}\} \) enantiomer pairing. Additionally one enantiomer pairing is observed in solution (Figure 6.12), the characteristic amine CH\(_2\) protons are represented as two doublets at 3.51 ppm and 2.67 ppm. In this case the doublet at 2.67 ppm also coincides with a CH proton from the DACH ring. There is significant broadening of the CH\(_2\) protons about the OBn moieties representing a degree of fluxionality about the OBn group.

![Figure 6.13: \(^1\)H NMR spectra of Al(23-25,28)OBn salalen complexes isolated with an enantiomer pair as the major product.]

Akin to the Al-Me salalen complexes the diastereomers isolated for the Al(22-30)OBn complexes is highly dependent upon crystallisation conditions. Al(24,25,28)OBn were obtained as the enantiomer pair \( \{ \text{Al-(}R\text{-N}_{\text{amine}}, \ (R,R)-1,2\text{-DACH}\}/\{ \text{Al-(}S\text{-N}_{\text{amine}}, \ (S,S)-1,2\text{-DACH}\} \) as the major product, as evident from the CH\(_2\) proton resonances of the \(^1\)H NMR spectra (Figure 6.13). Only Al(23)OBn formed the \( \{ \text{Al-(}S\text{-N}_{\text{amine}}, \ (R,R)-1,2\text{-DACH}\}/\{ \text{Al-(}R\text{-N}_{\text{amine}}, \ (S,S)-1,2\text{-DACH}\} \) enantiomer pair as the major product, indicated by the significant shift of the amine CH\(_2\) protons (Figure 6.13). The other aluminium benzyloxy \( \{ \text{Al}(22,26,27,29,30)\text{OBn} \) complexes were isolated as a mixtures of diastereomers in approximate 1:1 ratios.
Upon heating (80 °C, toluene) an aluminium salalen complex, which was isolated as a single enantiomer pairing, the alternate enantiomer pairing is formed. This observation is true for aluminium methyl salalen complexes and their benzyloxy derivatives. Significant inter-conversion occurs after exposure to elevated temperatures for 30 mins. This is clearly demonstrated by figure 6.14, Al(22)Me was heated (80 °C) for 4 hours and the resulting spectrum (figure 6.14) shows the presence of two diastereomers. The stereomeric mixture equilibrates at a 1:1 ratio so there is presumably little difference in energy between the various diastereomers in solution. This is of significant importance, as rac-lactide ROP was conducted above 80 °C. The complexes can be considered as mixtures of diastereomers within the polymerisations, irrelevant of the stereomeric form a specific aluminium salalen complex is isolated as.

![Figure 6.14](image)

**Figure 6.14**: a) ^1^H NMR spectrum of Al(22)Me at 20 °C. b) ^1^H NMR spectrum of Al(22)Me after heating (4h, 80 °C).

### 6.4 Ring-Opening-Polymerisation of rac-Lactide

The aluminium salalen complexes were trialled as initiators for the ROP of rac-lactide in solution and solvent free conditions. The aluminium methyl salalen complexes require the addition of one equivalent of benzyl alcohol as a co-initiator to
form the presumed *in-situ* benzyloxy complex. The isolated aluminium benzyloxy complexes were utilised without the addition of a co-initiator. Only the aluminium salalen benzyloxy complexes were used for solvent free ROP reactions due to practical complications.

### 6.4.1 Solution ROP of *rac*-lactide

Solution polymerisations were performed in 10 ml of toluene at 80 °C using 1.0 g of *rac*-lactide in all cases. A 100:1 lactide to initiator ratio was utilised and one equivalent of benzyl alcohol was introduced as a co-initiator where required. Aluminium salen complexes are typically slow,\(^5,6\) particularly in the case of salen complexes with a 1,2-DACH bridging group where 12 days was required to achieve appreciable conversion at 70 °C.\(^7\) Within this report a typical polymerisation required 4 days to reach acceptable conversions, the data is given in table 6.03. Polymerisations of *rac*-lactide using Al(25)OBn and Al(28)OBn initiators yielded low conversion and as such were repeated and allowed 10 days reaction time.

The reactions reached appreciable conversion although the presence of a \(^t\)Bu group on the salen moiety significantly reduced conversion. This is presumably a steric effect although this is in conjunction with the orientation of the salen phenoxy, as the same effect is not observed to such a degree when considering the salan section. The effect of the salen phenoxy substituent upon rate is investigated later in this chapter (see figure 6.18). Molecular weight distributions are narrow with PDI values ranging between 1.06 - 1.67. The resulting tacticity of the PLA is defined by the phenoxy group substituents upon the Al salalen initiators. The initiators containing \(^t\)Bu-phenoxy substituents on the imine and amine sections \{Al(22)Me, Al(R,R-22)Me, Al(22)OBn\} were the least active initiators investigated in this series. The molecular weights \((M_n)\) were much higher than anticipated for the low conversion polymers produced by Al(22)Me and Al(R,R-22)Me initiators. It was speculated that not all of the Al(22)Me and Al(R,R-22)Me initiators initiated a growing polymer chain.
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<td>12100</td>
<td>7700</td>
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</tr>
<tr>
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<td>40</td>
<td>5900</td>
<td>6400</td>
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</tr>
<tr>
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<tr>
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<td>13900</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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<td>14600</td>
<td>1.67</td>
</tr>
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<td>99</td>
<td>14400</td>
<td>19350</td>
<td>1.15</td>
</tr>
</tbody>
</table>

Table 6.03: Solution ROP of rac-lactide for Al(22-25,28)Me and Al(22-30)OBn initiators. 10 ml of toluene, 80 °C, 100:1:1 [rac-lactide]:[initiator]:[benzyl alcohol]*where required. a Conversion ascertained by \(^1\)H NMR spectroscopy. b Theoretical molecular weight calculated from conversion (Conv. × 100 × 144.13 + 108.14). c Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. d $P_R$ as calculated from \(^1\)H NMR homonuclear decoupling spectroscopy in CDCl₃.

A slight heterotactic bias was typically obtained when the salan phenoxy contained \(^t\)Bu moieties Al(23,24)Me/OBn. Interestingly, the introduction of \(^t\)Bu group upon the salen phenoxy resulted in the production of PLA with a slight isotactic bias for Al(25,28)OBn initiators (Figure 6.15), this was not observed for Al(22)OBn or analogous Al(25,28)Me initiators. Moreover, the in-situ reactions using Al(22-25,28)Me initiators with BnOH co-initiator gave different yields and selectivity than their Al(22-25,28)OBn analogues. It was postulated that multiple initiating species were being produced during the in-situ reactions, whereas the isolated Al(22-25,28)OBn initiators were comparatively well defined.
The introduction of chloro-substituents upon the salen phenoxy ring gave an increase in conversion all achieving > 96% conversion after 4 days at 80 °C in toluene (See table 6.03; Al(24)Me, Al(24,27,30)OBn). Narrow molecular weight distributions were still obtained and the resulting PLA revealed some heterotactic selectivity ($P_r = 0.54 – 0.73$). The homonuclear decoupled $^1$H NMR spectrum for PLA produced by Al(30)OBn is given in figure 6.16, a clear enhancement of the [isi] and [sis] tetrads at 5.15 ppm and 5.22 ppm is observed. This switch to a heterotactic preference and enhanced activity is presumably an electronic effect, a direct result of the chloro-phenoxy substituents. The 1,2-DACH salalen aluminium initiators series show enhanced rates when compared to prior 1,2-DACH salen aluminium initiators, although the stereoselectivity was not maintained.\textsuperscript{7, 8}
Figure 6.16: $^1$H NMR homonuclear decoupled spectrum showing tetrad resonances for the ROP of 
\( \text{rac-} \text{Lactide by Al(30)OBn in toluene at 80 °C.} \)

6.4.2 Solvent free ROP of rac-lactide

Solvent free polymerisations were performed at 130 °C where 1.0 g of 
\( \text{rac-} \text{Lactide was melted in the presence of Al(22-30)OBn initiators, the reaction was} \)
allowed to proceed for the amount of time given in table 6.04. The isolated 
benzyloxy initiators \{Al(22-30)OBn\} allowed the solvent free ROP reactions to be 
conducted. When the aluminium salalen initiator contained chloro or hydrogen 
substituents on both the salan and salen phenoxy groups good conversion is obtained 
in 2 h. On the other hand the steric bulk associated with the \(^1\text{Bu moieties of the} \)
initiator Al(22)OBn reduces activity, hence 48 hours is required for appreciable 
conversion to be obtained. It was speculated that isolated complex diastereomers 
interconvert at the higher temperatures in melt conditions, although direct analysis of 
the initiators under these condition is complicated.
| Al(22)OBn | 48 | 30 | 13100 | 7850 | 1.07 | 0.54 |
| Al(23)OBn | 24 | 85 | 36900 | 57600 | 1.51 | 0.58 |
| Al(24)OBn | 24 | 91 | 39500 | 48150 | 1.71 | 0.64 |
| Al(25)OBn | 24 | 27 | 11800 | 9100 | 1.06 | 0.41 |
| Al(26)OBn | 2  | 42 | 18300 | 28700 | 1.07 | 0.51 |
| Al(27)OBn | 2  | 94 | 40800 | 33350 | 1.10 | 0.57 |
| Al(28)OBn | 24 | 68 | 29500 | 14300 | 1.56 | 0.43 |
| Al(29)OBn | 2  | 98 | 42500 | 46550 | 1.47 | 0.61 |
| Al(30)OBn | 24 | 60 | 26100 | 23350 | 1.14 | 0.72 |

Table 6.04: Solvent free ROP of rac-lactide for initiators Al(22-30)OBn at 130 °C, 300:1 [rac-lactide]:[initiator] ratio. a Conversion ascertained by 1H NMR spectroscopy. b Theoretical molecular weight calculated from conversion (Conv. × 300 × 144.13 + 108.14). c Molecular weight and PDI determined by GPC (THF) using polystyrene standards without applying a correction factor. d P, as calculated from 1H NMR homonuclear decoupling spectroscopy in CDCl3.

The melt polymerisation data is shown in table 6.04, notably 1Bu moieties on either the salan or salen phenoxy groups gave lower conversions. At elevated temperature narrow molecular weight distributions could still be obtained for Al(22,25-27,30)OBn (PDI = 1.06 - 1.14). Parallel to the solution ROP of rac-lactide heterotactically biased PLA was obtained when chloro substituents were present on the salen phenoxy (P, = 0.57 – 0.72), no loss in stereoselectivity was observed at the elevated temperature. The homonuclear decoupled 1H NMR spectrum of PLA produced by Al(30)OBn used to determine PDI is given in figure 6.17, a significant enhancement of the [isi] and [sis] tetrads is shown. Analogous to the solution state polymerisations 1Bu groups on the salen segment results in a slight isotactic bias (P, = 0.41 – 0.43), with the exception of the Al(22)OBn initiator.
6.4.3 Kinetic investigation for the solution ROP of rac-lactide

Kinetic experiments were performed to analyse the apparent rate of propagation of the ROP of rac-lactide by 1,2-DACH aluminium salalen complexes. The effect of the changing the substituents on the salen phenoxy was investigated. The kinetic experiments were performed on an NMR scale using 0.05 g of rac-lactide in a 100:1 ratio with an aluminium initiator {Al(25-27)OBn} at 80 °C in d8-toluene. The graph of ln([LA]₀/[LA]ₜ) versus time gave pseudo first order linear plots (Figure 6.18). The aluminium salalen complexes chosen for kinetic analysis contained hydrogen substituents on the salan phenoxy, tBu, H, and Cl substituents were investigated on the salen phenoxy. The apparent first order rate constant was determined from the graph given in figure 6.18. When tBu and H substituents are present upon the phenoxy ring long reaction times are required hence the spectra were recorded in greater than 24 h intervals. Contrastingly Cl substituents resulted in very high conversion after 24 h, hence a spectrum was recorded at 15 mins intervals.
Figure 6.18: Pseudo first order plots for the ROP of rac-lactide by Al(25-27)OBn. 50 mg of rac-lactide in 0.6 ml of d₈-toluene at 80 °C at 100:1 [rac-lactide]:[initiator] ratio.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>$k_{app}$ (min⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(25)OBn</td>
<td>2.00(7)</td>
<td>0.9946</td>
</tr>
<tr>
<td>Al(26)OBn</td>
<td>24.0(7)</td>
<td>0.9972</td>
</tr>
<tr>
<td>Al(27)OBn</td>
<td>153.7(1)</td>
<td>1.0000</td>
</tr>
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</table>

Table 6.05: $k_{app}$ values and $R^2$ values for ROP of rac-lactide by Al(25-27)OBn initiators

It can be clearly seen that ⁴Bu salen phenoxy substituents hinder the ROP reaction rate, $k_{app} = 2.00 \times 10^{-5}$ min⁻¹ (Table 6.05). A significant enhancement of around two orders of magnitude ($152.71 \times 10^{-5}$ min⁻¹) is observed when Cl moieties are present on the salen phenoxy ring. Previous salalen aluminium initiators trialled for the ROP of rac-lactide within the Jones group gave first order $k_{app}$ between $13.80 \times 10^{-5} - 33.53 \times 10^{-5}$ min⁻¹ for ⁴Bu, Me, and H salan ortho-phenoxy substituents.¹¹ The 1,2-DACH salan complex synthesised by Feijen et al.¹⁰ analogous to Al(26)OBn, containing hydrogen phenoxy substituents, gave a $k_{app} = 448 \times 10^{-5}$ min⁻¹. Feijen et al.¹⁰ also reported that Cl substituents on salan phenoxy groups gave a reduction in apparent rate, $k_{app} = 93.7 \times 10^{-5}$ min⁻¹.
Previously reported salen rac-1,2-DACH complexes for the ROP of rac-lactide by Feijen et al.\textsuperscript{8} gave $k_{\text{app}} = 11.6 \times 10^{-5}$ min$^{-1}$ at 70 °C (62:1 rac-lactide to initiator ratio) this is comparable to the $k_{\text{app}}$ reported for the ROP of rac-lactide by the salalen complex Al(25)OBn.

Kinetic investigations of the ROP of rac-lactide by Al(28)Me and Al(28)OBn was conducted. The experiments were performed at 80 °C in d$_8$-toluene using 0.05 g of rac-lactide in a 20:1 ratio, one equivalent of BnOH was added to the Al(28)Me initiated polymerisation. Apparent rates of propagation ($k_{\text{app}}$) were obtained from the gradient of pseudo first order rate plots (Figure 6.19). The in-situ Al(28)Me + BnOH initiator system was more than two times faster ($k_{\text{app}} = 20.82 \times 10^{-5}$ min$^{-1}$) than the less active Al(28)OBn initiator ($k_{\text{app}} = 9.51 \times 10^{-5}$ min$^{-1}$) (Table 6.06). The expected initiating species from the in-situ reaction of Al(28)Me + BnOH is Al(28)OBn. This rate difference indicated the active species from the in-situ reaction of Al(28)Me + BnOH were not identical to the isolated Al(28)OBn initiator. This demonstrates the formation of a discrete metal co-initiator species cannot always be assumed within in-situ ROP reactions.

![Figure 6.19: Pseudo first order plots for the ROP of rac-lactide by Al(28)Me with one equivalent of benzyl alcohol and Al(28)OBn at 80 °C in d$_8$-toluene. 50 mg of rac-lactide in 0.6 ml of d$_8$-toluene at 80 °C at 20:1 [rac-lactide]:[initiator] ratio, one equivalent of BnOH was added in-situ to the Al(28)Me initiator.](image-url)
<table>
<thead>
<tr>
<th>$k_{app}$ (min$^{-1}$)</th>
<th>R$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(28)Me 20.8(6)</td>
<td>0.9971</td>
</tr>
<tr>
<td>Al(28)OBn 9.51(5)</td>
<td>0.9983</td>
</tr>
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</table>

Table 6.06: $k_{app}$ values and R$^2$ values for ROP of rac-lactide by Al(28)Me and Al(28)OBn initiators.

6.5 Conclusion

Further salalen ligands with a 1,2-DACH backbone {((22-30)H$_2$)} were synthesised and characterised to expand the derivatives library for these ligands. Aluminium methyl complexes Al(22-30)Me were synthesised along with their benzyloxy derivatives Al(22-30)OBn. The majority of aluminium complexes {Al(22-25,28)Me, Al(22-30)OBn} were characterised by $^1$H, $^{13}$C{($^1$H} NMR spectroscopy and CHN analysis. Solid-state structures for Al(22)Me, Al(R,R-22)Me, and Al(25)OBn were determined by X-ray diffraction. X-ray diffraction demonstrated; Al(22)Me existed as the {Al-(S)-N$_{amine}$, (R,R)-1,2-DACH}/{Al-(R)-N$_{amine}$, (S,S)-1,2-DACH} diastereomers, Al(R,R-22)Me existed as the {Al-(R)-N$_{amine}$, (R,R)-1,2-DACH} diastereomer, Al(25)OBn existed as the {Al-(R)-N$_{amine}$, (R,R)-1,2-DACH} diastereomers. NMR spectroscopic investigations showed the isolation of isomers was possible with a dependence upon crystallisation conditions. However, in solution these isomers interconvert at high temperature (80 °C).

The ROP of rac-lactide was conducted using Al(22-25,28)Me, Al(R,R-22)Me, and Al(22-30)OBn initiators to investigate the effect of substituents (R = 'Bu, H, and Cl) upon the imine (salen) side and amine (salan) side. Al(22-25,28)Me and Al(R,R-22)Me were investigated for the polymerisation of rac-lactide with benzyl alcohol as a co-initiator. The solution (toluene) ROP of rac-lactide attained appreciable conversion for the majority of cases in 4-10 days (80 °C, 100:1 [rac-lactide]:[initiator] ratio). The solvent free ROP of rac-lactide resulted in appreciable conversion for Al(22-30)OBn initiators between 2-48 hours dependent upon the phenoxy substituents. Bulky 'Bu phenoxy groups had a negative impact upon polymerisation rate, where rate follows Cl > H > 'Bu for Al(25-27)OBn.
initiators. Selectivity ranged from moderately isotactic to moderately heterotactic ($P_r = 0.31 - 0.73$). Al(25,28)OBn initiators gave the strongest isotactic bias ($P_r = 0.31 - 0.43$) and Al(30)OBn revealed the strongest heterotactic bias ($P_r = 0.72 - 0.73$). A greater than two fold rate difference was observed between Al(28)Me + BnOH ($k_{app} = 20.82 \times 10^{-5}$ min$^{-1}$) and isolated Al(28)OBn initiator ($k_{app} = 9.51 \times 10^{-5}$ min$^{-1}$). This prompted speculation that the active species from Al(28)Me + BnOH contained other initiating complexes than just the Al(28)OBn species.

6.6 Future Work

Further derivatives of 1,2-DACH salalen ligands could be synthesised, firstly the phenol substituents could be varied. The amine-methyl group could also be varied as previous work on salalen complexes has shown this substituent region can affect the initiator properties. Other metals can be trialled with this ligand set, e.g. group 4, indium, and lanthanides are possible candidates. The presence of one initiating benzyloxy group upon the aluminium metal makes these initiators candidates for initiating co-polymerisation reactions with other cyclic esters. Other salalen ligands could be synthesised with differing linking diamines, a notable candidate is based upon the salen ligands synthesised by Nomura et. al., the possible salalen variant is given in figure 6.20.

![Figure 6.20: Potential aluminium salalen complex for the ROP of rac-lactide.](image)

6.7 Final concluding remarks

The homo/piperazine based salan ligands gave 2:1 titanium to ligand complexes \{Ti$_2$(1-5,8-9,12-13)(O’Pr)$_6$\} with an interesting equilibrium based upon the steric demands of the ortho-phenoxy substituents. The bimetallic titanium
complexes were active for the ROP of lactide but lacked control over molecular weight and resulted in predominately atactic PLA. Homopiperaine salan group 4 monometallic complexes were formed and the titanium complexes \{Ti(6-11)(O^iPr)_2\} were poor initiators most likely due to hindrance about the titanium metal. The zirconium and hafnium homopiperazine salan complexes \{Zr/Hf(6-9,10)(O^iPr)_2\} resulted in mostly atactic lactide but the hafnium initiators \{Hf(6,7)(O^iPr)_2\} resulted in an isotactic biased PLA from rac-lactide in solvent and solvent free conditions. Aluminium benzyloxy and aluminium methyl homopiperazine salan complexes were synthesised as monometallic complexes. The aluminium benzyloxy homopiperazine salan complexes \{Al(6-9,11)OBn\} were shown to be active under solvent free conditions for the ROP of rac-lactide, \(\varepsilon\)-caprolactone, and \(\delta\)-valerolactone.

1,4-DACH salen titanium and aluminium bimetallic complexes \{Ti_2(16-18)(O^iPr)_6, Al_2(16-18)Me_4\} were isolated with bulky ortho-phenoxy substituents and proven to be active initiators for the ROP of lactide. The aluminium 1,4-DACH based salen complexes \{Al_2(16-18)Me_4\} were shown to polymerise lactide in an immortal manner and resulted in isotactic biased PLA. A systematic study of 1,2-DACH salalen complexes \{Al(22-25,28)Me, Al(22-30)OBn\} was conducted and the phenoxy substituents on the imine and amine side were systematically investigated. Imine phenoxy substituents were shown to have the most prominent effect upon activity and stereoselectivity. Additionally isolated aluminium benzyloxy 1,2-DACH salalen complexes and aluminium benzyloxy 1,2-DACH salalen complexes formed in-situ within a polymerisation were compared, where the initiators formed in-situ resulted in reduced selectivity.

6.8 References

Chapter 7

7. Experimental
7. Experimental

7.1 General Experimental Considerations

Metal complex preparations and characterisations were performed under dry inert gas atmosphere (N\textsubscript{2} or Ar) using standard Schlenk line and glove box techniques. Dry solvents were collected from an MBraun solvent purification system (SPS) for the handling of and preparation of metal complexes. Laboratory reagent grade solvents were used for the preparation of ligands. All chemicals were purchased from Sigma-Aldrich and used without further purification unless stated. Ti(O\textsubscript{i}Pr)\textsubscript{4} (97\%, Aldrich) was purified by vacuum distillation and stored under inert atmosphere within a young’s ampoule. Rac-lactide was crystallised from high purity toluene obtained from an MBraun SPS system and sequentially sublimed twice before glove-box storage under inert atmosphere. \(\varepsilon\)-caprolactone and \(\delta\)-valereolactone were purified by vacuum distillation before storage under inert atmosphere.

\(^1\text{H}\) and \(^{13}\text{C}\{^1\text{H}\}\) NMR spectra were recorded with a Bruker 250, 300, 400 or 500 MHz instrument and referenced to residual solvent peaks. NMR spectroscopy analysis was conducted in CDCl\textsubscript{3}, C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}, or C\textsubscript{4}D\textsubscript{8}O. CDCl\textsubscript{3} was dried by distillation from calcium hydride, before use with metal complexes. C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3} and C\textsubscript{4}D\textsubscript{8}O were dried over molecular sieves before use. NMR tubes fitted with Young’s taps were utilised for analysis of metal complexes, high temperature, and kinetic experiments. Ligands dissolved in acetonitrile were analysed by high resolution mass spectrometry on a micrOTOFQ (ESI-TOF) spectrometer in the positive mode. CHN elemental analysis data was recorded by either Mr. A. Craver (at the University of Bath, on an Exeter Analytical CE440 Elemental Analyzer) or by Mr Stephen Boyer (London Metropolitan University). X-ray diffraction data was collected on a Nonius Kappa CCD diffractometer using Mo-K\textsubscript{a} radiation (\(\lambda = 0.71073\) Å) at 150 K. X-ray diffraction data for Ti\textsubscript{2}(\textit{I})\textsubscript{2}O\textsubscript{i}Pr\textsubscript{4} was recorded at the diamond synchrotron facility using X-ray wavelength of \(\lambda = 0.6889\) Å at 150 K by Dr Mary Mahon. All structures were solved by direct methods and refined on all \(R^2\) data using the SHELXL-97 suite of programs. All hydrogen atoms were included in idealised positions and refined using the riding model.
7.2 General Polymerisation Procedures

\(^{1}\text{H}\) Homonuclear decoupled NMR spectroscopy was performed on a Bruker 400 MHz spectrometer for determination of \(P_r\) (\(P_r\) = the probability of heterotactic linkages) values of \(rac\)-lactide polymers. This was found through analysis of the decoupled methine region of the spectra by Bernoulli statistics discussed by Coates et al.\(^1\) Polymers were analysed by GPC on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μm MIXED-D 300 x 7.5 mm column at 35°C with a flow rate of 1 ml min\(^{-1}\). Samples were solubilised in THF and filtered through a PTFE 0.2 μm filter prior to auto-sampler injection. The polymers are analysed by refractive index which was referenced against 11 narrow molecular weight polystyrene polymer standards giving a calibrated range of \(M_w\) 615-568000 Da. The PDI is calculated from \(M_w/M_n\) (\(M_w\) = weight average molecular weight, \(M_n\) = number average molecular weight). MALDI-TOF mass spectrometry analysis of polymers was conducted by the EPSRC National Mass Spectrometry service Centre, Swansea, UK on the Applied Biosystems Voyager DE-STR instrument. The samples were dissolved in THF and analysed in positive-reflection mode using a dithranol matrix with a NaOAc additive to promote positive ionisation.

7.3 Homo/Piperazine Salan Ligand Preparation for Chapters 2-4

\(1\text{H}_2\). 2,4-di-methylphenol (8.50 g, 69.6 mmol), piperazine anhydrous (3.00 g, 34.8 mmol), and formaldehyde (38% in H\(_2\)O) (5.78 ml, 2.35 g, 78.1 mmol) were refluxed in MeOH (40 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (5.64 g, 15.9 mmol, 46 %). \(^{1}\text{H}\) NMR (CDCl\(_3\)): \(\delta\) 2.22 (6H, s, Me), 2.23 (6H, s, Me), 2.30 – 3.20 (8H, br, ring-CH\(_2\)), 3.67 (4H, s, N-CH\(_2\)-Ar), 6.65 (2H, d, \(J = 1.5\) Hz, ArH), 6.85 (2H, d, \(J = 1.5\) Hz, ArH), 10.54 (2H, br, OH). \(^{13}\text{C}\{^{1}\text{H}\}\) NMR (CDCl\(_3\)): \(\delta\) 15.7 (CH\(_3\)), 20.5 (CH\(_3\)), 52.4 (CH\(_2\)), 61.4 (CH\(_2\)), 119.9 (Ar), 124.7 (Ar), 126.9 (ArH), 127.9 (Ar), 138.8 (ArH), 153.4 (ArO). Calc. m/z [C\(_{22}\)H\(_{30}\)N\(_2\)O\(_2\) + H]\(^+\) 355.2385. Found 355.2488.

\(2\text{H}_2\). 2-methyl-4-\(\text{tert}\)-butylphenol (3.97 g, 22.4 mmol), piperazine anhydrous (1.00 g, 11.6 mmol), and formaldehyde (38% in H\(_2\)O) (1.92 ml, 0.78 g, 26.0 mmol) were refluxed in MeOH (25 ml) for 24 h. During which time a white precipitate was
observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.20 g, 2.7 mmol, 24%). $^1$H NMR (CDCl$_3$): δ 1.28 (18H, s, tBu), 2.24 (6H, s, CH$_3$), 2.30 – 3.20 (8H, br, ring-CH$_2$), 3.71 (4H, s, N-CH$_2$-Ar), 6.84 (2H, d, J = 2.0 Hz, ArH), 7.08 (2H, d, J = 2.0 Hz, ArH), 10.67 (2H, br, OH). $^{13}$C{$_1^1$H} NMR (CDCl$_3$): δ 16.1 (CH$_3$), 31.7 (CH$_3$), 33.9 (C), 52.5 (CH$_2$), 61.8 (C-H$_2$), 119.5 (Ar), 123.2 (ArH), 124.2 (Ar), 127.1 (ArH), 141.6 (Ar), 153.4 (ArO). Calc. m/z [C$_{28}$H$_{42}$N$_2$O$_2$ + H]$^+$ 439.3325. Found 439.3306.

3H$_2$. 2,4-di-tert-butylphenol (14.37 g, 69.7 mmol), piperazine anhydrous (3.00 g, 34.8 mmol), and formaldehyde (38% in H$_2$O) (5.78 ml, 2.35 g, 78.14 mmol) were refluxed in MeOH (40 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (13.31 g, 25.5 mmol, 73%). $^1$H NMR (CDCl$_3$): δ 1.28 (18H, s, tBu), 1.42 (18H, s, tBu), 2.10 – 3.20 (8H, br, ring-CH$_2$), 3.72 (4H, s, N-CH$_2$-Ar), 6.84 (2H, d, J = 2.5 Hz, ArH), 7.23 (2H, d, J = 2.5 Hz, ArH), 10.68 (2H, br, OH). $^{13}$C{$_1^1$H} NMR (CDCl$_3$): δ 29.7 (CH$_3$), 31.8 (CH$_3$), 34.3 (C), 35.0 (C), 52.3 (CH$_2$), 62.1 (CH$_2$), 120.4 (Ar), 123.2 (ArH), 123.7 (ArH), 135.7 (Ar), 140.9 (Ar), 154.2 (ArO). Calc. m/z [C$_{22}$H$_{30}$N$_2$O$_2$ + H]$^+$ 523.4263. Found 523.4366.

4H$_2$. 2-tert-butyl-4-methylphenol (7.63 g, 46.5 mmol), piperazine anhydrous (2.00 g, 23.2 mmol), and formaldehyde (38% in H$_2$O) (3.85 ml, 1.57 g, 52.1 mmol) were refluxed in MeOH (30 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (5.66 g, 12.9 mmol, 56%). $^1$H NMR (CDCl$_3$): δ 1.41 (18H, s, tBu), 2.25 (6H, s, Me), 2.30 – 3.20 (8H, b, ring-CH$_2$), 3.69 (4H, s, N-CH$_2$-Ar), 6.68, (2H, s, ArH), 7.01 (2H, s, ArH), 10.68 (2H, b, OH). $^{13}$C{$_1^1$H} NMR (CDCl$_3$): δ 20.9 (CH$_3$), 29.6 (CH$_3$), 34.7 (C), 52.2 (CH$_2$), 61.3 (CH$_2$), 121.0 (Ar), 126.9, 127.5 (ArH), 127.1 (Ar), 136.4 (Ar), 154.2 (ArO). Calc. m/z [C$_{28}$H$_{42}$N$_2$O$_2$ + H]$^+$ 439.3325. Found 439.3308.

5H$_2$. 2,4-di-tert-amylphenol (5.44 g, 23.2 mmol), piperazine anhydrous (1.00 g, 11.6 mmol), and formaldehyde (38% in H$_2$O) (1.92 ml, 0.78 g, 26.0 mmol) were refluxed in MeOH (25 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.84 g, 3.2
mmol, 28%). $^1$H NMR (CDCl$_3$): δ 0.62 (6H, t, J = 7.5 Hz, CH$_3$), 0.64 (6H, t, J = 7.5 Hz, CH$_3$), 1.24 (12H, s, CH$_3$), 1.36 (12H, s, CH$_3$), 1.57 (4H, q, J = 7.5 Hz, CH$_2$), 1.88 (4H, q, J = 7.5 Hz, CH$_2$), 2.30 – 3.20 (8H, br, ring-CH$_2$), 3.67 (4H, s, N-CH$_2$-Ar), 6.76 (2H, d, J = 2.0 Hz, ArH), 7.08 (2H, d, J = 2.0 Hz, ArH), 10.55 (2H, br, OH).

$^{13}$C{$^1$H} NMR (CDCl$_3$): δ 9.3 (CH$_3$), 9.7 (CH$_3$), 27.7 (CH$_2$), 28.7 (CH$_3$), 33.1 (CH$_2$), 37.3 (C), 38.5 (C), 52.2 (CH$_2$), 61.2 (CH$_2$), 120.1 (Ar), 124.3 (ArH), 125.3 (ArH), 133.9 (Ar), 139.0 (Ar), 153.9 (ArO). Calc. m/z [C$_{38}$H$_{63}$N$_2$O$_2$ + H]$^+$ 579.4890. Found 579.4906.

6H$_2$. 2,4-di-methyl-butylphenol (2.44 g, 20.0 mmol), homo-piperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H$_2$O) (1.67 ml, 0.68 g, 22.6 mmol) were refluxed in MeOH (20 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.84 g, 5.0 mmol, 50 %). $^1$H NMR (CDCl$_3$): δ 1.93 (2H, quin, J = 6.1 Hz, CH$_2$), 2.22 (12H, s, Me), 2.78 (4H, s, ring-CH$_2$), 2.83 (4H, t, J = 6.2 Hz, ring-CH$_2$), 3.74 (4H, s, N-CH$_2$-Ar), 6.62 (2H, s, ArH), 6.87 (2H, s, ArH), 10.82 (2H, br, OH). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 15.7 (CH$_3$), 20.5 (CH$_3$), 26.7 (CH$_2$), 53.5 (CH$_2$), 54.6 (CH$_2$), 62.0 (CH$_2$), 120.1 (Ar), 124.7 (Ar), 126.7 (ArH), 127.7 (Ar), 130.7 (ArH), 153.7, (ArO). Calc. m/z [C$_{23}$H$_{32}$N$_2$O$_2$ + H]$^+$ 369.2542. Found 369.2530.

7H$_2$. 2-methyl-4-tert-butylphenol (3.28 g, 20.0 mmol), homo-piperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H$_2$O) (1.66 ml, 0.67 g, 22.5 mmol) were refluxed in MeOH (20 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.68 g, 3.7 mmol, 37 %). $^1$H NMR (CDCl$_3$): δ 1.28 (18H, s, tBu), 1.95 (2H, quin, J = 6.0 Hz, CH$_2$), 2.25 (6H, s, CH$_3$), 2.80 (4H, s, ring-CH$_2$), 2.85 (4H, t, J = 6.0 Hz, ring-CH$_2$), 3.78 (4H, s, N-CH$_2$-Ar), 6.81 (2H, d, J = 2.3 Hz, ArH), 7.08 (2H, d, J = 2.3 Hz, ArH), 10.95 (2H, br, OH). $^{13}$C{$^1$H} NMR (CDCl$_3$): δ 16.1 (CH$_3$), 26.8 (CH$_2$), 31.8 (CH$_3$), 34.0 (C), 53.6 (CH$_2$), 54.8 (CH$_2$), 62.5 (CH$_2$), 120.4 (Ar), 123.0 (ArH), 124.2 (Ar), 127.1 (ArH), 141.4 (Ar), 153.7, (ArO). Calc. m/z [C$_{29}$H$_{44}$N$_2$O$_2$ + H]$^+$ 453.3481. Found 453.3497.
2H. 2,4-di-tert-butylphenol (4.12 g, 20.0 mmol), homo-piperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H₂O) (1.66 ml, 0.67 g, 24.5 mmol) were refluxed in MeOH (20 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.29 g, 2.4 mmol, 24 %). ¹H NMR (CDCl₃): δ 1.28 (18H, s, tBu), 1.42 (18H, s, tBu), 1.91 (2H, quintet, J = 6.0 Hz, ring-CH₂), 2.78 (4H, s, ring-CH₂), 2.83 (4H, t, J = 6.0 Hz, ring-CH₂), 3.77 (4H, s, N-CH₂), 6.84 (2H, d, J = 2.5 Hz, ArH), 7.23 (2H, d, J = 2.5 Hz, ArH), 10.68 (2H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 26.9 (CH₂), 29.7 (CH₃), 31.8 (CH₃), 34.2 (C), 35.0 (C), 52.2 (CH₂), 54.6 (CH₂), 62.6 (CH₂), 121.4 (Ar), 123.1 (ArH), 135.8 (Ar), 140.7 (Ar), 154.4, (ArO). Calc. m/z [C₃₅H₅₆N₂O₂ + H]+ 537.4420. Found 537.4442.

9H. 2-tert-butyl-4-methylphenol (3.28 g, 20.0 mmol), homo-piperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H₂O) (1.66 ml, 0.67 g, 22.5 mmol) were refluxed in MeOH (20 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.56 g, 3.5 mmol, 35 %). ¹H NMR (CDCl₃): δ 1.42 (18H, s, tBu), 1.89 (2H, quin, J = 6.1 Hz, CH₂), 2.24 (6H, s, CH₃), 2.77 (4H, s, ring-CH₂), 2.81 (4H, t, J = 6.0 Hz, ring-CH₂), 3.75 (4H, s, N-CH₂-Ar), 6.66 (2H, d, J = 1.9 Hz, ArH), 7.01 (2H, d, J = 2.3 Hz, ArH), 11.00 (2H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 20.9 (CH₂), 26.9 (CH₃), 29.6 (CH₃), 34.7 (C), 53.2 (CH₂), 54.6 (CH₂), 62.1 (CH₂), 122.0 (Ar), 126.9 (ArH), 127.3 (Ar), 127.4 (ArH), 136.6 (Ar), 154.6, (ArO). Calc. m/z [C₂₉H₄₄N₂O₂ + H]+ 453.3481. Found 453.3494.

10H. 2,4-di-tert-amylphenol (4.68 g, 20.0 mmol), homo-piperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H₂O) (1.67 ml, 0.68 g, 22.5 mmol) were refluxed in MeOH (20 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.85 g, 3.1 mmol, 31 %). ¹H NMR (CDCl₃): δ 0.64 (12H, q, J = 7.6 Hz CH₃), 1.23 (12H, s, CH₃), 1.37 (12H, s, CH₃), 1.57 (4H, quart, J = 7.5 Hz, CH₂), 1.90 (4H, quart, J = 7.3 Hz, CH₂), 1.90 (2H, s, ring-CH₂), 2.74 (4H, s, ring-CH₂), 2.81 (4H, t, J = 5.8 Hz, ring-CH₂), 3.76 (4H, s, N-CH₂-Ar), 6.74 (2H, d, J = 2.3 Hz, ArH), 7.07 (2H, d, J = 2.5 Hz, ArH), 10.87 (2H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 9.3 (CH₃), 9.7 (CH₃), 26.8
(CH₂), 27.8 (CH₃), 28.7 (CH₃), 33.2 (C), 37.3 (C), 37.4 (CH₂), 38.5 (CH₂), 53.1 (CH₂), 54.6 (CH₂), 62.6 (CH₂), 121.1 (Ar), 124.2 (ArH), 125.2 (ArH), 134.0 (Ar), 138.9 (Ar), 154.2 (ArO). Calc. m/z [C₃₉H₶₄N₂O₂ + H]+ 593.5046. Found 593.4993.

**11H₂.** Homopiperazine anhydrous (2.20 g, 25 mmol) and formaldehyde (38% in H₂O) (5.30 ml, 75.4 mmol) were refluxed (2 h) in MeOH (40 ml). The solution was then cooled to room temperature and 4-tert-butylphenol (7.51 g, 50.0 mmol) in methanol (60 ml) was added slowly then refluxed (16 h) and then cooled to room temperature. The solid was filtered, washed in cold MeOH then dried under vacuum to yield a white powder (2.31 g, 5.5 mmol, 22%). ¹H NMR (CDCl₃): δ 1.27 (18H, s, CH₃), 1.94 (2H, quintet, J = 6.0 Hz, CH₂), 2.79 (4H, s, CH₂), 2.84 (4H, t, J = 6.0 Hz, CH₂), 3.78 (4H, s, CH₂), 6.76 (2H, d, J = 8.50 Hz, ArH), 6.95 (2H, d, J = 2.5 Hz, ArH), 7.19 (2H, dd, J = 8.5 Hz, J = 2.5 Hz, ArH), 10.47 (2H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 26.8 (CH₂), 31.6 (CH₃), 34.0 (C), 53.6 (CH₂), 54.7 (CH₂), 62.4 (CH₂), 115.5 (ArH), 121.0 (Ar), 125.4 (ArH), 125.6 (ArH), 154.2 (ArO). Calc. m/z [C₂₇H₄₀N₂O₂ + H]+ 425.3168. Found 425.3233.

**12H₂.** 2,4-di-tert-butylphenol (4.11 g, 19.9 mmol), 2-methylpiperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H₂O) (1.62 ml, 0.66 g, 21.9 mmol) were refluxed in MeOH (20 ml ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (2.71 g, 5.0 mmol, 51%). ¹H NMR (CDCl₃): δ 1.23 (3H, d J = 6.5 Hz), 1.28 (9H, s, tBu), 1.29 (9H, s, tBu), 1.41 (18H, s, tBu), 2.10 – 3.20 (7H, br, ring-CH₂/CH), 3.69 (4H, m, N-CH₂-Ar), 6.82, (2H, br ArH), 7.21 (1H, d, J = 2.5 Hz, ArH), 7.23 (1H, d, J = 2.5 Hz, ArH), 10.71 (1H, br, OH), 10.82 (1H, br, OH). ¹³C{¹H} NMR (CDCl₃): δ 25.7 (CH₃), 29.7 (CH₃), 31.8 (CH₃), 34.2 (C), 35.0 (C), 52.5 (CH₂), 62.1 (CH₂), 120.8 (Ar), 122.9 (ArH), 123.0 (ArH), 123.5 (ArH), 123.6 (ArH), 135.6 (Ar), 135.7 (Ar), 140.9 (Ar), 140.9 (Ar), 154.1, (ArO). Calc. m/z [C₂₇H₄₀N₂O₂ + H]+ 537.4420. Found 537.4413.

**13H₂.** 2-tert-butyl-4-methylphenol (3.38 g, 20.5 mmol), 2-methylpiperazine (1.00 g, 10.0 mmol), and formaldehyde (38% in H₂O) (1.66 ml, 0.67 g, 22.5 mmol) were refluxed in MeOH (20 ml) for 24 h. During which time a white precipitate was
observed this was filtered and washed with cold MeOH and dried to yield a white solid (1.29 g, 2.8 mmol, 29 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.21 (3H, d, \(J = 6.5\) Hz, \(\text{ring-CH}_{3}\)), 1.42 (18H, s, \(^1\)Bu), 2.26 (6H, s, Me), 2.30 – 3.20 (7H, br, \(\text{ring-CH}_{2}/\text{CH}\)), 3.30 (1H, br, N-CH\(_2\)), 3.65 (2H, m, N-CH\(_2\)), 4.27 (1H, br, N-CH\(_2\)), 6.68 (1H, s, ArH), 6.68 (1H, s, ArH), 7.01 (1H, d, \(J = 2.0\) Hz, ArH), 7.02 (1H, d, \(J = 2.0\) Hz, ArH), 10.67 (2H, br, OH). \(^{13}\)C\(^{\text{[1]}\}\) NMR (CDCl\(_3\)): \(\delta\) 20.9 (CH\(_3\)), 24.1 (CH\(_3\)), 29.5 (CH\(_3\)), 29.5 (CH\(_2\)), 34.6 (C), 34.6 (C), 52.6 (CH\(_2\)), 57.4 (CH\(_2\)), 61.7 (CH\(_2\)), 121.1 (Ar), 126.7 (ArH), 127.0 (ArH), 127.4 (ArH), 127.4 (Ar), 127.5 (ArH), 136.4 (Ar), 134.4 (Ar), 154.3 (ArO). Calc. m/z \([\text{C}_{29}\text{H}_{44}\text{N}_{2}\text{O}_2 + \text{H}]^+\) 453.3481. Found 453.3462.

\(14\)H\(_2\). 2,4-di-\(\text{tert}\)-amylphenol (9.36 g, 40.0 mmol), 2-methylpiperazine (2.00 g, 20.0 mmol), and formaldehyde (38 % in H\(_2\)O) (3.31 ml, 1.35 g, 44.5 mmol) were refluxed in MeOH (30 ml) for 24 h. During which time a white precipitate was observed this was filtered and washed with cold MeOH and dried to yield a white solid (5.96 g, 10.3 mmol, 52 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 0.66 (12H, m, CH\(_3\)), 1.21 (3H, d, Me, \(J = 6.3\) Hz), 1.25 (12H, s, CH\(_3\)), 1.36 (12H, s, CH\(_3\)), 1.56 (4H, q, CH\(_2\)), 1.89 (4H, m, CH\(_2\)), 2.10 – 3.20 (7H, b, \text{ring-CH}_{2}), 3.30 (1H, b, N-CH\(_2/-\text{Ar}\)), 3.65 (2H, m, N-CH\(_2/-\text{Ar}\)), 4.25 (1H, b, N-CH\(_2/-\text{Ar}\)), 6.75 (2H, s, ArH), 7.07 (2H, m, ArH), 10.58 (2H, b, OH). \(^{13}\)C\(^{\text{[1]}\}\) NMR (CDCl\(_3\)): \(\delta\) 9.3 (CH\(_3\)), 9.7 (CH\(_3\)), 28.7 (CH\(_3\)), 33.1 (CH\(_2\)), 37.3 (C), 38.5 (C), 52.5 (\text{ring-CH}_{2}), 57.8 (\text{ring-CH}_{2}), 62.1 (N-CH\(_2\)), 120.1 (ArC), 120.2 (ArC), 124.2 (ArH), 124.3 (ArH), 125.1 (ArH), 125.3 (ArH), 133.9(Ar), 138.8 (Ar), 138.8 (Ar), 153.9 (ArO). Calc. m/z \([\text{C}_{39}\text{H}_{64}\text{N}_{2}\text{O}_2 + \text{H}]^+\) 593.5046. Found 593.5063.

\(15\)H\(_2\). 2-methyl-4-\(\text{tert}\)-butylphenol (3.38 g, 20.5 mmol), 2-methylpiperazine (1.00 g, 10.0 mmol), and formaldehyde (38 % in H\(_2\)O) (1.66 ml, 0.67 g, 22.5 mmol) were refluxed in MeOH (20 ml, 65 °C) to yield a white solid (1.20 g, 2.7 mmol, 27 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta\) 1.23 (3H, d, Me, \(J = 6.5\) Hz), 1.31 (18H, s, \(^1\)Bu), 2.25 (6H, s, Me), 2.30 – 3.20 (7H, b, \text{ring-CH}_{2}), 3.28 (1H, b, N-CH\(_2/-\text{Ar}\)), 3.68 (2H, m, N-CH\(_2/-\text{Ar}\)), 4.36 (1H, b, N-CH\(_2/-\text{Ar}\)), 6.84 (4H, s, ArH), 7.08 (4H, s, ArH), 10.66 (2H, b, OH). \(^{13}\)C\(^{\text{[1]}\}\) NMR (CDCl\(_3\)): \(\delta\) 16.1 (CH\(_3\)), 31.7 (CH\(_3\)), 34.0 (C), 52.7 (CH\(_2\)), 61.7 (CH\(_2\)), 119.5 (Ar), 119.9 (Ar), 123.1 (ArH), 123.2 (ArH), 126.9 (ArH), 127.1 (ArH), 124.1 (Ar), 141.6 (Ar), 141.7 (Ar), 141.6 (Ar), 153.4, (ArO). Calc. m/z \([\text{C}_{29}\text{H}_{44}\text{N}_{2}\text{O}_2 + \text{H}]^+\) 453.3481. Found 453.3475.
7.4 Preparation of Complexes for Chapter 2

7.4.1 Preparation of titanium bimetallic homo/piperazine salan complexes

Ti₂(1)(O'iPr)₆. 1H₂ (0.50 g, 1.41 mmol) and Ti(O'iPr)₄ (0.85 ml, 2.87 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield pale yellow crystals (0.51 g, 0.64 mmol, 45 %). The NMR was a mixture of Ti₂(1)(O'iPr)₆ and Ti₂(1)₂(O'iPr)₄ and Ti(O'iPr)₄ in a 4:1:2 ratio as discussed in the text. The NMR spectrum for the individual components follows: Ti₂(1)(O'iPr)₆ ¹H NMR (CDCl₃) (233 K): δ 1.26 (36H, d, J = 6.0 Hz, CH₃), 2.13 (6H, s, CH₃), 2.15 (3H, s, CH₃), 2.16 (3H, s, CH₃), 2.30 – 3.90 (8H, br, ring-CH₂), 4.09 (4H, m, N-CH₂-Ar), 4.89 (6H, br, CH), 6.69 (2H, s ArH), 6.83 (2H, s, ArH). Ti₂(1)₂(O'iPr)₄ ¹H NMR (233 K): δ 0.94 (3H, d, J = 6.0 Hz, Me), 0.97 (3H, d, J = 6.0 Hz, Me), 1.16 (6H, d, J = 6.0 Hz, Me), 1.20 – 1.40 (12H, br, CH₃), 2.08 (3H, s, Me), 2.10 – 2.25 (18H, br, Me), 2.28 (3H, s, Me), 2.30 – 3.90 (16H, br, ring-CH₂), 4.09 (8H, m, N-CH₂-Ar), 4.89 (4H, b, CH), 6.57 (2H, ArH), 6.76 (2H, ArH), 6.84 (2H, ArH), 6.92 (2H, ArH). Ti(O'iPr)₄ ¹H NMR (CDCl₃) (233 K): δ 1.26 (24H, d, J = 6.0 Hz, CH₃), 4.47 (4H, sept, J = 6.0 Hz, CH). ¹³C{¹H} NMR (CDCl₃): δ 16.8 (CH₃), 20.5 (CH₃), 26.7 (CH₃), 43.3 (CH₂), 52.0 (CH₂), 77.8 (CH), 122.7 (Ar), 124.8 (Ar), 127.0 (Ar), 127.7 (ArH), 130.8 (ArH), 158.2 (ArO).


Ti₂(2)(O'iPr)₆. 2H₂ (0.22g, 0.50 mmol) and Ti(O'iPr)₄ (0.30 ml, 1.01 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (20 ml) to yield a pale yellow crystals (0.19 g, 0.20 mmol, 41 %). The NMR was a mixture of Ti₂(2)(O'iPr)₆ and Ti₂(2)₂(O'iPr)₄ and Ti(O'iPr)₄ in a 4:1:2 ratio as discussed in the text. The NMRs for the individual components are: Ti₂(2)(O'iPr)₆ ¹H NMR (CDCl₃) (233 K): δ 1.23 (18H, s, CH₃), 1.26 (36H, d, J = 6.0 Hz, CH₃), 2.18 (6H, br, CH₃), 2.30 – 4.00 (8H, br, ring-CH₂), 4.15 (4H, br, N-CH₂-Ar), 4.90 (6H, br, CH), 6.89 (2H, br, ArH), 7.10 (2H, br ArH). Ti₂(2)₂(O'iPr)₄ ¹H NMR (CDCl₃) (233 K): δ 0.85 (3H, d, J = 6.0 Hz, CH₃), 0.87 (3H, d, J = 6.0 Hz, CH₃), 0.97 (3H, d, J = 6.0 Hz, CH₃), δ 1.14 (18H, s, CH₃), 1.10 – 1.50 (15H, br, CH₃), 1.34 (18H, s, CH₃), 2.13 (3H, s CH₃), 2.20 (6H, s, CH₃), 2.26 (3H, s,
Ti\(_2\)(O'Pr)\(_6\). 3H\(_2\) (0.49g, 0.94 mmol) and Ti(O'Pr)\(_4\) (0.70 ml, 2.36 mmol) were dissolved in CH\(_2\)Cl\(_2\) (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (20 ml) to yield pale yellow crystals (0.23 g, 0.26 mmol, 52 %). \(^1\)H NMR (CDCl\(_3\)): \(\delta 1.31\) (36H, d, J = 6.0 Hz, CH\(_3\)), 1.41 (18H, s, CH\(_3\)), 2.21 (6H, s, Me), 2.30 – 3.80 (8H, br, \(\text{ring-CH}_2\)), 4.12 (4H, s, N-CH\(_2\)-Ar), 4.93 (6H, sept, J = 6.0 Hz, CH), 6.78 (2H, d, J = 2.0 Hz, ArH), 6.97 (2H, d = 2.3 Hz, ArH). \(^{13}\)C\(^{\text{\text{\text{-}}}1\text{H}}\) NMR (CDCl\(_3\)): \(\delta 20.9\) (CH\(_3\)), 27.0 (CH\(_3\)), 29.6 (CH\(_3\)), 34.8 (C), 51.9 (N-CH\(_2\)), 77.6 (CH), 124.3 (Ar), 126.7 (Ar), 126.9 (ArH), 128.3 (ArH), 136.2 (Ar), 158.9 (ArO). Calc. (%) for C\(_{46}\)H\(_{82}\)N\(_2\)O\(_8\)Ti\(_2\): C 61.7, H 9.33, N 3.21.
mmol, 20 %). ¹H NMR (CDCl₃): δ 0.61 (12H, m, CH₃), 1.20 – 1.25 (12H, m, CH₃), 1.28 (36H, d, J = 6.0 Hz, CH₃), 1.35 (12H, s, CH₃), 1.54 (4H, m, CH₂), 1.96 (4H, m, CH₂), 2.20 – 2.80 (4H, br, ring-CH₂), 3.30 – 3.80 (4H, br, ring-CH₂), 4.10 (4H, s, N-CH₂-Ar), 4.90 (6H, sept, J = 6.0 Hz, ArH), 6.88 (2H, d, J = 2.0 Hz, ArH), 7.04 (2H, d, J = 2.0 Hz, ArH). ¹³C{¹H} NMR (CDCl₃): δ 26.9 (CH₂), 34.3 (C), 35.1 (C), 55.2 (CH₂), 64.3 (CH₂), 77.6 (CH), 123.2 (ArH), 124.1 (Ar), 124.6 (ArH), 135.5 (Ar), 140.0 (Ar), 159.9 (ArO). Calc. (%) for C₅₃H₁₀₂N₂O₈Ti₂, C 64.48, H 10.01, N 2.73. Found CHN (%), C 64.2, H 9.98, N 3.02.

Ti₂(8)(O’Pr)₆. 8H₂ (0.48g, 0.89 mmol) and Ti(O’Pr)₄ (0.80 ml, 2.70 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (30 ml) to yield pale yellow crystals (0.68 g, 0.69 mmol, 77 %). ¹H NMR (CDCl₃): δ 1.27 (36H, br, CH₃), 1.29 (18H, s, CH₃), 1.45 (18H, s, CH₃), 2.00 (2H, br, ring-CH₂), 2.98 (4H, br, ring-CH₂), 3.14 (4H, br, ring-CH₂), 3.92 (4H, s, N-CH₂-Ar), 4.90 (6H, sept, J = 6.0 Hz, CH), 6.86 (2H, d, J = 2.5 Hz, ArH), 7.19 (2H, d, J = 2.5 Hz, ArH). ¹³C{¹H} NMR (CDCl₃): δ 26.9 (CH₃), 31.8 (CH₃), 34.3 (C), 35.1 (C), 55.2 (CH₂), 64.3 (CH₂), 77.6 (CH), 123.2 (ArH), 124.1 (Ar), 124.6 (ArH), 135.5 (Ar), 140.0 (Ar), 159.9 (ArO). Calc. (%) for C₅₃H₁₀₂N₂O₈Ti₂, C 64.62, H 9.82, N 2.84. Found (%), C 64.4, H 9.61, N 2.95.

Ti₂(9)(O’Pr)₆. 9H₂ (0.51g, 1.13 mmol) and Ti(O’Pr)₄ (1.00 ml, 3.38 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane (10 ml) to yield yellow crystals (0.37 g, 0.24 mmol, 36 %). ¹H NMR (CDCl₃) (233 K): δ 1.26 (36H, b, CH₃-Pr), 1.42 (18H, d, 'Bu), 2.24 (6H, m, Me), 2.41 (1H, b, ring-CH₂), 2.59 (1H, b, ring-CH₂), 2.80 (1H, b, ring-CH₂), 2.99 (1H, b, ring-CH₂), 3.20 (2H, b, ring-CH₂), 3.43 (2H, b, ring-CH₂), 3.62 (2H, b, ring-CH₂), 3.80-4.20 (4H, m, N-CH₂-Ar), 4.90 (6H, b, CH), 6.64 (1H, s, ArH), 6.72 (1H, s, ArH), 6.95 (1H, s, ArH), 7.04 (1H, s, ArH). ¹³C{¹H} NMR (CDCl₃): δ 21.0 (CH₃), 26.9 (CH₃), 34.8 (C), 27.0 (CH₃), 21.2 (CH₂), 29.7 (CH₂), 30.0 (CH₂), 30.2 (CH₂), 30.6 (CH₂), 56.8 (N-CH₂), 77.6 (CH), 122.9 (Ar), 124.0 (Ar), 123.5 (ArH), 127.9 (ArH), 139.4 (Ar), 163.1 (ArO). Calc. (%) for C₄₇H₈₄N₂O₈Ti₂, C 62.66, H 9.40, N 3.11. Found (%), C 60.1, H 9.01, N 3.10.
Ti₂(12)(O'Pr)_6. 12H₂ (0.60 g, 1.11 mmol) and Ti(O'Pr)₄ (1.00 ml, 3.38 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane (2 ml) to yield yellow crystals (0.72 g, 0.73 mmol, 65 %). ¹H NMR (CDCl₃) (233 K): δ 0.97 (3H, d, J = 6.0 Hz, CH₃), 1.28 (36H, d J = 6.0 Hz, CH₃), 1.31 (9H, br, CH₃), 1.41 (9H, s, CH₃), 1.42 (9H, s, CH₃), 2.40 – 3.70 (7H, br, ring-CH₂), 3.95 (2H, br, N-CH₂-Ar), 4.12 (2H, m, N-CH₂-Ar), 4.80 (3H, sept, J = 6.0 Hz, CH), 4.89 (3H, sept, J = 6.0 Hz, CH), 6.90 (1H, d, J = 2.5 Hz, ArH), 7.14 (1H, d, J = 2.5 Hz, ArH), 7.18 (2H, br, ArH). ¹³C{¹H} NMR (CDCl₃): δ 26.7 (CH₃), 26.8 (CH₃), 26.8 (CH₃), 26.9 (CH₃), 29.7 (C), 29.8 (C), 31.8 (CH₃), 34.3 (C), 34.4 (C), 35.1 (CH₂), 76.5 (CH), 77.4 (CH), 77.8 (CH), 122.0 (ArH), 123.1 (ArH), 123.6 (ArH), 123.9 (Ar), 124.4 (ArH), 135.5 (Ar), 135.7 (Ar), 140.0 (Ar), 141.0 (Ar), 158.9 (ArO). Calc. (%) for C₅₃H₉₆N₂O₈Ti₂, C 64.62, H 9.82, N 2.84. Found (%), C 63.0, H 9.48, N 3.04

Ti₂(13)(O'Pr)_6. 13H₂ (0.51 g, 1.13 mmol) and Ti(O'Pr)₄ (1.00 ml, 3.38 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane (5 ml) to yield yellow crystals (0.59 g, 0.65 mmol, 58 %). ¹H NMR (CDCl₃): δ 1.07 (3H, d, J = 6.5, CH₃), 1.31 (18H, d, J = 6.0 Hz, CH₃), 1.33 (18H, d, J = 6.0 Hz, CH₃), 1.44 (9H, s, CH₃), 1.45 (9H, s, CH₃), 2.23 (3H, s, CH₃), 2.25 (3H, s, CH₃), 2.48 (1H, br, CH₂), 2.52 (1H, br, CH₂), 2.66, (1H, br, CH₂), 3.04 (1H, m, CH₂), 3.34 (1H, m, CH₂), 3.38 (1H, m, CH₂), 3.55 (1H, br, CH₂) 3.94 (2H, s, CH₂), 4.09 (2H, m, CH₂), 4.83 (3H, sept, J = 6.0 Hz, CH), 4.92 (3H, sept, J = 6.0 Hz, CH), 6.72 (1H, s, ArH), 6.95 (1H, s, ArH), 6.98 (1H, s, ArH), 7.01 (1H, s, ArH). ¹³C{¹H} NMR (CDCl₃): δ 17.9 (CH₃), 21.0 (CH₃), 21.1 (CH₃), 26.8 (CH₃), 26.9 (CH₃), 29.7 (C), 30.0 (C), 34.8 (CH₂), 44.9 (CH₂), 49.5 (CH₁), 50.2 (CH₂), 53.4 (CH₂), 77.5 (CH), 77.9 (CH), 124.4 (Ar), 125.7 (ArH), 126.5 (Ar), 126.7 (ArH), 127.6 (ArH), 127.6 (Ar), 128.2 (ArH), 136.2 (Ar), 136.5 (Ar), 159.1 (ArO), 159.7 (ArO). Calc. (%) for C₄₇H₈₄N₂O₈Ti₂, C 64.62, H 9.82, N 2.84. Found (%), C 63.0, H 9.48, N 3.04

Ti₂(14)(O'Pr)_₄. 1H₂ (0.60 g, 1.69 mmol) and Ti(O'Pr)₄ (0.50 ml, 1.69 mmol) were dissolved in Tol. (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield pale yellow crystals (0.27
g, 0.52 mmol, 31 %). $^1$H NMR (CDCl$_3$) (233 K): $\delta$ 0.92 (6H, d, J = 6.0 Hz, CH$_3$), 0.95 (6H, d, J = 6.0 Hz, CH$_3$), 1.15 (6H, d, J = 6.0 Hz, CH$_3$), 1.29 (6H, d, J = 6.0 Hz, CH$_3$), 1.86 (2H, t, J = 12.5 Hz, CH$_2$), 2.06 (6H, s, CH$_3$), 2.10 (6H, s, CH$_3$), 2.13 (6H, s, CH$_3$), 2.19 (4H, d, J = 7.5 Hz, CH$_2$), 2.27 (6H, s, CH$_3$), 2.61 (2H, d, J = 11.5 Hz, CH$_2$), 2.69 (2H, d, J = 11.0 Hz, CH$_2$), 2.82 (2H, t, J = 11.5 Hz, CH$_2$), 3.19 (2H, t, J = 12.0 Hz, CH$_2$), 3.32 (2H, d, J = 12.0 Hz, CH$_2$), 3.85 (2H, t, J = 11.5 Hz, CH$_2$), 4.03 (4H, m, CH$_2$), 4.19 (2H, d, J = 13.5 Hz, CH$_2$), 4.47 (2H, sept, J = 12.0 Hz, CH), 4.92 (2H, septet, J = 12.0 Hz, CH), 6.56 (2H, s, ArH), 6.74 (2H, s, ArH), 6.82 (2H, s, ArH), 6.91 (2H, s, ArH). $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 16.5 (CH$_3$), 16.7 (CH$_3$), 17.4 (CH$_3$), 20.6 (CH$_3$), 25.8 (CH$_3$), 26.5 (CH$_3$), 26.7 (CH$_3$), 27.0 (CH$_3$), 44.9 (CH$_2$), 47.5 (CH$_2$), 48.8 (CH$_2$), 51.4 (br, CH$_2$), 52.8 (br, CH$_2$), 59.3 (CH$_2$), 78.5 (CH), 79.3 (CH), 123.3 (ArH), 123.7 (ArH), 124.7 (ArH), 126.0 (ArH), 126.9 (ArH), 127.6 (ArH), 127.9 (Ar), 129.6 (Ar), 130.5 (Ar), 130.9 (Ar), 158.5 (ArO), 163.2 (ArO). Calc. (%) for C$_{33}$H$_{42}$N$_2$O$_4$Ti: C 64.86, H 8.16, N 5.40. Found (%), C 64.67, H 8.16, N 5.56.

### 7.4.2 Preparation of titanium monometallic homopiperazine salan complexes

Ti(6)(O$^3$Pr)$_2$. 6H$_2$ (0.37 g, 1.00 mmol) and Ti(O$^3$Pr)$_4$ (0.30 ml, 1.01 mmol) were dissolved in toluene (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield pale yellow crystals (0.14 g, 0.26 mmol, 26 %). 2 species identified in the solution state NMR spectra. $^1$H NMR (CDCl$_3$): $\delta$ 0.40 (3H, d, J = 5.5 Hz, CH$_3$), 1.14 (6H, br, CH$_3$), 1.19 (3H, d, J = 5.5 Hz, CH$_3$), 1.68 (1H, m, CH$_2$), 1.88 (1H, m, CH$_2$), 2.21 (9H, s, CH$_3$), 2.29 (3H, s, CH$_3$), 2.42 (2H, br, CH$_2$), 2.79 (1H, d, J = 6.0 Hz, CH$_2$), 3.11 (1H, d, J = 11.5 Hz, CH$_2$), 3.31 (2H, s, CH$_2$), 3.60 (1H, d, J = 6.5 Hz, CH$_2$), 3.72 (1H, m, CH$_2$), 3.95 (1H, m, CH$_2$), 4.20 (2H, d, J = 11.0 Hz, CH$_2$), 4.46 (1H, m, CH$_2$), 4.85 (1H, m, CH$_2$), 4.93 (1H, m, CH$_2$), 6.68 (2H, s, ArH), 6.91 (1H, s, ArH). 2nd species $^1$H NMR (CDCl$_3$): $\delta$ 0.45 – 1.45 (12H, br, CH$_3$), 2.00 – 2.50 (12H, br, CH$_3$), 2.00 – 2.50 (4H, br, CH$_2$), 3.00 – 5.00 (10H, br, CH$_2$), 3.00 – 5.00 (2H, br, CH), 6.58 (2H, s, ArH), 6.87 (2H, s, ArH). $^{13}$C($^1$H) NMR (CDCl$_3$): $\delta$ 16.5 (CH$_3$), 16.9 (CH$_3$), 20.8 (CH$_3$), 23.0 (CH$_2$), 23.7 (CH$_2$), 25.9 (CH$_3$), 26.1 (CH$_3$), 26.3 (CH$_3$), 50.8 (br, CH$_2$), 55.6 (CH$_2$), 58.0 (CH$_2$), 59.2 (br, CH$_2$), 62.7 (br, CH$_2$), 64.1 (CH$_2$), 72.1 (CH), 73.2 (CH), 75.7 (CH), 75.9 (CH), 123.4 (ArH), 124.6 (ArH), 125.4 (ArH), 127.4 (Ar), 122.0 – 132.0 (Ar),
131.5 (Ar), 163.0 (ArO). Calc. (%) for C_{29}H_{44}N_{2}O_{4}Ti: C 65.41, H 8.33, N 5.26. Found (%), C 65.29, H 8.27, N 5.37

Ti(7)(O{\textsuperscript{1}Pr})_{2}. 7H_{2} (0.46 g, 1.02 mmol) and Ti(O{\textsuperscript{1}Pr})_{4} (0.30 ml, 1.01 mmol) were dissolved in toluene (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield pale yellow crystals (0.48 g, 0.78 mmol, 77 %). 2 species identified in the solution state NMR spectra. \textsuperscript{1}H NMR (CDCl_{3}): \( \delta \) 0.32 (3H, d, J = 6.0 Hz, CH_{3}), 0.87 (6H, br, CH_{3}), 1.65 (9H, d, J = 6.0 Hz, CH_{3}), 1.26 (36H, s, CH_{3}), 1.71 (1H, m, CH_{2}), 1.90 (2H, m, CH_{2}), 2.16 (4H, br, CH_{2}), 2.28 (12H, s, CH_{3}), 2.24 (2H, br, CH_{2}), 2.80 (1H, d, J = 6.5 Hz, CH_{2}), 3.16 (1H, d, J = 11.5 Hz, CH_{2}), 3.30 (4H, br, CH_{2}), 3.61 (1H, d, J = 6.5 Hz, CH_{2}), 3.71 (2H, m, CH_{2}), 3.97 (1H, m, CH), 4.20 (2H, d, J = 11.5 Hz, CH_{2}), 4.22 (1H, br, CH_{2}), 4.45 (1H, m, CH), 4.80 (1H, m, CH), 4.92 (1H, m, CH), 6.74 (2H, br, ArH), 6.86 (2H, s, ArH), 7.05 (2H, br, ArH), 7.11 (2H, s, ArH). \textsuperscript{13}C[\textsuperscript{1}H] NMR (CDCl_{3}): \( \delta \) 16.5 (CH_{3}), 16.9 (CH_{3}), 20.7 (CH_{3}), 23.0 (C), 23.7 (C), 25.8 (CH_{3}), 26.1 (CH_{3}), 26.3 (CH_{3}), 55.6 (CH_{2}), 58.0 (CH_{2}), 59.2 (br, CH_{2}), 62.7 (br, CH_{2}), 64.1 (CH_{2}), 72.1 (CH), 73.1 (CH), 75.7 (CH), 75.9 (CH), 122.9 (Ar), 123.4 (ArH), 124.0 (Ar), 126.7 (br, Ar), 127.9 (ArH), 139.1 (Ar), 163.0 (ArO). Calc. (%) for C_{35}H_{56}N_{2}O_{4}Ti: C 68.17, H 9.15, N 4.54. Found (%), C 68.29, H 9.28, N 4.57

Ti(8)(O{\textsuperscript{1}Pr})_{2}. 8H_{2} (0.54 g, 1.01 mmol) and Ti(O{\textsuperscript{1}Pr})_{4} (0.30 ml, 1.01 mmol) were dissolved in toluene (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield pale yellow crystals (0.24 g, 0.34 mmol, 34 %). 2 species identified in the solution state NMR spectra in an approximate 50:50 ratio, a third species is present in a negligible ratio. \textsuperscript{1}H NMR (CDCl_{3}): \( \delta \) 0.39 (3H, d, J = 6.0 Hz, CH_{3}), 0.55 (3H, d, J = 6.0 Hz, CH_{3}), 0.72 (3H, d, J = 6.0 Hz, CH_{3}), 0.94 (3H, d, J = 6.0 Hz, CH_{3}), 0.97 (3H, d, J = 6.0 Hz, CH_{3}), 0.98 (3H, d, J = 6.0 Hz, CH_{3}), 1.01 (6H, d, J = 6.0 Hz, CH_{3}), 1.26 (18H, s, \textsuperscript{1}Bu), 1.28 (18H, s, \textsuperscript{1}Bu), 1.46 (9H, s, \textsuperscript{1}Bu), 1.47 (9H, s, \textsuperscript{1}Bu), 1.48 (18H, s, \textsuperscript{1}Bu), 1.82 (2H, m, CH_{2}), 2.23 (3H, m, CH_{2}), 2.38 (3H, m, CH_{2}), 2.45 (1H, m, CH_{2}), 2.72 (2H, m, CH_{2}), 3.05 (1H, d, J = 11.5 Hz, CH_{2}), 3.23 (2H, d, J = 11.5 Hz, CH_{2}), 3.44 (1H, d, J = 14.5 Hz, CH_{2}), 3.55 (2H, m, CH_{2}), 3.61 (2H, d, J = 6.5 Hz, CH_{2}), 3.88 (2H, m, CH_{2}), 3.97 (1H, br, CH_{2}), 4.01 (2H, d, J = 11.5 Hz, CH_{2}), 4.13 (1H, d, J = 11.5 Hz, CH_{2}), 4.17 (1H, m,
Ti(9)(O^tPr)_2. 9H_2 (0.46 g, 1.02 mmol) and Ti(O^tPr)_4 (0.30 ml, 1.01 mmol) were dissolved in toluene (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield pale yellow crystals (0.16 g, 0.26 mmol, 26 %). 2 species identified in the solution state NMR spectra in a approximate 50:50 ratio. ^1H NMR (CDCl_3): δ 0.41 (3H, br, CH_3), 0.55 (3H, d, J = 6.0 Hz, CH_3), 0.72 (3H, d, J = 6.0 Hz, CH_3), 0.83 (3H, d, J = 6.0 Hz, CH_3), 0.98 (3H, d, J = 6.0 Hz, CH_3), 1.02 (3H, d, J = 6.0 Hz, CH_3), 1.00 (3H, s, CH_3), 0.98 (6H, br, CH_3), 1.43 (54H, s, ^1Bu), 1.81 (3H, m, CH_2), 2.15–2.30 (7H, br, CH_2), 2.22 (6H, s, CH_3), 2.24 (6H, s, CH_3), 2.25 (6H, s, CH_3), 2.30–2.45 (6H, m, CH_2), 2.54 (1H, m, CH_2), 2.66 (2H, m, CH_2), 2.78 (1H, br, CH_2), 3.05 (2H, d, J = 12.0 Hz, CH_2), 3.22 (2H, d, J = 11.5 Hz, CH_2), 3.41 (2H, t, J = 13.0 Hz, CH_2), 3.43 (2H, br, CH_2), 3.54 (2H, br, CH_2), 3.68 (2H, d, J = 3.5 Hz, CH_2), 3.82 (2H, br, CH), 3.98 (3H, br, CH_2), 4.05 (2H, d, J = 12.0 Hz, CH_2), 4.12 (2H, m, CH_2), 4.24 (2H, m, CH), 4.51 (2H, d, J = 14.0 Hz, CH_2), 4.61 (2H, m, CH), 5.31 (1H, d, J = 13.0 Hz, CH_2), 6.61 (1H, s, ArH), 6.75 (2H, s, ArH), 6.77 (2H, s, ArH), 6.81 (1H, s, ArH), 6.97 (1H, s, ArH), 7.01 (4H, s, ArH), 7.09 (1H, s, ArH). ^13C(^1H) NMR (CDCl_3): δ 20.9 (CH_3), 21.0 (CH_3), 21.1 (CH_3), 22.9 (CH_3), 23.4 (CH_3), 25.8 (CH_3), 25.9 (CH_3), 26.0 (CH_3), 26.3 (CH_3), 26.4 (CH_3), 26.9 (CH_3), 29.9 (CH_3), 30.2 (CH_3), 30.6 (CH_3), 34.8 (C), 35.0 (C), 35.2 (C), 35.3 (C), 50.9 (CH_2), 52.6 (CH_2), 55.2 (CH_2), 55.5 (CH_2), 55.7 (CH_2), 57.8 (CH_2), 58.4 (CH_2), 59.1 (CH_2), 62.9 (CH_2), 64.3
(CH₂), 64.4 (CH₂), 64.7 (CH₂), 72.7 (CH), 73.0 (CH), 75.1 (CH), 75.9 (CH), 121.8 (Ar), 122.9 (Ar), 124.2 (Ar), 124.6 (Ar), 124.9 (Ar), 125.3 (Ar), 125.7 (ArH), 125.9 (Ar), 126.0 (Ar), 126.9 (ArH), 127.4 (ArH), 127.7 (ArH), 127.8 (ArH), 128.0 (ArH), 128.2 (ArH), 134.8 (Ar), 135.0 (Ar), 137.5 (Ar), 137.6 (Ar), 134.8 (Ar), 159.1 (ArO), 159.9 (ArO), 163.5 (ArO), 164.3 (ArO). Calc. (%) for C₃₅H₅₆N₂O₄Ti: C 68.17, H 9.15, N 4.54. Found (%), C 66.45, H 8.85, N 4.58.

Ti(10)(O'Pr)₂. 10H₂ (0.60 g, 1.01 mmol) and Ti(O'Pr)₄ (0.30 ml, 1.01 mmol) were dissolved in toluene (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in vacuo and recrystallised from hexane to yield pale yellow crystals (0.13 g, 0.17 mmol, 17 %). 2 species identified in the solution state NMR spectra in a approximate 50:50 ratio. ¹H NMR (CDCl₃): δ 0.33 (3H, d, J = 6.0 Hz, CH₃), 0.55 (3H, d, J = 6.0 Hz, CH₃), 0.67 (15H, m, CH₃), 0.76 (12H, m, CH₃), 0.99 (3H, d, J = 6.0 Hz, CH₃), 1.01 (3H, d, J = 6.0 Hz, CH₃), 1.12 (6H, d, J = 6.0 Hz, CH₃), 1.23 (6H, s, CH₃), 1.26 (12H, s, CH₃), 1.29 (6H, s, CH₃), 1.39 (3H, s, CH₃), 1.41 (3H, s, CH₃), 1.45 (9H, s, CH₃), 1.47 (9H, s, CH₃), 1.60 (8H, m, CH₂), 1.60 (8H, m, CH₂), 1.75 – 1.95 (6H, m, CH₂), 2.07 (3H, m, CH₂), 2.22 (4H, m, CH₂), 2.30 – 2.50 (4H, m, CH₂), 2.66 (1H, m, CH₂), 2.78 (2H, m, CH₂), 3.06 (1H, d, J = 11.5 Hz, CH₂), 3.20 (2H, d, J = 11.5 Hz, CH₂), 3.44 (1H, d, J = 14.5 Hz, CH₂), 3.53 (2H, d, J = 7.5 Hz, CH₂), 3.62 (2H, d, J = 6.5 Hz, CH₂), 3.90 (2H, m, CH₂), 4.00 (1H, br, CH₂), 4.10 (3H, d, J = 11.5 Hz, CH₂), 4.22 (1H, m, CH₂), 4.25 (1H, m, CH), 4.34 (1H, m, CH), 4.54 (1H, d, J = 13.5 Hz, CH₂), 4.59 (1H, m, CH), 4.68 (1H, m, CH), 6.68 (1H, d, J = 2.0 Hz, ArH), 6.83 (2H, d, J = 2.5 Hz, ArH), 6.85 (1H, d, J = 2.0 Hz, ArH), 7.05 (1H, d, J = 2.0 Hz, ArH), 7.14 (2H, d, J = 2.5 Hz, ArH), 7.16 (1H, br, ArH). ¹³C [¹H] NMR (CDCl₃): δ 9.3 (CH₃), 9.4 (CH₃), 9.7 (CH₃), 9.9 (CH₃), 22.9 (CH₂), 23.4 (CH₂), 25.7 (CH₃), 25.8 (CH₃), 26.2 (CH₃), 26.3 (CH₃), 26.4 (CH₃), 27.0 (CH₃), 27.4 (CH₃), 27.8 (CH₃), 27.8 (CH₃), 28.0 (CH₃), 28.1 (CH₃), 28.2 (CH₃), 28.3 (CH₃), 28.7 (CH₃), 28.7 (CH₃), 28.9 (CH₃), 29.0 (CH₃), 29.1 (CH₃), 29.2 (CH₃), 29.3 (CH₃), 32.9 (C), 33.3 (C), 33.8 (C), 37.2 (CH₂), 37.2 (CH₂), 37.3 (CH₂), 37.4 (CH₂), 37.6 (C), 38.3 (C), 38.5 (C), 38.9 (C), 51.1 (CH₂), 52.5 (CH₂), 55.4 (CH₂), 55.6 (CH₂), 57.6 (CH₂), 58.2 (CH₂), 59.0 (CH₂), 63.2 (CH₂), 64.7 (CH₂), 64.8 (CH₂), 65.2 (CH₂), 72.7 (CH), 73.0 (CH), 74.8 (CH), 75.9 (CH), 120.9 (Ar), 121.9 (Ar), 123.3 (Ar), 123.4 (Ar), 123.8 (ArH), 124.5 (ArH), 124.6 (ArH), 125.3 (ArH), 125.9 (ArH), 126.5
(ArH), 132.9 (Ar), 133.0 (Ar), 134.9 (Ar), 135.1 (Ar), 136.1 (Ar), 136.2 (Ar), 137.2 (Ar), 137.4 (Ar), 158.8 (ArO), 159.7 (ArO), 163.5 (ArO), 164.1 (ArO). CHN Calc. (%) for C_{45}H_{76}N_{2}O_{4}Ti: C 71.40, H 10.12, N 3.70. Found (%), C 71.38, H 9.97, N 3.78.

Ti(II)(O\textsuperscript{1}Pr)\textsubscript{2}, 11H\textsubscript{2} (0.43 g, 1.01 mmol) and Ti(O\textsuperscript{3}Pr)\textsubscript{4} (0.30 ml, 1.01 mmol) were dissolved in toluene (30 ml) then heated (80 °C) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield pale yellow crystals (0.39 g, 0.66 mmol, 65 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 0.63 (6H, d, J = 6.0 Hz, CH\textsubscript{3}), 1.61 (6H, d, J = 6.0 Hz, CH\textsubscript{3}), 1.28 (18H, s, \textsuperscript{1}Bu), 1.72 (1H, m, CH\textsubscript{2}), 1.72 (1H, m, CH\textsubscript{2}), 2.19 (1H, m, CH\textsubscript{2}), 2.28 (2H, m, CH\textsubscript{2}), 2.81 (2H, d, J = 6.5 Hz, CH\textsubscript{2}), 3.20 (2H, d, J = 11.5 Hz, CH\textsubscript{2}), 3.61 (2H, d, J = 6.0 Hz, CH\textsubscript{2}), 3.61 (2H, br, CH\textsubscript{2}), 3.84 (1H, m, CH), 4.22 (2H, d, J = 11.5 Hz, CH\textsubscript{2}), 4.82 (1H, m, CH), 6.79 (1H, s, ArH), 6.82 (1H, s, ArH), 7.02 (2H, d, J = 2.0 Hz, ArH), 7.18 (1H, s, ArH), 7.27 (1H, s, ArH). \textsuperscript{13}C\textsuperscript{[\textsuperscript{1}H]} NMR (CDCl\textsubscript{3}): δ 23.0 (CH\textsubscript{2}), 26.1 (CH\textsubscript{3}), 26.2 (CH\textsubscript{3}), 31.9 (CH\textsubscript{3}), 34.0 (C), 55.3 (CH\textsubscript{2}), 58.0 (CH\textsubscript{2}), 64.1 (CH\textsubscript{2}), 72.0 (CH), 73.0 (CH), 116.6 (ArH), 123.6 (Ar), 125.9 (ArH), 126.5 (ArH), 139.7 (Ar), 164.1 (ArO). CHN Calc. (%) for C\textsubscript{33}H\textsubscript{52}N\textsubscript{2}O\textsubscript{4}Ti: C 67.33, H 8.90, N 4.76. Found (%), C 67.42, H 8.89, N 4.70.

7.4.3 Preparation of titanium catechol homo/piperazine salan complexes

Ti(II)Catechol, 1H\textsubscript{2} (0.60 g, 1.69 mmol) and Ti(O\textsuperscript{3}Pr)\textsubscript{4} (0.50 ml, 1.69 mmol) were dissolved in CH\textsubscript{2}Cl\textsubscript{2} (30 ml) and stirred (1 h). Catechol (0.185 g, 1.68 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in-vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.71 g, 1.39 mmol, 83 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): δ 2.18 (2H, d, J = 6.5 Hz, CH\textsubscript{2}), 2.25 (6H, s, CH\textsubscript{3}), 2.26 (6H, s, CH\textsubscript{3}), 2.63 (2H, d, J = 5.5 Hz, CH\textsubscript{2}), 3.23 (2H, d, J = 6.5 Hz, CH\textsubscript{2}), 3.38 (2H, d, J = 14.0 Hz, CH\textsubscript{2}), 3.80 (2H, d, J = 5.5 Hz, CH\textsubscript{2}), 4.51 (2H, d, J = 13.5 Hz, CH\textsubscript{2}), 6.40 (1H, d, J = 3.5 Hz, ArH), 6.42 (1H, d, J = 3.5 Hz, ArH), 6.62 (1H, d, J = 3.5 Hz, ArH), 6.64 (1H, d, J = 3.5 Hz, ArH), 6.65 (2H, s, ArH), 6.96 (2H, s, ArH). \textsuperscript{13}C\textsuperscript{[\textsuperscript{1}H]} NMR (CDCl\textsubscript{3}): δ 16.7 (CH\textsubscript{3}), 20.7 (CH\textsubscript{3}), 49.7 (CH\textsubscript{2}), 50.1 (CH\textsubscript{2}), 58.5 (CH\textsubscript{2}), 111.2 (ArH), 119.1 (ArH), 121.9 (Ar), 126.1 (Ar), 126.8 (ArH), 129.0, (Ar), 131.4, (ArH), 157.3, (ArO), 158.7, (ArO). Calc. (%) for C\textsubscript{28}H\textsubscript{32}N\textsubscript{2}O\textsubscript{4}Ti: C 66.14, H 6.34, N 5.51. Found (%), C 66.28, H 6.20, N 5.55.
Ti(1)-3,5-Di-tert-butylcatechol. 1H2 (0.36 g, 1.02 mmol) and Ti(OiPr)4 (0.30 ml, 1.01 mmol) were dissolved in CH2Cl2 (30 ml) and stirred (1 h). 3,5-Di-tert-butylcatechol (0.225 g, 1.01 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.42 g, 0.68 mmol, 67 %). 1H NMR (CDCl3): δ 1.12 (9H, s, tBu), 1.26 (9H, s, tBu), 2.19 (2H, d, J = 6.0 Hz, CH2), 2.24 (6H, s, CH3), 2.27 (6H, s, CH3), 2.65 (2H, d, J = 5.5 Hz, CH2), 3.24 (2H, d, J = 6.0 Hz, CH2), 3.40 (2H, d, J = 13.5 Hz, CH2), 3.91 (2H, d, J = 5.5 Hz, CH2), 4.51 (2H, d, J = 13.5 Hz, CH2), 6.34 (1H, d, J = 2.5 Hz, ArH), 6.62 (1H, d, J = 4.5 Hz, ArH), 6.61 (2H, s, ArH), 6.96 (2H, s, ArH). 13C{1H} NMR (CDCl3): δ 16.5 (CH3), 20.7 (CH3), 29.6 (CH3), 32.1 (CH3), 34.3 (C), 34.5 (C), 49.8 (CH2), 55.1 (CH2), 58.6 (CH2), 106.9 (ArH), 112.9 (ArH), 121.7 (Ar), 126.2 (Ar), 126.6 (ArH), 128.5 (Ar), 131.1 (ArH), 131.3 (Ar), 141.1 (Ar), 154.8 (ArO), 157.6, (ArO), 158.8, (ArO). Calc. (%) for C36H48N2O4Ti: C 69.67, H 7.80, N 4.51. Found (%), C 64.47, H 7.25, N 4.23.

Ti(1)-Methoxy catechol. 1H2 (0.36 g, 1.02 mmol) and Ti(OiPr)4 (0.30 ml, 1.01 mmol) were dissolved in CH2Cl2 (30 ml) and stirred (1 h). 3-Methoxy catechol (0.142 g, 1.01 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.25 g, 0.46 mmol, 46 %). 1H NMR (CDCl3): δ 2.19 (2H, d, J = 6.5 Hz, CH2), 2.23 (6H, s, CH3), 2.25 (6H, s, CH3), 2.63 (2H, d, J = 5.5 Hz, CH2), 3.22 (2H, d, J = 6.0 Hz, CH2), 3.38 (2H, d, J = 13.5 Hz, CH2), 3.69 (3H, s, CH3), 3.83 (2H, d, J = 5.5 Hz, CH2), 4.53 (2H, d, J = 13.5 Hz, CH2), 6.12 (1H, dd, J = 8.0 Hz, J = 1.0 Hz, ArH), 6.33 (1H, dd, J = 8.5 Hz, J = 1.5 Hz, ArH), 6.54 (1H, t, J = 8.0 Hz, ArH), 6.64 (2H, s, ArH), 6.94 (2H, s, ArH). 13C{1H} NMR (CDCl3): δ 16.6 (CH3), 20.7 (CH3), 49.7 (CH2), 55.2 (CH2), 56.9 (CH3), 58.6 (CH2), 115.7 (ArH), 115.9 (ArH), 118.3 (ArH), 122.0 (Ar), 126.1 (Ar), 126.7 (ArH), 128.9 (Ar), 131.3 (ArH), 144.1 (Ar), 146.7 (ArO), 157.4 (ArO), 160.0 (ArO). Calc. (%) for C29H48N2O5Ti: C 64.69, H 6.36, N 5.20. Found (%), C 64.74, H 6.29, N 5.39.

Ti(1)-4-Nitro catechol. 1H2 (0.36 g, 1.02 mmol) and Ti(OiPr)4 (0.30 ml, 1.01 mmol) were dissolved in CH2Cl2 (30 ml) and stirred (1 h). 4-Nitro catechol (0.16 g, 1.03
mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in-vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.44 g, 0.80 mmol, 78%). $^1$H NMR (CDCl$_3$): δ 2.25 (6H, s, CH$_3$), 2.27 (6H, s, CH$_3$), 2.31 (2H, d, J = 7.0 Hz, CH$_2$), 2.75 (2H, d, J = 5.5 Hz, CH$_2$), 3.32 (2H, d, J = 6.0 Hz, CH$_2$), 3.47 (2H, d, J = 14.0 Hz, CH$_2$), 3.79 (2H, d, J = 6.0 Hz, CH$_2$), 4.48 (2H, d, J = 14.0 Hz, CH$_2$), 6.38 (1H, d, J = 8.5 Hz, ArH), 6.70 (2H, s, ArH), 6.98 (2H, s, ArH), 7.25 (1H, s, ArH), 7.70 (1H, dd, J = 8.5 Hz, J = 2.5 Hz, ArH). $^{13}$C($^1$H) NMR (CDCl$_3$): δ 16.5 (CH$_3$), 20.8 (CH$_3$), 49.8 (CH$_2$), 55.2 (CH$_2$), 58.5 (CH$_2$), 106.2 (ArH), 110.0 (ArH), 117.5 (ArH), 121.7 (Ar), 125.9 (Ar), 126.8 (ArH), 130.1 (Ar), 131.7 (ArH), 144.5 (Ar), 157.1 (ArO), 158.2 (ArO), 166.3 (ArO). Calc. (%) for C$_{28}$H$_{31}$N$_3$O$_6$Ti: C 60.77, H 5.65, N 7.59. Found (%), C 60.81, H 5.79, N 7.49.

Ti(2)Catechol. $^{2}$H$_2$ (0.74 g, 1.69 mmol) and Ti(O$^i$Pr)$_4$ (0.50 ml, 1.69 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (1 h). Catechol (0.186 g, 1.69 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in-vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.72 g, 1.22 mmol, 72%). $^1$H NMR (CDCl$_3$): δ 1.29 (18H, s, $^1$Bu), 2.17 (2H, d, J = 6.5 Hz, CH$_2$), 2.29 (6H, s, CH$_3$), 2.23 (6H, s, CH$_3$), 2.64 (2H, d, J = 5.5 Hz, CH$_2$), 3.22 (2H, d, J = 6.5 Hz, CH$_2$), 3.40 (2H, d, J = 13.5 Hz, CH$_2$), 3.79 (2H, d, J = 5.5 Hz, CH$_2$), 4.53 (2H, d, J = 13.5 Hz, CH$_2$), 6.39 (1H, d, J = 3.5 Hz, ArH), 6.41 (1H, d, J = 4.0 Hz, ArH), 6.61 (1H, d, J = 4.0 Hz, ArH), 6.63 (1H, d, J = 3.5 Hz, ArH), 6.83 (2H, d, J = 2.5, ArH), 7.14 (2H, d, J = 2.5, ArH). $^{13}$C($^1$H) NMR (CDCl$_3$): δ 17.0 (CH$_3$), 31.8 (CH$_3$), 34.1 (C), 49.6 (CH$_2$), 55.1 (CH$_2$), 58.8 (CH$_2$), 111.1 (ArH), 119.0 (ArH), 121.5 (Ar), 123.0 (ArH), 125.3 (Ar), 127.7 (ArH), 142.4 (Ar), 144.5 (Ar), 157.2 (ArO), 158.9 (ArO). Calc. (%) for C$_{34}$H$_{44}$N$_3$O$_8$Ti: C 68.91, H 5.65, N 7.59. Found (%), C 60.81, H 5.79, N 4.71.

Ti(6)Catechol. $^{6}$H$_2$ (0.37 g, 1.00 mmol) and Ti(O$^i$Pr)$_4$ (0.30 ml, 1.01 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (1 h). Catechol (0.11 g, 1.00 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in-vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.33 g, 0.63 mmol, 62%). $^1$H NMR (CDCl$_3$): δ 2.00 (2H, m,
CH₂), 2.12 (6H, s, CH₃), 2.23 (6H, s, CH₃), 2.41 (2H, d, J = 7.5 Hz, CH₂), 2.54 (1H, d, J = 7.0 Hz, CH₂), 2.58 (1H, d, J = 6.5 Hz, CH₂), 3.16 (2H, d, J = 7.0 Hz, CH₂), 3.22 (2H, d, J = 13.5 Hz, CH₂), 4.14 (2H, br, CH₂), 4.39 (2H, d, J = 13.0 Hz, CH₂), 6.40 (1H, d, J = 3.5 Hz, ArH), 6.42 (1H, d, J = 3.5 Hz, ArH), 6.62 (1H, d, J = 3.5 Hz, ArH), 6.64 (1H, d, J = 3.5 Hz, ArH), 6.65 (2H, s, ArH), 6.96 (2H, s, ArH). ¹³C{¹H} NMR (CDCl₃): δ 16.5 (CH₃), 20.8 (CH₃), 23.2 (CH₂), 49.3 (CH₂), 58.7 (CH₂), 63.1 (CH₂), 111.6 (ArH), 119.5 (ArH), 123.1 (ArH), 125.5 (Ar), 127.0 (ArH), 129.1 (Ar), 131.5 (ArH), 158.2 (br, ArO), 158.8 (br, ArO). Calc. (%) for C₂₇H₃₄N₂O₄Ti: C 66.67, H 6.56, N 5.36. Found (%), C 66.28, H 6.20, N 5.55.

Ti(6)-3-Methoxycatechol. 6H₂ (0.37 g, 1.00 mmol) and Ti(O′Pr)₄ (0.30 ml, 1.01 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (1 h). 3-Methoxycatechol (0.142 g, 1.01 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in-vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.50 g, 0.91 mmol, 89 %). ¹H NMR (CDCl₃): δ 2.01 (2H, d, J = 6.5 Hz, CH₂), 2.12 (6H, br, CH₃), 2.36 (6H, s, CH₃), 2.40 (2H, d, J = 7.5 Hz, CH₂), 2.56 (2H, m, CH₂), 3.15 (2H, d, J = 7.0 Hz, CH₂), 3.22 (2H, d, J = 13.5 Hz, CH₂), 3.75 (3H, s, CH₃), 3.80 – 4.40 (2H, br, CH₂) 4.41 (2H, d, J = 13.5 Hz, CH₂), 6.14 (1H, dd, J = 8.0 Hz, J = 1.5 Hz, ArH), 6.37 (1H, dd, J = 8.0 Hz, J = 1.5 Hz, ArH), 6.58 (1H, t, J = 8.0 Hz, ArH), 6.65 (1H, br, ArH), 6.92 (1H, br, ArH). ¹³C{¹H} NMR (CDCl₃) (328 K): δ 16.4 (CH₃), 20.7 (CH₃), 23.5 (CH₂), 49.6 (CH₂), 57.2 (CH₃), 58.9 (CH₂), 63.3 (CH₂), 106.3 (ArH), 106.7 (ArH), 118.9 (ArH), 123.2 (Ar), 125.6 (Ar), 126.9 (ArH), 129.1 (Ar), 131.6 (ArH), 144.5 (Ar), 158.4 (ArO), 160.4 (ArO), 177.6, (ArO). Calc. (%) for C₃₀H₃₆N₂O₅Ti: C 65.22, H 6.57, N 5.07. Found (%), C 65.18, H 6.65, N 5.16.

Ti(6)-4-Nitroocatechol. 6H₂ (0.50 g, 1.36 mmol) and Ti(O′Pr)₄ (0.40 ml, 1.35 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (1 h). 4-Nitro catechol (0.21 g, 1.35 mmol) was added to the yellow solution and the resulting dark red solution was stirred (16 h) before the solvent was removed in-vacuo and recrystallised from hot toluene (30 ml) to yield orange crystals (0.34 g, 0.60 mmol, 44 %). ¹H NMR (CDCl₃): δ 2.06 (2H, m, CH₂), 2.15 (6H, s, CH₃), 2.27 (6H, s, CH₃), 2.32 (2H, m, CH₂), 2.37 (Toluene-CH₃), 2.53 (2H, d, J = 7.5 Hz, CH₂), 2.63 (2H, m, CH₂), 3.26 (2H, d, J =
7.0 Hz, CH₂), 3.37 (2H, d, J = 14.0 Hz, CH₂), 4.30 (2H, d, J = 13.5 Hz, CH₂), 6.41 (1H, d, J = 9.0 Hz, ArH), 6.72 (2H, s, ArH), 6.98 (2H, s, ArH), 7.15-7.30 (m, Toluene-ArH) 7.27 (1H, s, ArH), 7.74 (1H, dd, J = 8.5 Hz, J = 2.5 Hz, ArH). \(^{13}\)C\({}^1\)H NMR (CDCl₃): δ 16.4 (CH₃), 20.8 (CH₃), 23.1 (CH₂), 58.6 (CH₂), 58.9 (CH₂), 63.3 (CH₂), 106.6 (ArH), 110.4 (ArH), 117.7 (ArH), 122.5 (Ar), 125.1 (Ar), 127.1 (ArH), 130.2 (Ar), 131.8 (ArH) 140.8 (ArO), 157.5 (ArO), 166.8 (ArO). Calc. (%) for C₁₉H₃₃N₂O₆Ti: C 61.38, H 5.86, N 7.40. Found (%), C 61.47, H 6.00, N 7.11.

7.5 Preparation of Complexes for Chapter 3

7.5.1 Preparation of zirconium homopiperazine salan complexes

Zr(6)(OiPr)₂. 6H₂ (0.48 g, 1.29 mmol) and Zr(OiPr)₄,iPrOH (0.5 g, 1.29 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed \textit{in-vacuo} and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.34 g, 0.59 mmol, 46 %). \(^1\)H NMR (CDCl₃) (233 K): δ 0.27 (6H, d, J = 6.8 Hz, Me), 1.24 (6H, d, J = 6.8 Hz, Me), 1.41 (1H, d, J = 5.8 Hz, CH₂), 1.68 (1H, br, CH₂), 2.17 (6H, s, Me), 2.19 (6H, s, Me), 2.24 (2H, m, CH₂), 2.88 (2H, d, J = 6.8 Hz, CH₂), 3.07 (2H, d, J = 11.6 Hz, CH₂), 3.30 (1H, br, CH₂), 3.55 (2H, d, J = 6.8 Hz, CH₂), 4.37 (2H, d, J = 11.6 Hz, N-CH₂-Ar), 4.50 (1H, m, CH), 6.67 (2H, s, ArH), 6.90 (2H, s, ArH) \(^{13}\)C\({}^1\)H NMR (CDCl₃) (253 K): δ 17.1 (CH₃), 20.6 (CH₃), 22.5 (CH₂), 26.4 (CH₃), 27.2 (CH₃), 54.2 (CH₂), 56.0 (CH₂), 63.2 (CH₂), 67.5 (CH), 69.2 (CH), 122.4 (Ar), 124.8 (Ar), 126.3 (Ar), 127.8 (ArH) 131.9 (ArH) 159.8 (ArO). Calc. (%) for C₂₉H₄₄N₂O₄Zr: C 60.48, H 7.70, N 4.86. Found (%), C 60.54, H 7.66, N 4.71.

Zr(7)(OiPr)₂. 7H₂ (0.58 g, 1.29 mmol) and Zr(OiPr)₄,iPrOH (0.5 g, 1.29 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed \textit{in-vacuo} and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.49 g, 0.74 mmol, 58 %). \(^1\)H NMR (CDCl₃) (233 K): δ 0.15 (6H, d, J = 5.8 Hz, Me), 1.21 (18H, s, tBu), 1.23 (6H, s, Me), 1.73 (1H, br, CH₂), 2.15 (1H, br, CH₂), 2.20 (6H, s, Me), 2.26 (2H, br, CH₂), 2.89 (2H, d, J = 6.6 Hz, CH₂), 3.12 (2H, d, J = 11.6 Hz, CH₂), 3.27 (2H, m, CH₂), 3.27 (1H, m, CH), 3.53 (2H, d, J = 6.8 Hz, N-CH₂-Ar), 4.38 (2H, d, J = 11.6 CH), 4.43 (1H, s, J = 6.1 Hz, CH), 6.83 (2H, s, ArH), 7.09 (2H, s, ArH) \(^{13}\)C\({}^1\)H NMR (CDCl₃) (233 K): δ 17.4 (CH₃), 22.5 (CH₂), 26.0 (CH₃), 27.1 (CH₃),
31.7 (CH₃), 33.7 (C), 54.2 (CH₂), 55.8 (CH₂), 63.4 (CH₂), 67.6 (CH), 69.9 (CH), 121.7 (Ar), 123.8 (ArH), 125.7 (Ar), 128.4 (ArH), 138.4 (Ar), 159.8, (ArO). Calc. (%) for C₃₁H₅₆N₂O₄Zr: C 63.69, H 8.55, N 4.24. Found (%), C 62.7, H 8.55, N 4.65.

Zr(8)(OiPr)₂. 8H₂ (0.67 g, 1.25 mmol) and Zr(OiPr)₄.iPrOH (0.5 g, 1.29 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.31 g, 0.42 mmol, 33 %). ¹H NMR (CDCl₃) (253 K): δ 0.01 (6H, s, CH₃), 1.23 (18H, s, tBu), 1.23 (6H, br, CH₃), 1.42 (18H, s, tBu), 1.80 (1H, br, CH₂), 2.21 (1H, br, CH₂), 2.35 (2H, br, CH₂), 2.88 (2H, d, J = 6.3 Hz, CH₂), 3.14 (2H, d, J = 10.4 Hz, CH₂), 3.53 (2H, d, J = 7.1 Hz, CH₂), 3.60 (2H, br, N-CH₂-Ar), 3.60 (1H, br, CH), 4.30 (2H, br, N-CH₂-Ar), 4.32 (1H, br, CH), 6.88 (2H, s, ArH), 7.24 (2H, s, ArH) ¹³C{¹H} NMR (CDCl₃): δ 23.1 (CH₂), 26.0 (CH₃), 27.1 (CH₃), 30.2 (CH₃), 31.9 (CH₃), 34.1 (C), 35.3 (C), 56.5 (CH₂), 63.9 (CH₂), 68.6 (CH), 69.6 (CH), 122.8 (Ar), 124.4 (Ar), 136.3 (Ar), 138.0 (Ar). due to poor solubility 2 Ar resonances were not detected. Calc. (%) for C₄₁H₆₈N₂O₄Zr: C 66.17, H 9.21, N 3.76. Found (%), C 66.1, H 9.30, N 4.16.

Zr(9)(OiPr)₂. 9H₂ (0.58 g, 1.29 mmol) and Zr(OiPr)₄.iPrOH (0.5 g, 1.29 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.19 g, 0.29 mmol, 22 %). ¹H NMR (CDCl₃) (233 K): δ 0.07 (6H, d, J = 5.1 Hz, Me), 1.21 (6H, d, J = 5.8 Hz, Me), 1.39 (18H, s, tBu), 1.42 (1H, br, CH₂), 1.74 (1H, br, CH₂), 2.19 (6H, s, CH₃), 2.32 (2H, m, CH₂), 2.89 (2H, d, J = 6.3 Hz, CH₂), 3.10 (2H, d, J = 11.6 Hz, CH₂), 3.50 (2H, d, J = 6.6 Hz, CH₂), 3.59 (2H, br, N-CH₂-Ar), 3.59 (1H, br, CH), 4.27 (2H, br, N-CH₂-Ar), 4.27 (1H, br, CH), 6.72 (2H, s, ArH), 7.00 (2H, s, ArH) ¹³C{¹H} NMR (CDCl₃) (233 K): δ 20.9 (CH₃), 22.5 (CH₂), 26.0 (CH₃), 27.2 (CH₃), 29.8 (CH₃), 34.9 (C), 54.3 (CH₂), 56.0 (CH₂), 63.5 (CH₂), 67.9 (CH), 69.1 (CH), 123.4 (Ar), 123.8 (ArH), 128.0 (Ar), 128.7 (ArH), 136.1 (Ar), 161.3, (ArO). Calc. (%) C₃₃H₅₆N₂O₄Zr: C 63.69, H 8.55, N 4.24. Found (%), C 63.68, H 8.66, N 4.24.

Zr(10)(OiPr)₂. 10H₂ (0.61 g, 1.03 mmol) and Zr(OiPr)₄.iPrOH (0.4 g, 1.03 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in-
vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.37 g, 0.46 mmol, 45 %). $^1$H NMR (CDCl$_3$ (233 K): $\delta$ 0.02 (6H, br, CH$_3$), 0.72 (6H, t, J = 7.2 Hz, CH$_3$), 1.16 (6H, br, CH$_3$), 1.19 (12H, s, CH$_3$), 1.34 (6H, s, CH$_3$), 1.36 (6H, s, CH$_3$), 1.50 (4H, m, CH$_2$), 1.65 (2H, m, CH$_2$), 1.79 (1H, br, CH$_2$), 2.11 (2H, m, CH$_2$), 2.19 (1H, br, CH$_2$), 2.33 (2H, m, CH$_2$), 2.88 (2H, d, J = 6.6 Hz, CH$_2$), 3.13 (2H, d, J = 11.4 Hz, CH$_2$), 3.49 (2H, d, J = 7.1 Hz, CH$_2$), 3.66 (1H, br, CH), 3.66 (2H, br, N-CH$_2$-Ar), 4.24 (1H, br, CH), 4.28 (2H, d, J = 11.6 Hz, CH$_2$), 6.80 (2H, s, ArH), 7.10 (2H, s, ArH) $^{13}$C{$^1$H} NMR (CDCl$_3$) (253 K): $\delta$ 9.2 (CH$_3$), 9.8 (CH$_3$), 22.7 (CH$_3$), 26.0 (CH$_3$), 27.0 (CH$_3$), 27.2 (CH$_3$), 27.7 (CH$_3$), 28.6 (CH$_3$), 29.4 (CH$_3$), 33.1 (C), 37.0 (C), 37.1 (CH$_2$), 38.3 (CH$_2$), 54.4 (CH$_2$), 56.1 (CH$_2$), 64.0 (CH$_2$), 68.2 (CH), 69.1 (CH), 123.5 (Ar), 125.4 (ArH), 126.2 (ArH), 134.7 (Ar), 135.2 (Ar), 161.4 (ArO). Calc. (%) for C$_{45}$H$_{76}$N$_2$O$_4$Zr: C 67.53, H 9.57, N 3.50. Found (%), C 64.38, H 9.22, N 3.11.

### 7.5.2 Preparation of hafnium homopiperazine salan complexes

Hf(6)(O$^t$Pr)$_2$. 6H$_2$ (0.39 g, 1.05 mmol) and Hf(O$^t$Pr)$_4$.iPrOH (0.5 g, 1.05 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.30 g, 0.45 mmol, 43 %). $^1$H NMR (CDCl$_3$) (233 K): $\delta$ 0.25 (6H, d, J = 5.8 Hz, Me), 1.23, (6H, d, J = 5.8 Hz, Me), 1.68 (1H, br, CH$_2$), 2.15 (1H, br, CH$_2$), 2.17 (6H, s, Me), 2.20 (6H, s, Me), 2.34 (2H, m, CH$_2$), 2.95 (2H, d, J = 6.3 Hz, CH$_2$), 3.12 (2H, d, J = 11.6 Hz, CH$_2$), 3.37 (1H, br, CH$_2$), 3.37 (2H, br CH$_2$), 3.56 (2H, d, J = 6.8 Hz, CH$_2$), 4.31 (2H, d, J = 11.6 Hz, N-CH$_2$-Ar), 4.57 (1H, sept, J = 5.8 Hz, CH), 6.66 (2H, s, ArH), 6.92 (2H, s, ArH) $^{13}$C{$^1$H} NMR (CDCl$_3$) (233 K): $\delta$ 17.1 (CH$_3$), 20.6 (CH$_3$), 22.5 (CH$_2$), 26.6 (CH$_3$), 27.4 (CH$_3$), 54.3 (CH$_2$), 56.3 (CH$_2$), 63.1 (CH$_2$), 67.3 (CH), 69.0 (CH), 122.4 (Ar), 124.9 (Ar), 126.9 (Ar), 127.8 (ArH) 131.9 (ArH) 159.6 (ArO). Calc. (%) for C$_{29}$H$_{44}$N$_2$O$_4$Hf: C 52.52, H 6.69, N 4.22. Found (%), C 52.4, H 6.71, N 4.28.

Hf(7)(O$^t$Pr)$_2$. 7H$_2$ (0.48 g, 1.05 mmol) and Hf(O$^t$Pr)$_4$.iPrOH (0.5 g, 1.05 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.37 g, 0.46 mmol, 45 %). $^1$H NMR (CDCl$_3$) (233 K): $\delta$ 0.02 (6H, br, CH$_3$), 0.52 (6H, t, J = 7.2 Hz, CH$_3$), 0.72 (6H, t, J = 7.2 Hz, CH$_3$), 1.16 (6H, br, CH$_3$), 1.19 (12H, s, CH$_3$), 1.34 (6H, s, CH$_3$), 1.36 (6H, s, CH$_3$), 1.50 (4H, m, CH$_2$), 1.65 (2H, m, CH$_2$), 1.79 (1H, br, CH$_2$), 2.11 (2H, m, CH$_2$), 2.19 (1H, br, CH$_2$), 2.33 (2H, m, CH$_2$), 2.88 (2H, d, J = 6.6 Hz, CH$_2$), 3.13 (2H, d, J = 11.4 Hz, CH$_2$), 3.49 (2H, d, J = 7.1 Hz, CH$_2$), 3.66 (1H, br, CH), 3.66 (2H, br, N-CH$_2$-Ar), 4.24 (1H, br, CH), 4.28 (2H, d, J = 11.6 Hz, CH$_2$), 6.80 (2H, s, ArH), 7.10 (2H, s, ArH) $^{13}$C{$^1$H} NMR (CDCl$_3$) (253 K): $\delta$ 9.2 (CH$_3$), 9.8 (CH$_3$), 22.7 (CH$_3$), 26.0 (CH$_3$), 27.0 (CH$_3$), 27.2 (CH$_3$), 27.7 (CH$_3$), 28.6 (CH$_3$), 29.4 (CH$_3$), 33.1 (C), 37.0 (C), 37.1 (CH$_2$), 38.3 (CH$_2$), 54.4 (CH$_2$), 56.1 (CH$_2$), 64.0 (CH$_2$), 68.2 (CH), 69.1 (CH), 123.5 (Ar), 125.4 (ArH), 126.2 (ArH), 134.7 (Ar), 135.2 (Ar), 161.4 (ArO). Calc. (%) for C$_{45}$H$_{76}$N$_2$O$_4$Zr: C 67.53, H 9.57, N 3.50. Found (%), C 64.38, H 9.22, N 3.11.
2.35 (2H, m, CH$_2$), 2.95 (2H, d, J = 6.6 Hz, CH$_2$), 3.16 (2H, d, J = 11.6 Hz, CH$_2$), 3.36 (2H, br, CH$_2$), 3.36 (1H, br, CH), 3.55 (2H, d, J = 6.8 Hz, N-CH$_2$-Ar), 4.42 (2H, d, J = 11.4 Hz, N-CH$_2$-Ar), 4.51 (1H, sept, J = 6.0 Hz, CH), 6.83 (2H, d, J = 2.3 Hz, ArH), 7.11 (2H, d, J = 2.0 Hz, ArH). 13C{[1H] NMR (CDCl$_3$) (233 K): δ 17.4 (CH$_3$), 22.5 (CH$_2$), 26.2 (CH$_3$), 27.3 (CH$_3$), 31.7 (CH$_3$), 33.7 (C), 54.3 (CH$_2$), 56.1 (CH$_2$), 63.4 (CH$_2$), 67.4 (CH), 69.0 (CH), 121.7 (Ar), 123.7 (ArH), 126.3 (Ar), 128.4 (ArH), 138.5 (Ar), 159.7 (ArO). Calc. (%)

C$_3$H$_5$N$_2$O$_4$Hf: C 56.25, H 7.55, N 3.75. Found (%): C 56.24, H 7.48, N 3.63.

Hf($\text{O}^\text{iPr})_2$. 8H$_2$ (0.53 g, 0.99 mmol) and Hf(O$i$Pr)$_4$.$^4$PrOH (0.47 g, 0.99 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.14 g, 0.17 mmol, 17 %). 1H NMR (CDCl$_3$) (233 K): δ -0.02 (6H, d, J = 4.5 Hz, Me), 1.18 (6H, d, J = 5.7 Hz, $^4$Bu), 1.20 (18H, s, $^4$Bu), 1.79 (1H, br, CH$_2$), 2.19 (1H, br, CH$_2$), 2.44 (2H, br, CH$_2$), 2.95 (2H, d, J = 6.1 Hz, CH$_2$), 3.17 (2H, d, J = 11.6 Hz, CH$_2$), 3.52 (2H, d, J = 6.8 Hz, CH$_2$), 3.63 (2H, br, N-CH$_2$-Ar), 3.63 (1H, br, CH), 4.32 (2H, d, J = 11.6 Hz, N-CH$_2$-Ar), 4.32 (1H, br, CH), 6.86 (2H, s, ArH), 7.24 (2H, s, ArH). 13C{[1H] NMR (CDCl$_3$) (258 K): δ 22.6 (CH$_2$), 25.8 (CH$_3$), 27.5 (CH$_3$), 30.0 (CH$_3$), 31.8 (CH$_3$), 34.0 (C), 35.1 (C), 54.5 (CH$_2$), 56.3 (CH$_2$), 63.7 (CH$_2$), 68.0 (CH), 69.0 (CH), 122.6 (Ar), 124.5 (ArH), 124.6 (ArH), 136.3 (Ar), 136.3 (Ar), 137.6 (Ar), 161.3 (ArO). Calc. (%) for C$_3$H$_{56}$N$_2$O$_4$Hf: C 56.25, H 7.55, N 3.75. Found (%): C 56.24, H 7.48, N 3.63.

Hf($\text{O}^\text{iPr})_2$. 9H$_2$ (0.48 g, 1.05 mmol) and Hf(O$i$Pr)$_4$.$^4$PrOH (0.5 g, 1.05 mmol) were dissolved in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.14 g, 0.17 mmol, 17 %). 1H NMR (CDCl$_3$) (233 K): δ 0.07 (6H, s, Me), 1.20 (6H, d, J = 5.3 Hz, Me), 1.40 (18H, s, $^4$Bu), 1.41 (1H, br, CH$_2$), 1.74 (1H, br, CH$_2$), 2.20 (6H, s, CH$_3$), 2.42 (2H, m, CH$_2$), 2.95 (2H, d, J = 6.8 Hz, CH$_2$), 3.13 (2H, d, J = 11.6 Hz, CH$_2$), 3.52 (2H, d, J = 7.1 Hz, CH$_2$), 3.65 (2H, br, N-CH$_2$-Ar), 3.67 (1H, br, CH), 4.31 (2H, d, J = 11.6 Hz, N-CH$_2$-Ar), 4.38 (1H, br, CH), 6.72 (2H, s, ArH), 7.03 (2H, s, ArH). 13C{[1H] NMR (CDCl$_3$) (233 K): δ 20.8 (CH$_3$), 22.5 (CH$_2$), 26.3 (CH$_3$), 27.5 (CH$_3$), 29.9 (CH$_3$), 34.8 (C), 54.5 (CH$_2$), 56.2 (CH$_2$), 63.4 (CH$_2$), 67.7 (CH), 68.9 (CH), 247
123.4 (Ar), 123.9 (ArH), 128.0 (Ar), 128.6 (ArH), 136.6 (Ar), 161.2 (ArO). Calc. (%) for C₃₅H₅₆N₂O₄Hf: C 56.25, H 7.55, N 3.75. Found (%), C 56.35, H 7.43, N 3.64.

Hf(10)(O’Pr)₂. 10H₂ (0.62 g, 1.05 mmol) and Hf(O’Pr)₄⋅PrOH (0.5 g, 1.05 mmol) were dissolved in CH₂Cl₂ (30 ml) and stirred (16 h). The solvent was removed in vacuo and recrystallised from hot hexane (40 ml) to yield colourless crystals (0.30 g, 0.34 mmol, 32 %). ¹H NMR (CDCl₃) (233 K): δ 0.03 (6H, s, CH₃), 0.52 (6H, t, J = 7.3 Hz, CH₃), 0.72 (6H, t, J = 7.3 Hz, CH₃), 1.16 (12H, s, CH₃), 1.20 (6H, s, CH₃), 1.35 (6H, s, CH₃), 1.37 (6H, s, CH₃), 1.50 (4H, m, CH₂), 1.69 (2H, m, CH₂), 1.78 (1H, br, CH₂), 2.09 (2H, m, CH₂), 2.20 (1H, br, CH₂), 2.43 (2H, m, CH₂), 2.95 (2H, d, J = 6.3 Hz, CH₂), 3.16 (2H, d, J = 11.4 Hz, CH₂), 3.51 (2H, d, J = 7.3 Hz, CH₂), 3.74 (2H, br, N-CH₂-Ar), 3.74 (1H, br, CH), 4.32 (2H, d, J = 11.4 Hz, N-CH₂-Ar), 4.33 (1H, br, CH), 6.80 (2H, s, ArH), 7.12 (2H, s, ArH). ¹³C{¹H} NMR (233 K): δ 9.2 (CH₃), 9.8 (CH₃), 22.9 (CH₂), 26.3 (CH₃), 27.1 (CH₃), 27.6 (CH₃), 27.7 (CH₃), 28.4 (CH₃), 29.8 (CH₃), 33.0 (C), 37.1 (C), 37.2 (CH₂), 38.2 (CH₂), 54.6 (CH₂), 56.4 (CH₂), 63.8 (CH₂), 68.0 (CH₂), 68.9 (CH₂), 122.5 (Ar), 125.4 (ArH), 126.3 (ArH), 135.1 (Ar), 135.1 (Ar), 161.2 (ArO). Calc. (%) for C₄₅H₇₆N₂O₄Hf: C 60.89, H 8.63, N 3.16. Found (%), C 51.99, H 7.82, N 2.50.

7.6 Preparation of Complexes for Chapter 4

7.6.1 Preparation of methyl aluminium homopiperazine salan complexes

Al(6)Me. A solution of 6H₂ (0.69 g, 1.87 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe₃ (0.93 ml, 1.86 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.45 g, 1.1 mmol, 59 %). ¹H NMR (298 K) (CD₅CD₃): δ −0.59 (1.5H, s, Al-Me), −0.43 (1.5H, s, Al-Me), 0.50 (0.5H, d, J = 15.5 Hz, CH₂), 0.89 (1H, m, CH₂), 1.04 (0.5H, br, CH₂), 1.22 (1H, m, CH₂), 1.35 (2H, m, CH₂), 1.51 (1H, m, CH₂), 1.68 (1H, m, CH₂), 2.28 (3H, s, CH₃), 2.30 (3H, s, CH₃), 2.43 (3H, s, CH₃), 2.58 (2H, m, CH₂), 2.62 (3H, s, CH₃), 2.66 (2H, m, CH₃), 2.92 (1H, m, CH₂), 3.68 (1H, d, J = 13.0 Hz, CH₃), 4.04 (1H, d, J = 13.0 Hz, CH₂), 6.45 (2H, d, J = 4.5 Hz, ArH), 6.95 (2H, s, ArH). ¹³C{¹H} NMR (CD₂CD₃): δ 16.7 (CH₃), 17.0 (CH₃), 20.8 (CH₃), 22.0 (CH₂), 22.4 (CH₂), 248
46.2 (CH₂), 49.5 (CH₂), 51.1 (CH₂), 55.5 (CH₂), 61.7 (CH₂), 62.8 (CH₂), 119.0 (Ar), 120.5 (Ar), 123.6 (Ar), 124.3 (Ar), 126.5 (ArH), 126.7 (ArH), 128.0 (Ar), 128.9 (Ar), 131.7 (ArH), 131.9 (ArH), 157.7 (ArO), 157.9 (ArO). Calc. (%) for C₄₉H₃₃N₂O₂Al, C 70.56, H 8.14, N 6.86. Found (%), C 70.68, H 8.08, N 6.69.

Al(7)Me. A solution of 7H₂ (0.91 g, 2.01 mmol) in toluene (40 ml) was heated to 50°C and 2M AlMe₃ (1.0 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.25 g, 0.51 mmol, 25 %). ¹H NMR (233 K) (C₆D₅CD₃): δ −0.45 (3H, s, Al-Me), 0.18 (1H, br, CH₂), 0.73 (1H, br, CH₂), 1.12 (2H, d, J = 7.5 Hz, CH₂), 1.39 (2H, d, J = 7.0 Hz, CH₂), 1.51 (18H, s, CH₃), 2.06 (1H, m, CH₂), 2.45 (2H, d, J = 13.0 Hz, CH₂), 2.54 (2H, br, CH₂), 2.64 (1H, br, CH₂), 2.82 (6H, s, CH₃), 3.97 (2H, d, J = 13.0 Hz, CH₂), 6.80 (2H, d, J= 2.0 Hz, ArH), 7.40 (2H, d, J = 2.0 Hz, ArH). ¹³C{¹H} NMR (C₆D₅CD₃): δ 17.3 (CH₃), 21.9 (C), 32.2 (CH₃), 40.0 (CH₂), 49.4 (CH₂), 52.1 (CH₂), 63.2 (CH₂), 118.5 (Ar), 122.3 (ArH), 127.8 (Ar), 127.9 (ArH), 137.5 (Ar), 157.6 (ArO). Calc. (%) for C₃⁶H₄₅N₂O₂Al, C 73.14, H 9.21, N 5.69. Found (%), C 72.99, H 9.09, N 5.78.

Al(8)Me. A solution of 8H₂ (0.54 g, 1.01 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe₃ (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). The crude mixture was recrystallised from a toluene:hexane mix to yield clear crystals suitable for X-ray diffraction (0.25 g, 0.43 mmol, 43 %). ¹H NMR (233 K) (C₄D₈O): δ −0.87 (3H, s, Al-Me), 1.26 (18H, s, CH₃), 1.44 (9H, s, CH₃), 1.50 (9H, s, CH₃), 1.86 (1H, br, CH₂), 2.33 (2H, br, CH₂), 2.41 (1H, br, CH₂), 2.62 (1H, br, CH₂), 3.15 (2H, br, CH₂), 3.23 (2H, m, CH₂), 3.32 (2H, m, CH₂), 3.41 (1H, br, CH₂), 4.06 (1H, d, J = 11.5 Hz, CH₂), 4.27 (1H, d, J = 14.0 Hz, CH₂), 6.79 (1H, s, ArH), 6.86 (1H, s, ArH), 7.16 (1H, s, ArH), 7.20 (1H, s, ArH). ¹³C{¹H} NMR (233 K) (C₄D₈O): δ 21.9 (CH₂), 29.8 (CH₃), 29.1 (CH₃), 31.3 (CH₃), 31.4 (CH₃), 33.7 (C), 33.8 (C), 34.8 (C), 35.1 (C), 43.9 (CH₂), 51.9 (CH₂), 54.2 (CH₂), 55.6 (CH₂), 59.4 (CH₂), 65.0 (CH₂), 120.5 (Ar), 121.8 (Ar), 122.4 (Ar), 122.7 (Ar), 123.2 (Ar), 123.5 (Ar), 135.8 (Ar), 136.4
Al(9)Me. A solution of 9H₂ (0.45 g, 1.00 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe₃ (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.21 g, 0.43 mmol, 43%). ¹H NMR (233 K) (C₆D₅CD₃): δ −0.59 (3H, s, Al-Me), 0.54 (1H, d, J = 13.5 Hz, CH₂), 0.92 (1H, br, CH₂), 1.08 (1H, br, CH₂), 1.16 (2H, br, CH₂), 1.30 (1H, d, J = 7.5 Hz, CH₂), 1.55 (1H, br, CH₂), 1.92 (9H, s, CH₃), 1.95 (9H, s, CH₃), 2.27 (1H, d, J = 11.5 Hz, CH₂), 2.40 (1H, d, J = 14.5 Hz, CH₂), 2.43 (1H, br, CH₂), 2.43 (3H, s, 2.76), 2.48 (3H, s, 2.76), 2.57 (1H, br, CH₂), 2.87 (1H, br, CH₂), 3.63 (1H, d, J = 11.5 Hz, CH₂), 3.81 (1H, d, J = 14.0 Hz, CH₂), 6.54 (1H, s, ArH), 6.60 (1H, s, ArH), 7.36 (1H, s, ArH), 7.41 (1H, s, ArH). ¹³C{¹H} NMR (233 K) (C₄D₈O): δ 21.3 (CH₃), 21.4 (CH₃), 22.9 (CH₂), 30.2 (CH₃), 30.9 (CH₃), 35.6 (C), 35.9 (C), 44.8 (CH₂), 52.7 (CH₂), 55.3 (CH₂), 56.8 (CH₂), 60.2 (CH₂), 65.6 (CH₂), 122.1 (Ar), 123.3 (Ar), 123.4 (Ar), 124.8 (Ar), 127.4 (Ar), 127.5 (Ar), 128.1 (Ar), 128.5 (Ar), 138.2 (Ar), 139.4 (Ar), 156.8 (ArO), 161.0 (ArO). Calc. (%) for C₃₀H₴₅N₂O₂Al, C 73.14, H 9.21, N 5.69. Found (%), C 73.02, H 9.25, N 5.73.

Al(11)Me. A solution of 11H₂ (0.85 g, 2.00 mmol) in toluene (40 ml) was heated to 50°C and 2M AlMe₃ (1.0 ml, 2.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.55 g, 1.18 mmol, 59%). ¹H NMR (233 K) (C₆D₅O): δ −0.53 (3H, s, Al-Me), 1.23 (18H, s, CH₃), 1.23 (2H, br, CH₂), 2.30 (2H, m, CH₂), 2.94 (2H, br, CH₂), 3.04 (2H, br, CH₂), 3.13 (2H, br, CH₂), 3.40 (2H, d, J = 13.5 Hz, CH₂), 4.30 (2H, d, J = 13.0 Hz, CH₂), 6.58 (2H, d, J = 8.5 Hz, ArH), 6.87 (2H, d, J = 2.0 Hz, ArH), 7.07 (2H, dd, J = 8.5 Hz, J = 2.0 Hz, ArH). ¹³C{¹H} NMR (C₄D₈O): δ 22.5 (CH₂), 31.6 (CH₃), 33.7 (C), 50.2 (CH₂), 52.7 (CH₂), 63.1 (CH₂), 119.3 (ArH), 119.7 (Ar), 124.6 (ArH), 126.0 (ArH), 137.5 (Ar), 159.4 (ArO). Calc. (%) for C₂₈H₄₁N₂O₂Al, C 72.38, H 8.89, N 6.03. Found (%), C 72.35, H 8.88, N 6.17.

7.6.2 Preparation of benzoxy aluminium homopiperazine salan complexes
Al(6)OBn. A solution of 6H₂ (0.37 g, 1.00 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe₃ (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). Excess benzyl alcohol (0.52 ml, 5.02 mmol) was carefully added to the hot solution and allowed to stir (3 h, 80 °C) the reaction was then cooled and the solvent removed under vacuum. The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.22 g, 0.44 mmol, 44 %). ¹H NMR (233 K) (C₆D₅CD₃): δ 0.22 (1H, d, J = 13.5 Hz, CH₂), 0.75 (1H, br, CH₂), 1.10 (2H, br, CH₂), 1.45 (2H, br, CH₂), 2.40 (6H, s, CH₃), 2.45 (4H, m, CH₂), 2.71 (2H, br, CH₂), 2.81 (6H, s, CH₃), 4.30 (2H, d, J = 12.5 Hz, CH₂), 5.25 (2H, s, CH₂), 6.51 (2H, s, ArH), 7.15 (1H, br, ArH), 7.15 (2H, br, ArH), 7.23 (2H, m, ArH), 7.41 (2H, d, J = 7.5 Hz, ArH). ¹³C{¹H} NMR (C₆D₅CD₃): δ 16.8 (CH₃), 20.8 (CH₃), 21.9 (C), 22.4 (C), 45.6 (CH₂), 50.0 (CH₂), 52.5 (CH₂), 55.7 (CH₂), 61.9 (CH₂), 62.4 (CH₂), 64.9 (CH₂), 66.4 (CH₂), 119.6 (Ar), 120.5 (Ar), 124.3 (Ar), 124.7 (Ar), 126.1 (ArH), 126.5 (ArH), 126.6 (ArH), 127.3 (ArH), 126.8 (ArH), 128.1 (Ar), 128.1 (ArH), 128.3 (ArH), 128.8 (Ar), 131.8 (ArH), 132.0 (ArH), 157.4 (ArO), 157.3 (ArO). Calc. (%) for C₃₀H₃₇N₂O₃Al, C 71.98, H 7.45, N 5.60. Found (%), C 72.12, H 7.50, N 5.52.

Al(7)OBn. A solution of 7H₂ (0.45 g, 0.99 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe₃ (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). Excess benzyl alcohol (0.52 ml, 5.02 mmol) was carefully added to the hot solution and allowed to stir (3 h, 80°C) the reaction was then cooled and the solvent removed under vacuum. The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.47 g, 0.81 mmol, 81 %). ¹H NMR (233 K) (C₆D₅CD₃): δ 0.11 (1H, d, J = 12.0 Hz, CH₂), 0.70 (1H, br, CH₂), 1.10 (2H, d, J= 8.0 Hz, CH₂), 1.47 (2H, br, CH₂), 1.50 (18H, s, CH₃), 2.43 (4H, m, CH₂), 2.71 (2H, d, J = 6.5 Hz, CH₂), 2.85 (6H, s, CH₃), 4.31 (2H, d, J = 12.5 Hz, CH₂), 5.29 (2H, s, CH₂), 6.79 (2H, s, ArH), 7.15 (1H, br, ArH), 7.24 (2H, t, J = 7.5 Hz, ArH), 7.40 (4H, m, ArH). ¹³C NMR (C₆D₅CD₃): δ 17.6 (CH₃), 22.3 (CH₂), 32.5 (C), 32.6 (CH₃), 34.5 (CH₂), 50.4 (CH₂), 52.9 (CH₂), 63.2 (CH₂), 66.7 (CH₂), 119.5 (Ar), 122.7 (ArH), 126.5 (ArH), 127.2 (ArH), 128.1 (Ar), 128.4 (ArH), 128.5 (ArH), 138.4 (Ar), 147.3 (Ar), 157.7
(ArO). Calc. (%) for C$_{36}$H$_{49}$N$_2$O$_3$Al, C 73.94, H 8.45, N 4.79. Found (%), C 73.91, H 8.50, N 4.72.

Al(8)OBn. A solution of 8H$_2$ (0.54 g, 1.00 mmol) in toluene (40 ml) was heated to 50°C and 2M AlMe$_3$ (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). Excess benzyl alcohol (0.31 ml, 3.0 mmol) was carefully added to the hot solution and allowed to stir (3 h, 80°C) the reaction was then cooled and the solvent removed under vacuum. The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.24 g, 0.36 mmol, 36 %). $^1$H NMR (233 K) (C$_6$D$_5$CD$_3$): $\delta$ 0.29 (1H, br, CH$_2$), 0.76 (1H, br, CH$_2$), 1.48 (4H, br, CH$_2$), 1.51 (18H, s, CH$_3$), 2.00 (18H, s, CH$_3$), 2.56 (4H, m, CH$_2$), 2.64 (2H, m, CH$_2$), 4.32 (2H, d, J = 13.5 Hz, CH$_2$), 5.26 (2H, s, CH$_2$), 6.77 (2H, s, ArH), 7.15 (1H, s, ArH), 7.21 (2H, t, J = 7.5 Hz, ArH), 7.36 (2H, d, J = 7.5 Hz, ArH), 7.66 (2H, s, ArH). $^{13}$C{$^1$H} NMR (C$_6$D$_5$CD$_3$): $\delta$ 22.1 (CH$_2$), 30.1 (CH$_3$), 32.1 (CH$_3$), 34.2 (C), 36.1 (C), 50.7 (CH$_2$), 52.3 (CH$_2$), 63.7 (CH$_2$), 65.9 (CH$_2$), 119.8 (Ar), 122.8 (ArH), 124.0 (ArH), 126.1 (ArH), 126.7 (ArH), 128.1 (ArH), 137.9 (Ar), 139.0 (Ar), 147.0 (Ar), 157.6 (ArO). Calc. (%) for C$_{42}$H$_{61}$N$_2$O$_3$Al, C 75.41, H 9.19, N 4.19. Found (%), C 75.37, H 9.04, N 4.12.

Al(9)OBn. A solution of 9H$_2$ (0.45 g, 0.99 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe$_3$ (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). Excess benzyl alcohol (0.52 ml, 5.02 mmol) was carefully added to the hot solution and allowed to stir (5 h, 80°C) the reaction was then cooled and the solvent removed under vacuum. The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.20 g, 0.34 mmol, 34 %). $^1$H NMR (233 K) (C$_6$D$_5$CD$_3$): $\delta$ 0.40 (1H, d, J = 13.5 Hz, CH$_2$), 0.76 (1H, br, CH$_2$), 1.20 (2H, d, J = 9.0 Hz, CH$_2$), 1.40 (2H, br, CH$_2$), 1.96 (18H, s, CH$_3$), 2.43 (6H, s, CH$_3$), 2.51 (4H, m, CH$_2$), 2.66 (2H, m, CH$_2$), 4.27 (2H, d, J = 13.0 Hz, CH$_2$), 5.25 (2H, s, CH$_2$), 6.48 (2H, s, ArH), 7.14 (1H, s, ArH), 7.21 (2H, t, J = 7.5 Hz, ArH), 7.40 (4H, m, ArH). $^{13}$C{$^1$H} NMR (C$_6$D$_5$CD$_3$): $\delta$ 21.0 (CH$_3$), 22.1 (CH$_2$), 30.9 (CH$_3$), 35.7 (C), 50.6 (CH$_2$), 52.2 (CH$_2$), 63.2 (CH$_2$), 65.9 (CH$_2$), 120.3 (Ar), 124.3 (Ar), 126.1 (ArH), 126.7 (ArH), 126.9
Al(11)OBn. A solution of 11H2 (0.43 g, 1.01 mmol) in toluene (30 ml) was heated to 50°C and 2M AlMe3 (0.5 ml, 1.00 mmol) was added slowly while stirring (30 mins, 50°C), after which the solution was further heated and stirred (3 h, 80°C). Excess benzyl alcohol (0.31 ml, 3.00 mmol) was carefully added to the hot solution and allowed to stir (16 h, 70°C) the reaction was then cooled and the solvent removed under vacuum. The crude mixture was recrystallised from a toluene:hexane mix to yield a white powder (0.41 g, 0.74 mmol, 74 %).

1H NMR (C6D5CD3): \(\delta = 0.80 (1H, m, \text{CH}_2), 1.14 (1H, m, \text{CH}_2), 1.35 (1H, s, \text{CH}_3), 1.50 (4H, m, \text{CH}_2), 2.59 (2H, d, J = 7.5 Hz, \text{CH}_2), 3.22 (2H, d, J = 12.5 Hz, \text{CH}_2), 3.36 (2H, m, \text{CH}_2), 3.58 (2H, m, \text{CH}_2), 5.16 (2H, s, \text{CH}_2), 6.85 (2H, d, J = 2.5 Hz, ArH), 7.04 (1H, m, ArH), 7.12 (2H, m, ArH), 7.14 (1H, s, ArH), 7.14 (1H, br, ArH), 7.22 (1H, d, J = 2.5 Hz, ArH), 7.25 (1H, d, J = 2.5 Hz, ArH), 7.29 (1H, m, ArH), 7.32 (1H, br, ArH).

13C{1H} NMR (C6D5CD3): \(\delta = 22.1 (\text{CH}_2), 32.0 (\text{CH}_3), 34.0 (\text{C}), 46.8 (\text{CH}_2), 50.1 (\text{CH}_2), 52.4 (\text{CH}_2), 55.2 (\text{CH}_2), 62.6 (\text{CH}_2), 66.3 (\text{CH}_2), 120.9 (\text{ArH}), 121.4 (\text{Ar}), 125.3 (\text{ArH}), 126.3 (\text{ArH}), 127.6 (\text{ArH}), 128.4 (\text{ArH}), 139.3 (\text{Ar}), 147.3 (\text{Ar}), 159.6 (\text{ArO}).

Calc. (%) for C36H49N2O3Al, C 73.94, H 8.45, N 4.79. Found (%), C 73.86, H 8.51, N 4.75.

7.7 Preparation of Ligands and Complexes for Chapter 5

7.7.1 Preparation of trans-1,4-DACH salen ligands

3-(tert-butyl)-2-hydroxy-5-methylbenzaldehyde. 2-(tert-butyl)-4-methylphenol (15 g, 91.3 mmol) was dissolved in dry acetonitrile (150 ml) in an argon charged vessel. Then triethylamine (36.96 g, 365.3 mmol) and MgCl2 (17.39 g, 182.6 mmol) were added and allowed to stir (15 mins). At which point paraformaldehyde (19.20 g, 639.4 mmol) was added and the mixture was stirred (15 mins) before refluxing (4 h) in an inert atmosphere. The solution was allowed to cool to room temperature before addition of 5% HCl (100ml). The product was extracted into diethyl ether (50 ml x 6), the organic layers were washed with saturated brine (20 ml x 3) and dried with MgSO4. The MgSO4 was removed by filtration and the solvent removed in-vacuo,
the solid was dissolved in hexane (10 ml) and run through a silica plug before crystallisation yielding beige solid (5.61 g, 29.2 mmol, 32 %). $^1$H NMR (CDCl$_3$): $\delta$ 1.32 (9H, s, CH$_3$), 2.23 (3H, s, CH$_3$), 7.06 (1H, s, ArH), 7.24 (1H, s, ArH), 9.73 (1H, s, CH), 11.51 (1H, s, OH).

4-methyl-2-tritylphenol. p-Cresol (39.00 g, 360.6 mmol) was melted (100 °C) under an inert atmosphere and sodium metal (2.14 g, 93.1 mmol) was slowly added while vigorously stirring (1 h). Trityl chloride (20 g, 71.7 mmol) was added and the reaction was further heated (140 °C) and stirred (5 h). The reaction was cooled (~25 °C) then NaOH solution (1 M, 100 ml) and diethyl ether (100 ml) was added, the organic layer was isolated and washed with NaOH solution (1 M, 50 ml x 5). The organic phase was washed with water (50 ml x 2) then saturated brine (50 ml) before drying with MgSO$_4$. MgSO$_4$ was filtered and the solvent removed in-vacuo, the product was recrystallised from ethanol to yield a solid (16.45 g, 46.9 mmol, 65 %). $^1$H NMR (CDCl$_3$): $\delta$ 2.16 (3H, s, CH$_3$), 2.80 (1H, s, OH), 6.71 (1H, d, $J$ =8 Hz, ArH), 6.84 (1H, s, ArH), 7.01 (1H, d, $J$ = 6.6 Hz, ArH), 7.15 – 7.30 (15H, m, ArH).

2-hydroxy-5-methyl-3-tritylbenzaldehyde. 4-methyl-2-tritylphenol (12.0 g, 34.2 mmol), hexamethylenetetramine (9.60 g, 68.5 mmol), and trifluoroacetic acid (35 ml) were added to a vessel and heated while stirring (120 °C, 4 h). The reaction was cooled (~75 °C) before addition of H$_2$SO$_4$ (33 % aq, 50 ml), the mixture was heated (125 °C) and further stirred (2 h). The reaction was then cooled to ambient conditions then water (50 ml) and ethyl acetate (50 ml) was added. The organic phase was isolated and the aqueous phase was further extracted with ethyl acetate (30 ml x 3) at which point the organic layers were combined and washed with water (50 ml) and brine (20 ml). The organic layer was dried with MgSO$_4$ then filtered, the solvent was removed in-vacuo and recrystallised from ethanol to yield a white solid (9.04 g, 23.9 mmol, 70 %). $^1$H NMR (CDCl$_3$): $\delta$ 2.20 (3H, s, CH$_3$), 7.05 – 7.35 (17H, m, ArH), 9.72 (1H, s, CH), 11.10 (1H, s, OH).

16H$_2$ 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1.03 g, 4.4 mmol) and trans-1,4-diaminocyclohexane (0.25 g, 2.2 mmol) were stirred in MeOH (40 ml) for 4 h. The resulting yellow precipitate was filtered and washed with cold MeOH and dried in
vacuo to yield a white solid (1.16 g, 2.1 mmol, 97 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 1.32 (18H, s, \textsuperscript{t}Bu), 1.47 (18H, s, \textsuperscript{t}Bu), 1.74 (4H, m, ring-CH\textsubscript{2}), 1.98 (4H, m, ring-CH\textsubscript{2}), 3.28 (2H, br, ring-CH), 7.12 (2H, d, \(J = 2.0\) Hz, ArH), 7.40 (2H, d, \(J = 2.0\) Hz, ArH), 8.45 (2H, s, N=CH) 13.88 (2H, br, OH). \textsuperscript{13}C{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}): \(\delta\) 29.6 (CH\textsubscript{3}), 31.7 (CH\textsubscript{3}), 32.7 (CH\textsubscript{2}), 34.3 (C), 35.2 (C), 67.2 (CH), 118.0 (Ar), 129.6 (ArH), 126.9 (ArH), 136.7 (Ar), 140.1 (Ar), 158.2 (ArO), 164.3 (N=CH). Calc. m/z [C\textsubscript{36}H\textsubscript{54}N\textsubscript{2}O\textsubscript{2} + H]\textsuperscript{+} 547.4258. Found 547.4320.

17H\textsubscript{2} 3-(\textsuperscript{t}er\textsuperscript{t}t\textsuperscript{t}butyl)-2-hydroxy-5-methylbenzaldehyde (1.88 g, 9.8 mmol) and \textit{trans}-1,4-diaminocyclohexane (0.56 g, 4.9 mmol) were stirred in MeOH (40 ml) for 4 h. The resulting yellow precipitate was filtered and washed with cold MeOH and dried in vacuo to yield a white solid (2.17 g, 4.7 mmol, 96 %). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 1.45 (18H, s, \textsuperscript{t}Bu), 1.74 (4H, m, ring-CH\textsubscript{2}), 1.98 (4H, m, ring-CH\textsubscript{2}), 2.30 (6H, s, CH\textsubscript{3}), 3.27 (2H, br, ring-CH), 6.94 (2H, br, ArH), 7.14 (2H, d, \(J = 2.0\) Hz, ArH), 8.39 (2H, s, N=CH) 13.80 (2H, br, OH). \textsuperscript{13}C{\textsuperscript{1}H} NMR (C\textsubscript{6}D\textsubscript{5}CD\textsubscript{3}): \(\delta\) 20.8 (CH\textsubscript{3}), 29.5 (CH\textsubscript{3}), 32.6 (CH\textsubscript{2}), 34.9 (C), 67.1 (CH), 118.5 (Ar), 126.8 (Ar), 129.5 (ArH), 130.6 (ArH), 137.3 (Ar), 158.2 (ArO), 164.0 (N=CH). Calc. m/z [C\textsubscript{30}H\textsubscript{42}N\textsubscript{2}O\textsubscript{2} + H]\textsuperscript{+} 463.3319. Found 463.3362.

18H\textsubscript{2} 2-hydroxy-5-methyl-3-tritylbenzaldehyde (3.0 g, 7.9 mmol) and \textit{trans}-1,4-diaminocyclohexane (0.45 g, 3.9 mmol) were stirred in MeOH (40 ml) for 4 h. The resulting yellow precipitate was filtered and washed with cold MeOH and dried in vacuo to yield a white solid (2.64 g, 3.2 mmol, 80 %) \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta\) 1.54 (4H, br, ring-CH\textsubscript{2}), 1.76 (4H, br, ring-CH\textsubscript{2}), 2.22 (6H, s, CH\textsubscript{3}), 3.08 (2H, br, ring-CH), 7.09 (2H, s, ArH), 7.22 (32H, br, ArH), 8.30 (2H, s, N=CH) 13.34 (2H, br, OH). \textsuperscript{13}C{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}) (333 K): \(\delta\) 20.9 (CH\textsubscript{2}), 30.9 (CH\textsubscript{2}), 32.6 (CH\textsubscript{3}), 63.6 (CH), 67.1 (C), 119.1 (Ar), 125.6 (ArH), 127.3 (ArH), 127.5 (Ar), 130.9 (ArH), 131.2 (Ar), 131.3 (ArH), 134.5 (ArH), 134.7 (Ar), 146.0 (Ar), 158.2 (ArO), 163.3 (N=CH). Calc. m/z [C\textsubscript{60}H\textsubscript{54}N\textsubscript{2}O\textsubscript{2} + H]\textsuperscript{+} 835.4264. Found 835.4267.

7.7.2 Preparation of titanium \textit{trans}-1,4-DACH salen complexes

Ti\textsubscript{2}(16)(O\text{Pr})\textsubscript{6}. Ti(O\text{Pr})\textsubscript{4} (0.31 ml, 1.03 mmol) was added to a solution of 16H\textsubscript{2} (0.28 g, 0.51 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (30 ml) and stirred (16 h). The solvent was removed \textit{in-}
vacuo and recrystallised from hexane to yield yellow crystals (0.22 g, 0.22 mmol, 43 %). $^1$H NMR (CDCl$_3$): $\delta$ 1.26 (36H, d, $J = 6.0$ Hz, $^t$Bu), 1.36 (18H, s, $^t$Bu), 1.49 (18H, s, $^t$Bu), 1.61 (4H, m, ring-CH$_2$), 2.26 (4H, d, $J = 7.0$ Hz, ring-CH$_2$), 4.39 (2H, br, ring-CH), 4.91 (6H, Sept, $J = 6.0$ Hz, ArH), 7.17 (2H, d, $J = 2.5$ Hz, ArH), 7.47 (2H, d, $J = 2.5$ Hz, ArH), 8.32 (2H, s, N=CH). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 26.8 (CH$_3$), 29.6 (CH$_3$), 31.7 (CH$_3$), 32.6 (CH$_2$), 34.3 (C), 35.4 (C), 62.6 (CH), 77.3 (CH), 121.5 (Ar), 127.6 (ArH), 128.5 (ArH), 138.0 (Ar), 140.0 (Ar), 159.7 (ArO), 162.7 (N=CH). Calc. (%) for C$_{54}$H$_{94}$Ti$_2$N$_2$O$_8$, C 65.18, H 9.52, N 2.82. Found (%), C 63.5, H 9.37, N 2.78.

Ti$_2$($^{17}$O$i$Pr)$_6$. Ti(O$i$Pr)$_4$ (0.0.5 ml, 1.69 mmol) was added to a solution of $^{17}$H$_2$ (0.39 g, 0.84 mmol) in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield yellow crystals (0.19 g, 0.21 mmol, 25 %). $^1$H NMR (CDCl$_3$): $\delta$ 1.26 (36H, d, $J = 6.0$ Hz, CH$_3$), 1.48 (18H, s, $^t$Bu), 1.59 (4H, m, ring-CH$_2$), 2.25 (4H, d, $J = 8.0$ Hz ring-CH$_2$), 2.32 (6H, s, Me), 4.39 (2H, br, ring-CH), 4.91 (6H, Sept, $J = 6.0$ Hz, CH), 7.02 (2H, d, $J = 1.5$ Hz, ArH), 7.20 (2H, d, $J = 2.0$ Hz, ArH), 8.29 (2H, s, N=CH). $^{13}$C{$^1$H} NMR (CDCl$_3$): $\delta$ 20.8 (CH$_3$), 26.8 (CH$_3$), 29.6 (CH$_3$), 32.5 (CH$_2$), 35.1 (C), 62.5 (CH), 77.3 (CH), 122.0 (Ar), 126.6 (Ar), 131.3 (ArH), 132.2 (ArH), 138.4 (Ar), 159.8 (ArO), 162.3 (N=CH). Calc. (%) for C$_{48}$H$_{82}$N$_2$O$_8$Ti$_2$, C 63.29, H 9.07, N 3.08. Found (%), C 63.15, H 8.94, N 3.23.

Ti$_2$($^{18}$O$i$Pr)$_6$. Ti(O$i$Pr)$_4$ (0.30 ml, 1.01 mmol) was added to a solution of $^{18}$H$_2$ (0.42 g, 0.50 mmol) in CH$_2$Cl$_2$ (30 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield yellow crystals (0.31 g, 0.24 mmol, 48 %). $^1$H NMR (CDCl$_3$) (328 K): $\delta$ 0.98 (36H, d, $J = 5.5$ Hz, $^t$Bu), 1.47 (4H, br, ring-CH$_2$), 2.13 (4H, br, ring-CH$_2$), 2.19 (2H, s, CH$_3$), 4.22 (2H, br, ring-CH), 4.42 (6H, br, CH), 7.00 – 7.30 (34H, br, ArH), 8.17 (2H, s, N=CH). $^{13}$C{$^1$H} NMR (CDCl$_3$) (328 K): $\delta$ 20.8 (CH$_3$), 26.6 (CH$_3$), 32.8 (CH$_2$), 62.4 (CH), 63.9 (C), 77.1 (CH), 122.9 (Ar), 125.5 (ArH), 126.2 (Ar), 127.2 (ArH), 131.5 (ArH), 133.0 (ArH), 136.2 (ArH), 136.3 (ArH), 159.7 (ArO), 161.7 (N=CH). Calc. (%) for C$_{78}$H$_{94}$N$_2$O$_8$Ti$_2$, C 73.00, H 7.38, N 2.18. Found (%), C 72.85, H 7.25, N 2.20.

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7.7.3 Preparation of aluminium trans-1,4-DACH salen complexes

Al₂(16)Me₄. 2M AlMe₃ (0.84 ml, 1.68 mmol) in heptane was added to a solution of 16H₂ (0.46 g, 0.84 mmol) in toluene (40 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from hexane to yield yellow crystals (0.19 g, 0.29 mmol, 34 %). ¹H NMR (D₈-Tol): δ -0.27 (12H, s, Al-Me ) 1.37 (18H, s, 'Bu), 1.57 (18H, s, 'Bu), 1.45 – 1.70 (8H, m, ring-CH₃), 2.60 (2H, br, ring-CH), 6.94 (2H, d, J = 2.5 Hz, ArH), 7.40 (2H, s, N=CH), 7.69 (2H, d, J = 2.5 Hz, ArH). ¹³C{¹H} NMR (D₈-Tol): δ -5.7 (Al-Me), 30.6 (CH₃), 32.6 (CH₃), 33.4 (CH₂), 35.3 (C), 36.3 (CH₂), 69.5 (CH), 119.8 (Ar), 130.1 (ArH), 133.2 (ArH), 138.5 (Ar), 140.1 (Ar), 163.3 (ArO), 172.7 (N=CH). Calc. (%) for C₄₀H₆₄Al₂N₂O₂, C 72.91, H 9.79, N 4.25. Found (%), C 73.03, H 9.66, N 4.19.

Al₂(17)Me₄. 2M AlMe₃ (0.60 ml, 1.20 mmol) in heptane was added to a solution of 17H₂ (0.28 g, 0.61 mmol) in toluene (40 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from a hexane:toluene mixture to yield yellow crystals (0.13 g, 0.23 mmol, 37 %). ¹H NMR (D₈-Tol): δ -0.28 (12H, s, Al-Me ) 1.55 (18H, s, 'Bu), 1.45 – 1.70 (8H, m, ring-CH₃), 2.22 (6H, s, CH₃), 2.59 (2H, br, ring-CH), 6.59 (2H, d, J = 1.5 Hz, ArH), 7.29 (2H, s, N=CH), 7.39 (2H, d, J = 2.5 Hz, ArH). ¹³C{¹H} NMR (D₈-Tol): δ -7.0 (Al-Me), 20.6 (CH₃), 29.5 (CH₃), 32.6 (CH₂), 32.3 (C), 35.2 (CH₂), 68.5 (CH), 119.2 (Ar), 125.5 (Ar), 132.7 (ArH), 135.7 (ArH), 141.2 (Ar), 162.3 (ArO), 171.2 (N=CH). Calc. (%) for C₃₄H₅₂Al₂N₂O₂, C 71.05, H 9.79, N 4.25. Found (%), C 70.95, H 9.13, N 5.09.

Al₂(18)Me₄. 2M AlMe₃ (0.50 ml, 1.00 mmol) in heptane was added to a solution of 18H₂ (0.42 g, 0.50 mmol) in toluene (40 ml) and stirred (16 h). The solvent was removed in-vacuo and recrystallised from a hexane:toluene mixture to yield yellow crystals (0.22 g, 0.17 mmol, 34 %). ¹H NMR (D₈-Tol): δ -0.70 (12H, s, Al-Me ) 1.39 (8H, br, ring-CH₂), 2.10 (6H, s, CH₃), 2.46 (2H, br, ring-CH), 6.61 (2H, d, J = 2.0 Hz, ArH), 6.95 – 7.15 (18H, m, ArH), 7.12 (2H, s, N=CH), 7.40 (6H, s, ArH), 7.43 (6H, s, ArH), 7.58 (2H, d, J = 2.5 Hz, ArH). ¹³C{¹H} NMR (D₈-Tol): δ -6.9 (Al-Me), 20.6 (CH₃), 32.3 (CH₂), 63.9 (C), 68.1 (CH), 119.4 (Ar), 125.8 (ArH), 127.5 (ArH), 131.6 (ArH), 139.3 (Ar), 139.4 (ArH), 146.1 (Ar), 161.8 (ArO), 170.6 (N=CH). Calc. (%) for C₆₄H₆₄Al₂N₂O₂, C 81.16, H 6.81, N 2.96. Found (%), C 81.01, H 6.78, N 3.04.
7.8 Preparation of Ligands and Complexes for Chapter 6

7.8.1 Preparation of trans-1,2-DACH salalen ligands

tert-Butyl (2-aminocyclohexyl)carbamate. A solution of di-tert-butyl dicarbonate (9.61 g, 44.04 mmol) in CH$_2$Cl$_2$ (50 ml) was added dropwise to a cooled (0 °C) solution of trans-1,2-diaminecyclohexane (15.08 g, 70.47 mmol) in CH$_2$Cl$_2$ (50 ml) over a period of 30 mins while stirring. The solution was allowed to warm to room temperature and stirred overnight. CH$_2$Cl$_2$ (50 ml) and water (50 ml) were added to the resulting suspension to dissolve the precipitate and the organic phase was separated then the solvent was removed in-vacuo. The residue was dissolved in ethyl ether (50 ml) and water (50 ml) and the solution was acidified to pH 5 with 4M HCl, the mixture was separated and the aqueous layer was washed with ethyl ether (3 x 50 ml). 2M NaOH was added to the aqueous layer until pH 10.5 was reached, at which point the product was extracted with AcOEt (3 x 50 ml). The organic phase was washed with saturated brine (20 ml) and dried with anhydrous MgSO$_4$. After filtration the solvent was removed in-vacuo to yield a pale beige solid (7.17 g, 33.46 mmol, 47 %). $^1$H NMR (CDCl$_3$): δ 1.00 – 1.30 (4H, m, CH$_2$), 1.38 (2H, s, NH$_2$), 1.41 (9H, s, tBu), 1.65 (2H, m, CH$_2$), 1.95 (2H, m, CH$_2$), 2.29 (1H, td, J = 10 Hz, J = 4.0 Hz, CH), 3.08 (1H, br, CH), 4.52 (1H, br, NH).

19HBoc. tert-Butyl (2-aminocyclohexyl)carbamate (2.00 g, 9.33 mmol) was added to a solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (2.18 g, 9.30 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. Sodium borohydride (2.12 g, 56.03 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed in-vacuo. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H$_2$O, 2.12 ml, 26.74 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed in-vacuo and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0 °C), then sodium borohydride (2.12 g, 56.03 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed in-vacuo. Water (50 ml) was then used to precipitate a
white solid, which was then filtered and washed with water (3 x 50 ml) and dried to yield a white solid (3.40 g, 7.61 mmol, 82 %). ¹H NMR (CDCl₃): δ 1.00 – 1.20 (2H, m, CH₂), 1.28 (9H, s, 'Bu), 1.43 (9H, s, 'Bu), 1.48 (9H, s, 'Bu), 1.60 – 2.10 (6H, m, CH₂), 2.29 (3H, s, CH₃), 2.36 (1H, m, CH), 3.62 (1H, m, CH), 3.75 (1H, m, NH), 3.79 (1H, d, J = 4.5 Hz, CH₂), 4.55 (1H, d, J = 10.0 Hz, CH₂), 6.81 (1H, d, J = 2.5 Hz, ArH), 7.21 (1H, d, J = 2.5 Hz, ArH), 11.10 (1H, br, ArOH).

19H₃. 19HBoc (2.40 g, 5.37 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (20 ml x 4). The organic phase was washed with saturated brine (20 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed in-vacuo to yield an oily residue which was used without further purification (1.80 g, 5.19 mmol, 97 %) ¹H NMR (CDCl₃): δ 1.10 – 1.30 (4H, m, CH₂), 1.28 (9H, s, 'Bu), 1.48 (9H, s, 'Bu), 1.65 – 2.05 (4H, m, CH₂), 2.25 (3H, s, CH₃), 2.35 (1H, m, CH), 2.79 (1H, m, CH), 3.72 (1H, d, J = 13.5 Hz, CH₂), 3.86 (1H, d, J = 13.5 Hz, CH₂), 4.12 (1H, q, J = 7.5 Hz, NH) 3.50 – 4.00 (3H, br, NH₂, ArOH), 6.83 (1H, d, J = 2.5 Hz, ArH), 7.21 (1H, d, J = 2.5 Hz, ArH).

20HBoc. tert-Butyl (2-aminocyclohexyl)carbamate (2.43 g, 11.34 mmol) was added to a solution of 2-hydroxybenzaldehyde (1.39 g, 11.38 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. Sodium borohydride (1.29 g, 34.10 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed in-vacuo. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H₂O, 2.58 ml, 31.79 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed in-vacuo and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0 °C), then sodium borohydride (2.00 g, 52.87 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed in-vacuo. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 50 ml) and dried to
yield a white solid (3.33 g, 9.96 mmol, 81%). $^1$H NMR (CDCl$_3$): δ 1.00 – 1.30 (4H, m, CH$_2$), 1.41 (9H, s, $^t$Bu), 1.60 – 2.05 (4H, m, CH$_2$), 2.21 (3H, s, CH$_3$), 2.34 (1H, td, J = 11.0 Hz, J = 3.5 Hz, CH), 3.60 (1H, m, CH), 3.75 (1H, q, J = 14.0 Hz, CH$_2$), 4.40 (1H, br, NH), 6.71 (2H, m, ArH), 6.88 (1H, dd, J = 7.5 Hz, J = 1.5 Hz, ArH), 7.08 (1H, td, J = 7.5 Hz, J = 1.5 Hz, ArH).

20H$_3$. 20HBoc (3.25 g, 9.72 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (30 ml x 4). The organic phase was washed with saturated brine (20 ml) then dried with MgSO$_4$, the solid was removed by filtration and the solvent removed $\text{in-vacuo}$ to yield a white solid (1.85, 7.89 mmol, 81%). $^1$H NMR (CDCl$_3$): δ 1.10 – 1.35 (4H, m, CH$_2$), 1.65 – 2.05 (4H, m, CH$_2$), 2.22 (3H, s, CH$_3$), 2.34 (1H, td, J = 10.0 Hz, J = 3.5 Hz, CH), 2.78 (1H, td, J = 10.0 Hz, J = 4.5 Hz, CH), 3.61 (1H, d, J = 13.5 Hz, CH$_2$), 3.89 (1H, d, J = 13.5 Hz, CH$_2$), 4.39 (3H, br, NH$_2$, ArOH), 6.76 (1H, td, J = 7.5 Hz, J = 1.0 Hz, ArH), 6.82 (1H, dd, J = 8.0 Hz, J = 1.0 Hz, ArH), 6.97 (1H, dd, J = 7.5 Hz, J = 1.5 Hz, ArH), 7.15 (1H, td, J = 7.5 Hz, J = 1.5 Hz, ArH).

21HBoc. tert-Butyl (2-aminocyclohexyl)carbamate (3.00 g, 14.00 mmol) was added to a solution of 3,5-dichloro-2-hydroxybenzaldehyde (2.67 g, 13.98 mmol) in MeOH (30 ml) / THF (30 ml) and stirred for 1 h. Sodium borohydride (1.60 g, 42.29 mmol) was added slowly to the yellow solution and then stirred for 16 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed $\text{in-vacuo}$. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 50 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H$_2$O, 3.18 ml, 39.18 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed $\text{in-vacuo}$ and the residue was dissolved in MeOH (30 ml) / THF (30 ml) and cooled (0 °C), then sodium borohydride (2.50 g, 66.09 mmol) was slowly added and the solution was stirred for 2 h. The reaction was quenched with water (10 ml) and the solvent partially removed $\text{in-vacuo}$. Water (50 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 50 ml) and dried to yield a white solid (4.30 g, 10.66 mmol, 76 %). $^1$H NMR (CDCl$_3$): δ 1.10 – 1.35 (4H,
m, CH₂), 1.48 (9H, s, 'Bu), 1.70 – 2.10 (4H, m, CH₂), 2.27 (3H, s, CH₃), 2.40 (1H, td, J = 11.0 Hz, J = 3.5 Hz, CH), 3.69 (1H, m, CH), 3.71 (1H, d, J = 14.0 Hz, CH₂), 3.87 (1H, d, J = 14.0 Hz, CH₂), 4.48 (1H, d, J = 10.0 Hz, NH), 6.82 (1H, d, J = 2.5 Hz, ArH), 7.22 (1H, d, J = 2.5 Hz, ArH), 9.87 (1H, br, ArOH).

**21H₂.** 21HBOc (4.20 g, 10.41 mmol) was dissolved in methanol (30 ml) and 3M HCl (30 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (30 ml x 4). The organic phase was washed with saturated brine (20 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed in vacuo to yield a white solid (2.66, 8.77 mmol, 84%). ¹H NMR (CDCl₃): δ 1.00 – 1.25 (4H, m, CH₂), 1.61 (1H, br, CH₂), 1.71 (1H, br, CH₂), 1.85 (2H, br, CH₂), 2.21 (3H, s, CH₃), 2.25 (1H, br, CH₂), 2.84 (1H, br, CH), 3.08 (1H, d, J = 12.0 Hz, CH₂), 3.79 (1H, d, J = 12.5 Hz, CH₂), 4.92 (3H, br, NH₂, ArOH), 6.80 (1H, d, J = 2.5 Hz, ArH), 7.14 (1H, d, J = 2.5 Hz, ArH).

**22H₂.** 19HBOc (1.00 g, 2.24 mmol) was dissolved in methanol (20 ml) and 3M HCl (20 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (15 ml x 4). The organic phase was washed with saturated brine (10 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed in vacuo. The oily residue was dissolved in MeOH (30 ml) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.52 g, 2.24 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in vacuo to yield a yellow solid (0.50 g, 0.89 mmol, 40%). ¹H NMR (CDCl₃): δ 1.15 (9H, s, 'Bu), 1.28 (9H, s, 'Bu), 1.32 (9H, s, 'Bu), 1.35 – 1.45 (3H, m, ring-CH₂), 1.51 (9H, s, 'Bu), 1.63 – 2.07 (5H, m, ring-CH₂), 2.26 (3H, s, CH₃), 3.00 (1H, m, ring-CH), 3.33 (1H, m, ring-CH), 3.75 (1H, d, J = 13.0 Hz, CH₂), 3.91 (1H, d, J = 13.0 Hz, CH₂), 6.83 (1H, d, J = 2.5 Hz, ArH), 7.06 (1H, d, J = 2.5 Hz, ArH), 7.14 (1H, d, J = 2.5 Hz, ArH), 7.41 (1H, d, J = 2.5 Hz, ArH), 8.40 (1H, s, CH), 10.61 (1H, br, OH), 13.59 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.8 (CH₂), 25.3 (CH₂), 29.5 (CH₃), 29.8 (CH₃), 31.7 (CH₃), 31.9 (CH₃), 34.2 (C), 34.9 (C), 35.2 (CH₂), 35.4 (CH₂), 66.6 (CH), 70.3 (CH), 118.1 (Ar), 121.0 (Ar), 122.5 (ArH), 123.3 (ArH), 125.8 (ArH), 126.9(ArH), 135.4 (Ar), 136.6 (Ar), 139.8 (Ar), 139.8 (Ar),
(R,R-22)H₂. tert-butyl (1S,2S)-2-aminocyclohexyl)carbamate (0.375 g, 1.75 mmol) was added to a solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.41 g, 1.75 mmol) in MeOH (15 ml) / THF (15 ml) and stirred for 1 h. Sodium borohydride (0.30 g, 9.99 mmol) was added slowly to the yellow solution and then stirred for 5 h until the solution became colourless. The reaction was quenched with water (10 ml) and the solvent partially removed in-vacuo. Water (30 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 30 ml). The resulting solid was dissolved in MeOH (30 ml) and formaldehyde solution (37 % in H₂O, 0.40 ml, 4.93 mmol) was slowly added and allowed to stir for 1 h. The solvent was removed in-vacuo and the residue was dissolved in MeOH (15 ml) / THF (15 ml) and cooled (0 °C), then sodium borohydride (0.30 g, 9.99 mmol) was slowly added and the solution was stirred for 16 h. The reaction was quenched with water (10 ml) and the solvent partially removed in-vacuo. Water (30 ml) was then used to precipitate a white solid, which was then filtered and washed with water (3 x 30 ml) and dried to yield a white solid. The white solid was dissolved in methanol (20 ml) and 3M HCl (20 ml) then heated to 60 °C and allowed to stir (16 h). The mixture was neutralised with 3M NaOH and the white precipitate was extracted with AcOEt (10 ml × 4). The organic phase was washed with saturated brine (10 ml) then dried with MgSO₄, the solid was removed by filtration and the solvent removed in-vacuo. The residue was dissolved in MeOH (20 ml) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.41 g, 1.75 mmol) was added. The solution was stirred for 16 h then the solid was filtered and further dried in-vacuo to yield a pale yellow solid (0.49 g, 0.87 mmol, 50 %). ¹H NMR (CDCl₃): δ 1.12 (9H, s, ¹Bu), 1.25 (9H, s, ¹Bu), 1.29 (9H, s, ¹Bu), 1.35 – 1.45 (3H, m, ring-CH₂), 1.48 (9H, s, ¹Bu), 1.63 – 2.07 (5H, m, ring-CH₂), 2.23 (3H, s, CH₃), 2.98 (1H, m, ring-CH), 3.31 (1H, m, ring-CH), 3.72 (1H, d, J = 12.0 Hz, CH₂), 3.88 (1H, d, J = 12.0 Hz, CH₂), 6.80 (1H, d, J = 2.5 Hz, ArH), 7.03 (1H, d, J = 2.5 Hz, ArH), 7.11 (1H, d, J = 2.5 Hz, ArH), 7.38 (1H, d, J = 2.5 Hz, ArH), 8.38 (1H, s, CH), 10.61 (1H, br, OH), 13.58 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 24.8 (CH₂), 25.3 (CH₂), 29.5 (CH₃), 29.7 (CH₃), 31.6 (CH₃), 31.9 (CH₃), 34.2 (C), 34.8 (C), 35.2 (CH₂), 35.5 (CH₂), 66.7 (CH), 70.4 (CH), 118.2 (Ar),
23H₂. 19H₃ (1.00 g, 2.89 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.31 ml, 2.91 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.98 g, 2.17 mmol, 75 %). ¹H NMR (CDCl₃): δ 1.11 (9H, s, tBu), 1.25 (9H, s, tBu), 1.31 – 1.53 (3H, m, ring-CH₂), 1.63 – 2.08 (5H, m, ring-CH₂), 2.20 (3H, s, CH₃), 2.97 (1H, m, ring-CH), 3.36 (1H, m, ring-CH), 3.70 (1H, br, CH₂), 3.80 (1H, d, J = 13.0 Hz, CH₂), 6.77 (1H, d, J = 2.0 Hz, ArH), 6.86 (1H, t, J = 7.5 Hz, ArH), 6.99 (1H, d, J = 8.0 Hz, ArH), 7.11 (1H, br, ArH), 7.23 (1H, d, J = 7.5 Hz, ArH), 7.42 (1H, t of d, J = 2.0 Hz, J = 8.0 Hz, ArH), 8.38 (1H, s, CH), 10.62 (1H, br, OH), 13.15 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 23.1 (CH₂), 24.6 (CH₂), 25.1 (CH₂), 29.3 (CH₃), 34.1 (C), 34.6 (C), 34.9 (CH₂), 58.5 (CH₂), 67.2 (CH), 70.1 (CH), 117.0 (ArH), 118.4 (ArH), 119.1 (Ar), 120.7 (Ar), 122.5 (ArH), 123.1 (ArH), 131.3 (ArH), 132.1 (ArH), 135.4 (Ar), 139.8 (Ar), 154.6 (ArO), 161.2 (ArO), 164.7 (CH). Calc. m/z [C₂₉H₄₂N₂O₂ + Na]⁺ 473.3144. Found 473.3166

24H₂. 19H₃ (0.80 g, 2.31 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.44 ml, 2.30 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.77 g, 1.48 mmol, 64 %). ¹H NMR (CDCl₃): δ 1.10 (9H, s, tBu), 1.25 (9H, s, tBu), 1.28 – 1.50 (3H, m, ring-CH₂), 1.64 – 2.08 (5H, m, ring-CH₂), 2.18 (3H, s, CH₃), 2.94 (1H, m, ring-CH), 3.36 (1H, m, ring-CH), 3.70 (1H, d, J = 13.0 Hz, CH₂), 3.81 (1H, d, J = 13.0 Hz, CH₂), 6.76 (1H, d, J = 2.0 Hz, ArH), 7.10 (1H, br, ArH), 7.14 (1H, d, J = 2.0 Hz, ArH), 7.42 (1H, d, J = 2.5 Hz, ArH), 8.29 (1H, s, CH), 10.50 (1H, br, OH), 14.20 (1H, s, OH). ¹³C{¹H} NMR (CDCl₃): δ 22.5 (CH₂), 24.5 (CH₂), 25.1 (CH₂), 29.3 (CH₂), 31.8 (CH₃), 34.2 (C), 34.6 (C), 34.7 (CH₃), 67.8 (CH), 69.5 (CH), 120.2 (Ar), 120.4 (Ar), 122.7 (Ar), 122.8 (Ar), 122.8 (ArH), 123.2 (ArH), 129.2 (ArH), 132.0 (ArH), 135.5 (Ar), 140.2 (Ar), 154.5 (ArO), 156.6 (ArO), 163.2 (CH). Calc. m/z [C₂₉H₄₀Cl₂N₂O₂ + H]⁺ 519.2545. Found 519.2564
26H₂. 20H₃ (0.60 g, 2.56 mmol) was dissolved in MeOH (30 ml) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.60 g, 2.56 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.92 g, 2.04 mmol, 80 %). ¹H NMR (CDCl₃): δ 1.20 – 1.44 (3H, m, ring-CH₂), δ 1.33 (9H, s, tBu), 1.49 (9H, s, tBu), 1.60 – 2.06 (5H, m, ring-CH₂), 2.30 (3H, s, CH₃), 3.03 (1H, m, ring-CH), 3.36 (1H, td, J = 10.5 Hz, J = 4.5 Hz, ring-CH), 3.92 (2H, m, CH₂), 6.69 – 6.77 (2H, m, ArH), 6.94 (1H, m, ArH), 7.09 (1H, d, J = 2.5 Hz, ArH), 7.13 (1H, m, ArH), 7.41 (1H, d, J = 2.5 Hz, ArH), 8.42 (1H, s, CH), 9.6 – 11.8 (1H, br, OH), 12.1 – 14.2 (1H, br, OH). ¹³C [¹H] NMR (CDCl₃): δ 24.7 (CH₂), 25.3 (CH₂), 25.5 (CH₂), 29.6 (CH₃), 31.7 (CH₃), 34.3 (C), 35.2 (C), 35.6 (CH₃), 35.7 (CH₂), 58.7 (CH₂), 66.1 (CH), 70.1 (CH), 116.5 (ArH), 118.0 (Ar), 119.7 (ArH), 121.9 (Ar), 126.1 (ArH), 127.3 (ArH), 128.8 (ArH), 128.8 (ArH), 136.7 (Ar), 140.1 (Ar), 158.2 (ArO), 158.4 (ArO), 165.8 (CH). Calc. m/z [C₂₉H₄₂N₂O₂ + Na]+ 473.3144. Found 473.3154

27H₂. 20H₃ (0.60 g, 2.56 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.31 g, 2.54 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.70 g, 2.07 mmol, 81 %). ¹H NMR (CDCl₃): δ 1.19 – 1.43 (3H, m, ring-CH₂), 1.48 – 1.63 (1H, m, ring-CH₂), 1.68 (1H, br, ring-CH₂), 1.72 (1H, br, ring-CH₂), 1.80 (1H, m, ring-CH₂), 1.92 (1H, m, ring-CH₂), 2.16 (3H, s, CH₃), 2.88 (1H, m, ring-CH), 3.25 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.61 (1H, d, J = 13.5 Hz, CH₂), 3.70 (1H, d, J = 13.5 Hz, CH₂), 6.60 – 6.68 (2H, m, ArH), 6.78 – 6.88 (2H, m, ArH), 6.94 (1H, d, J = 8.0 Hz, ArH), 7.02 (1H, td, J = 7.5 Hz, J = 2.0 Hz ArH), 7.18 (1H, m, ArH), 7.25 (1H, m, ArH), 8.31 (1H, s, CH), 9.5 – 14.0 (2H, br, OH). ¹³C [¹H] NMR (CDCl₃): δ 23.8 (CH₂), 24.7 (CH₂), 25.1 (CH₂), 35.6 (CH₂), 35.6 (CH₃), 58.1 (CH₂), 66.5 (CH), 70.0 (CH), 116.3 (ArH), 117.2 (ArH), 118.7 (ArH), 118.8 (ArH), 119.0 (Ar), 121.8 (Ar), 128.5 (ArH), 128.6 (ArH), 131.5 (ArH), 132.4 (ArH), 158.3 (ArO), 161.2 (ArO), 164.7 (CH). Calc. m/z [C₂₁H₂₆N₂O₂ + Na]+ 361.1892. Found 361.1895

25H₂. 20H₃ (0.60 g, 2.56 mmol) was dissolved in MeOH (30 ml) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.60 g, 2.56 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.79 g,
1.91 mmol, 75%). $^1$H NMR (CDCl$_3$): δ 1.25 – 1.50 (3H, m, ring-CH$_2$), 1.62 (1H, m, ring-CH$_2$), 1.70 (2H, br, ring-CH$_2$), 1.90 (1H, br, ring-CH$_2$), 2.02 (1H, m, ring-CH$_2$), 2.92 (1H, m, ring-CH), 3.38 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.72 (1H, d, J = 13.5 Hz, CH$_2$), 3.87 (1H, d, J = 13.5 Hz, CH$_2$), 6.63 – 6.77 (2H, m, ArH), 7.10 (1H, td, J = 8.0 Hz, ArH), 7.17 (1H, d, J = 2.5 Hz, ArH), 7.41 (1H, td, J = 8.0 Hz, J = 1.5 Hz, ArH), 7.17 (1H, d, J = 2.5 Hz, ArH), 7.41 (1H, d, J = 2.5 Hz, ArH), 8.28 (1H, s, CH), 9.0 – 11.5 (1H, br, OH), 12.5 – 15.0 (1H, br, OH).

$^{13}$C{$_1$H} NMR (CDCl$_3$): δ 23.0 (CH$_2$), 24.5 (CH$_2$), 25.0 (CH$_2$), 35.2 (CH$_2$), 36.3 (CH$_3$), 57.4 (CH$_2$), 66.7 (CH), 69.2 (CH), 116.4 (ArH), 118.9 (ArH), 119.9 (Ar), 121.5 (Ar), 122.7 (Ar), 122.8 (Ar), 128.6 (ArH), 128.8 (ArH), 129.3 (ArH), 132.3 (ArH), 156.6 (ArO), 158.0 (ArO), 163.3 (CH). Calc. m/z [C$_{21}$H$_{24}$Cl$_2$N$_2$O$_2$ + Na$^+$] 429.1113. Found 429.1119

28H$_2$. 21H$_3$ (0.75 g, 2.47 mmol) was dissolved in MeOH (30 ml) and 3,5-di-tert-butyl-2-hydroxybenzaldehyde (0.58 g, 2.48 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (1.08 g, 2.08 mmol, 84 %). $^1$H NMR (CDCl$_3$): δ 1.24 – 1.44 (3H, m, ring-CH$_2$), δ 1.32 (9H, s, $^t$Bu), 1.48 (9H, s, $^t$Bu), 1.60 – 2.00 (5H, m, ring-CH$_2$), 2.28 (3H, s, CH$_3$), 3.01 (1H, m, ring-CH), 3.36 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.85 (1H, d, J = 14.5 Hz, CH$_2$), 3.95 (1H, d, J = 14.5 Hz, C$_2$H$_2$), 6.83 (1H, d, J = 2.5 Hz, ArH), 7.09 (1H, d, J = 2.5 Hz, ArH), 7.19 (1H, d, J = 2.5 Hz, ArH), 7.42 (1H, d, J = 2.5 Hz, ArH), 8.43 (1H, s, CH), 11.4 – 14.7 (1H, br, OH). $^{13}$C{$_1$H} NMR (CDCl$_3$): δ 24.7 (CH$_2$), 25.2 (CH$_2$), 29.6 (CH$_3$), 31.6 (CH$_3$), 34.3 (C), 35.2 (C), 35.3 (CH$_3$), 35.7 (CH$_2$), 59.5 (CH$_2$), 66.5 (CH), 70.1 (CH), 117.9 (Ar), 121.5 (Ar), 123.1 (Ar), 124.0 (Ar), 126.1 (ArH), 126.8 (ArH), 127.5 (ArH), 128.6 (ArH), 137.1 (Ar), 140.3 (Ar), 153.3 (ArO), 158.1 (ArO), 166.1 (CH). Calc. m/z [C$_{29}$H$_{30}$Cl$_2$N$_2$O$_2$ + Na$^+$] 541.2365. Found 541.2393

29H$_2$. 21H$_3$ (0.75 g, 2.47 mmol) was dissolved in MeOH (30 ml) and 2-hydroxybenzaldehyde (0.30 g, 2.46 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.63 g, 1.55 mmol, 63 %). $^1$H NMR (CDCl$_3$): δ 1.23 – 2.05 (8H, m, ring-CH$_2$), 2.27 (3H, s, CH$_3$), 2.97 (1H, m, ring-CH), 3.35 (1H, td, J = 10.5 Hz, J = 4.5, Hz, ring-CH), 3.79 (1H, d, J = 14.5 Hz, CH$_2$), 3.90 (1H, d, J = 14.5 Hz, CH$_2$), 6.80 (1H, d, J = 2.5 Hz,
ArH), 6.91 (1H, td, J = 7.5 Hz, J = 1.0 Hz, ArH), 7.01 (1H, m, ArH), 7.18 (1H, d, J = 2.5 Hz, ArH), 7.26 (1H, dd, J = 7.5 Hz, J = 1.5 Hz, ArH), 7.35 (1H, ddd, J = 8.5 Hz, J = 7.5 Hz, J = 1.5 Hz, ArH), 8.41 (1H, s, CH), 10.5 – 14.0 (2H, br, OH).

$\text{^13C\{^1H\}}\text{NMR (CDCl}_3\text{): }\delta$ 24.5 (CH$_2$), 25.1 (CH$_2$), 25.7 (CH$_2$), 35.4 (CH$_2$), 35.7 (CH$_3$), 58.6 (CH$_2$), 66.9 (CH), 70.0 (CH), 117.2 (ArH), 118.8 (ArH), 118.8 (Ar), 121.6 (Ar), 123.1 (Ar), 123.9 (Ar), 126.7 (ArH), 128.6 (ArH), 131.6 (ArH), 132.7 (ArH), 153.1 (ArO), 156.3 (ArO), 161.2 (ArO), 165.0 (CH). Calc. m/z $[C_{21}H_{24}Cl_2N_2O_2 + Na]^+$ 429.1113. Found 429.1102.

$30\text{H}_2$. $21\text{H}_3$ (0.75 g, 2.47 mmol) was dissolved in MeOH (30 ml) and 3,5-dichloro-2-hydroxybenzaldehyde (0.46 g, 2.46 mmol) was added. The solution was stirred for 2 h then the solid was filtered and further dried in-vacuo to yield a yellow solid (0.94 g, 1.97 mmol, 80 %). $^1\text{H NMR (CDCl}_3\text{): }\delta$ 1.23 – 2.06 (8H, m, ring-CH$_2$), 2.25 (3H, s, CH$_3$), 2.91 (1H, m, ring-CH), 3.37 (1H, td, J = 10.5 Hz, 4.5 Hz, ring-CH), 3.73 (1H, d, J = 14.5 Hz, CH$_2$), 3.86 (1H, d, J = 14.5 Hz, CH$_2$), 6.80 (1H, d, J = 2.5 Hz, ArH), 7.18 (1H, m, ArH), 7.42 (1H, d, J = 2.5 Hz, ArH), 8.30 (1H, s, CH), 11.0 – 14.5 (1H, br, OH). $^{13}\text{C\{^1H\}}\text{NMR (CDCl}_3\text{): }\delta$ 24.0 (CH$_2$), 24.4 (CH$_2$), 25.0 (CH$_2$), 35.1 (CH$_2$), 36.1 (CH$_3$), 57.8 (CH$_2$), 67.0 (CH), 69.4 (CH), 119.8 (Ar), 121.8 (Ar), 122.8 (Ar), 123.0 (Ar), 123.3 (Ar), 123.6 (Ar), 126.6 (ArH), 128.8 (ArH), 129.3 (ArH), 132.4 (ArH), 152.9 (ArO), 156.3 (ArO), 163.5 (CH). Calc. m/z $[C_{21}H_{22}Cl_2N_2O_2 + Na]^+$ 497.0333. Found 497.0350.

### 7.8.2 Preparation of aluminium trans-1,2-DACH salalen complexes

$\text{Al(22)Me. } 22\text{H}_2$ (0.45 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe$_3$ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from hexane to yield yellow crystals (0.29 g, 0.48 mmol, 60 %). $^1\text{H NMR (D}_8\text{-Tol)} (233 K): \delta$ -0.35 (3H, s, Al-Me), 0.50 (2H, m, ring-CH$_2$), 0.63 (2H, br, ring-CH$_2$), 1.05 – 1.30 (4H, m, ring-CH$_2$), 1.40 (9H, s, $^1\text{Bu}$), 1.49 (9H, s, $^1\text{Bu}$), 1.60 (3H, s, CH$_3$), 1.82 (9H, s, $^1\text{Bu}$), 1.86 (9H, s, $^1\text{Bu}$), 2.35 (2H, m, ring-CH), 2.78 (1H, d, J = 13.0 Hz, CH$_2$), 3.98 (1H, d, J = 13.0 Hz, CH$_2$), 6.84 (1H, s, ArH), 6.98 (1H, s, ArH), 7.52 (1H, s, ArH), 7.58 (1H, s, ArH), 7.76 (1H, s, CH). $^{13}\text{C NMR (D}_8\text{-Tol)}: \delta$ 21.5 (CH$_2$), 24.1 (CH$_2$), 24.8 (CH$_2$), 30.0 (CH$_3$), 30.1 (CH$_3$), 31.5 (CH$_3$), 32.1 (CH$_3$), 33.1 (CH$_2$), 34.1 (C),
Despite significant efforts elemental analysis could not be obtained for complexes containing ligand 1H2, clean NMRs and the single crystal data supports the complex.

Al(R,R-22)Me. R,R-22H2 (0.225 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe3 in heptane (0.20 ml, 0.40 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from hexane to yield yellow crystals (0.08 g, 0.13 mmol, 33 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. 1H NMR (d8-Tol): δ -0.48 (3H, s, Al-Me), -0.41 (3H, s, Al-Me), 0.50 - 0.85 (8H, m, ring-CH2), 1.15 – 1.35 (8H, m, ring-CH2), 1.35 (9H, s, tBu), 1.37 (9H, s, tBu), 1.41 (9H, s, tBu), 1.45 (9H, s, tBu), 1.69 (9H, s, tBu), 1.74 (9H, s, tBu), 1.76 (3H, s, CH3), 1.77 (9H, s, tBu), 1.78 (9H, s, tBu), 1.85 (3H, s, CH3), 2.35 – 2.50 (2H, m, ring-CH), 2.59 (1H, m, ring-CH), 2.80 (1H, d, J = 12.0 Hz, CH2), 2.83 (1H, m, ring-CH), 2.94 (1H, d, J = 13.0 Hz, CH2), 2.71 (1H, d, J = 12.0 Hz, CH2), 4.08 (1H, d, J = 13.0 Hz, CH2), 6.81 (1H, d, J = 2.5 Hz, ArH), 6.92 (1H, d, J = 2.5 Hz, ArH), 6.96 (2H, t, J = 2.5 Hz, ArH), 7.49 (1H, d, J = 2.5 Hz, ArH), 7.54 (1H, d, J = 2.5 Hz, ArH), 7.71 (1H, d, J = 2.5 Hz, ArH), 7.73 (1H, d, J = 2.5 Hz, ArH), 7.74 (1H, d, J = 1.0 Hz, ArH), 7.77 (1H, d, J = 1.0 Hz, ArH). 13C{1H} NMR (d8-Tol): δ 21.2 (CH2), 21.6 (CH2), 23.1 (CH2), 24.2 (CH2), 24.8 (CH2), 25.0 (CH2), 30.0 (CH3), 30.2 (CH3), 30.4 (CH3), 30.5 (CH3), 31.5 (CH3), 31.6 (CH3), 32.0 (CH2), 32.1 (CH3), 32.2 (CH3), 32.6 (CH2), 33.1 (C), 34.1 (C), 34.3 (C), 34.3 (C), 35.6 (C), 35.7 (C), 35.8 (C), 35.8 (C), 36.3 (CH3), 41.1 (CH3), 52.3 (CH2), 58.6 (CH2), 60.3 (CH), 61.2 (CH), 66.4 (CH), 118.1 (Ar), 120.9 (Ar), 122.2 (Ar), 123.7 (ArH), 123.7 (ArH), 123.8 (ArH), 123.9 (ArH), 127.5 (ArH), 127.8 (ArH), 131.7 (ArH), 132.0 (ArH), 136.7 (Ar), 136.8 (Ar), 138.0 (Ar), 138.2 (Ar), 138.4 (Ar), 141.4 (Ar), 141.8 (Ar), 157.1 (ArO), 157.4 (ArO), 166.1 (ArO), 166.5 (ArO), 171.4 (N=CH), 171.7 (N=CH). CHN analysis - see comment for Al(21)Me.

Al(22)OBn. 22H2 (0.45 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe3 in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with
hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.092 ml, 0.89 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from hexane to yield a yellow solid (0.06 g, 0.09 mmol, 11 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. \(^1\)H NMR (D₈-Tol): δ 0.45 – 0.9 (8H, m, ring-CH₂), 1.10 – 1.55 (8H, m, ring-CH₂), 1.35 (9H, s, \(^1\)Bu), 1.37 (9H, s, \(^1\)Bu), 1.39 (9H, s, \(^1\)Bu), 1.44 (9H, s, \(^1\)Bu), 1.62 (9H, s, \(^1\)Bu), 1.73 (9H, s, \(^1\)Bu), 1.74 (9H, s, \(^1\)Bu), 1.78 (9H, s, \(^1\)Bu), 2.18 (3H, s, CH₃), 2.23 (3H, s, CH₃), 2.30 (1H, td, J = 11.5 Hz, J = 3.0 Hz, ring-CH), 2.60 – 2.80 (3H, m, ring-CH), 2.83 (1H, d, J = 12.0 Hz, CH₂), 3.00 (1H, d, J = 13.0 Hz, CH₂), 3.71 (1H, d, J = 12.0 Hz, CH₂), 4.50 (1H, d, J = 13.0 Hz, CH₂), 5.20 (4H, br, CH₂), 6.80 (1H, d, J = 2.5 Hz, ArH), 6.93 (1H, d, J = 2.5 Hz, ArH), 6.96 (1H, s, ArH), 7.00 (1H, d, J = 2.5 Hz, ArH), 7.04 (2H, br, ArH), 7.15 – 7.40 (8H, br, ArH), 7.47 (1H, d, J = 2.5 Hz, ArH), 7.54 (1H, d, J = 2.5 Hz, ArH), 7.71 (1H, s, N=CH), 7.74 (1H, d, J = 2.5 Hz, ArH), 7.78 (1H, d, J = 2.5 Hz, ArH), 7.80 (1H, s, N=CH). \(^13\)C NMR (D₈-Tol): δ 24.1 (CH₂), 24.8 (CH₂), 30.0 (CH₃), 30.4 (CH₃), 30.5 (CH₃), 30.7 (CH₃), 31.5 (CH₃), 31.5 (CH₃), 32.0 (CH₂), 32.1 (CH₃), 32.2 (CH₃), 32.2 (CH₂), 34.1 (C), 34.2 (C), 34.3 (C), 34.3 (C), 35.5 (C), 35.7 (C), 35.8 (C), 35.9 (C), 37.6 (CH₃), 41.7 (CH₃), 52.1 (CH₂), 59.2 (CH₂), 60.2 (CH), 60.2 (CH), 60.7 (CH), 66.2 (CH), 118.4 (Ar), 121.2 (Ar), 122.1 (Ar), 123.6 (ArH), 123.7 (ArH), 123.8 (ArH), 123.9 (ArH), 126.8 (ArH), 127.8 (ArH), 128.0 (ArH), 128.2 (ArH), 132.1 (ArH), 132.3 (ArH), 137.3 (Ar), 137.3 (Ar), 138.5 (Ar), 141.4 (Ar), 141.5 (Ar), 156.9 (ArO), 157.3 (ArO), 166.4 (ArO), 171.2 (N=CH), 171.5 (N=CH). CHN analysis - see comment for Al(21)Me

Al(23)Me. 23H₂ (0.45 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from toluene to yield yellow crystals (0.10 g, 0.20 mmol, 20 %). \(^1\)H NMR (D₈-Tol): δ -0.36 (3H, s, Al-Me), 0.70 - 1.00 (4H, br, ring-CH₂), 1.30 – 1.60 (4H, m, ring-CH₂), 1.45 (9H, s, \(^1\)Bu), 1.75 (9H, s, \(^1\)Bu), 1.86 (3H, s, CH₃), 2.45 – 2.65 (2H, m, ring-CH), 2.72 (1H, d, J = 12.0 Hz, CH₂), 3.49 (1H, d, J = 12.0 Hz, CH₂), 6.53 (1H, ddd, J = 8.0 Hz, J = 6.5 Hz, J = 1.5 Hz, ArH), 6.90 (1H, d, J = 1.5 Hz, ArH), 6.93 (1H, d, J = 2.0 Hz, ArH), 7.14 (1H, d, J = 1.5 Hz, ArH), 7.18 (1H, dd, J = 6.5 Hz, J = 2.0 Hz, ArH), 7.52 (1H, d,
Ar. Ar. Ar 3 ed (16 h). The solvent was removed. AlMe3 (1H, d, J = 2.5 Hz, ArH), 34.8 (CH3), 70.9 (CH), 120.1 (ArH), 123.4 (Ar), 126.4 (Ar), 127.8 (ArH), 128.3 (ArH), 128.5 (ArH), 138.7 (ArH), 142.1 (ArH), 142.7 (Ar), 143.3 (Ar), 162.1 (ArO), 173.9 (ArO), 176.3 (N=CH). Calc. (%) for C30H43AlN2O2, C 73.44, H 8.83, N 5.71. Found (%), C 73.57, H 8.83, N 5.80.

Al(23)OBn. 23H2 (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe3 in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo, then the residue was dissolved in toluene (30 ml). Benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added to the reaction and allowed to stir (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from hexane to yield a yellow solid (0.06 g, 0.09 mmol, 11 %). 1H NMR (D8-Tol) (233 K): δ 0.40 – 0.65 (4H, m, ring-CH2), 1.05 – 1.30 (4H, m, ring-CH2), 1.46 (9H, s, 'Bu), 1.74 (9H, s, 'Bu), 2.21 (3H, s, CH3), 2.29 (2H, br, ring-CH), 2.88 (1H, d, J = 13.5 Hz, CH2), 4.56 (1H, d, J = 13.5 Hz, CH2), 5.31 (1H, d, J = 14.0 Hz, CH2), 5.57 (1H, d, J = 14.0 Hz, CH2), 6.56 (1H, t, J = 7.5 Hz, ArH), 6.82 (1H, s, ArH), 6.87 (1H, d, J = 7.5 Hz, ArH), 7.04 (1H, s, ArH), 7.20 (1H, s, ArH), 7.23 (1H, s, ArH), 7.29 (2H, t, J = 7.5 Hz, ArH), 7.41 (1H, s, ArH), 7.56 (1H, s, ArH), 7.60 (1H, s, ArH), 7.62 (1H, s, CH). 13C NMR (D8-Tol): δ 25.0 (CH2), 25.6 (CH2), 30.9 (CH3), 32.7 (C), 33.2 (CH3), 36.4 (C), 38.6 (CH3), 60.3 (CH2), 60.7 (CH), 60.9 (CH), 67.5 (CH2), 116.9 (ArH), 118.9 (Ar), 121.3 (Ar), 122.0 (Ar), 123.1 (ArH), 124.0 (ArH), 126.0 (ArH), 126.2 (ArH), 127.3 (ArH), 128.4 (ArH), 129.7 (ArH), 134.2 (ArH), 137.5 (ArH), 138.7 (Ar), 138.8 (Ar), 143.3 (Ar), 157.2 (ArO), 168.1 (ArO), 170.6 (N=CH). Calc. (%) for C36H47AlN2O3, C 74.20, H 8.13, N 4.81. Found (%), C 72.31, H 7.86, N 4.47.

Al(24)Me. 24H2 (0.41 g, 0.79 mmol) was dissolved in toluene (30 ml) then 2M AlMe3 in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.34 g, 0.61 mmol, 77 %). 1H NMR (D8-Tol) (233 K): δ -0.41 (3H, s, Al-Me), 0.70 – 0.95 (4H, br, ring-CH2), 1.30 – 1.50 (4H, m, ring-CH2), 1.43 (9H, s, 'Bu), 1.73 (9H, s, 'Bu), 1.81 (3H, s, CH3), 2.50 (1H, m.
ring-CH), 2.70 (1H, br, ring-CH), 2.71 (1H, d, J = 12.0 Hz, CH₂), 3.44 (1H, d, J = 12.0 Hz, CH₂), 6.65 (1H, d, J = 2.5 Hz, ArH), 6.92 (1H, d, J = 2.5 Hz, ArH), 7.34 (1H, s, ArH), 7.35 (1H, s, CH), 7.52 (1H, d, J = 2.5 Hz, ArH).¹³C NMR (D₈-Tol): δ 24.7 (CH₂), 24.9 (CH₂), 30.0 (CH₃), 32.2 (CH₃), 33.0 (C), 34.3 (C), 35.5 (CH₂), 40.8 (CH₂), 52.3 (CH₂), 62.2 (CH), 60.9 (CH), 66.0 (CH₂), 116.5 (ArH), 117.9 (Ar), 120.7 (ArH), 122.2 (Ar), 127.4 (ArH), 128.8 (ArH), 130.0 (ArH), 131.9 (ArH), 136.8 (Ar), 141.6 (Ar), 161.5 (ArO), 166.4 (ArO), 172.1 (N=CH). Calc. (%) for C₃₆H₄₁AlCl₅N₂O₂, C 64.40, H 7.39, N 5.01. Found (%), C 64.39, H 7.46, N 5.18.

Al(24)OBn. 24H₂ (0.42 g, 0.81 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.091 ml, 0.88 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from hexane to yield a yellow solid (0.22 g, 0.34 mmol, 42 %).¹H NMR (D₈-Tol) (K): δ 0.65 – 0.85 (4H, br, ring-CH₂), 1.30 – 1.55 (4H, m, ring-CH₂), 1.42 (9H, s, ¹Bu), 1.74 (9H, s, ¹Bu), 2.23 (3H, s, CH₃), 2.74 (2H, br, CH₂), 2.77 (1H, br, CH), 3.51 (1H, d, J = 12.0 Hz, CH), 5.14 (2H, br, CH₂), 6.64 (1H, d, J = 2.0 Hz, ArH), 6.93 (1H, s, ArH), 7.03 (1H, s, ArH), 7.12 (1H, s, ArH), 7.13 (1H, s, CH), 7.30 (1H, s, ArH), 7.33 (1H, s, ArH), 7.35 (1H, s, ArH), 7.53 (1H, d, J = 2.5 Hz, ArH).¹³C NMR (D₈-Tol): δ 24.6 (CH₂), 24.7 (CH₂), 30.0 (CH₂), 31.8 (CH₂), 32.2 (C), 34.3 (C), 35.5 (CH₂), 41.6 (CH₃), 52.3 (CH₂), 61.0 (CH), 65.9 (CH₂), 66.2 (CH), 118.8 (Ar), 119.1 (Ar), 121.1 (Ar), 123.4 (ArH), 124.0 (ArH), 126.0 (ArH), 127.1 (ArH), 128.0 (ArH), 130.9 (ArH), 135.8 (ArH), 138.7 (Ar), 138.9 (Ar), 156.8 (ArO), 162.0 (ArO), 169.7 (N=CH). Calc. (%) for C₃₆H₄₅AlCl₅N₂O₃, C 66.35, H 6.96, N 4.30. Found (%), C 66.20, H 7.08, N 4.28

Al(25)Me. 25H₂ (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.18 g, 0.37 mmol, 46 %).¹H NMR (D₈-Tol) (233 K): δ -0.35 (3H, s, Al-Me), 0.70 – 0.90 (4H, br, ring-CH₂), 1.35 – 1.55
(4H, m, ring-CH₂), 1.40 (9H, s, 1^Bu), 1.79 (9H, s, 1^Bu), 1.86 (3H, s, CH₃), 2.55 (1H, m, ring-CH), 2.66 (1H, d, J = 12.0 Hz, CH₂), 3.49 (1H, d, J = 12.0 Hz, CH₂), 6.73 (1H, t, J = 7.0 Hz, ArH), 6.86 (1H, d, J = 7.0 Hz, ArH), 6.94 (1H, d, J = 2.5 Hz, ArH), 7.05 (1H, d, J = 8.0 Hz, ArH), 7.19 (1H, t, J = 7.5 Hz, ArH), 7.72 (1H, s, ArH), 7.73 (1H, s, CH). ¹³C NMR (D₈-Tol): δ 24.9 (CH₂), 25.0 (CH₂), 29.7 (CH₃), 31.6 (CH₂), 33.4 (C), 34.2 (C), 35.7 (CH₂), 40.8 (CH₃), 51.7 (CH₂), 61.5 (CH), 66.3 (CH), 118.9 (Ar), 119.0 (Ar), 121.3 (Ar), 123.5 (ArH), 124.0 (ArH), 128.1 (Ar), 130.9 (ArH), 135.9 (ArH), 138.4 (Ar), 138.9 (Ar), 156.9 (ArO), 162.0 (ArO), 170.4 (N=CH). Calc. (%) for C₃₀H₄₇AlN₃O₂, C 73.44, H 8.83, N 5.71. Found (%), C 73.37, H 8.90, N 5.82.

Al(25)OBn. 25H₂ (0.36 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.23 g, 0.39 mmol, 49%). ¹H NMR (D₈-Tol) (233 K): δ 0.40 – 0.80 (4H, m, ring-CH₂), 1.15 – 1.55 (4H, m, ring-CH₂), 1.48 (9H, s, 1^Bu), 1.88 (9H, s, 1^Bu), 2.24 (3H, s, CH₃), 2.25 (1H, br, ring-CH), 2.59 (1H, d, J = 12.0 Hz, CH₂), 2.77 (1H, t, J = 11.0 Hz, ring-CH), 3.39 (1H, d, J = 12.0 Hz, CH₂), 5.34 (1H, d, J = 13.0 Hz, CH₂), 5.44 (1H, d, J = 13.0 Hz, CH₂), 6.86 (1H, t, J = 7.0 Hz, ArH), 6.93 (1H, d, J = 7.5 Hz, ArH), 7.15 – 7.30 (5H, m, ArH), 7.48 (2H, d, J = 7.5 Hz, ArH), 7.60 (1H, s, ArH), 7.85 (1H, s, ArH). ¹³C NMR (D₈-Tol): δ 24.9 (CH₂), 25.0 (CH₂), 30.0 (CH₃), 31.6 (CH₃), 32.4 (C), 34.2 (C), 35.8 (CH₂), 41.4 (CH₃), 51.5 (CH₂), 60.7 (CH), 66.1 (CH), 66.2 (CH₂), 116.9 (ArH), 118.2 (Ar), 120.6 (ArH), 122.1 (Ar), 125.9 (ArH), 127.3 (ArH), 128.0 (ArH), 128.7 (ArH), 130.0 (ArH), 132.1 (ArH), 137.3 (Ar), 141.8 (Ar), 161.3 (ArO), 166.6 (ArO), 171.8 (N=CH). Calc. (%) for C₃₆H₄₁AlN₃O₂, C 74.20, H 8.13, N 4.81. Found (%), C 74.29, H 8.11, N 4.72.

Al(26)OBn. 26H₂ (0.34 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with
hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.11 ml, 1.06 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.27 g, 0.57 mmol, 57 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. 

$^1$H NMR (D$_8$-Tol): $\delta$ 0.45 – 0.90 (8H, m, ring-CH$_2$), 1.15 – 1.55 (8H, m, ring-CH$_2$), 2.16 (3H, s, CH$_3$), 2.22 (3H, s, CH$_3$), 2.39 (1H, td, J = 12.0 Hz, J = 2.5 Hz, ring-CH), 2.52 (1H, t, J = 11.0 Hz, ring-CH), 2.64 (1H, br, ring-CH), 2.67 (1H, d, J = 12.0 Hz, CH$_2$), 2.74 (1H, t, J = 11.0 Hz, ring-CH), 2.99 (1H, d, J = 13.5 Hz, CH$_2$), 3.05 (1H, d, J = 12.5 Hz, CH$_2$), 4.51 (1H, d, J = 12.5 Hz, CH$_2$), 5.09 (4H, br, CH$_2$), 6.54 (2H, t, J = 6.5 Hz, ArH), 6.70 (2H, m, ArH), 6.76 (1H, d, J = 7.5 Hz, ArH), 6.86 (2H, t, J = 8.0 Hz, ArH), 6.92 (1H, d, J = 7.5 Hz, ArH), 7.03 – 7.09 (5H, m, ArH), 7.16 (8H, m, ArH), 7.38 (4H, br, ArH), 7.56 (1H, s, ArH), 7.67 (1H, s, ArH). 

$^{13}$C NMR (D$_8$-Tol): $\delta$ 21.3 (CH$_2$), 23.9 (CH$_2$), 24.6 (CH$_2$), 24.7 (CH$_2$), 24.8 (CH$_2$), 31.0 (CH$_2$), 32.0 (CH$_2$), 37.4 (CH$_3$), 41.6 (CH$_3$), 51.6 (CH$_2$), 58.3 (CH$_3$), 59.7 (CH), 59.8 (CH), 60.5 (CH), 66.1 (CH), 66.2 (CH$_2$), 115.7 (ArH), 115.7 (ArH), 117.0 (ArH), 117.2 (ArH), 118.6 (Ar), 118.7 (Ar), 120.4 (ArH), 120.5 (ArH), 121.1 (Ar), 122.2 (Ar), 122.6 (ArH), 122.8 (ArH), 125.9 (ArH), 127.1 (ArH), 128.1 (ArH), 130.1 (ArH), 130.2 (ArH), 133.9 (ArH), 134.0 (ArH), 137.1 (ArH), 137.2 (ArH), 160.9 (ArO), 161.3 (ArO), 168.4 (ArO), 168.8 (ArO), 170.8 (N=CH), 171.1 (N=CH). Calc. (%) for C$_{28}$H$_{31}$AlN$_2$O$_3$: C 71.47, H 6.64, N 5.95. Found (%), C 71.38, H 6.65, N 6.02.

Al(27)OBn. 27H$_2$ (0.41 g, 1.00 mmol) was dissolved in toluene (30 ml) then 2M AlMe$_3$ in heptane (0.50 ml, 1.00 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with hexane to remove any traces of AlMe$_3$. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.11 ml, 1.06 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.20 g, 0.37 mmol, 37 %). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. 

$^1$H NMR (D$_8$-Tol): $\delta$ 0.30 – 0.80 (8H, m, ring-CH$_2$), 1.30 – 1.50 (8H, m, ring-CH$_2$), 1.66 (1H, m, CH$_2$), 2.12 (3H, s, CH$_3$), 2.16 (3H, s, CH$_3$), 2.36 (1H, m, ring-CH), 2.57 (1H, m, ring-CH), 2.65 (1H, d, J = 12.5 Hz, CH$_2$), 2.72 (1H, d, J =
12.5 Hz, ring-CH), 2.79 (1H, m, ring-CH), 2.96 (1H, d, J = 13.5 Hz, CH₂), 3.51 (1H, d, J = 12.5 Hz, CH₂), 4.45 (1H, d, J = 13.5 Hz, CH₂), 5.13 (4H, br, CH₂), 6.50 – 6.85 (7H, m, ArH), 7.03 (2H, m, ArH), 7.14 (5H, m, ArH), 7.25 – 7.40 (7H, m, ArH), 7.51 (1H, s, N=CH). 13C NMR (D₈-Tol): δ 21.3 (CH₃), 23.8 (CH₂), 24.5 (CH₂), 24.7 (CH₂), 24.8 (CH₂), 30.9 (CH₂), 32.0 (CH₂), 37.5 (CH₃), 41.7 (CH₃), 51.6 (CH₂), 58.3 (CH₃), 59.5 (CH), 60.2 (CH), 60.9 (CH), 65.9 (CH₂), 66.1 (CH), 117.3 (ArH), 117.5 (ArH), 118.9 (Ar), 119.0 (Ar), 119.2 (Ar), 119.3 (Ar), 120.4 (ArH), 120.6 (ArH), 120.8 (Ar), 121.9 (Ar), 126.2 (ArH), 127.0 (ArH), 128.1 (ArH), 130.2 (ArH), 130.3 (ArH), 131.0 (ArH), 131.1 (ArH), 135.7 (ArH), 135.82 (ArH), 160.5 (ArO), 160.8 (ArO), 161.3 (ArO), 161.8 (ArO), 169.7 (N=CH), 170.3 (N=CH). Calc. (%) for C₂₉H₂₉AlCl₂N₂O₃, C 62.34, H 5.42, N 5.19. Found (%), C 62.28, H 5.46, N 5.07.

Al(28)Me. 28H₂ (0.41 g, 0.79 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.32 g, 0.57 mmol, 72 %). 1H NMR (D₆-Tol): δ -0.43 (3H, s, Al-Me), 0.60 – 1.00 (4H, m, ring-CH₂), 1.20 – 1.60 (4H, br, ring-CH₂), 1.37 (9H, s, 1Bu), 1.63 (3H, s, CH₃), 1.78 (9H, s, 1Bu), 2.42 (2H, m, ring-CH), 2.61 (1H, m, CH), 3.26 (1H, d, J = 11.5 Hz, CH₂), 6.65 (1H, s, ArH), 6.94 (1H, s, ArH), 7.34 (1H, s, ArH), 7.72 (1H, s, ArH), 7.73 (1H, s, CH). 13C NMR (D₆-Tol): δ 24.8 (CH₂), 24.9 (CH₂), 29.9 (CH₃), 31.5 (CH₃), 32.2 (C), 34.2 (C), 35.7 (CH₂), 40.7 (CH₂), 51.0 (CH₂), 61.3 (CH), 66.3 (CH), 117.8 (Ar), 120.2 (Ar), 124.7 (Ar), 125.4 (Ar), 127.1 (ArH), 127.4 (ArH), 129.8 (ArH), 127.5 (ArH), 132.3 (ArH), 137.3 (Ar), 141.9 (Ar), 155.7 (ArO), 166.2 (ArO), 172.3 (N=CH). Calc. (%) for C₃₀H₄₁AlCl₂N₂O₂, C 64.40, H 7.39, N 5.01. Found (%), C 64.47, H 7.51, N 5.13.

Al(28)OBl. 28H₂ (0.42 g, 0.81 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.083 ml, 0.80 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.34 g, 0.52 mmol,
Al(29)OBn. 29H2 (0.33 g, 0.81 mmol) was dissolved in toluene (30 ml) then 2M AlMe3 in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed in-vacuo and the crude mixture was briefly washed with hexane to remove any traces of AlMe3. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.091 ml, 0.88 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed in-vacuo and the crude mixture was recrystallised twice from a toluene / hexane mix to yield a yellow solid (0.19 g, 0.35 mmol, 43%). The following analysis shows a diastereomeric compound in an approximate 1:1 ratio. Analysis also shows impurities were present in this sample despite extensive efforts to isolate a pure product. 1H NMR (d8-Tol): δ 0.30 – 0.90 (8H, m, ring-CH2), 1.10 – 1.65 (8H, m, ring-CH2), 2.07 (3H, s, CH3), 1.95 – 2.15 (3H, m, CH3), 2.30 – 2.70 (4H, m, CH), 2.73 (1H, d, J = 13.5 Hz, CH2), 3.10 – 4.10 (2H, m, CH2), 4.24 (1H, d, J = 13.5 Hz, CH2), 4.50 – 5.30 (4H, br, CH2), 6.45 – 6.75 (4H, m, ArH), 6.80 – 6.90 (2H, m, ArH), 7.05 (1H, s, ArH), 7.07 (1H, s, ArH), 7.10 – 7.23 (6H, m, ArH), 7.29 (2H, m, ArH), 7.35 (2H, s, ArH), 7.38 (2H, s, ArH), 7.48 (1H, br, ArH), 7.54 (1H, s, N=CH), 7.55 – 7.90 (2H, m, ArH, N=CH). 13C{1H} NMR (d8-Tol): δ 21.2 (CH2), 23.7 (CH2), 24.4 (CH2), 24.6 (CH2), 24.7 (CH2), 30.7 (CH2), 31.8 (CH2), 37.4 (CH3), 41.5 (CH3), 50.8 (CH2), 57.4 (CH2), 59.6 (CH), 60.2 (CH), 60.3 (CH), 66.1 (CH2), 66.1 (CH), 116.0 (ArH), 118.4 (Ar), 118.5 (Ar), 120.8 (Ar), 120.9 (Ar), 122.7 (ArH), 122.7 (ArH), 123.5 (Ar), 124.2 (Ar), 24.6 (Ar), 126.2 (ArH), 274
126.9 (ArH), 127.1 (ArH), 127.1 (ArH), 128.1 (ArH), 129.8 (ArH), 129.9 (ArH), 133.8 (ArH), 133.9 (ArH), 137.4 (ArH), 137.6 (ArH), 155.3 (ArO), 155.5 (ArO), 168.3 (ArO), 168.8 (ArO), 170.9 (N=CH), 171.1 (N=CH).

Calc. (%) for C_{28}H_{29}AlCl_{2}N_{2}O_{3}, C 62.34, H 5.42, N 5.19. Found (%), C 57.91, H 5.78, N 4.39.

Al(30)OBn. 30H₂ (0.38 g, 0.80 mmol) was dissolved in toluene (30 ml) then 2M AlMe₃ in heptane (0.40 ml, 0.80 mmol) was slowly added and stirred (16 h). The solvent was removed \textit{in-vacuo} and the crude mixture was briefly washed with hexane to remove any traces of AlMe₃. The residue was dissolved in toluene (30 ml) then benzyl alcohol (0.091 ml, 0.88 mmol) was slowly added and the reaction was stirred (16 h). The solvent was removed \textit{in-vacuo} and the crude mixture was recrystallised from a toluene:hexane mix to yield a yellow solid (0.16 g, 0.26 mmol, 33 %). The major diastereomer is characterised, the minor diastereomer is present at an approximate 3:1 ratio. \(^1\)H NMR (D₈-Tol): δ 0.25 – 0.40 (2H, m, ring-CH₂), 0.50 – 0.75 (2H, m, ring-CH₂), 1.17 (2H, m, ring-CH₂), 1.32 (1H, m, ring-CH₂), 1.44 (1H, m, ring-CH₂), 2.09 (3H, s, CH₃), 2.45 (1H, m, ring-CH), 2.68 (1H, m, ring-CH), 3.22 (1H, d, J = 12.5 Hz, CH₂), 4.18 (1H, d, J = 12.5 Hz, CH₂), 5.11 (2H, br, CH₂), 6.56 (2H, ArH), 7.05 (1H, d, J = 7.5 Hz, ArH), 7.17 (2H, t, J = 7.5 Hz, ArH), 7.25 (1H, s, ArH), 7.29 (2H, m, ArH), 7.37 (1H, s, ArH), 7.39 (1H, s, CH). Calc. (%) for C_{29}H_{27}AlCl₄N₂O₃, C 55.28, H 4.47, N 4.61. Found (%), C 55.17, H 4.54, N 4.64. \(^{13}\)C\(^{1}\)H NMR analysis was not possible due to solubility.

7.9 References

8.0 Appendix

X-ray diffraction data
8.1 X-ray diffraction data

8.1.1 Chapter 2

1H₂

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
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<td>Temperature</td>
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<td>Wavelength</td>
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<td>Crystal system, space group</td>
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<td>Unit cell dimensions</td>
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<td></td>
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Empirical formula \( C_{19}H_{31}NO \)

Formula weight 289.41

Temperature 150(2) K

Wavelength 0.68890 Å

Crystal system, space group Triclinic, \( P\)-1

Unit cell dimensions \( a = 7.229(7) \) Å \( \alpha = 102.458(14) ^\circ \) 
\( b = 9.916(9) \) Å \( \beta = 96.862(5) ^\circ \) 
\( c = 14.129(12) \) Å \( \gamma = 104.919(11) ^\circ \) 

Volume 939.1(14) Å³

\( Z, \) Calculated density 2, 1.24 Mg/m³

Absorption coefficient 0.062 mm⁻¹

\( F(000) \) 320

Crystal size 0.07 x 0.06 x 0.02 mm

Theta range for data collection 2.13 to 22.50 °

Limiting indices \(-8 \leq h \leq 8, -9 \leq k \leq 11, -15 \leq l \leq 15\) 

Reflections collected / unique 6488 / 2639 [\( R(\text{int}) = 0.0334 \) ]

Data Completeness 0.984

Absorption correction Semi-empirical from equivalents

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 2639 / 0 / 200

Goodness-of-fit on \( F^2 \) 1.653

Final \( R \) indices \([I > 2\sigma(I)]\) \( R_1 = 0.1211, \) \( wR_2 = 0.3648 \)

\( R \) indices (all data) \( R_1 = 0.1391, \) \( wR_2 = 0.3898 \)

Largest diff. peak and hole 1.226 and -0.367 eÅ⁻³
$\text{C}_{35}\text{H}_{56}\text{N}_2\text{O}_2$

Empirical formula  

Formula weight 536.82

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group  Triclinic, P-1

Unit cell dimensions  
\[ a = 10.0750(2) \text{ Å}, \alpha = 65.7700(10) ^\circ \]
\[ b = 13.3950(3) \text{ Å}, \beta = 88.2360(10) ^\circ \]
\[ c = 14.3470(3) \text{ Å}, \gamma = 71.9810(10) ^\circ \]

Volume 1668.67(6) Å$^3$

Z, Calculated density 2, 1.068 Mg/m$^3$

Absorption coefficient 0.065 mm$^{-1}$

$\text{F}(000)$ 592

Crystal size 0.12 x 0.10 x 0.10 mm

Theta range for data collection 3.53 to 27.48 °

Limiting indices $-13 \leq h \leq 13, -17 \leq k \leq 17, -18 \leq l \leq 18$

Reflections collected / unique 31839 / 7601 [$R(\text{int}) = 0.0633$]

Completeness to theta = 27.48 99.3 %

Absorption correction  None

Max. and min. transmission 0.9935 and 0.9923

Refinement method Full-matrix least-squares on $F^2$

Data / restraints / parameters 7601 / 0 / 364

Goodness-of-fit on $F^2$ 1.041

Final R indices [$I>2\sigma(I)$] $R_1 = 0.0549$, $wR_2 = 0.1391$

R indices (all data) $R_1 = 0.0796$, $wR_2 = 0.1577$

Largest diff. peak and hole 0.268 and -0.372 eÅ$^{-3}$
Ti$_2$(I)$_2$(OiPr)$_4$

Empirical formula C$_{59}$H$_{91}$N$_4$O$_8$Ti$_2$

Formula weight 1080.16

Temperature 150(2) K

Wavelength 0.68890 Å

Crystal system, space group Monoclinic, $P2_1/c$

Unit cell dimensions $a = 23.224(6) \text{ Å}$, $\alpha = 90 ^\circ$

$b = 16.478(5) \text{ Å}$, $\beta = 96.782(3) ^\circ$

$c = 31.844(9) \text{ Å}$, $\gamma = 90 ^\circ$

Volume 12101(6) Å$^3$

Z, Calculated density 8, 1.186 Mg/m$^3$

Absorption coefficient 0.317 mm$^{-1}$

F(000) 4648

Crystal size 0.08 x 0.05 x 0.02 mm

Theta range for data collection 2.83 to 25.17 °

Limiting indices $-22 \leq h \leq 28$, $-20 \leq k \leq 20$, $-39 \leq l \leq 38$

Reflections collected / unique 102329 / 23430 [R(int) = 0.0710]

Data Completeness 0.982

Absorption correction Semi-empirical from equivalents

Refinement method Full-matrix least-squares on F$^2$

Data / restraints / parameters 23430 / 0 / 1365

Goodness-of-fit on F$^2$ 1.061

Final R indices [I>2σ(I)] $R_1 = 0.0727$, $wR_2 = 0.1813$

R indices (all data) $R_1 = 0.1017$, $wR_2 = 0.2020$

Largest diff. peak and hole 0.646 and -0.471 eÅ$^{-3}$
Ti$_2$(2)(OiPr)$_6$

Empirical formula \(\text{C}_{23}\text{H}_{41}\text{NO}_4\text{Ti}\)

Formula weight 443.47

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \(\text{P2}_1/\text{c}\)

Unit cell dimensions \(a = 9.5960(5)\) Å \(\alpha = 90^\circ\)
\(b = 23.1890(14)\) Å \(\beta = 91.398(3)^\circ\)
\(c = 11.4210(8)\) Å \(\gamma = 90^\circ\)

Volume 2540.7(3) Å³

Z, Calculated density 4, 1.159 Mg/m³

Absorption coefficient 0.362 mm⁻¹

\(F(000)\) 960

Crystal size 0.20 x 0.15 x 0.10 mm

Theta range for data collection 3.68 to 27.48 °

Limiting indices \(-12\leq h\leq 12, -28\leq k\leq 30, -14\leq l\leq 14\)

Reflections collected / unique 27064 / 5764 [R(int) = 0.0931]

Completeness to theta = 27.48 98.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9647 and 0.9311

Refinement method Full-matrix least-squares on \(F^2\)

Data / restraints / parameters 5764 / 0 / 303

Goodness-of-fit on \(F^2\) 1.049

Final R indices [I>2σ(I)] \(R_1 = 0.0572, \ wR_2 = 0.1373\)

R indices (all data) \(R_1 = 0.0852, \ wR_2 = 0.1525\)

Largest diff. peak and hole 0.575 and -0.539 e. Å⁻³
**Ti₂(3)(OiPr)₆**

- **Empirical formula**: \( \text{C}_{52}\text{H}_{94}\text{N}_2\text{O}_8\text{Ti}_2 \)
- **Formula weight**: 971.09
- **Temperature**: 150(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system, space group**: Monoclinic, \( \text{P}_2_1/\text{n} \)
- **Unit cell dimensions**:
  - \( a = 10.8260(6) \text{ Å} \)  \( \alpha = 90 \, ^\circ \)
  - \( b = 18.8930(9) \text{ Å} \)  \( \beta = 104.050(2) \, ^\circ \)
  - \( c = 14.5330(10) \text{ Å} \)  \( \gamma = 90 \, ^\circ \)
- **Volume**: 2883.6(3) Å³
- **Z, Calculated density**: 2, 1.118 Mg/m³
- **Absorption coefficient**: 0.324 mm⁻¹
- **\( F(000) \)**: 1056
- **Crystal size**: 0.10 x 0.05 x 0.05 mm
- **Theta range for data collection**: 3.54 to 24.00 °
- **Limiting indices**: \(-12 \leq h \leq 12, -21 \leq k \leq 21, -16 \leq l \leq 16\)
- **Reflections collected / unique**: 42193 / 4506 [\( R(\text{int}) = 0.1040 \)]
- **Completeness to theta = 24.00**: 99.7 %
- **Absorption correction**: None
- **Refinement method**: Full-matrix least-squares on \( F^2 \)
- **Data / restraints / parameters**: 4506 / 0 / 301
- **Goodness-of-fit on \( F^2 \)**: 1.064
- **Final R indices \([I>2\sigma(I)]\)**: \( R_1 = 0.0434, \, wR_2 = 0.0873 \)
- **R indices (all data)**: \( R_1 = 0.0682, \, wR_2 = 0.0985 \)
- **Largest diff. peak and hole**: 0.233 and -0.354 eÅ⁻³
**Ti₃(4)(OiPr)₆**

**Empirical formula**  
C₅₂H₉₆N₂O₈Ti₂

**Formula weight**  
973.11

**Temperature**  
150(2) K

**Wavelength**  
0.71073 Å

**Crystal system, space group**  
Triclinic, P-1

**Unit cell dimensions**  
\[a = 9.4410(3) \text{ Å}, \alpha = 79.5090(10) ^\circ\]
\[b = 10.0110(3) \text{ Å}, \beta = 84.6760(10) ^\circ\]
\[c = 15.1580(5) \text{ Å}, \gamma = 87.7970(10) ^\circ\]

**Volume**  
1402.28(8) Å³

**Z, Calculated density**  
1, 1.152 Mg/m³

**Absorption coefficient**  
0.334 mm⁻¹

**F(000)**  
530

**Crystal size**  
0.20 x 0.20 x 0.15 mm

**Theta range for data collection**  
3.72 to 27.53 °

**Limiting indices**  
-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -18 ≤ l ≤ 19

**Reflections collected / unique**  
19702 / 6423 [R(int) = 0.0458]

**Completeness to theta = 27.53**  
99.2 %

**Absorption correction**  
Semi-empirical from equivalents

**Max. and min. transmission**  
0.9517 and 0.9363

**Refinement method**  
Full-matrix least-squares on F²

**Data / restraints / parameters**  
6423 / 0 / 350

**Goodness-of-fit on F²**  
1.025

**Final R indices [I>2σ(I)]**  
R₁ = 0.0541, wR₂ = 0.1354

**R indices (all data)**  
R₁ = 0.0735, wR₂ = 0.1509

**Largest diff. peak and hole**  
0.951 and -0.932 eÅ⁻³
Ti₂(5)(OiPr)₆

Empirical formula          C₃₁H₅₈NO₄Ti
Formula weight             556.68
Temperature               150(2) K
Wavelength                0.71073 Å
Crystal system, space group Triclinic, P-1
Unit cell dimensions      
                          a = 11.0450(10) Å  α = 115.990(5) °  
                          b = 13.2550(11) Å  β = 109.683(5) °  
                          c = 13.9140(14) Å  γ = 91.805(5) °  
Volume                    1685.0(3) Å³
Z, Calculated density     2, 1.097 Mg/m³
Absorption coefficient    0.285 mm⁻¹
F(000)                    610
Crystal size              0.10 x 0.10 x 0.10 mm
Theta range for data collection 4.09 to 27.52 °
Limiting indices          -14 ≤ h ≤ 14, -16 ≤ k ≤ 17, -18 ≤ l ≤ 18
Reflections collected / unique 33515 / 7641 [R(int) = 0.0614]
Completeness to theta = 27.52 % 98.8 %
Absorption correction     None
Max. and min. transmission 0.9720 and 0.9720
Refinement method         Full-matrix least-squares on F²
Data / restraints / parameters 7641 / 0 / 347
Goodness-of-fit on F²      1.017
Final R indices [I>2σ(I)]  R₁ = 0.0590, wR₂ = 0.1504
R indices (all data)       R₁ = 0.0903, wR₂ = 0.1713
Largest diff. peak and hole 0.761 and -0.626 eÅ⁻³
Ti$_2$(8)(OiPr)$_6$

Empirical formula \( \text{C}_{56}\text{H}_{103}\text{N}_2\text{O}_8\text{Ti}_2 \)
Formula weight 1028.20
Temperature 150(2) K
Wavelength 0.71073 Å
Crystal system, space group Triclinic, \( \text{P-1} \)
Unit cell dimensions
\( a = 14.2220(3) \) Å \( \alpha = 69.6250(10) ^\circ \)
\( b = 15.3740(4) \) Å \( \beta = 89.943(2) ^\circ \)
\( c = 17.4080(4) \) Å \( \gamma = 62.8660(10) ^\circ \)
Volume 3118.09(13) Å$^3$
Z, Calculated density 2, 1.095 Mg/m$^3$
Absorption coefficient 0.303 mm$^{-1}$
F(000) 1122
Crystal size 0.20 x 0.10 x 0.10 mm
Theta range for data collection 3.75 to 27.50 ^\circ
Limiting indices -18≤h≤18, -19≤k≤19, -22≤l≤22
Reflections collected / unique 53817 / 14138 [R(int) = 0.0624]
Completeness to theta = 27.50 98.7 %
Absorption correction None
Refinement method Full-matrix least-squares on F$^2$
Data / restraints / parameters 14138 / 0 / 717
Goodness-of-fit on F$^2$ 1.007
Final R indices [I>2σ(I)] \( R_1 = 0.0576, \) \( wR_2 = 0.1516 \)
R indices (all data) \( R_1 = 0.0942, \) \( wR_2 = 0.1780 \)
Largest diff. peak and hole 0.706 and -0.519 eÅ$^{-3}$
**Ti$_2$(12)(OiPr)$_6$**

Empirical formula \( \text{C}_{53}\text{H}_{96}\text{N}_2\text{O}_8\text{Ti}_2 \)

Formula weight 985.12

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group monoclinic, \( P2_1/n \)

Unit cell dimensions
- \( a = 9.24600(10) \) Å \( \alpha = 90^\circ \)
- \( b = 24.3060(3) \) Å \( \beta = 91.5990(10)^\circ \)
- \( c = 26.2840(3) \) Å \( \gamma = 90^\circ \)

Volume 5904.59(12) Å\(^3\)

\( Z, \) Calculated density 4, 1.108 Mg/m\(^3\)

Absorption coefficient 0.318 mm\(^{-1}\)

\( F(000) \) 2144

Crystal size 0.20 x 0.15 x 0.10 mm

Theta range for data collection 3.53 to 24.99 °

Limiting indices \(-10\leq h\leq10, -28\leq k\leq28, -31\leq l\leq31\)

Reflections collected / unique 67951 / 10306 \([R(\text{int}) = 0.0726]\)

Completeness to theta = 24.99 99.4 %

Absorption correction None

Max. and min. transmission 0.9689 and 0.9392

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 10306 / 93 / 589

Goodness-of-fit on \( F^2 \) 1.150

Final \( R \) indices \([I>2\sigma(I)]\) \( R_1 = 0.0822, \) \( wR_2 = 0.2120 \)

\( R \) indices (all data) \( R_1 = 0.1025, \) \( wR_2 = 0.2276 \)

Largest diff. peak and hole 0.867 and -0.505 eÅ\(^{-3}\)
Ti$_2$(13)(OiPr)$_6$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{23.50}$H$</em>{41.50}$O$_4$Ti</td>
</tr>
<tr>
<td>Formula weight</td>
<td>449.98</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Triclinic, P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 9.4140(4) Å, α = 92.550(2) °</td>
</tr>
<tr>
<td></td>
<td>b = 9.9250(4) Å, β = 94.4870(10) °</td>
</tr>
<tr>
<td></td>
<td>c = 13.9710(12) Å, γ = 92.879(3) °</td>
</tr>
<tr>
<td>Volume</td>
<td>1298.18(13) Å$^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.151 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.355 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>487</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.35 to 27.51 °</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-12≤h≤12, -12≤k≤12, -18≤l≤18</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>18880 / 5909 [R(int) = 0.0247]</td>
</tr>
<tr>
<td>Completeness to theta = 27.51</td>
<td>99.1 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9653 and 0.9323</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5909 / 3 / 299</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.056</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>R$_1$ = 0.0643, wR$_2$ = 0.1731</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R$_1$ = 0.0720, wR$_2$ = 0.1823</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.912 and -0.754 eÅ$^{-3}$</td>
</tr>
</tbody>
</table>
Ti(7)(OiPr)$_2$

Empirical formula: $C_{35}H_{56}N_2O_4Ti$

Formula weight: 616.72

Temperature: 150(2) K

Wavelength: 0.71073 Å

Crystal system, space group: Triclinic, $P$-1

Unit cell dimensions:

- $a = 11.234(1)$ Å, $\alpha = 83.037(7)^\circ$
- $b = 12.431(2)$ Å, $\beta = 71.297(6)^\circ$
- $c = 13.347(1)$ Å, $\gamma = 89.540(5)^\circ$

Volume: 1751.5(4) Å$^3$

Z, Calculated density: 2, 1.169 Mg/m$^3$

Absorption coefficient: 0.282 mm$^{-1}$

$F(000)$: 668

Crystal size: 0.20 x 0.15 x 0.10 mm

Theta range for data collection: 3.75 to 27.52 °

Limiting indices: $-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-17 \leq l \leq 17$

Reflections collected / unique: 36743 / 7965 [R(int) = 0.0877]

Completeness to theta = 27.52: 98.8 %

Absorption correction: None

Refinement method: Full-matrix least-squares on $F^2$

Data / restraints / parameters: 7965 / 0 / 391

Goodness-of-fit on $F^2$: 1.034

Final R indices [I>2$\sigma$(I)]: $R_1 = 0.0564$, $wR_2 = 0.1265$

R indices (all data): $R_1 = 0.1066$, $wR_2 = 0.1497$

Largest diff. peak and hole: 0.299 and -0.473 eÅ$^{-3}$
Ti(9)(OiPr)$_2$

Empirical formula: $\text{C}_{35}\text{H}_{56}\text{N}_2\text{O}_4\text{Ti}$

Formula weight: 616.72

Temperature: 150(2) K

Wavelength: 0.71073 Å

Crystal system, space group: Monoclinic, $P2_1/\alpha$

Unit cell dimensions:
- $a = 19.3720(7)$ Å, $\alpha = 90$°
- $b = 9.6520(4)$ Å, $\beta = 116.015(2)$°
- $c = 20.3950(10)$ Å, $\gamma = 90$°

Volume: 3427.0(3) Å$^3$

$Z$, Calculated density: 4, 1.195 Mg/m$^3$

Absorption coefficient: 0.288 mm$^{-1}$

$F(000)$: 1336

Crystal size: 0.10 x 0.10 x 0.10 mm

Theta range for data collection: 3.61 to 24.17°

Limiting indices: $-22 \leq h \leq 22$, $-10 \leq k \leq 11$, $-23 \leq l \leq 23$

Reflections collected / unique: 21094 / 5422 [R(int) = 0.1729]

Completeness to theta = 27.52: 99.0%

Absorption correction: Sortav

Refinement method: Full-matrix least-squares on $F^2$

Data / restraints / parameters: 5422 / 0 / 391

Goodness-of-fit on $F^2$: 1.079

Final R indices [I>2σ(I)]: $R_1 = 0.0837$, $wR_2 = 0.1960$

R indices (all data): $R_1 = 0.1272$, $wR_2 = 0.2254$

Largest diff. peak and hole: 1.219 and -0.422 eÅ$^{-3}$
Ti(10)(OiPr)$_2$

Empirical formula \( \text{C}_{45}\text{H}_{69}\text{N}_2\text{O}_4\text{Ti} \)

Formula weight 749.92

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Orthorhombic, \( \text{P2}_1\text{2}_1\text{2}_1 \)

Unit cell dimensions
\[
\begin{align*}
a &= 10.9250(7) \text{ Å} & \alpha &= 90^\circ \\
b &= 14.7200(12) \text{ Å} & \beta &= 90^\circ \\
c &= 27.1040(14) \text{ Å} & \gamma &= 90^\circ
\end{align*}
\]

Volume 4358.8(5) Å$^3$

Z, Calculated density 4, 1.143 Mg/m$^3$

Absorption coefficient 0.238 mm$^{-1}$

\( F(000) \) 1628

Crystal size 0.10 x 0.10 x 0.10 mm

Theta range for data collection 3.66 to 24.10 °

Limiting indices \(-12 \leq h \leq 12, -16 \leq k \leq 16, -31 \leq l \leq 31 \)

Reflections collected / unique 52730 / 6899 \([R(\text{int}) = 0.1339]\)

Completeness to theta = 24.10 99.4 %

Absorption correction None

Max. and min. transmission 0.9766 and 0.9766

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 6899 / 4 / 514

Goodness-of-fit on \( F^2 \) 1.039

Final R indices [I>2\( \sigma (I) \)] \( R_1 = 0.0607, \ wR_2 = 0.1452 \)

R indices (all data) \( R_1 = 0.0918, \ wR_2 = 0.1651 \)

Absolute structure parameter -0.03(4)

Largest diff. peak and hole 0.344 and -0.350 eÅ$^{-3}$
Ti(11)(OiPr)₂

Empirical formula \( \text{C}_{40}\text{H}_{60}\text{N}_{2}\text{O}_{4}\text{Ti} \)

Formula weight 680.80

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( \text{P}2_1/\text{n} \)

Unit cell dimensions
\begin{align*}
a &= 14.0530(2) \text{ Å} \quad &\alpha &= 90 \degree \\
b &= 13.5820(2) \text{ Å} \quad &\beta &= 91.528(1) \degree \\
c &= 20.1480(4) \text{ Å} \quad &\gamma &= 90 \degree \\
\end{align*}

Volume 3844.24(11) Å³

\( Z, \text{ Calculated density} \) 4, 1.176 Mg/m³

Absorption coefficient 0.263 mm⁻¹

\( F(000) \) 1472

Crystal size 0.1 x 0.1 x 0.1 mm

Theta range for data collection 3.58 to 25.00 °

Limiting indices \(-16\leq h\leq16, \ -16\leq k\leq16, \ -23\leq l\leq23 \)

Reflections collected / unique 66001 / 6743 \([R(\text{int}) = 0.1218]\)

Completeness to theta = 25.00 99.6 %

Absorption correction Multi-scan

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 6743 / 15 / 563

Goodness-of-fit on \( F^2 \) 1.027

Final R indices \([I>2\sigma(I)]\) \( R_1 = 0.0503, \ wR_2 = 0.1156 \)

R indices (all data) \( R_1 = 0.0830, \ wR2 = 0.1348 \)

Largest diff. peak and hole 0.298 and -0.371 eÅ⁻³
Ti(1)(catechol)

Empirical formula  
\( C_{58}H_{64}Cl_4N_4O_8Ti_2 \)

Formula weight  
1186.76

Temperature  
150(2) K

Wavelength  
0.71073 Å

Crystal system, space group  
Monoclinic, \( P2_1/a \)

Unit cell dimensions  
\[ a = 12.2350(4) \text{ Å} \quad \alpha = 90^\circ \]
\[ b = 17.2330(8) \text{ Å} \quad \beta = 96.642(2)^\circ \]
\[ c = 13.4000(5) \text{ Å} \quad \gamma = 90^\circ \]

Volume  
2806.37(19) Å³

Z, Calculated density  
2, 1.404 Mg/m³

Absorption coefficient  
0.533 mm⁻¹

\( F(000) \)  
1240

Crystal size  
0.10 x 0.10 x 0.10 mm

Theta range for data collection  
3.52 to 26.76 °

Limiting indices  
\(-15 \leq h \leq 15, -21 \leq k \leq 21, -16 \leq l \leq 16\)

Reflections collected / unique  
48977 / 59 [R(int) = 0.1302]

Completeness to theta = 26.76 °  
99.1 %

Absorption correction  
None

Max. and min. transmission  
0.9486 and 0.9486

Refinement method  
Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters  
5929 / 0 / 347

Goodness-of-fit on \( F^2 \)  
1.069

Final R indices [I>2σ(I)]  
\( R_1 = 0.0684, \quad wR_2 = 0.1672 \)

R indices (all data)  
\( R_1 = 0.1199, \quad wR_2 = 0.2017 \)

Largest diff. peak and hole  
0.556 and -1.231 eÅ⁻³
**Ti(I)(3,5-di-tert-butylcatechol)**

**Empirical formula**  
C$_{37}$H$_{50}$Cl$_2$N$_2$O$_4$Ti

**Formula weight**  
705.59

**Temperature**  
150(2) K

**Wavelength**  
0.71073 Å

**Crystal system, space group**  
Monoclinic, $P2_1/c$

**Unit cell dimensions**  

\[
\begin{align*}
a & = 19.8000(2) \text{ Å} & \alpha & = 90^\circ \\
b & = 12.5740(2) \text{ Å} & \beta & = 103.8080(10)^\circ \\
c & = 30.7360(5) \text{ Å} & \gamma & = 90^\circ \\
\end{align*}
\]

**Volume**  
7431.05(18) Å$^3$

**Z, Calculated density**  
8, 1.261 Mg/m$^3$

**Absorption coefficient**  
0.414 mm$^{-1}$

**F(000)**  
2992

**Crystal size**  
0.50 x 0.30 x 0.10 mm

**Theta range for data collection**  
3.53 to 27.52 °

**Limiting indices**  
$-25 \leq h \leq 25$, $-16 \leq k \leq 16$, $-39 \leq l \leq 39$

**Reflections collected / unique**  
98628 / 16983 [R(int) = 0.1423]

**Completeness to theta = 27.52**  
99.2 %

**Absorption correction**  
None

**Refinement method**  
Full-matrix least-squares on $F^2$

**Data / restraints / parameters**  
16983 / 6 / 874

**Goodness-of-fit on $F^2$**  
1.050

**Final R indices [I>2σ(I)]**  
$R_1 = 0.0867$, $wR_2 = 0.2228$

**R indices (all data)**  
$R_1 = 0.1194$, $wR_2 = 0.2455$

**Largest diff. peak and hole**  
1.155 and -1.307 eÅ$^{-3}$
**Ti(1)(4-NO₂-catechol)**

**Empirical formula**  
C₂₈.₅₀H₃₂ClN₃O₆Ti

**Formula weight**  
595.92

**Temperature**  
150(2) K

**Wavelength**  
0.71073 Å

**Crystal system, space group**  
Monoclinic, *P*₂₁/n

**Unit cell dimensions**  
\[ \begin{align*} 
& a = 12.7780(2) \text{ Å} \quad \alpha = 90^\circ \\
& b = 13.3090(2) \text{ Å} \quad \beta = 101.097(1)^\circ \\
& c = 16.4640(3) \text{ Å} \quad \gamma = 90^\circ 
\end{align*} \]

**Volume**  
2747.56(8) Å³

**Z, Calculated density**  
4, 1.441 Mg/m³

**Absorption coefficient**  
0.457 mm⁻¹

**F(000)**  
1244

**Crystal size**  
0.20 x 0.10 x 0.10 mm

**Theta range for data collection**  
3.58 to 27.49 °

**Limiting indices**  
\(-16 \leq h \leq 16, -17 \leq k \leq 17, -21 \leq l \leq 21\)

**Reflections collected / unique**  
40787 / 6270 \[R(int) = 0.0700\]

**Completeness to theta = 27.49**  
99.2 %

**Absorption correction**  
None

**Max. and min. transmission**  
0.9557 and 0.9141

**Refinement method**  
Full-matrix least-squares on F²

**Data / restraints / parameters**  
6270 / 0 / 366

**Goodness-of-fit on F²**  
1.012

**Final R indices [I>2σ(I)]**  
\[ R_1 = 0.0638, \quad wR_2 = 0.1590 \]

**R indices (all data)**  
\[ R_1 = 0.0785, \quad wR_2 = 0.1733 \]

**Largest diff. peak and hole**  
1.766 and -1.588 eÅ⁻³

294
Ti(6)(4-NO₂-catechol)

Empirical formula: C₄₃H₄₉N₃O₆Ti

Formula weight: 751.75

Temperature: 150(2) K

Wavelength: 0.71073 Å

Crystal system, space group: Monoclinic, P2₁/c

Unit cell dimensions:
- a = 20.0540(5) Å, α = 90°
- b = 18.6670(5) Å, β = 113.361(2)°
- c = 22.6240(6) Å, γ = 90°

Volume: 7775.0(4) Å³

Z, Calculated density: 8, 1.284 Mg/m³

Absorption coefficient: 0.272 mm⁻¹

F(000): 3184

Crystal size: 0.10 x 0.10 x 0.10 mm

Theta range for data collection: 3.51 to 27.49°

Limiting indices: -26≤h≤25, -24≤k≤24, -29≤l≤29

Reflections collected / unique: 153642 / 17723 [R(int) = 0.0657]

Completeness to theta = 27.49°: 99.3%

Absorption correction: None

Max. and min. transmission: 0.9734 and 0.9734

Refinement method: Full-matrix least-squares on F²

Data / restraints / parameters: 17723 / 0 / 1021

Goodness-of-fit on F²: 1.054

Final R indices [I>2σ(I)]: R₁ = 0.0507, wR₂ = 0.1190

R indices (all data): R₁ = 0.0829, wR₂ = 0.1357

Largest diff. peak and hole: 0.351 and -0.450 eÅ⁻³


8.1.2 Chapter 3

Zr(6)(OiPr)2

Empirical formula  \( \text{C}_{29}\text{H}_{44}\text{N}_{2}\text{O}_{4}\text{Zr} \)

Formula weight  575.88

Temperature  150(2) K

Wavelength  0.71073 Å

Crystal system, space group  Monoclinic, \( \text{P}2_1/\text{n} \)

Unit cell dimensions  
\[ a = 8.5750(6) \text{ Å} \quad \alpha = 90^\circ \]
\[ b = 16.5030(14) \text{ Å} \quad \beta = 99.220(5) ^\circ \]
\[ c = 20.7000(15) \text{ Å} \quad \gamma = 90^\circ \]

Volume  2891.5(4) Å³

Z, Calculated density  4, 1.323 Mg/m³

Absorption coefficient  0.415 mm⁻¹

\( F(000) \)  1216

Crystal size  0.10 x 0.10 x 0.05 mm

Theta range for data collection  3.53 to 27.49 °

Limiting indices  
\[-11 \leq h \leq 10, \quad -21 \leq k \leq 21, \quad -26 \leq l \leq 26 \]

Reflections collected / unique  45579 / 6603 [R(int) = 0.0584]

Completeness to theta = 27.49  99.5 %

Absorption correction  Semi-empirical from equivalents

Max. and min. transmission  0.9795 and 0.9597

Refinement method  Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters  6603 / 0 / 333

Goodness-of-fit on \( F^2 \)  1.107

Final R indices [I>2\( \sigma(I) \)]  
\( R_1 = 0.0349, \quad wR_2 = 0.0789 \)

R indices (all data)  
\( R_1 = 0.0524, \quad wR_2 = 0.0897 \)

Largest diff. peak and hole  0.417 and -0.700 eÅ⁻³
Zr(6)(OiPr)₂.0.5THF.0.5IPA

Empirical formula \( \text{C}_{32.50} \text{H}_{52} \text{N}_{2} \text{O}_{5} \text{Zr} \)

Formula weight \( 641.98 \)

Temperature \( 150(2) \, \text{K} \)

Wavelength \( 0.71073 \, \text{Å} \)

Crystal system, space group Monoclinic, \( \text{P}2_1/\text{n} \)

Unit cell dimensions
\[
\begin{align*}
& a = 14.3840(2) \, \text{Å} \, \alpha = 90^\circ \\
& b = 10.8140(2) \, \text{Å} \, \beta = 95.0460(10) \, ^\circ \\
& c = 20.7480(3) \, \text{Å} \, \gamma = 90^\circ 
\end{align*}
\]

Volume \( 3214.81(9) \, \text{Å}^3 \)

\( Z, \) Calculated density \( 4, 1.326 \, \text{Mg/m}^3 \)

Absorption coefficient \( 0.383 \, \text{mm}^{-1} \)

\( F(000) \) \( 1364 \)

Crystal size \( 0.25 \times 0.20 \times 0.10 \, \text{mm} \)

Theta range for data collection 3.88 to 27.46 °

Limiting indices \(-18\leq h\leq18, \, -14\leq k\leq14, \, -26\leq l\leq26 \)

Reflections collected / unique \( 59866 / 7319 \) [R(int) = 0.0617]

Completeness to theta = 27.46 99.6 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.9627 and 0.9103

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 7319 / 0 / 445

Goodness-of-fit on \( F^2 \) 1.085

Final R indices [I>2\( \sigma(I) \)] \( R_1 = 0.0392, \, wR_2 = 0.0989 \)

R indices (all data) \( R_1 = 0.0573, \, wR_2 = 0.1108 \)

Largest diff. peak and hole 0.473 and -0.942 eÅ\(^{-3} \)
Zr(7)(OiPr)$_2$

Empirical formula      \( C_{35}H_{56}N_2O_4Zr \)
Formula weight         660.04
Temperature            150(2) K
Wavelength             0.71073 Å
Crystal system, space group \( Cm \), monoclinic
Unit cell dimensions   \( a = 11.7950(5) \) Å \( \alpha = 90^\circ \)
                        \( b = 24.3760(10) \) Å \( \beta = 124.476(2) ^\circ \)
                        \( c = 7.6360(4) \) Å \( \gamma = 90^\circ \)
Volume                 1809.86(14) Å$^3$
Z, Calculated density  \( 2, 1.211 \) Mg/m$^3$
Absorption coefficient 0.340 mm$^{-1}$
\( F(000) \)            704
Crystal size           0.10 x 0.10 x 0.10 mm
Theta range for data collection 4.19 to 25.04 °
Limiting indices       \(-13 \leq h \leq 14, -28 \leq k \leq 28, -9 \leq l \leq 9\)
Reflections collected / unique 7278 / 3018 \([R(\text{int}) = 0.0452]\)
Completeness to theta = 25.04 99.3 %
Absorption correction  None
Max. and min. transmission 0.9668 and 0.9668
Refinement method      Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 3018 / 2 / 206
Goodness-of-fit on \( F^2 \) 1.029
Final R indices [I>2\( \sigma(I) \)] \( R_1 = 0.0360, \) \( wR_2 = 0.0799 \)
R indices (all data)    \( R_1 = 0.0394, \) \( wR2 = 0.0816 \)
Absolute structure parameter \(-0.01(4)\)
Largest diff. peak and hole 0.462 and -0.579 eÅ$^{-3}$
Zr(10)(OiPr)$_2$

Empirical formula\hspace{1cm} C$_{45}$H$_{76}$N$_2$O$_4$Zr
Formula weight\hspace{1cm} 800.30
Temperature\hspace{1cm} 150(2) K
Wavelength\hspace{1cm} 0.71073 Å
Crystal system, space group\hspace{1cm} Orthorhombic, P$_2_1$2$_1$2$_1$
Unit cell dimensions\hspace{1cm} a = 12.0070(4) Å \hspace{1cm} α = 90 °
b = 14.6590(5) Å \hspace{1cm} β = 90 °
c = 25.1760(10) Å \hspace{1cm} γ = 90 °
Volume\hspace{1cm} 4431.2(3) Å$^3$
Z, Calculated density\hspace{1cm} 4, 1.200 Mg/m$^3$
Absorption coefficient\hspace{1cm} 0.289 mm$^{-1}$
F(000)\hspace{1cm} 1728
Crystal size\hspace{1cm} 0.10 x 0.10 x 0.10 mm
Theta range for data collection\hspace{1cm} 3.52 to 24.09 °
Limiting indices\hspace{1cm} -13≤h≤13, -16≤k≤16, -28≤l≤28
Reflections collected / unique\hspace{1cm} 34743 / 6996 [R(int) = 0.1963]
Completeness to theta = 24.09 \hspace{1cm} 99.3 %
Absorption correction\hspace{1cm} Semi-empirical from equivalents
Max. and min. transmission\hspace{1cm} 0.9717 and 0.9717
Refinement method\hspace{1cm} Full-matrix least-squares on F$^2$
Data / restraints / parameters\hspace{1cm} 6996 / 0 / 485
Goodness-of-fit on F$^2$\hspace{1cm} 1.054
Final R indices [I>2σ(I)]\hspace{1cm} R$_1$ = 0.0825, wR$_2$ = 0.1712
R indices (all data)\hspace{1cm} R$_1$ = 0.1264, wR$_2$ = 0.1972
Absolute structure parameter\hspace{1cm} -0.10(9)
Largest diff. peak and hole\hspace{1cm} 1.783 and -0.723 eÅ$^{-3}$
Hf(6)(OiPr)$_2$

Empirical formula \( \text{C}_{29}\text{H}_{44}\text{HfN}_2\text{O}_4 \)

Formula weight 663.15

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( P2_1/n \)

Unit cell dimensions
\[
\begin{align*}
\text{a} &= 8.5680(3) \text{ Å} \quad \alpha = 90^\circ \\
\text{b} &= 16.4690(7) \text{ Å} \quad \beta = 99.410(3)^\circ \\
\text{c} &= 20.6830(7) \text{ Å} \quad \gamma = 90^\circ
\end{align*}
\]

Volume 2879.23(19) Å$^3$

Z, Calculated density 4, 1.530 Mg/m$^3$

Absorption coefficient 3.658 mm$^{-1}$

F(000) 1344

Crystal size 0.20 x 0.10 x 0.10 mm

Theta range for data collection 3.52 to 27.50 °

Limiting indices \(-11\leq h \leq 11, -21\leq k \leq 21, -26\leq l \leq 26\)

Reflections collected / unique 50883 / 6592 \([R(\text{int}) = 0.0760]\)

Completeness to theta = 27.50 99.6 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7112 and 0.5282

Refinement method Full-matrix least-squares on $F^2$

Data / restraints / parameters 6592 / 0 / 333

Goodness-of-fit on $F^2$ 1.185

Final R indices \([I>2\sigma(I)]\) \( R_1 = 0.0414, \ wR_2 = 0.0888 \)

R indices (all data) \( R_1 = 0.0614, \ wR_2 = 0.0977 \)

Largest diff. peak and hole 1.963 and \(-1.601 \text{ eÅ}^{-3}\)
Hf(7)(OiPr)$_2$

Empirical formula $\text{C}_{17.50}\text{H}_{26}\text{Hf}_{0.50}\text{NO}_2$

Formula weight 371.64

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, Cm

Unit cell dimensions
\begin{align*}
a &= 11.7460(2) \text{ Å} & \alpha &= 90^\circ \\
b &= 24.2790(5) \text{ Å} & \beta &= 124.5040(10)^\circ \\
c &= 7.6000(2) \text{ Å} & \gamma &= 90^\circ \\
\end{align*}

Volume 1786.10(7) Å$^3$

Z, Calculated density 4, 1.382 Mg/m$^3$

Absorption coefficient 2.957 mm$^{-1}$

F(000) 760

Crystal size 0.20 x 0.15 x 0.10 mm

Theta range for data collection 3.58 to 27.49 °

Limiting indices $-15 \leq h \leq 15$, $-31 \leq k \leq 31$, $-9 \leq l \leq 9$

Reflections collected / unique 17045 / 4042 [R(int) = 0.0338]

Completeness to theta = 27.49 % 99.6 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7564 and 0.5893

Refinement method Full-matrix least-squares on $F^2$

Data / restraints / parameters 4042 / 2 / 204

Goodness-of-fit on $F^2$ 1.065

Final R indices [I>2σ(I)] $R_1 = 0.0201$, $wR_2 = 0.0491$

R indices (all data) $R_1 = 0.0201$, $wR_2 = 0.0491$

Absolute structure parameter 0.000(8)

Largest diff. peak and hole 0.789 and -1.438 eÅ$^{-3}$
**Hf(8)(OiPr)₂**

- **Empirical formula**: C\textsubscript{23.50}H\textsubscript{41}Hf\textsubscript{0.50}NO\textsubscript{2}
- **Formula weight**: 458.82
- **Temperature**: 150(2) K
- **Wavelength**: 0.71073 Å
- **Crystal system, space group**: Triclinic, P\text{-}1
- **Unit cell dimensions**:
  - \(a = 8.7915(3)\) Å, \(\alpha = 66.874(3)°\)
  - \(b = 16.8368(6)\) Å, \(\beta = 79.532(3)°\)
  - \(c = 17.6504(6)\) Å, \(\gamma = 84.196(3)°\)
- **Volume**: 2361.41(14) Å\textsuperscript{3}
- **Z, Calculated density**: 4, 1.291 Mg/m\textsuperscript{3}
- **Absorption coefficient**: 2.250 mm\textsuperscript{-1}
- **F(000)**: 964
- **Crystal size**: 0.50 x 0.20 x 0.03 mm
- **Theta range for data collection**: 2.88 to 27.48°
- **Limiting indices**: -11≤h≤11, -21≤k≤21, -22≤l≤22
- **Reflections collected / unique**: 23772 / 10822 [R(int) = 0.0696]
- **Completeness to theta = 27.48**: 99.8 %
- **Absorption correction**: None
- **Max. and min. transmission**: 0.9356 and 0.3992
- **Refinement method**: Full-matrix least-squares on \(F^2\)
- **Data / restraints / parameters**: 10822 / 0 / 505
- **Goodness-of-fit on \(F^2\)**: 0.980
- **Final R indices [I>2σ(I)]**: \(R_1 = 0.0492, \text{ wR}_2 = 0.0745\)
- **R indices (all data)**: \(R_1 = 0.0792, \text{ wR}_2 = 0.0830\)
- **Largest diff. peak and hole**: 1.101 and -1.352 eÅ\textsuperscript{-3}
**Hf(10)(OiPr)₂**

Empirical formula  
\[ \text{C}_{45}\text{H}_{76}\text{HfN}_{2}\text{O}_{4} \]

Formula weight  
887.57

Temperature  
150(2) K

Wavelength  
0.71073 Å

Crystal system, space group  
Orthorhombic, \( P2_12_12_1 \)

Unit cell dimensions  
a = 12.00200(10) Å  \( \alpha = 90^\circ \)
b = 14.66100(10) Å  \( \beta = 90^\circ \)
c = 25.1240(2) Å  \( \gamma = 90^\circ \)

Volume  
4420.85(6) Å³

Z, Calculated density  
4, 1.334 Mg/m³

Absorption coefficient  
2.401 mm⁻¹

\( F(000) \)  
1856

Crystal size  
0.10 x 0.10 x 0.10 mm

Theta range for data collection  
3.53 to 27.49 °

Limiting indices  
\(-15 \leq h \leq 15, -19 \leq k \leq 19, -32 \leq l \leq 32\)

Reflections collected / unique  
71328 / 10103 [\( R(\text{int}) = 0.0771 \)]

Completeness to theta = 27.49 °  
99.6 %

Absorption correction  
None

Max. and min. transmission  
0.7953 and 0.7953

Refinement method  
Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters  
10103 / 0 / 493

Goodness-of-fit on \( F^2 \)  
1.080

Final R indices \([I>2\sigma(I)]\)  
\( R_1 = 0.0332, \; wR_2 = 0.0643 \)

R indices (all data)  
\( R_1 = 0.0504, \; wR_2 = 0.0693 \)

Absolute structure parameter  
-0.034(8)

Largest diff. peak and hole  
1.319 and -1.303 eÅ⁻³
Zr₄(1)(OiPr)₆(HOiPr)₂

Empirical formula \( \text{C}_{76}\text{H}_{156}\text{N}_2\text{O}_{18}\text{Zr}_4 \)

Formula weight 1750.91

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( \text{C}2/\text{c} \)

Unit cell dimensions
\( a = 21.8419(4) \text{ Å} \), \( \alpha = 90° \)
\( b = 15.0338(3) \text{ Å} \), \( \beta = 104.8290(10)° \)
\( c = 29.6284(5) \text{ Å} \), \( \gamma = 90° \)

Volume 9404.9(3) Å³

Z, Calculated density 4, 1.237 Mg/m³

Absorption coefficient 0.488 mm⁻¹

\( F(000) \) 3720

Crystal size 0.1 x 0.1 x 0.15 mm

Theta range for data collection 3.68 to 25.03°

Limiting indices -25 ≤ h ≤ 25, -17 ≤ k ≤ 17, -34 ≤ l ≤ 35

Reflections collected / unique 42398 / 7919 [R(int) = 0.0794]

Completeness to theta = 25.03 96.1%

Absorption correction None

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 7991 / 8 / 489

Goodness-of-fit on \( F^2 \) 1.046

Final R indices [I>2σ(I)] \( R_1 = 0.0541 \), \( wR_2 = 0.1022 \)

R indices (all data) \( R_1 = 0.0916 \), \( wR_2 = 0.1170 \)

Largest diff. peak and hole 0.508 and -0.653 eÅ⁻³
Zr$_2$(15)(OiPr)$_6$

Empirical formula  \( \text{C}_{47}\text{H}_{64}\text{N}_2\text{O}_8\text{Zr}_2 \)

Formula weight  987.60

Temperature  150(2) K

Wavelength  0.71073 Å

Crystal system, space group  orthorhombic, \( \text{C}_{2}\text{cb} \)

Unit cell dimensions  
\( a = 14.3530(6) \text{ Å} \quad \alpha = 90^\circ \)
\( b = 39.3260(15) \text{ Å} \quad \beta = 90^\circ \)
\( c = 19.3250(7) \text{ Å} \quad \gamma = 90^\circ \)

Volume  10907.9(7) Å$^3$

\( Z, \text{Calculated density} \)  8, 1.203 Mg/m$^3$

Absorption coefficient  0.428 mm$^{-1}$

\( F(000) \)  4192

Crystal size  0.20 x 0.10 x 0.10 mm

Theta range for data collection  3.76 to 25.02 °

Limiting indices  -17≤h≤17, -46≤k≤46, -22≤l≤22

Reflections collected / unique  64279 / 9549 \([R\text{(int)} = 0.0949]\)

Completeness to theta = 25.02  99.4 %

Absorption correction  None

Max. and min. transmission  0.9585 and 0.9193

Refinement method  Full-matrix least-squares on F$^2$

Data / restraints / parameters  9549 / 2 / 563

Goodness-of-fit on F$^2$  1.098

Final R indices \([I>2\sigma(I)]\)  \( R_1 = 0.0536, \text{ wR}_2 = 0.1273 \)

R indices (all data)  \( R_1 = 0.0889, \text{ wR}_2 = 0.1513 \)

Absolute structure parameter  0.00(5)

Largest diff. peak and hole  0.665 and -0.561 eÅ$^{-3}$
**Hf(1)(OiPr)₆**

Empirical formula \( \text{C}_{80}\text{H}_{140}\text{Hf}_4\text{N}_4\text{O}_{16} \)

Formula weight 2127.92

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Triclinic, \( P\bar{1} \)

Unit cell dimensions
- \( a = 12.8800(6) \) Å \( \alpha = 108.912(2) \) °
- \( b = 17.1940(9) \) Å \( \beta = 93.491(3) \) °
- \( c = 21.3410(10) \) Å \( \gamma = 93.019(3) \) °

Volume 4449.6(4) Å³

Z, Calculated density 2, 1.588 Mg/m³

Absorption coefficient 4.711 mm⁻¹

\( F(000) \) 2128

Crystal size 0.10 x 0.05 x 0.05 mm

Theta range for data collection 4.74 to 24.00 °

Limiting indices \(-14\leq h\leq 13, -19\leq k\leq 19, -23\leq l\leq 24 \)

Reflections collected / unique 34810 / 13794 [\( R(int) = 0.1529 \)]

Completeness to theta = 24.00 98.7 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7986 and 0.6502

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 13794 / 0 / 908

Goodness-of-fit on \( F^2 \) 1.023

Final R indices [\( I>2\sigma(I) \)] \( R_1 = 0.0655, \) \( wR_2 = 0.1120 \)

R indices (all data) \( R_1 = 0.1482, \) \( wR_2 = 0.1420 \)

Largest diff. peak and hole 1.145 and -1.315 eÅ⁻³
Hf$_2$(3)(OiPr)$_6$

Empirical formula \( \text{C}_{26}\text{H}_{47}\text{HfN}_6\text{O}_4 \)

Formula weight 616.14

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( Pn \)

Unit cell dimensions
\[
\begin{align*}
a & = 10.3720(5) \text{ Å} & \alpha & = 90 ^\circ \\
b & = 17.1010(9) \text{ Å} & \beta & = 105.698(3) ^\circ \\
c & = 16.7140(7) \text{ Å} & \gamma & = 90 ^\circ \\
\end{align*}
\]

Volume 2854.0(2) Å$^3$

Z, Calculated density 4, 1.434 Mg/m$^3$

Absorption coefficient 3.683 mm$^{-1}$

\( F(000) \) 1256

Crystal size 0.10 x 0.10 x 0.10 mm

Theta range for data collection 3.79 to 25.37 °

Limiting indices \(-12\leq h \leq 12, -20\leq k \leq 20, -20\leq l \leq 18\)

Reflections collected / unique 28088 / 10193 [\( R(\text{int}) = 0.0707 \)]

Completeness to theta = 25.37 99.1 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.7096 and 0.7096

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 10193 / 8 / 602

Goodness-of-fit on \( F^2 \) 1.047

Final R indices [I>2\( \sigma(I) \)] \( R_1 = 0.0414 \), \( wR_2 = 0.0812 \)

R indices (all data) \( R_1 = 0.0752 \), \( wR2 = 0.0957 \)

Absolute structure parameter -0.034(14)

Largest diff. peak and hole 1.258 and -0.748 eÅ$^{-3}$
8.1.3 Chapter 4

Al(7)Me

Empirical formula \( \text{C}_{33.55} \text{H}_{49} \text{AlN}_{2} \text{O}_{2} \)

Formula weight \( 538.73 \)

Temperature \( 150(2) \text{ K} \)

Wavelength \( 0.71073 \text{ Å} \)

Crystal system, space group Orthorhombic, \( \text{P2}_1\text{2}_1\text{2}_1 \)

Unit cell dimensions
\begin{align*}
a &= 14.7810(2) \text{ Å} & \alpha &= 90^\circ \\
b &= 15.1010(2) \text{ Å} & \beta &= 90^\circ \\
c &= 29.1190(4) \text{ Å} & \gamma &= 90^\circ \\
\end{align*}

Volume \( 6499.59(15) \text{ Å}^3 \)

\( Z, \) Calculated density \( 8, 1.101 \text{ Mg/m}^3 \)

Absorption coefficient \( 0.092 \text{ mm}^{-1} \)

\( F(000) \) 2344

Crystal size \( 0.30 \times 0.20 \times 0.20 \text{ mm} \)

Theta range for data collection \( 3.69 \text{ to } 27.44^\circ \)

Limiting indices \(-19\leq h \leq 19, -19\leq k \leq 19, -37\leq l \leq 37 \)

Reflections collected / unique \( 81419 / 14759 \) \( [R(\text{int}) = 0.0780]\)

Completeness to theta = 27.44 \( 99.3\% \)

Absorption correction Multi-scan

Max. and min. transmission \( 0.9818 \text{ and } 0.9729 \)

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters \( 14759 / 0 / 733 \)

Goodness-of-fit on \( F^2 \) 1.091

Final \( R \) indices \([I>2\sigma(I)]\) \( R_1 = 0.0619, \text{ wR}_2 = 0.1606 \)

\( R \) indices (all data) \( R_1 = 0.0676, \text{ wR}_2 = 0.1651 \)

Absolute structure parameter \( 0.06(14) \)

Largest diff. peak and hole \( 0.450 \text{ and } -0.264 \text{ eÅ}^{-3} \)
Al(8)Me

Empirical formula \( \text{C}_{36}\text{H}_{57}\text{AlN}_{2}\text{O}_{2} \)

Formula weight 576.82

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( \text{C}2/c \)

Unit cell dimensions
- \( a = 35.6710(9) \) Å, \( \alpha = 90^\circ \)
- \( b = 10.4360(3) \) Å, \( \beta = 116.4370(10)^\circ \)
- \( c = 24.9340(8) \) Å, \( \gamma = 90^\circ \)

Volume 8311.3(4) Å\(^3\)

Z, Calculated density 8, 0.922 Mg/m\(^3\)

Absorption coefficient 0.075 mm\(^{-1}\)

\( F(000) \) 2528

Crystal size 0.30 x 0.30 x 0.25 mm

Theta range for data collection 3.64 to 27.49 °

Limiting indices \(-45\leq h\leq 46, -13\leq k\leq 13, -32\leq l\leq 32\)

Reflections collected / unique 70559 / 9479 [\( R(\text{int}) = 0.0411 \)]

Completeness to theta = 27.49 % 99.3 %

Absorption correction None

Max. and min. transmission 0.9814 and 0.9777

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 9479 / 9 / 514

Goodness-of-fit on \( F^2 \) 1.112

Final R indices \([I>2\sigma(I)]\) \( R_1 = 0.1139, \) \( wR_2 = 0.3087 \)

R indices (all data) \( R_1 = 0.1264, \) \( wR2 = 0.3178 \)

Largest diff. peak and hole 0.630 and \(-0.523 \text{ eÅ}^{-3} \)
Al(11)Me

Empirical formula \( \text{C}_{34.30} \text{H}_{47.76} \text{AlN}_2 \text{O}_2 \)

Formula weight 547.02

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( \text{C}_2/c \)

Unit cell dimensions
- \( a = 32.935(3) \) Å, \( \alpha = 90^\circ \)
- \( b = 7.0560(10) \) Å, \( \beta = 114.289(5)^\circ \)
- \( c = 31.375(4) \) Å, \( \gamma = 90^\circ \)

Volume 6645.8(14) Å\(^3\)

Z, Calculated density 8, 1.093 Mg/m\(^3\)

Absorption coefficient 0.091 mm\(^{-1}\)

\( F(000) \) 2372

Crystal size 0.10 x 0.10 x 0.10 mm

Theta range for data collection 3.53 to 24.98 °

Limiting indices \(-38 \leq h \leq 38, -8 \leq k \leq 8, -35 \leq l \leq 37\)

Reflections collected / unique 24788 / 5755 \( [R(\text{int}) = 0.1342] \)

Completeness to theta = 24.98 ° 98.5 %

Absorption correction None

Max. and min. transmission 0.9909 and 0.9909

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 5755 / 10 / 394

Goodness-of-fit on \( F^2 \) 1.078

Final R indices \([I>2\sigma(I)]\) \( R_1 = 0.1279, \ wR_2 = 0.3141 \)

R indices (all data) \( R_1 = 0.1946, \ wR2 = 0.3564 \)

Largest diff. peak and hole 0.722 and -0.458 eÅ\(^{-3}\)
8.1.4 Chapter 5

Ti$_2$(16)(OiPr)$_6$

Empirical formula \( \text{C}_{60}\text{H}_{108}\text{N}_2\text{O}_8\text{Ti}_2 \)

Formula weight 1081.28

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( \text{P2}_1/\text{n} \)

Unit cell dimensions
- \( a = 17.1370(12) \) Å \( \alpha = 90 \) °
- \( b = 11.4570(16) \) Å \( \beta = 95.355(5) \) °
- \( c = 17.2330(15) \) Å \( \gamma = 90 \) °

Volume 3368.7(6) Å$^3$

Z, Calculated density 2, 1.066 Mg/m$^3$

Absorption coefficient 0.284 mm$^{-1}$

\( F(000) \) 1180

Crystal size 0.10 x 0.10 x 0.10 mm

Theta range for data collection 3.52 to 25.03 °

Limiting indices \(-20 \leq h \leq 19, -12 \leq k \leq 13, -20 \leq l \leq 20\)

Reflections collected / unique 26382 / 5924 [\( R(\text{int}) = 0.1132 \)]

Completeness to theta = 25.03 99.3 %

Absorption correction None

Max. and min. transmission 0.9722 and 0.9722

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 5924 / 0 / 401

Goodness-of-fit on \( F^2 \) 1.022

Final R indices [\( I > 2 \sigma (I) \)] \( R_1 = 0.0576, wR_2 = 0.1211 \)

R indices (all data) \( R_1 = 0.1157, wR_2 = 0.1481 \)

Largest diff. peak and hole 0.530 and -0.357 eÅ$^{-3}$
Ti$_2$(17)(OiPr)$_6$

Empirical formula  \( \text{C}_{24}\text{H}_{41}\text{NO}_4\text{Ti} \)

Formula weight  455.48

Temperature  150(2) K

Wavelength  0.71073 Å

Crystal system, space group  Monoclinic, \( \text{P2}_1/\text{c} \)

Unit cell dimensions  
\[ a = 10.4230(2) \text{ Å} \quad \alpha = 90^\circ \]
\[ b = 22.8100(5) \text{ Å} \quad \beta = 114.617(1)^\circ \]
\[ c = 12.5010(2) \text{ Å} \quad \gamma = 90^\circ \]

Volume  \( 2701.97(9) \text{ Å}^3 \)

Z, Calculated density  4, 1.120 Mg/m$^3$

Absorption coefficient  0.342 mm$^{-1}$

F(000)  984

Crystal size  0.40 x 0.20 x 0.20 mm

Theta range for data collection  3.59 to 27.54 °

Limiting indices  \(-13 \leq h \leq 13, -29 \leq k \leq 29, -16 \leq l \leq 16 \)

Reflections collected / unique  39062 / 6195 [R(int) = 0.1081]

Completeness to theta = 27.54 °  99.4 %

Absorption correction  Semi-empirical from equivalents

Max. and min. transmission  0.9347 and 0.8753

Refinement method  Full-matrix least-squares on F$^2$

Data / restraints / parameters  6195 / 6 / 323

Goodness-of-fit on F$^2$  1.110

Final R indices [I>2σ(I)]  
\[ R_1 = 0.0691, \, wR_2 = 0.1764 \]

R indices (all data)  
\[ R_1 = 0.0892, \, wR_2 = 0.1912 \]

Largest diff. peak and hole  0.901 and -0.656 eÅ$^{-3}$
**Ti₂(18)(OiPr)₆**

**Empirical formula**  
C₄₀H₄₉Cl₂N₄O₄Ti

**Formula weight**  
726.60

**Temperature**  
150(2) K

**Wavelength**  
0.71073 Å

**Crystal system, space group**  
Triclinic, P-1

**Unit cell dimensions**  

\[
a = 8.8350(2) \text{ Å} \quad \alpha = 95.5030(10) ^\circ \\
b = 10.7560(3) \text{ Å} \quad \beta = 90.5850(10) ^\circ \\
c = 20.4880(7) \text{ Å} \quad \gamma = 97.9200(10) ^\circ
\]

**Volume**  
1918.96(10) Å³

**Z, Calculated density**  
2, 1.258 Mg/m³

**Absorption coefficient**  
0.402 mm⁻¹

**F(000)**  
768

**Crystal size**  
0.20 x 0.20 x 0.10 mm

**Theta range for data collection**  
3.52 to 25.07 °

**Limiting indices**  
-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -24 ≤ l ≤ 23

**Reflections collected / unique**  
25157 / 6767 [R(int) = 0.0538]

**Completeness to theta = 25.07**  
99.1 %

**Absorption correction**  
None

**Refinement method**  
Full-matrix least-squares on F²

**Data / restraints / parameters**  
6767 / 0 / 440

**Goodness-of-fit on F²**  
1.046

**Final R indices [I>2σ(I)]**  
R₁ = 0.0493, wR₂ = 0.1165

**R indices (all data)**  
R₁ = 0.0685, wR₂ = 0.1291

**Largest diff. peak and hole**  
0.579 and -0.593 eÅ⁻³
Al₂(16)Me₄

Empirical formula \( \text{C}_{48}\text{H}_{80}\text{Al}_2\text{N}_2\text{O}_4 \)
Formula weight 803.10
Temperature 150(2) K
Wavelength 0.71073 Å
Crystal system, space group triclinic, \( \text{P}-1 \)
Unit cell dimensions
\[ a = 9.5690(10) \text{ Å} \quad \alpha = 109.497(5) {}^\circ \]
\[ b = 11.6000(7) \text{ Å} \quad \beta = 96.776(4) {}^\circ \]
\[ c = 11.8190(13) \text{ Å} \quad \gamma = 93.635(5) {}^\circ \]
Volume 1220.6(2) Å³
Z, Calculated density 1, 1.093 Mg/m³
Absorption coefficient 0.101 mm⁻¹
F(000) 440
Crystal size 0.20 x 0.10 x 0.05 mm
Theta range for data collection 3.56 to 24.16 °
Limiting indices \(-11\leq h\leq 11, -13\leq k\leq 11, -13\leq l\leq 13\)
Reflections collected / unique 7936 / 3792 [R(int) = 0.0831]
Completeness to theta = 24.16 % 96.9 %
Absorption correction None
Refinement method Full-matrix least-squares on \( F^2 \)
Data / restraints / parameters 3792 / 6 / 261
Goodness-of-fit on \( F^2 \) 1.013
Final R indices \([I>2\sigma(I)]\) \( R_1 = 0.0782, \ wR_2 = 0.1813 \)
R indices (all data) \( R_1 = 0.1313, \ wR_2 = 0.2188 \)
Largest diff. peak and hole 0.490 and -0.615 eÅ⁻³
**Al_{2}(17)Me_{4}**

**Empirical formula**  
C_{34}H_{52}Al_{2}N_{2}O_{2}

**Formula weight**  
574.74

**Temperature**  
150(2) K

**Wavelength**  
0.71073 Å

**Crystal system, space group**  
Triclinic, P-1

**Unit cell dimensions**  

\[
\begin{align*}
a &= 6.4870(6) \text{ Å} & \alpha &= 98.515(5) ^\circ \\
b &= 7.6680(7) \text{ Å} & \beta &= 90.729(5) ^\circ \\
c &= 17.3850(14) \text{ Å} & \gamma &= 94.709(5) ^\circ
\end{align*}
\]

**Volume**  
852.08(13) Å³

**Z, Calculated density**  
1, 1.120 Mg/m³

**Absorption coefficient**  
0.116 mm⁻¹

**F(000)**  
312

**Crystal size**  
0.20 x 0.20 x 0.20 mm

**Theta range for data collection**  
3.85 to 27.50 ^\circ

**Limiting indices**  
-8 ≤ h ≤ 8, -9 ≤ k ≤ 9, -22 ≤ l ≤ 22

**Reflections collected / unique**  
13796 / 3854 [R(int) = 0.0423]

**Completeness to theta = 27.50**  
98.4 %

**Absorption correction**  
None

**Max. and min. transmission**  
0.9772 and 0.9772

**Refinement method**  
Full-matrix least-squares on F²

**Data / restraints / parameters**  
3854 / 0 / 187

**Goodness-of-fit on F²**  
1.040

**Final R indices [I>2σ(I)]**  
R₁ = 0.0429, wR₂ = 0.1084

**R indices (all data)**  
R₁ = 0.0571, wR₂ = 0.1198

**Largest diff. peak and hole**  
0.238 and -0.294 eÅ⁻³
### Zn$_2$(17)Me$_2$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>{46}$H$</em>{68}$N$_2$O$_4$Zn$_2$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>843.76</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system, space group</td>
<td>Monoclinic, P21/n</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 14.2740(2) Å, α = 90 °</td>
</tr>
<tr>
<td></td>
<td>b = 7.98300(10) Å, β = 101.4560(10) °</td>
</tr>
<tr>
<td></td>
<td>c = 20.1200(4) Å, γ = 90 °</td>
</tr>
<tr>
<td>Volume</td>
<td>2246.98(6) Å $^3$</td>
</tr>
<tr>
<td>Z, Calculated density</td>
<td>2, 1.247 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>1.109 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>900</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.10 x 0.10 mm</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>4.02 to 27.45 °</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-18≤h≤18, -10≤k≤10, -26≤l≤26</td>
</tr>
<tr>
<td>Reflections collected / unique</td>
<td>37316 / 5113 [R(int) = 0.0670]</td>
</tr>
<tr>
<td>Completeness to theta = 27.45</td>
<td>99.2 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.8972 and 0.8086</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on $F^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>5113 / 0 / 275</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.028</td>
</tr>
<tr>
<td>Final R indices [I&gt;2σ(I)]</td>
<td>$R_1 = 0.0363$, $wR_2 = 0.0869$</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>$R_1 = 0.0538$, $wR_2 = 0.0950$</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.283 and -0.389 eÅ$^{-3}$</td>
</tr>
</tbody>
</table>
8.1.5 Chapter 6

Al(22)Me

Empirical formula \( \text{C}_{38}\text{H}_{59}\text{AlN}_{2}\text{O}_{2} \)

Formula weight 602.85

Temperature 150(2) K

Wavelength 0.71073 Å

Crystal system, space group Monoclinic, \( \text{P}2_1/n \)

Unit cell dimensions
\[
\begin{align*}
    a &= 11.8730(6) \text{ Å} & \alpha &= 90^\circ \\
    b &= 10.6560(7) \text{ Å} & \beta &= 94.668(5) ^\circ \\
    c &= 28.8840(18) \text{ Å} & \gamma &= 90^\circ \\
\end{align*}
\]

Volume 3642.2(4) Å³

Z, Calculated density 4, 1.099 Mg/m³

Absorption coefficient 0.089 mm⁻¹

\( F(000) \) 1320

Crystal size 0.10 x 0.10 x 0.02 mm

Theta range for data collection 3.72 to 23.80 °

Limiting indices \(-13 \leq h \leq 13, -12 \leq k \leq 12, -29 \leq l \leq 32 \)

Reflections collected / unique 18682 / 5538 [\( R(\text{int}) = 0.1690 \)]

Completeness to theta = 23.80 % 99.2 %

Absorption correction Multi-scan

Max. and min. transmission 0.9982 and 0.9912

Refinement method Full-matrix least-squares on \( F^2 \)

Data / restraints / parameters 5538 / 0 / 402

Goodness-of-fit on \( F^2 \) 1.065

Final R indices [\( I>2\sigma(I) \)] \( R_1 = 0.1076 \), \( wR_2 = 0.2127 \)

R indices (all data) \( R_1 = 0.2002 \), \( wR_2 = 0.2528 \)

Largest diff. peak and hole 0.275 and -0.246 eÅ⁻³
Al(R,R-22)Me

Identification code               h12mdj15
Empirical formula               C_{44}H_{73}AlN_{2}O_{2}
Formula weight               689.02
Temperature               150(2) K
Wavelength               0.71073 Å
Crystal system, space group       Monoclinic, P2_1
Unit cell dimensions
  a = 14.159(2) Å  α = 90 °
  b = 10.235(4) Å  β = 92.574(7) °
  c = 14.801(2) Å  γ = 90 °
Volume               2142.8(10) Å³
Z, Calculated density             2, 1.068 Mg/m³
Absorption coefficient               0.083 mm⁻¹
F(000)               760
Crystal size               0.30 x 0.10 x 0.10 mm
Theta range for data collection       4.08 to 27.49 °
Limiting indices
  -18≤h≤18, -13≤k≤13, -19≤l≤18
Reflections collected / unique       38513 / 9665 [R(int) = 0.0612]
Completeness to theta = 27.49 %               99.4 %
Absorption correction               None
Refinement method               Full-matrix least-squares on F²
Data / restraints / parameters       9665 / 1 / 458
Goodness-of-fit on F²               1.033
Final R indices [I>2σ(I)]
  R₁ = 0.0457, wR₂ = 0.0993
R indices (all data)
  R₁ = 0.0691, wR₂ = 0.1097
Absolute structure parameter               -0.01(13)
Largest diff. peak and hole               0.308 and -0.317 eÅ⁻³
Al(25)OBn

Identification code               k12mdj12
Empirical formula                 C₃₉.₅₅H₅₁AlN₂O₃
Formula weight                    628.80
Temperature                       150(2) K
Wavelength                        0.71073 Å
Crystal system, space group       Monoclinic, C₂/c
Unit cell dimensions              a = 25.7960(3) Å , α = 90 °
                                      b = 12.55700(10) Å , β = 100.521(1) °
                                      c = 21.7940(2) Å , γ = 90 °
Volume                            6940.84(12) Å³
Z, Calculated density             8, 1.203 Mg/m³
Absorption coefficient            0.098 mm⁻¹
F(000)                            2712
Crystal size                      0.20 x 0.20 x 0.15 mm
Theta range for data collection   3.62 to 27.45 °
Limiting indices                  -33≤h≤30, -16≤k≤16, -28≤l≤28
Reflections collected / unique    55806 / 7910 [R(int) = 0.0619]
Completeness to theta = 27.45     99.5 %
Absorption correction             None
Max. and min. transmission        0.9854 and 0.9806
Refinement method                 Full-matrix least-squares on F²
Data / restraints / parameters    7910 / 0 / 420
Goodness-of-fit on F²             1.033
Final R indices [I>2σ(I)]         R₁ = 0.0422, wR₂ = 0.0903
R indices (all data)              R₁ = 0.0634, wR₂ = 0.1006
Largest diff. peak and hole       0.330 and −0.293 eÅ⁻³