New Main Group and Rare Earth Complexes and Their Applications in the Ring-Opening Polymerisation of Cyclic Esters

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Thesis submitted to the University of Oxford for the degree of Doctor of Philosophy, July 2011.
The work described in this Thesis was carried out in the Chemistry Research Laboratory, University of Oxford from October 2007 to July 2011 under the supervision of Professor Philip Mountford. All work is my own unless stated to the contrary, and has not previously been submitted for any degree at this or any other university.

Michael Gregory Cushion

July 2011
Abstract

Michael Gregory Cushion
Merton College

This Thesis describes the synthesis and characterisation of new Main Group and Rare Earth alkyl, amide, alkoxide and borohydride complexes and their use as catalysts for the ring-opening polymerisation (ROP) of ε-caprolactone and rac-lactide.

Chapter 1 introduces ROP from an industrial and academic perspective, as well as polymer characterisation techniques. A literature review is given, with an emphasis placed on Main Group catalysts.

Chapter 2 describes the synthesis and characterisation of new homo- and hetero-scorpionate Main Group complexes. An introduction to homo- and hetero-scorpionate ligands is given, as well as a discussion of the ε-caprolactone and rac-lactide ROP activity displayed by the new complexes.

Chapter 3 describes the synthesis and characterisation of new neutral and cationic Main Group borohydride complexes supported by the tris(pyrazolyl)methane and tris(pyrazolyl)hydroborate ligands. A review of borohydride complexes is also given. The ε-caprolactone and rac-lactide ROP activity shown by the complexes presented is also discussed.

Chapter 4 describes the synthesis and characterisation of new mono- and di-cationic yttrium complexes supported by the tris(pyrazolyl)methane and triazacyclononane ligands. An introduction to the synthesis of neutral and cationic Rare Earth complexes is given. An overview of immortal ROP is also provided. The activity of the new complexes towards the immortal ROP of rac-lactide is also discussed.

Chapter 5 contains experimental details and characterising data for the new complexes reported in this thesis.

CD Appendix contains .cif files for all of the new crystallographically characterised complexes.
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Acknowledgements

Firstly I would like to thank my supervisor, Professor Philip Mountford, for his help and support throughout the course of my studies. I’ve learned a lot and this has provided me with a solid foundation to build on. Also, don’t worry, I’ll be (relatively) clean-shaven for my viva!

I also express gratitude to the rest of the Mountford group for being pleasant to work with, and I wish them the best for the future. Thanks in particular to Matt, Lawrence, Liban, Richard and Dr. Andrew Schwarz for helping to proof read my Chapters and making many useful suggestions. Thanks must also go to Alexander Kilpatrick for being an excellent Part II student and a good guy to work with. Unfortunately I haven’t been able to discuss any of your project since you worked on Chromium! We all know Calcium is a much better metal to work on (despite what Chemistry Top Trumps might say). Also, good luck to Guun with the rest of your DPhil. Keep on ROPin’ in the free world.

I would also like to thank my contemporary, Robert ‘Coops’ Cooper, for being a good friend and also for many entertaining nights out in Oxford. It was good to have somebody else around that started at the same time as me, albeit under a different supervisor. I’m also grateful to Colin Sparrow and Dr Nick Rees for their help with mass spectroscopy and NMR. Dr Amber L. Thompson and Dr David J. Watkin also deserve special mention for helping me to collect data for many crystals.

Additionally, I am very grateful to the support provided to me throughout my life by my family and close friends at home. It hasn’t always been easy but the comfort you have provided me has given me inspiration through the difficult times. That’s not to say there haven’t been good times too, and I’m also lucky to have shared these with you. I look forward to sharing many more. Finally, thanks must also go to Holly for everything recently. With any luck I’ll be a doctor soon too.
## Abbreviations

### General

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>Å</td>
<td>Ångstrom</td>
</tr>
<tr>
<td>av.</td>
<td>average</td>
</tr>
<tr>
<td>ca.</td>
<td><em>circa</em>, about</td>
</tr>
<tr>
<td>calc.</td>
<td>calculated</td>
</tr>
<tr>
<td>°</td>
<td>degrees</td>
</tr>
<tr>
<td>ºC</td>
<td>degrees Celsius</td>
</tr>
<tr>
<td>d</td>
<td>day(s)</td>
</tr>
<tr>
<td>g</td>
<td>gram(s)</td>
</tr>
<tr>
<td>GPC</td>
<td>gel permeation chromatography</td>
</tr>
<tr>
<td>h</td>
<td>hour(s)</td>
</tr>
<tr>
<td>K</td>
<td>Kelvin</td>
</tr>
<tr>
<td>k&lt;sub&gt;i&lt;/sub&gt;</td>
<td>rate constant of initiation</td>
</tr>
<tr>
<td>k&lt;sub&gt;p&lt;/sub&gt;</td>
<td>rate constant of propagation</td>
</tr>
<tr>
<td>min</td>
<td>minute(s)</td>
</tr>
<tr>
<td>s</td>
<td>second(s)</td>
</tr>
<tr>
<td>rt</td>
<td>room temperature</td>
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### Chemical

<table>
<thead>
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<tbody>
<tr>
<td>Ar</td>
<td>aryl group</td>
</tr>
<tr>
<td>Bn</td>
<td>benzyl</td>
</tr>
<tr>
<td>Cp</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cp*</td>
<td>C&lt;sub&gt;5&lt;/sub&gt;Me&lt;sub&gt;5&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cy</td>
<td>cyclohexyl</td>
</tr>
<tr>
<td>D-lactide</td>
<td>(R,R)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione</td>
</tr>
<tr>
<td>E</td>
<td>generic chalcogen atom</td>
</tr>
<tr>
<td>Et</td>
<td>ethyl</td>
</tr>
<tr>
<td>i&lt;sup&gt;Bu&lt;/sup&gt;</td>
<td><em>iso</em>-butyl</td>
</tr>
<tr>
<td>i&lt;sup&gt;Pr&lt;/sup&gt;</td>
<td><em>iso</em>-propyl</td>
</tr>
<tr>
<td>i&lt;sup&gt;PrOH&lt;/sup&gt;</td>
<td>isopropyl alcohol</td>
</tr>
<tr>
<td>L</td>
<td>a supporting ligand (set)</td>
</tr>
<tr>
<td>L-lactide</td>
<td>(S,S)-cis-3,6-dimethyl-1,4-dioxane-2,5-dione</td>
</tr>
<tr>
<td>Me</td>
<td>methyl</td>
</tr>
</tbody>
</table>
Mes $\rightarrow$ 2,4,6-C$_6$H$_2$Me$_3$

meso- lactide $(R,S)$-cis-3,6-dimethyl-1,4-dioxane-2,5-dione

$M_n$ number average molecular weight

$M_p$ peak molecular weight

M-OR metal alkoxide

$M_w$ weight average molecular weight

$^n$Bu $n$-butyl

PDI poly dispersity index

PET or PETE polyethylene terephthalate

Ph phenyl

$P_m$ probability of meso- linkages

PLA poly(lactic acid)

PCL poly(ε-caprolactone)

$P_r$ probability of racemic linkages

$p$-Tol 4-C$_6$H$_4$Me

py pyridine

pz pyrazolyl

R generic aryl or alkyl

rac-lactide a racemic mixture of $D$- and $L$-lactide

ROP ring-opening polymerisation

Sn(Oct)$_2$ Tin octanoate

$t$Bu tert-butyl

THF tetrahydrofuran

X Generic halide

### Mass Spectrometry

EI electron impact

FI field ionisation

$m/z$ mass to charge ratio

MS mass spectrometry

MALDI-ToF MS matrix-assisted laser desorption/ionization - time of flight mass spectrometry
### Nuclear Magnetic Resonance Spectroscopy

- $^{13}\text{C}\{^1\text{H}\}$: proton-decoupled $^{13}\text{C}$
- $^{11}\text{B}\{^1\text{H}\}$: proton-decoupled $^{11}\text{B}$
- app.: apparent
- br: broad
- COSY: correlation spectroscopy
- d: doublet
- HETCOR: heteronuclear correlation
- HMBC: heteronuclear multiple bond correlation
- HMQC: heteronuclear single quantum correlation
- i: ipso
- J: coupling constant
- m: meta
- m: multiplet
- NMR: nuclear magnetic resonance
- nOe: nuclear Overhauser effect
- o: ortho
- p: para
- ppm: parts per million
- q: quartet
- ROESY: rotating-frame nuclear Overhauser Effect spectroscopy
- s: singlet
- sept: septet
- t: triplet
- $\delta$: chemical shift in ppm

### Infrared Spectroscopy

- br: broad
- FT-IR: fourier transform infrared red
- IR: infrared red
- m: medium
- s: strong
- w: weak
- v: frequency
Notes about the numbering of compounds described in this Thesis

Literature compounds described in this Thesis are numbered 1.x, 2.x, 3.x, 4.x according to the Chapter in which they first occur. The new compounds described in this Thesis are numbered 1 – 30.
Chapter One

Introduction
1.0 Outline

This Chapter provides an introduction to the ring-opening polymerisation (ROP) of cyclic esters. Discussion will include an overview of the industrial and academic research carried out in this area. An emphasis on main group and rare earth metal catalysed ROP will be placed, with notable exceptions from other areas of the periodic table also discussed. Catalysts employing cyclopentadienyl ligands will be discussed, with a progression to post-metallocene systems, most specifically systems employing O-, N- and mixed N,O-donor ancillary ligands. An introduction to the analytical techniques used in polymer characterisation will also be presented.

1.1 Background

Polymers derived from petrochemical resources have had a tremendous industrial impact in modern times.\(^1\) Despite the numerous advantages presented by these materials, there are two major drawbacks. Firstly, the use of non-renewable oil based resources in their production, and secondly their non-biodegradable nature.\(^1, 2\) As a result of this and the growing cost of crude oil, significant attention over the past three decades has turned to the synthesis of biocompatible polymers from renewable resources.

Of the extensive range of biodegradable polymers known, linear aliphatic polyesters have been the most widely studied.\(^1-6\) Arguably the most prominent examples of this emerging class of polyesters are poly(\(\varepsilon\)-caprolactone) (PCL), poly(lactide) (PLA) and poly(glycolide) (PGA).\(^1\) These have attracted considerable recent attention due to their biomedical and pharmaceutical applications, for example as drug delivery agents and post-operative stitches and pins.\(^4\) PLA is also notably produced as a commodity thermoplastic in the packaging industry.\(^3\) The remainder of this Thesis focuses on PCL and PLA.

The most common and efficient method for the preparation of PCL and PLA is by the ROP of the parent cyclic monomers (the structures of which are shown in Figure 1.0). This offers a higher degree of control in terms of molecular weight and molecular weight distribution \((M_w/M_n)\) than traditional step-growth processes (i.e. polycondensation reactions) of the appropriate \(\alpha\)-hydroxy acids.\(^3\)
In the case of PLA a variety of stereoregular polymer microstructures are possible, each with their own specific properties (this is discussed further in Section 1.6). Therefore, interest has focussed particularly on the production of PLA, which is derived from corn, sugar beet and other annually renewable resources. It should be noted at this point that $\varepsilon$-CL is prepared industrially by the Baeyer-Villiger oxidation of cyclohexanone with peroxyacetic acid (i.e. from non-renewable resources). However, despite this, PCL is biodegradable. Millions of tonnes of cyclohexanone are produced annually (by the oxidation of cyclohexane), mainly as a precursor to nylon. The most common use of PCL is in the manufacture of speciality polyurethanes. PCL imparts good water, oil, solvent and chlorine resistance to the polyurethane produced. The life cycle of PLA is shown in Figure 1.1.

**Figure 1.0.** The structures of $\varepsilon$-caprolactone ($\varepsilon$-CL) and lactide (LA).

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**Figure 1.1.** The life cycle of PLA. $R =$ initiating group (e.g. alkyl, amide, alkoxide) from the catalyst.
1.2 ROP Mechanisms

There are a number of known mechanisms for the ROP of CL and LA, these include: coordination-insertion, activated monomer (a description of which is given in Chapter 4), anionic, cationic, organo-catalytic and enzymatic. These are the subject of recent reviews in the area.\(^1\)-\(^6\) This Thesis focuses on coordination-insertion ROP, since this pathway is the most widely present in ROP catalysed by Main Group, transition metal and lanthanide metal complexes.\(^3\)

The coordination-insertion mechanism proceeds by three main steps (Figure 1.2). Firstly, the carbonyl oxygen atom of the monomer coordinates to a Lewis acidic metal centre, making the carbonyl carbon more prone to nucleophilic attack. Secondly, insertion of the monomer into the M-R group of the initiator (R = typically an alkyl, amide or alkoxide group) occurs via nucleophilic attack of the R group on the carbonyl carbon of the monomer. Finally, acyl oxygen bond cleavage occurs. The coordination of subsequent monomers leads to propagation and the continuation of the cycle. Protolytic work-up liberates the polymer from the metal centre.

**Figure 1.2.** Coordination-insertion mechanism (using LA as an example). R = initiating group, e.g. alkyl, amide or alkoxide and \(k_i\) and \(k_p\) are the respective rate constants for initiation and propagation.
The majority of catalysts used for the ROP of cyclic esters suffer from a number of detrimental issues. These include inter- and intra-molecular transesterification (Figure 1.3), termination/ chain transfer reactions and a slow rate of initiation (relative to the rate of propagation). During intramolecular transesterification (‘back-biting’), the non-metal bound end of growing polymer chain coordinates to the metal centre, leading to insertion and the formation of cyclic PLA units, also leading to the generation of an active species. This often leads to broad molecular weight distributions and shorter than expected polymer chains, particularly in the later stages of the polymerisation.

During intermolecular transesterification, the non-metal bound end of a growing polymer chain coordinates to a different metal centre of an adjacent polymer chain, giving rise to chain redistribution. This process also leads to the broadening of molecular weight distributions and poor control over the length of polymer chains. Similarly the presence of residual protic impurities can induce early termination reactions, and/or chain transfer.

**Figure 1.3.** Transesterification side reactions. Top: Intramolecular transesterification. Bottom: Intermolecular transesterification.
The degree of transesterification during a polymerisation is highly dependent on the Lewis acidity of the metal present in the catalyst, which in turn is influenced by the ancillary ligand(s) present and the nature of the initiating group.\(^1\)\(^,\)\(^4\)\(^,\)\(^8\) For example Spassky \textit{et al}. synthesised a family of Schiff-base supported aluminium complexes, finding that Schiff-base ligands with electron withdrawing substituents on the backbone produced catalysts with a greater activity and lower degree of transesterification.\(^9\) It was proposed that the electron withdrawing substituents served to enhance the electrophilicity of the metal centre, and/or increase the polarisation of the initiating/propagating Al-X bond.\(^4\)\(^,\)\(^9\)

Also, it was found that transesterification can occur from the onset of polymerisations with Sn(Oct)\(_2\) \((M_w/M_n = 2.0)\), whereas the less active Al(OiPr)\(_3\) showed significantly lower degrees of transesterification \((M_w/M_n = 1.5)\) throughout the polymerisation process.\(^1\)\(^,\)\(^10\)\(^,\)\(^11\) The occurrence of post-polymerisation transesterification is also possible, where the polymerisation has reached a high monomer conversion and is not quenched sufficiently quickly. This process is evident by a shortening of polymer chains and increasing molecular weight distribution at high conversions.\(^25\)

\section*{1.3 Polymer Description}

Due to the aforementioned commonly occurring side reactions, it is extremely rare for a polymer to contain chains of uniform length. For this reason, polymers are described by an average molecular weight, calculated as a number \((M_n)\) or weight \((M_w)\) average, alongside the distribution of molecular weights \((M_w/M_n)\), most frequently referred to as the polydispersity index (PDI). \(M_n\) is defined by Equation 1.0, where \(N_i\) is the number of polymers having a molar mass \(M_i\).

\[
M_n = \frac{\sum N_i M_i}{\sum N_i} \quad \text{Equation 1.0}
\]

Similarly, \(M_w\) is given by Equation 1.1, where \(W_i\) is the mass of polymers having a molar mass \(M_i\).

\[
M_w = \frac{\sum W_i M_i}{\sum W_i} \quad \text{Equation 1.1}
\]

The PDI is given by the ratio of \(M_w/M_n\), shown in Equation 1.2.
Chapter 1

\[
PDI = \frac{M_w}{M_n}
\]

Equation 1.2

In the field of ROP, the \(M_n\) and PDI of a given polymer are the most frequently quoted values. In a perfect system the polymer chains are of uniform length and have identical \(M_n\) and \(M_w\) values, and therefore have a PDI of 1.0. However, in practice the length of polymer chains is given by a Gaussian distribution (largely due to transesterification and slow rates of initiation relative to propagation), with a bias of \(M_w\) towards higher values. Therefore, experimentally, PDI are always greater than 1.0, even for extremely well controlled systems. It follows that the further a PDI value deviates from 1.0 for a given system, the more extensive the transesterification reactions are, and/or the less well balanced the ratio of the rate of initiation to the rate of propagation is.

Generally speaking, PDI values of 1.0-1.2 are considered narrow, 1.2-1.8 moderate and 1.8 and above broad. Additionally, a comparison of experimental \(M_n\) values with calculated (based on the percentage monomer conversion) \(M_n\) is usually carried out. Thus, well controlled polymerisations usually produce polymers with narrow (1.0-1.2) PDIs and a close agreement between expected and calculated \(M_n\) values. Generally, \(M_n\) vs monomer conversion is monitored throughout a polymerisation and/or \(M_n\) is measured for a range of [monomer]_0/[catalyst]_0 ratios. This is important for separating out the different (and sometimes opposing) effects of \(k_i/k_p\) or \(k_{tr}/k_p\) relative magnitudes (where \(k_{tr}\) is the rate of transesterification). These are the criteria used for the discussion of the performance of the catalysts discussed in this thesis.

1.4 Living polymerisation

‘Living’ polymerisations are defined by the following set of characteristics: A linear increase of \(M_n\) with monomer conversion, narrow PDI values (due to minimal transesterification side reactions or their complete absence) and the ability to undergo sequential monomer addition (i.e. the ability to form block co-polymers).\(^5\), \(^6\), \(^12\) The narrow PDI values in living systems are largely due to high \(k_i/k_p\) and \(k_{tr}/k_p\) ratios.\(^6\) Excellent examples of catalysts for living ROP are given in Chapters 3 and 4, a good example for instance is shown in Figure 3.11 in Chapter 3. In the case of highly active systems (i.e. 80-100% monomer conversion in under 2 minutes), it may not be possible to determine kinetic polymerisation profiles. In these cases, evidence for a
living polymerisation process often comes by the observation of a linear increase in $M_n$ from a range of [monomer]$_0$:[catalyst]$_0$ ratios. A good example of this can be seen in Chapter 3 (Figure 3.8). Deviations from the aforementioned criteria of a living polymerisation are generally a consequence of a slow rate of initiation compared with propagation, and/or extensive transesterification and termination reactions competing with propagation.

Ideally, living polymerisation leads to the production of as many growing polymer chains as there are number of initiating groups. A special case of living polymerisation exists in immortal polymerisation, where it is possible to generate more growing polymer chains than there are initiating groups. This is achieved by the addition of chain transfer reagents to the polymerisation mixture. This is discussed in detail in Chapter 4.

1.5 Polymer Analysis

Polyesters such as PCL and PLA are characterised by a number of analytical techniques. These include: $^1$H and $^{13}$C NMR spectroscopy, gel permeation chromatography (GPC) and matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry (MALDI-ToF MS). NMR techniques generally provide information on polymer end groups (and tacticity in the case of PLA), and can also be used to determine polymer $M_n$ (generally for $M_n$ values less than ca. 2,000 g mol$^{-1}$) and the extent of monomer conversion. GPC analysis is used to quantify the $M_n$ and PDI of a given polymer sample. MALDI-ToF MS is used to determine polymer end-groups and as evidence for the presence (or lack of) transesterification. In most cases, the combination of these techniques is used to analyse polymers and investigate the polymerisation process. In some cases, DSC techniques are also used to determine the glass transition and melting points of the polymer, providing a measure of polymer crystallinity.

1.5.1 NMR Spectroscopy

In many cases, especially where high molecular weight polymers are produced, it is not possible to determine the end-group of a polymer by $^1$H NMR. This is due to the extremely high proportion of polymer backbone resonances relative to those corresponding to the end-groups. However, using a low [monomer]$_0$:[catalyst]$_0$ ratio
often provides a solution to this (since lower ratios generally produce polymer of lower molecular weight). An example of a PLA sample with BnNH-capped end groups is shown in Figure 1.4. Additionally, in this case the $M_n$ of the polymer sample has been determined by $^1$H NMR (2690 g mol$^{-1}$). This is in excellent agreement to that measured by GPC (2660 g mol$^{-1}$). A further drawback to this technique is that cyclic polymer backbone resonances overlap with those of linear polymer backbones. For this reason, it is not possible to determine the degree of transesterification using NMR techniques.

**Figure 1.4.** $^1$H NMR spectrum (CDCl$_3$) of BnNH-capped PLA.$^{13}$

1.5.2 Gel Permeation Chromatography

In this technique, polymer samples are dissolved in an organic solvent and passed through a styrene divinyl benzene copolymer column. The column is filled with porous beads of various sizes and these serve to separate the polymer chains by their hydrodynamic radius, a measure of the dynamic volume of a polymer chain based on its solution behaviour, i.e. its interactions with solvent molecules. Shorter length chains enter the pores and their path through the column is increased, whereas longer
chains pass through the column along a shorter path due to their lower degree of interaction with the pores. Therefore, shorter polymer chains have a greater retention time than longer chains. A normal distribution results and this allows a measurement of $M_n$, $M_w$ and PDI.

The instrument is calibrated against linear polystyrene samples of known molecular weight and PDI. However, the hydrodynamic radius of polystyrene is very different to that of polyesters (polar polymers). Therefore, a polystyrene and polyester sample with the same $M_n$ would have different retention times (and therefore different measured $M_n$ values). This problem is solved by application of the appropriate Mark-Houwink corrections ($K$ and $\alpha$) for a given polymer. These constants are specific to each polymer class and so, for example, are different for PCL and PLA.\textsuperscript{16}

The absolute molecular weight of a polymer is defined by Equation 1.3, which relates the intrinsic viscosity at infinite dilution, $[\eta]$, and the molecular weight of the given polymer.

$$[\eta] = K.M^\alpha$$ \textbf{Equation 1.3}

The Mark-Houwink corrections are experimentally determined by a plot of log[$\eta$] against log(M) over a large molecular weight range. Clearly, these are solvent and temperature specific. The GPC measurements reported in this Thesis were obtained by analysis in THF at 30 °C, with the appropriate corrections as previously determined for PCL\textsuperscript{17} and PLA\textsuperscript{18} after calibration against polystyrene standards.

Whist GPC is an essential tool in polymer analysis for linear polymer chains, cyclic polymer units are not accurately described. Additionally, some examples in ROP literature report GPC data having not applied the Mark-Houwink corrections. This can make definitive comparisons between research originating from different origins difficult.

\textbf{1.5.3 MALDI-ToF MS}

In MALDI-ToF MS, polymer chains are embedded in a protective matrix, for example crystalline 4-hydroxy-3-methoxy-cinnamic acid.\textsuperscript{19} A laser beam is then focussed on the matrix and this is ionised. The matrix then transfers some of its energy to the embedded polymer. Through this process, the polymer sample is energetically excited
but shielded from the full energy of the laser (preventing unwanted fragmentation). An added ion (for MALDI-ToF MS results in this thesis K⁺) binds with the polymer molecules, forming [polymer-K]⁺ ions. These ions then pass through a time-of-flight spectrometer where they are resolved by their mass-to-charge ratio. MALDI-ToF is used in polymer analysis as traditional vaporisation techniques used in mass spectrometry lead to unwanted ionisation and fragmentation of the polymer. An example MALDI-ToF MS spectrum of BnNH-capped PLA is shown in Figure 1.5. Also notable is the separation of peaks (144 m/z), which is characteristic of minimal transesterification. Contrastingly, MALDI-ToF-MS spectra from systems with significant transesterification show a peak separation of 72 m/z.

**Figure 1.5.** MALDI-ToF-MS spectrum of the BnNH-capped PLA. The cationisation agent used was potassium trifluoroacetate. The peak at m/z = 2885.4 corresponds to 

\[
[BnNH-[LA]_{14}-H + K]^+. 
\]

### 1.6 Stereocontrol of lactide polymerisation

Lactide exists as three diastereomers, L-, D- and meso-LA (see Figures 1.0 and 1.6). The epimerisation of naturally occurring L-LA, and subsequent separation, leads to the isolation of D- and meso-LA. The enantio-pure isomers are available commercially either as rac-LA (a racemic mixture) or as single enantiomers. As such, there is a
range of ordered polymer microstructures (Figure 1.6). The controlled ROP of either \(L\)- or \(D\)-LA (in the absence of epimerisation), results in isotactic PLA in which all of the sterocentres are aligned along the same side of the polymer chain.\(^{20}\) The ROP of rac-LA or meso-LA leads to a wider range of microstructures such as heterotactic (doubly alternating sterocentres) and isotactic PLA, in the case of rac-LA, and syndiotactic PLA (singly alternating sterocentres) in the case of meso-LA. Atactic PLA, with no ordered sterocentres, arises from epimerisation and/or a poor degree of control over tacticity.

**Figure 1.6.** Lactide stereoisomers and PLA microstructures.\(^{21}\)

The material originally presented here is not currently available in ORA.
of degradation. Additionally, a mixture of co-crystallised isotactic $L$-PLA and $D$-PLA has different bulk properties to that of either polymer on its own.\textsuperscript{2} For example, this mixed PLA has a melting point up to 230 °C, approximately 50 °C higher than either $L$-PLA or $D$-PLA (heterotactic PLA has a melting point of 130 °C).\textsuperscript{22} Therefore the best LA catalysts possess an ability to produce PLA with a degree of stereocontrol as well as the attributes listed for a good living polymerisation catalyst, for example a high $k_i/k_p$ ratio (see also Section 1.4). Other desirable qualities include low cost and toxicity as well as minimal colour and odour.\textsuperscript{2} In recent years, a number of such catalysts have been discovered and are the topic of many excellent reviews.\textsuperscript{1-6} The most widely studied monomer of LA is \textit{rac}-LA, due to its widespread availability and wider range of possible PLA microstructures.

The two methods used for the synthesis of stereoregular PLA using homogenous ROP catalysts are chain-end control and enantiomorphic site control. Chain-end control arises when the stereocentre of the last inserted monomer influences the stereochemistry of the next monomer to undergo addition. This usually occurs using achiral catalysts, generally with a significant degree of steric bulk around the metal centre. Chain-end control typically accounts for heterotactic PLA,\textsuperscript{13, 23-27} although in some cases isotactic PLA has also been produced.\textsuperscript{28-30} Conversely, enantiomorphic site control is induced by the chirality of the catalyst where preferential differentiation of monomer stereocentres occurs. Using such racemic systems it is possible to synthesise isotactic PLA from \textit{rac}-LA\textsuperscript{31-33} and syndiotactic PLA from \textit{meso}-LA.\textsuperscript{34, 35}

The microstructure of PLA is determined by \textsuperscript{13}C{\textsuperscript{1}H} and homodecoupled \textsuperscript{1}H NMR spectroscopy at the tetrad level and the conclusive assignments were determined by Hillmyer and Munson (Figure 1.7).\textsuperscript{36} Homonuclear decoupling of the methyl signals of PLA decouples the methyl and methine signals of the polymer. This results in a set of singlet resonances in the range 5.15-5.25 ppm.\textsuperscript{20} In Figure 1.7, and frequently elsewhere, ‘$i$’ denotes and isotactic link between adjacent stereocentres (i.e. $R,R$) and ‘$s$’ denotes a syndiotactic link between adjacent stereocentres (i.e. $S,R$). Using this notation, highly isotactic PLA has the repeating sequence $iii$ at the tetrad level and, similarly, heterotactic PLA is described by the sequences $isi$ and $sis$. As can be seen in Figure 1.7, PLA formed from \textit{rac}-LA and \textit{meso}-LA results in different sequences.
The degree of stereoregularity present in a given PLA chain is expressed as a probability, where $P_r$ is the probability of forming a racemic link (heterotactic enrichment) and $P_m$ is the probability of forming a meso link (isotactic). Hence, for the ROP of rac-LA, $P_r = 1.00$ and $P_m = 0.00$ for perfectly heterotactic PLA. Similarly, $P_r = 0.00$ and $P_m = 1.00$ describes perfectly isotactic PLA formed from rac-LA.\textsuperscript{20} Figures 1.8 and 1.9 show good examples of the homodecoupled $^1$H NMR spectra of isotactic, heterotactic and atactic PLA. Figure 3.15 in Chapter 3 also gives a good example of heterotactically enriched PLA.

**Figure 1.7.** Schematic representation of the currently accepted assignments (CH) for PLA at the tetrad level.$^{37}$

The material originally presented here is not currently available in ORA
Figure 1.8. The methine resonances in the homonuclear decoupled $^1$H NMR spectrum of PLA illustrating isotactic block PLA chains (a) and heterotactic PLA chains (b).  

The material originally presented here is not currently available in ORA

Figure 1.9. The methine resonances in the homonuclear decoupled $^1$H NMR spectrum of PLA illustrating atactic PLA chains.  

The material originally presented here is not currently available in ORA

1.7 Literature Review

Over the past two decades substantial research effort has been devoted to the development of catalytic systems for the ROP of $\varepsilon$-CL and LA. Highly desirable systems are those that promote ROP under ambient conditions with a high activity and the control (extending to tacticity control in the case of LA). This section provides a selective overview of the varied approaches used in this area. An emphasis is based on
Main Group catalysts, since Chapters 2 and 3 focus mainly on this area. The use of these catalysts is also highly desirable due to their biologically benign nature and abundance.\textsuperscript{23}

Additionally, notable examples of ROP catalysts based on metals across the periodic table are discussed. The area of ROP has been reviewed extensively on numerous occasions in the past decade and this is a reflection of the amount of widespread research existing in the area. The reader is directed to these reviews for detailed accounts.\textsuperscript{1-6} ROP catalysts are based on many metals such as magnesium,\textsuperscript{2, 40-43} zinc,\textsuperscript{35, 40, 42-46} calcium,\textsuperscript{2, 23, 24, 47-51} aluminium,\textsuperscript{52-56} Rare Earth metals,\textsuperscript{13, 25, 57-64} Group IV metals,\textsuperscript{8, 14, 26, 65-68} iron,\textsuperscript{69, 70} tin\textsuperscript{71-73} and indium.\textsuperscript{74, 75}

\subsection*{1.7.1 Industrial ROP and the Development of Simple Systems}

PLA is synthesised on a 140,000 tonne scale annually by Natureworks LLC in the USA and on a smaller scale elsewhere in the EU and Japan.\textsuperscript{6} The commonly used industrial catalyst used for the preparation of PLA is tin (II) 2-ethylhexanoate (stannous octanoate, see Figure 1.10). The advantages of this simple system are the production of high molecular weight polymer, high activity and low levels of epimerisation.\textsuperscript{76} An additional benefit of this system is the solvent free (melt) conditions used. The monomer and catalyst are simply heated together at 180-210 °C and 95 \% monomer conversion is achieved in 2.5 hours. The addition of alcohols to the process is sometimes carried out to accelerate the rate of polymerisation and/or to form lower molecular weight polymer.\textsuperscript{76} Also of high importance is the fact that the catalyst has been approved as a food additive by the FDA in the USA (despite being a potentially toxic Sn(II) species).\textsuperscript{76, 77}

Despite being an approved food additive, Sn(Oct)\textsubscript{2} has been restricted from use in biomedical applications, owing to the possible retention of tin residues in the PLA formed (which could go on to form highly toxic organo-tin species).\textsuperscript{78} For these reasons, lots of subsequent early research focussed on attempts to find a truly biocompatible homoleptic catalyst, for example Zn(lactate)\textsubscript{2} and Al(O\textsubscript{3}Pr)\textsubscript{3} (Figure 1.10).
The most extensively studied homoleptic aluminium alkoxide is \( \text{Al(O}^\text{iPr})_3 \), which was shown to be active for the ROP of LA.\(^{10, 54}\) However, this catalyst is substantially less active than \( \text{Sn(Oct)}_2 \), taking several days at 125-180 °C to reach high monomer conversions and also producing PLA with a lower than desired \( M_n \).\(^{1, 10}\) Furthermore, whilst the consumption of LA generally followed first order kinetics, induction periods were commonly found. This was attributed to aggregation phenomena, further complicated by the fact that \( \text{Al(O}^\text{iPr})_3 \) actually exists as an equilibrium mixture of a trimer and tetramer in solution (THF).\(^{54}\) An additional disadvantage of aluminium catalysts in general is that aluminium has been linked with the development of Alzheimer’s disease.\(^1\) Compared to aluminium, homoleptic zinc complexes such as zinc octanoate, zinc stearate, zinc salicylate and zinc lactate were found to be improved catalysts.\(^1, 6, 79, 80\) For example, zinc lactate polymerised LA to moderate conversions over 24 hours under similar melt conditions (140 °C) used in the testing of \( \text{Sn(Oct)}_2 \).\(^80\) However, such homoleptic zinc species were found to perform poorly compared to \( \text{Sn(Oct)}_2 \).\(^1, 6\)

In related work, Feijen et al. tested commercially available calcium dimethoxide and found this to be an active catalyst for the ROP of \( L \)-LA and \( \varepsilon \)-CL in the melt at 120 °C.\(^81\) However, the epimerisation of \( L \)-LA was observed and this was attributed to the formation of aggregated species. An improved system was found using \textit{in situ} generated calcium methoxide, formed by addition of 2 equivalents of MeOH to \( \text{Ca}\{\text{N(SiMe}_3\text{)}_2\}\) in the presence of LA.\(^81\) This polymerised both \( \varepsilon \)-CL and \( L \)-LA in
THF at room temperature, with no epimerisation of \( L\)-LA, i.e. solely isotactic PLA was formed. In this case polymers with narrow PDI\(_s\) and close to expected \( M_n\) values were observed.\(^8\) Interestingly, the attempted isolation of the alkoxide complex in the absence of LA led to the formation of insoluble, oligomeric species. Rare earth homoleptic alkoxide complexes have also been studied for the ROP of \( \varepsilon\)-CL\(^8\) and were also shown to have formed aggregated species in the early stages of polymerisation, evident by the observation of induction periods in the kinetic profiles.\(^8\)

It can be seen that homoleptic polymerisation systems are generally plagued by aggregation phenomena, poor control and non-ideal kinetic polymerisation profiles. Generally, more recent academic research has focussed on the development of well-defined single site catalysts, inspired by earlier developments in polyolefin technology. The advantages of this approach are the ability to modify the Lewis acidity of a metal centre (and therefore the activity of a catalyst), as well as the selectivity of the catalyst through the manipulation of inert ancillary ligand(s).

### 1.7.2 Cyclopentadienyl Based ROP Initiators

Cyclopentadienyl ligands are the most ubiquitous ancillary ligands in organometallic chemistry. Reasons for this include their relatively straightforward preparation, crystallinity and wide ranging possibilities for substitution at the ring substituents. As such there are a number of ROP catalysts with cyclopentadienyl supporting motifs (see also Chapter 3 for cyclopentadienyl borohydride complexes).

The dimeric samarium hydride complex 1.0 was prepared by Yasuda et al.\(^8\) and found to be fairly active for the ROP of \( \varepsilon\)-CL at room temperature in toluene, yielding PCL with a high molecular weight and a narrow PDI (<1.1).\(^8\) The methyl complexes \( \text{Cp}^*\text{M}(\text{Me})(\text{THF})\) (\( \text{M} = \text{Sm} (1.1) \) and \( \text{Yb} (1.2) \)) were also prepared in the same study by Yasuda and were found to have a superior activity to 1.0, attributed to the relatively high sensitivity of the latter. The lower activity of 1.2 compared to 1.1 was also thought to be due to reduction (Yb(III) to Yb(II)) during the polymerisation process, which is less favoured in the case of 1.1 (i.e. Sm(III) to Sm(II)).\(^3\)

In a later study by Agarwal et al.,\(^8\) the alkoxide complexes \( \text{Cp}^*\text{M}(\text{OR})(\text{THF})\) (\( \text{M} = \text{Sm} (R = \text{Et} (1.3) \) or \( \text{Yb} (R = \text{Me} (1.4) \) were synthesised alongside the dimeric
Chapter 1

[\text{Cp}_2\text{Y(μ-OEt)}]_2 \text{(1.5)}. These were tested for the ROP of ε-CL and compared with 1.1 under identical polymerisation conditions. It was found that 1.1 displayed higher activity and also gave superior control over the $M_n$ and PDI values of the polymers formed. It was also shown through NMR studies that 1.3-1.5 initiated ROP by classical coordination-insertion, whereas 1.1 was shown to first form an acetal prior to an ongoing coordination-insertion mechanism.\textsuperscript{84}

**Figure 1.11.** ROP catalysts supported by cyclopentadienyl based ligands.

![ROP catalysts](image)

1.0 \hspace{10cm} M = \text{Sm (1.1) or Yb (1.2)}

M = Sm (1.3, R = Et) or Yb (1.4, R = Me)

1.5

1.7.3 ROP Initiators with O-Donor Supporting Ligands

The bis(phenolates) have been studied extensively as supporting ligands for aluminium, titanium, zirconium and the rare earth metals (Figure 1.12).\textsuperscript{52, 85-88} The aluminium bis(phenolate) 1.6 displayed a low activity for the ROP of rac-lactide, taking a number of days to polymerise 20-50 equivalents in refluxing toluene, although narrow polymers with narrow PDIs were yielded. The low activity of this catalyst is most likely due to its dimeric structure and significant degree of steric crowding around the metal centre.\textsuperscript{88} The titanium bis(phenolate) 1.7 was prepared by Nakamura\textsuperscript{87} and was active for the polymerisation of ε-CL over a period of five hours at room temperature, giving polymers with a good agreement between expected and
observed $M_n$ and a narrow PDI (1.2).\textsuperscript{87} However, no activity for the ROP of rac-LA was reported.

In 2008 Arnold \textit{et al.} reported the synthesis of a family of homoleptic phosphine oxide-alkoxide complexes (see 1.8 for an example).\textsuperscript{89} Such complexes were shown to produce isotactically enriched PLA ($P_r = 0.80$) from rac-LA at low temperature ($-18$°C). The polymers produced also had a good $M_n$ agreement and moderate PDIs (1.2-1.4).\textsuperscript{89}

\textbf{Figure 1.12}. ROP catalysts supported by O-donor ligands.

The calcium $\beta$-diketone complex 1.9 was prepared by Westerhausen and Feijen by protonolysis of an amide precursor with $^t$PrOH.\textsuperscript{90} 1.9 was shown to polymerise either $\varepsilon$-CL or rac-LA rapidly at room temperature in THF, albeit producing polymers with higher than expected $M_n$ values and broad PDIs.\textsuperscript{90} The dimeric neodymium and ytterbium bis(phenolate) alkoxides 1.10 and 1.11 were also shown to be active initiators for the ROP of $\varepsilon$-CL in toluene at room temperature over one hour (1.10) or up to eight hours (1.11). A very good $M_n$ agreement in the polymers formed was
observed, together with narrow PDIs (1.1-1.3). The extended reaction times were attributed to the dimeric nature of the complexes and the subsequently high degree of steric crowding around the metal centres (as argued in the case of 1.6). The higher activity of 1.10 relative to 1.11 is most likely due to the larger size of the metal ion in the former.

1.7.4 ROP Initiators with N,O-Donor Supporting Ligands

Mixed N,O-donor ligands have also been studied very successfully for the ROP of cyclic esters. The titanatrane aryloxide complex 1.12 (Figure 1.13) was synthesised by Verkade in 2002. This was shown to polymerise either L- or rac-LA over the course of 24 hours at 130 °C in the melt, yielding isotactic or atactic PLA respectively. In all cases polymers with higher than expected $M_n$ values (approximately twice the expected value) and broad PDIs (1.8-2.0) were observed. The amine bis(phenolate) titanium bis(alkoxide) 1.13 was prepared by Davidson and co-workers in 2006 and studied for the ROP of ε-CL. 1.13 polymerised 100 equivalents of ε-CL over 24 hours at room temperature, giving a polymer $M_n$ value consistent with two growing chains per metal centre, and a PDI of 1.2. In related work by Carpentier, the related amine bis(phenolate) yttrium amide (1.14) and alkyl (1.15) complexes were synthesised. These were shown to polymerise up to 500 equivalents of rac-LA at room temperature in THF, giving heterotactically enriched PLA ($P_r = 0.80$) with fairly narrow PDIs (1.2-1.4) and a good $M_n$ agreement. Carpentier later showed the capacity of this system towards the immortal polymerisation of lactide with alcohol co-initiators, yielding multiple polymer chains per metal centre alongside the aforementioned control of tacticity. Subsequent and ongoing work within the Mountford group has also shown the capability of the zwitterionic yttrium complex 1.16 to facilitate the immortal ROP of LA in the presence of alcohol and amine co-initiators, yielding excellent $M_n$ control, narrow PDI values (1.0-1.1) and highly heterotactically enriched polymers ($P_r$ values up to ca. 0.9).

Research based on the amine phenolate ligands was later extended further by the group of Davidson, where notably the amine tris(phenolate) Group 4 alkoxide complexes 1.17-1.19 were synthesised. Whilst the titanium complex 1.17 produced atactic PLA in
the melt at 130 °C with a higher than expected $M_n$ and a moderate PDI of 1.4, the zirconium (1.18) and hafnium (1.19) complexes gave highly heterotactically enriched polymer ($P_r = 0.96$ and 0.88 respectively) under identical conditions. The zirconium catalyst also showed excellent $M_n$ control, whilst the hafnium catalyst gave polymer with an $M_n$ value approximately twice that expected.

**Figure 1.13.** ROP catalysts supported by N,O-donor ligands.
Schiff base ligands have also been used as ancillary ligands in the preparation of ROP catalysts. For example, the calcium complex 1.20 was prepared recently by Darensbourg and co-workers in 2008. This was reported to polymerise up to 700 equivalents of rac-LA over 30 minutes at room temperature in THF, giving atactic PLA with a narrow (1.0-1.1) PDI and slightly higher than predicted \( M_n \) values. However, it was also shown that heterotactically enriched PLA could be obtained by carrying out the polymerisation at -33 °C. Chisholm had previously studied the related Schiff base zinc complexes 1.21 and 1.22 for the ROP of rac-LA. However, they displayed low and required times of 4 and 72 hours respectively at room temperature in THF to polymerise 20 equivalents. The relatively low activity of these complexes compared to 1.20 is likely to be a consequence of the smaller size of zinc(II) compared to calcium(II).

Spasský demonstrated the first stereoselective polymerisation of rac-LA employing methoxide complexes bearing the (R)-stereoisomer of the aluminium salen complex 1.23. It was shown that this complex selectively polymerised D-LA over L-LA (using rac-LA), forming isotactic PLA. The (R)-stereoisomer of 1.23 was subsequently shown by Coates to give highly syndiotactically enriched PLA from meso-LA.

1.7.5 ROP initiators with N-donor supporting ligands

With a view to alleviating the aggregation difficulties often associated with O-donor ligands, N-donor ligands have been widely studied. With the additional substitution site available for nitrogen when compared to oxygen, it would be expected that N-donor ligands would provide a more sterically encumbering environment around a metal centre.

The tris(pyrazolyl)hydroborate (Tp) and \( \beta \)-diketiminate ligands have been amongst the most widely exploited classes of N-donor ligands studied for ROP. The main advantages of these two ligand classes are their ease of preparation, the tuneability for substitution with bulky substituents and generally robust nature. Chisholm prepared the calcium amide and aryloxide Tp\( \text{tBu} \) complexes 1.24 and 1.25, which are amongst the most active initiators for the ROP of rac-LA to date, polymerising 200 equivalents at room temperature in THF in one minute (1.24) and five minutes (1.25).
Complex 1.24 yielded highly heterotactic PLA ($P_t > 0.90$) with a slightly higher than expected $M_n$ and a broad PDI (1.74). Similar 1.25 yielded highly heterotactic PLA ($P_t > 0.90$) with a very similar $M_n$ to that produced by 1.24 and a slightly narrower PDI (1.68). Both of these complexes were found to be more active than either the magnesium (1.26) or zinc (1.27) Tp£â€œBu alkoxide complexes prepared by the same group.24, 96 The order of activity was postulated to depend on the polarity of the initiating metal oxygen bond in the order Ca > Mg > Zn, with 1.26 and 1.27 also giving polymers with narrower PDIs (approximately 1.2). The compromise between activity and control is a feature common to ROP initiators across the periodic table when employing the same ancillary ligands on different metals. The zinc siloxide complex 1.28 had earlier been prepared by Chisholm;35 presumably it was anticipated that the presence of the CF$_3$ groups would enhance the Lewis acidity of the metal centre. However, it was found that this catalyst was almost inactive for the ROP of rac-LA at room temperature.35

**Figure 1.14.** ROP catalysts supported by N-donor ligands.
The $\beta$-diketiminate magnesium (1.29) and zinc (1.30) alkoxide complexes were reported by Coates in 2001\textsuperscript{40} and were both shown to be highly active for the ROP of rac-LA at room temperature in CH$_2$Cl$_2$, requiring 2 minutes and 20 minutes respectively to reach high monomer conversions. Atactic PLA with a moderate PDI of 1.6 and a higher than expected $M_n$ was formed in the case of 1.29, whereas highly heterotactic PLA ($P_t = 0.90$) with a very narrow PDI (1.10) and a close to expected $M_n$.\textsuperscript{40} Chisholm later reported that the $\beta$-diketiminate magnesium (1.31) and calcium (1.32) amides were active for the ROP of rac-LA.\textsuperscript{24} Interestingly, whilst 1.31 polymerised 200 equivalents of the monomer within 5 minutes in CH$_2$Cl$_2$ at room temperature yielding heterotactic PLA ($P_t = 0.90$), 1.32 required 2 hours and gave atactic PLA. This is the reverse of the trend seen for the Tp$^{\text{Bu}}$ complexes 1.25-1.27. The unexpectedly low activity and selectivity of 1.32 was attributed to the formation of aggregated species formed during the polymerisation process.\textsuperscript{24}

The bis(phosphinimino) zinc complexes 1.33 and 1.34 were reported by Hill in 2002.\textsuperscript{97} Interestingly, these were both found to be inactive for the ROP of rac-LA at room temperature in CH$_2$Cl$_2$ unlike the high activity of the $\beta$-diketiminate complexes 1.29-1.32. This was thought to be largely due to the relatively high degree of steric bulk present around the metal centre, as well as the possibility of non-innocent behaviour of the bridgehead carbon atom present in the PCP ligand. Despite this, 1.33 and 1.34 were shown to produce atactic PLA in toluene at 60 °C over a period of five and four hours, respectively.\textsuperscript{97}

The tridentate diamidoamino aluminium complexes 1.35 and 1.36 were found to be active for the ROP of rac-LA in benzene at 80 °C, with the hydride complex (1.36) proving to be approximately twice as active as the methyl complex (1.37). Both catalysts produced atactic PLA with broad PDIs (1.7).\textsuperscript{98} In other work by Tolman and Hillmyer\textsuperscript{71}, the Sn(II) amidinate complexes 1.37 and 1.38 were prepared. These were both active for the ROP of rac-LA, although both catalysts required a temperature of 80 °C in toluene. In both cases reasonable control was observed, producing polymers with slightly higher than expected $M_n$ values and narrow-to-moderate PDIs (1.2-1.5).\textsuperscript{98}
1.8 Summary

This Chapter has highlighted many important examples of research in the very active field of ROP. It can be seen that, whilst underdeveloped, catalysts of the main group are amongst the most active to date. Generally it is found that calcium complexes show a greater activity than those of magnesium, which are in turn more active than those of zinc. An extensive number of catalysts have also been prepared for the rare earth metals, Group 4 metals and tin, employing a diversity of supporting ancillary ligands bearing a range of substituents.

The activity and selectivity of a given catalyst has also been shown to generally be influenced by the choice of ancillary ligand. Hence there is a growing interest in the design and application of novel supporting ligand systems (as well as exploring new applications of existing systems). Chapters 3 and 4 provide further introductory material for borohydride based ROP catalysts and immortal ROP respectively.

1.9 Aims and Outlook

This thesis describes the synthesis, characterisation and ROP capability towards ε-CL and rac-LA of calcium, magnesium, zinc and yttrium N-donor ligand supported amide, alkoxide and borohydride catalysts. The solution state behaviour of the complexes synthesised will be discussed alongside solid state structural determinations that have been undertaken to elucidate the structure and bonding of the complexes presented. The study includes neutral, zwitterionic and cationic systems as well as the application of the latter towards the immortal ROP of rac-LA.

2.0 References

Chapter 1

Chapter Two

New Group 2 and 12 Scorpionate complexes and their activity towards the ROP of \(\varepsilon\)-caprolactone and rac-lactide
2.0 Overview

This Chapter will provide an introduction into Group 2 and 12 scorpionate complexes. An overview of the synthesis and characterisation of Group 2 and 12 neutral and zwitterionic halide and amide complexes supported by homo- and hetero-scorpionate ligands will be presented. Their solid state structures and solution behaviour will be discussed, in conjunction with their application to the ring-opening polymerisation (ROP) of cyclic esters. Comparison of the newly reported complexes and previously reported related complexes will be undertaken within the context of the solid state structures and the ROP activity and selectivity observed. The majority of this work has recently been published.\(^1\)

2.1 Introduction

The anionic poly(pyrazolyl)borates and their neutral poly(pyrazolyl)methane counterparts are among the most widely used ligands in coordination and organometallic chemistry. Figure 2.0 depicts in general terms the tris(pyrazolyl)hydroborate (I) and tris(pyrazolyl)methane (II) homologues. The development of these and other scorpionate type ligands, and the synthesis and reactions of their complexes, have been the subject of many reviews.\(^2\)-\(^9\)

Figure 2.0. Tris(pyrazolyl)hydroborate (I), tris(pyrazolyl)methane (II) and tris(pyrazolyl)methanide (III) ligands.

Removal of the C-bound apical proton from II generates the anionic tris(pyrazolyl)methanide III (Figure 2.0). III is isoelectronic with the hydroborate system I, but features ambidentate characteristics and two possible binding sites, namely the anionic carbon or the pyrazolyl ring nitrogens.\(^10\) Stone was the first to report a structurally authenticated derivative of tris(pyrazolyl)methanide, namely the trimetallic species 2.0 (Figure 2.1) which has an anionic \(\text{C(pz)}_3\) moiety bound through both the apical carbon and all three 2-position pyrazolyl nitrogens.\(^11\).\(^12\) Compound 2.0 was prepared from Pt(norbornene)(PMe\(_2\)Ph)\(_2\) and Ar\(^F\)Au\{κ\(^3\)C, κ\(^3\)N-C(pz)\(_3\)}W(CMe)(CO)\(_2\). The latter was not
isolated but prepared in situ by sequential treatment of cationic \([W\{HC(pz)_3\}(CMe)(CO)_2]^+\) with NaOEt and Au(ArF)(THT) (ArF = C_6F_5; THT = tetrahydrothiophene). Previous work in the Mountford group found that deprotonation of the apical C-H moiety of Ti\{HC(Me_2pz)_3\}(NR)Cl_2 with MeLi or LiN^Pr_2 in the presence of THF gave the zwitterionic species Ti\{C(Me_2pz)_3\}(NR)Cl(THF) (R = 'Bu (2.1a) or 2-C_6H_4'tBu (2.1b)). These complexes, containing a formally cationic titanium, were the first structurally authenticated examples of a “naked” \(sp^3\) hybridized carbanion.\(^{13, 14}\) Direct reaction of HC(Me_2pz)_3 with MeLi in THF also afforded a zwitterionic carbanion-containing species, namely Li\{C(Me_2pz)_3\}(THF) (2.2). The structural integrity of the latter was investigated in detail, both in solution and in the solid-state.\(^{13, 15, 16}\)

The 5-position methyl groups of the \(-C(Me_2pz)_3\) moiety in 2.1 and 2.2 offer significant steric protection around the carbanionic centre. Compound 2.2 is nonetheless an effective reagent for delivery of the \(-C(Me_2pz)_3\) moiety: reaction of Ti(N'tBu)Cl_2(py)_3 with 2.2 formed Ti\{C(Me_2pz)_3\}(N'tBu)Cl(py), analogous to 2.1a,\(^{13}\) and with CuCl(PPh_3) or (PPh_3)AgNO_3 the compounds 2.3 and 2.4 were obtained, each of which possesses a \(\kappa^3N-C(Me_2pz)_3\) ligand.\(^{17}\) Interestingly, reaction with AuCl(PMe_3) gave Au\{\kappa^1C-C(Me_2pz)_3\}(PMe_3) (2.5),\(^{17}\) a monometallic relative of the organogold complex (2.0) of Stone. Homoleptic first row transition metal methanide complexes have also been prepared by deprotonation of bound pyrazolylmethane ligands, namely M\{C(Me_2pz)_3\}_2 (M = Fe (2.6) or Co (2.7)), each of which show interesting electronic properties.\(^{18}\) Mixed-sandwich complexes of ruthenium(II) containing cyclopentadienyl and tris(pyrazolyl)methane ligands have been prepared recently,\(^{19}\) and zwitterionic complexes of the general formula Ru\{C(R_2pz)_3\}Cp^{R'} (Cp^{R'} = Cp, R = none or Me_2; Cp^{R'} = Cp*, R_2 = none) are thereby made accessible.\(^{10, 20}\) DFT studies of the various half-sandwich and sandwich-type complexes have supported the proposal of a localized carbanionic lone pair as depicted in Figures 2.0 and 2.1, and the electronic structures and metal charges are very similar to those of the tris(pyrazolyl)hydroborate analogues.\(^{13, 18, 21}\)
Figure 2.1. Examples of main group and transition metal tris(pyrazolyl)methanide complexes.

In addition to 2.2, other main group tris(pyrazolyl)methanide complexes have been reported recently.\textsuperscript{21} Reaction of BuMgCl with HC(Me$_2$pz)$_3$ gave the highly insoluble (and probably polymeric) [Mg{C(Me$_2$pz)$_3$}Cl]$_x$ (2.9). Reaction of MgBu$_2$ with HC(Me$_2$pz)$_3$ formed the magnesium sandwich complex Mg{C(Me$_2$pz)$_3$}$_2$, regardless of stoichiometry. Only on reaction with a large excess of MgPh$_2$ at low temperature, and after multiple recrystallisations, could the half-sandwich complex Mg{C(Me$_2$pz)$_3$}Ph(THF) (2.10) be obtained (in trace quantities). In contrast, reaction of ZnMe$_2$ with HC(Me$_2$pz)$_3$ only occurred after several days of heating to form Zn{C(Me$_2$pz)$_3$}Me (2.11). No reaction at all took place between ZnPh$_2$ and HC(Me$_2$pz)$_3$, and nor could a sandwich complex Zn{C(Me$_2$pz)$_3$}$_2$ (analogous to Mg{C(Me$_2$pz)$_3$}$_2$ (2.8)) be obtained. Detailed DFT studies of the reactions of magnesium and zinc alkyls with HC(Me$_2$pz)$_3$ were also reported.\textsuperscript{21}
While *homoscorpionate* ligands have the same three moieties appended to the apical group (e.g., BH, CH), another important class of poly(pyrazolyl) ligands are the *heteroscorpionates*. Here one of the pyrazolyl groups has been replaced by a different C-, O-, S- or N-donor moiety (Figure 2.2).8

**Figure 2.2.** The general structure of a bis(pyrazolyl)methane (IV) ligand (L = C-, O-, S- or N-donor group).

While much of the early work with heteroscorpionate complexes was concerned with synthetic and structural studies, several reports have focussed more on their applications in the areas of ring-opening polymerisation of cyclic esters22-25 (e.g. Mg{([Me₂pz]₂CHArO){N(SiHMe₂)₂} (2.12)26) and Ziegler-Natta polymerization catalysis27 (e.g. Ti{([Me₂pz]₂CHArO)Me₃ (2.13, Ar = C₆H₄Bu₂),28 Zr{([Me₂pz]₂CHSiMe₂NPr}-(CH₃SiMe₃)₃ (2.14) and Sc{([Me₂pz]₂CHSiMe₂NPr}((CH₃SiMe₃)₂ (2.15)27). Recently, preliminary results for Cr(III) ethylene trimerisation precatalysts 2.17 – 2.19 (Figure 2.3) featuring heteroscorpionate ligands were disclosed by Braunstein and Hor29-31, as well as in the Mountford group (2.20).32
Figure 2.3. Examples of heteroscorpionate complexes used as polymerisation and ethylene trimerisation catalysts.

2.2 Synthesis of Group 2 tris(pyrazolyl)methane and tris(pyrazolyl)methanide complexes

Scheme 2.0 summarises the reactions of HC(Me$_2$pz)$_3$ with Mg[N(SiMe$_3$)$_2$]$_2$ and the sterically less demanding Mg[N(SiHMe$_2$)$_2$]$_2$. The reaction with Mg[N(SiMe$_3$)$_2$]$_2$ proceeded smoothly at room temperature over 24 h to afford the half-sandwich compound Mg[C(Me$_2$pz)$_3$]{N(SiMe$_3$)$_2$} (1) in 50% recrystallised yield. In contrast to the reactions of HC(Me$_2$pz)$_3$ with MgBu$_2$ or MgPh$_2$ (see above),$^{21}$ there was no evidence of formation of Mg[C(Me$_2$pz)$_3$]$_2$ (2.8) under these conditions. 2.8 was nonetheless obtained from Mg[N(SiHMe$_2$)$_2$]$_2$ or Mg[N(SiMe$_3$)$_2$]$_2$ by reaction with 2 equivalents of HC(Me$_2$pz)$_3$ at 70 °C in C$_6$D$_6$ for 2 or 4 days, respectively.

The NMR spectra of 1 are consistent with the structure proposed in Scheme 2.0, assuming fast rotation about the Mg-N(SiMe$_3$)$_2$ bond. The solid state structure of 1 is shown in Figure 2.4 and confirms its zwitterionic nature and the presence of a cationic {Mg-N(SiMe$_3$)$_2$}$^+$ moiety. The approximately tetrahedral magnesium is κ$^3$N bound to a tris(pyrazolyl)methanide ligand featuring a naked carbanion at C(16).
Scheme 2.0. Reactions of Mg\{N(SiRMe₂)₂\}₂ (R = Me or H) with HC(Me₂pz)₃ or DC(Me₂pz)₃.
The Mg-N\textsubscript{pz} bond lengths (avg. 2.115 Å) are reasonably comparable to those in Mg\{C(Me\textsubscript{2}pz\textsubscript{3})\}Ph(THF) (avg. 2.135 Å)\textsuperscript{21} but significantly shorter than in Mg\{C(Me\textsubscript{2}pz\textsubscript{3})\}\textsubscript{2} (2.189(1) Å), consistent with the various steric factors and coordination number effects in the three compounds. The Mg-N(SiMe\textsubscript{3})\textsubscript{2} distance is within the expected range.\textsuperscript{33} The largest N\textsubscript{pz}-Mg-N(SiMe\textsubscript{3})\textsubscript{2} angle and longest Mg-N\textsubscript{pz} bond is associated with N(3) due to steric repulsions between the C(20) and C(21) methyl groups attached to Si(2) and the C(9) methyl group. The Si(1)Me\textsubscript{3} group has less steric impact on the other pyrazolyl rings (containing N(1,2) and N(5,6)) as it is able to lodge into the cleft between these rings.

**Figure 2.4.** Displacement ellipsoid plots (20% probability) of one of the two crystallographically independent molecules of Mg\{C(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiMe\textsubscript{3})\}\textsubscript{2} (1, left) and Mg\{κ\textsuperscript{2}N-HC(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiHMMe\textsubscript{2})\}\textsubscript{2} (2, right). C-bound H atoms omitted and remaining H atoms drawn as spheres of an arbitrary radius.

Table 2.0. Selected bond distances (Å) and angles (°) for Mg\{C(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiMe\textsubscript{3})\}\textsubscript{2} (1).

<table>
<thead>
<tr>
<th>Bond (Å)</th>
<th>Angle (°)</th>
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<tr>
<td>Mg(1)-N(1)</td>
<td>2.094(2)</td>
</tr>
<tr>
<td>Mg(1)-N(3)</td>
<td>2.152(2)</td>
</tr>
<tr>
<td>Mg(1)-N(5)</td>
<td>2.098(2)</td>
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<td>Mg(1)-N(7)</td>
<td>1.987(2)</td>
</tr>
<tr>
<td>N(1)-Mg(1)-N(7)</td>
<td>122.35(8)</td>
</tr>
<tr>
<td>N(3)-Mg(1)-N(7)</td>
<td>136.48(8)</td>
</tr>
<tr>
<td>N(5)-Mg(1)-N(7)</td>
<td>118.22(8)</td>
</tr>
</tbody>
</table>
Table 2.1. Selected bond distances (Å) and angles (°) for Mg{κ²N-HC(Me₂pz)₃}⁻·
{N(SiHMe₂)₂}₂ (2).

<p>| | | | |</p>
<table>
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<tbody>
<tr>
<td>Mg(1)-N(1)</td>
<td>2.147(3)</td>
<td>Mg(1)-N(8)</td>
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<tr>
<td>Mg(1)-N(3)</td>
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<td>N(1)-Mg(1)-N(3)</td>
<td>87.1(1)</td>
</tr>
<tr>
<td>Mg(1)-N(7)</td>
<td>2.008(3)</td>
<td>N(7)-Mg(1)-N(8)</td>
<td>127.8(1)</td>
</tr>
</tbody>
</table>

In related work carried out in collaboration with the Breher group at the University of Karlsruhe¹ further insights into possible intermediates formed en route to 1 were obtained. NMR studies were performed at low temperature. HC(Me₂pz)₃ was mixed in an NMR tube with an excess of Mg{N(SiMe₃)₂}₂ and toluene-<sub>d₈</sub> was condensed into the mixture. The sample was mixed and thawed at −100 °C and immediately transferred to a pre-cooled NMR probe. The initial ¹H NMR spectrum obtained at −100 °C is depicted in Figure 4. Several resonances for different pyrazolyl CH and methyl groups, trimethylsilyl groups as well as the apical C-H moiety were detected. Based on ROESY data, the individual resonances were assigned to the compound Mg{κ²N-HC(Me₂pz)₃}{N(SiMe₃)₂}₂ (2.21) containing a κ²N-HC(Me₂pz)₃ ligand.

**Figure 2.5.** The proposed structure of 2.21.

Three sets of resonances for three different Me₂pz groups were observed suggesting restricted rotation of the non-coordinated Me₂pz group. Due to this, both coordinated Me₂pz ligands become inequivalent (two broad pairs of signals at 2.69/2.57 and 1.65/0.88 (Me) and a pair of pyrazolyl H atoms at 5.13/4.81 ppm (CH₉)). The non-coordinated Me₂pz ring shows three signals at 2.18 and 1.24 (Me) and 5.67 (CH₉). Furthermore, four different signals for inequivalent SiMe₃ groups were detected at 1.03, 0.70, 0.54 and 0.06 ppm. The proposed structure of 2.21 is consistent with the structurally characterized complex 2 discussed below. Warming the sample to between −80 and −60 °C (see Figure 2.6) leads to
an exchange regime in which the two coordinated Me₂pz ligands become equivalent (free rotation of the pendant Me₂pz unit on the NMR time-scale). At higher temperatures, a second fluxional process is observed in which the two different types of Me₂pz groups are in exchange. At temperatures above 0 °C the formation of 1 and HN(SiMe₃)₂ is observed leading to a clean sample without any by-products after leading the sample overnight at room temperature (top trace in Figure 2.6).

**Figure 2.6.** Variable temperature \(^1\)H NMR spectra of a mixture of HC(Me₂pz)₃ and Mg{N(SiMe₃)₂}₂ in toluene-\(d_8\) (~ = signals of HC(Me₂pz)₃; * = signals of Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1); # = residual solvent peaks of toluene).

It is well-established that changing from the bulky N(SiMe₃)₂ to the smaller N(SiHMe₂)₂ can reduce steric compression within complexes and help stabilize otherwise highly
crowded complexes. Therefore studies were extended to the less bulky amide \( \text{Mg}\{\text{N(SiHMe}_2\text{)}_2\}_2 \). Indeed, reaction of \( \text{HC(Me}_2\text{pz)}_3 \) with \( \text{Mg}\{\text{N(SiHMe}_2\text{)}_2\}_2 \) at room temperature for 2 h gave the relatively stable complex \( \text{Mg}\{\kappa^2\text{N-}} \text{HC(Me}_2\text{pz)}_3\}\{\text{N(SiHMe}_2\text{)}_2\}_2 \) (2) in 65% recrystallised yield. In agreement with the NMR studies on unstable 2.21, compound 2 is an adduct between a neutral bidentate \( \text{HC(Me}_2\text{pz)}_3 \) and a bent \( \text{Mg}\{\text{N(SiHMe}_2\text{)}_2\}_2 \) moiety. \( \kappa^2\text{N-} \)Bound \( \text{HC(Me}_2\text{pz)}_3 \) ligands have been reported previously, in particular for later transition metals with \( d^8 \) valence configurations. Four-coordinate compounds of the type \( \text{Mg}\{\text{N(SiMe}_3\text{)}_2\}_2\{(L)\}_2 \) have also been structurally characterized previously. The solid state structure of 2 is shown in Figure 2.4 along with selected bond distances and angles. The geometry about Mg(1) is distorted tetrahedral with the largest angle between the amide nitrogens N(7) and N(8). The Mg-N\text{pz}_3 distances (avg. 2.143 Å) are considerably shorter than those in six-coordinate \( \text{Mg}\{\text{HC(Me}_2\text{pz)}_3\}\text{Cl}_2(\text{THF}) \) (avg. 2.271 Å), the only other crystallographically characterized neutral \( \text{HC(Me}_2\text{pz)}_3 \) adduct of a Group 2 metal. The Mg-N(SiHMe2)_2 distances in 2 are comparable to those in the aforementioned \( \text{Mg}\{\text{N(SiMe}_3\text{)}_2\}_2\{(L)\}_2 \) species. The non-coordinated \( \text{Me}_2\text{pz} \) group containing N(5,6) is orthogonally orientated to both other pyrazolyl moieties due to steric factors, supporting the structure of 2.21 proposed on the basis of NMR measurements.

The NMR spectra of 2 are broad at room temperature indicative of one or more fluxional processes. Cooling to \( -65 \) °C in CD\(_2\)Cl\(_2\) resulted in a sharp \( ^1\text{H} \) NMR spectrum consistent with the solid state structure and comparable to those obtained for 2.21. Two sets of resonances (relative ratio 1:2) for \( \text{Me}_2\text{pz} \) groups were observed, consistent with a \( \kappa^2\text{N-} \)HC(Me\(_2\)pz\(_3\)) ligand. Three broad doublets for the methyl groups of different SiHMe\(_2\) groups were observed in the ratio 12H:6H:6H at \( -0.30, 0.01 \) and \( -0.48 \) ppm. These are assigned to the methyl groups of Si(1, 2) (made equivalent by the approximate \( C_s \) molecular symmetry), Si(3) and Si(4), respectively, assuming restricted rotation about Mg(1)-N(8). The low-frequency shift of the Si(4) methyl groups is due to magnetic anisotropy effects from the nearby Me\(_2\)pz rings. Warming the sample to \( -40 \) °C leads to fast exchange between Si(3)HMe\(_2\) and Si(4)HMe\(_2\) on the NMR timescale. Further warming to room temperature leads to an intermediate exchange regime in which the two N(SiHMe\(_2\)) ligands and two different types of Me\(_2\)pz group are now undergoing exchange. Importantly, no exchange was found between the bound HC(Me\(_2\)pz\(_3\)) ligand of 2 and free HC(Me\(_2\)pz\(_3\)) purposefully added to the NMR sample, showing that the Me\(_2\)pz group exchange process is an intramolecular process.
Figure 2.7. The proposed structure of \textit{Int\_exchange}.

![Int\_exchange](image)

The Me\textsubscript{2}pz group exchange process could in principle proceed either through a five-coordinate intermediate Mg\{κ\textsuperscript{3}N-HC(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiHMe\textsubscript{2})\textsubscript{3}\}\textsubscript{2} (\textit{Int\_exchange}) or a three-coordinate alternative Mg\{κ\textsuperscript{1}N-HC(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiHMe\textsubscript{2})\textsubscript{3}\}\textsubscript{2}. The rate constants for Me\textsubscript{2}pz group exchange were therefore determined at 6 different temperatures in the range \(\text{\textdegree}C\) and the relevant Eyring plot is shown in Figure 2.8.\textsuperscript{37} The derived activation parameters are \(\Delta H^\ddagger = 46.1(1)\) kJ mol\(^{-1}\) and \(\Delta S^\ddagger = -39(3)\) J mol\(^{-1}\) K\(^{-1}\) \((\Delta G^\ddagger_{(273K)} = 56.7(2)\) kJ mol\(^{-1}\)). The negative \(\Delta S^\ddagger\) term is consistent with a more ordered transition state, and therefore more indicative of a five-coordinate intermediate (associative-type exchange) such as \textit{Int\_exchange}. Related exchange mechanisms are known for tris(pyrazolyl)hydroborate complexes of transition metals.\textsuperscript{38} Structurally characterized analogues of \textit{Int\_exchange} include Mg\{C(Me\textsubscript{2}pz\textsubscript{3})\}\textsubscript{2}Ph(THF) (2.21),\textsuperscript{21} Mg\{HB(Me\textsubscript{2}pz\textsubscript{3})\}\textsubscript{2}Et(THF),\textsuperscript{39} Ca\{HB(\textit{i}Prpz)\}\textsubscript{3}\{N(SiMe\textsubscript{3})\textsubscript{2}\}(THF) (\textit{i}Prpz = 3\textit{-iso}propyl pyrazolyl),\textsuperscript{40} and Ca\{C(Me\textsubscript{2}pz\textsubscript{3})\}\textsubscript{2}\{N(SiMe\textsubscript{3})\textsubscript{2}\}(THF) (4).

Figure 2.8. Eyring plot for Me\textsubscript{2}pz ring exchange in Mg\{κ\textsuperscript{2}N-HC(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiHMe\textsubscript{2})\textsubscript{2}\}\textsubscript{2} (2). Derived activation parameters: \(\Delta H^\ddagger = 46.1(1)\) kJ mol\(^{-1}\); \(\Delta S^\ddagger = -39(3)\) J mol\(^{-1}\) K\(^{-1}\); \(\Delta G^\ddagger_{(273K)} = 56.7(2)\) kJ mol\(^{-1}\).
While 2.21 was found to lead to 1 readily at temperatures above 0 °C, the analogous conversion of 2 takes place only at higher temperatures. Heating a solution of 2 in C₆D₆ at 70 °C for several hours led quantitatively to the zwitterionic mono(amide) compound Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3, Scheme 2.0) and 1 equiv. of HN(SiHMe₂)₂. Compound 3 is the homologue of Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1) and was obtained on a preparative scale directly from HC(Me₂pz)₃ and Mg{N(SiHMe₂)₂}₂ in 49% yield after recrystallization from toluene. The ¹H and ¹³C NMR spectra of 1 and 3 are very similar. In particular, the carbanion carbon resonance C(Me₂pz) appears at 72.5 and 71.9 ppm, respectively, in the ¹³C NMR spectra of the two compounds.

The isolation of the intermediate 2 as a relatively stable and crystalline material at room temperature, and its well-behaved conversion to 3, provided the opportunity to probe the C–H bond breaking event that leads from pyrazolylmethane to pyrazolylmethanide in the reactions of main group alkyls and amides with HC(Me₂pz)₃ (i.e., the formation of compounds of the type M{C(Me₂pz)₃}X in general (Figure 2.1 and Scheme 2.0). To this end the deuterated analogue of 2, namely Mg{κ²N-DC(Me₂pz)₃}{N(SiHMe₂)₂}₂, was also synthesised (2-d), from DC(Me₂pz)₃ and Mg{N(SiHMe₂)₂}₂. Isotopomer 2-d is identical to 2 except for the presence of an apical C–D in the pyrazolylmethane ligand. As for 2, heating a solution of 2-d in C₆D₆ for several hours quantitatively formed 3 (along with 1 equiv. of DN(SiHMe₂)₂).

Figure 2.9 shows the first order log plots for the conversion of Mg{κ²N-HC(Me₂pz)₃}{N(SiHMe₂)₂}₂ (2) and Mg{κ²N-DC(Me₂pz)₃}{N(SiHMe₂)₂}₂ (2-d) to Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3) in C₆D₆ at 50 °C. The linear nature of the plots and near-unity R² values are consistent with first order, intramolecular processes. The first order rate constants are k(H) = 2.07(1) x 10⁻⁴ s⁻¹ and k(D) = 1.08(1) x 10⁻⁴ s⁻¹ for the protio- and deutero-systems, respectively, and show a clear primary kinetic isotope effect (KIE = k(H)/k(D) = 1.91(2)). Therefore the C–H (for 2) or C–D (for 2-d) bond cleavage occurs in the rate-limiting step (as opposed to some other reorganisation step being critical). The magnitude of k(H)/k(D) is within the usual ranges for concerted processes.⁴¹
Figure 2.9. First order plots for the conversion of Mg{κ²N-HC(Me₂pz)₃}{N(SiHMe₂)₂}₂ (2, red circles, \( R^2 = 0.997 \)) and Mg{κ²N-DC(Me₂pz)₃}{N(SiHMe₂)₂}₂ (2-d, blue squares, \( R^2 = 0.998 \)) to Mg{C(Me₂pz)₃}{N(SiHMe₂)₂}₂ (3) in C₆D₆ at 50 °C. \( I \) and \( I_0 \) refer to the normalized concentrations of 2 or 2-d at the given time and at time = 0, respectively. \( k(H) = 2.07(1) \times 10^{-4} \) s⁻¹; \( k(D) = 1.08(1) \times 10^{-4} \) s⁻¹; \( k(H)/k(D) = 1.91(2) \).

![Figure 2.9](image)

Figure 2.10. The proposed structure of Int_C–H

Although not detectable by NMR spectroscopy, it is proposed that the reaction coordinate leading to C–H activation (i.e., \( 2 \rightarrow 3 \) and also \( 2.21 \rightarrow 1 \)) is related to that suggested above for intramolecular pyrazolyl ring exchange within 2 (i.e., Int_exchange), but instead may proceed through a first formed intermediate of the type Mg{κ⁴C,κ²N-C(Me₂pz)₃}{N(SiMe₂)₂}{HN(SiMe₂)₂} (Int_C–H) (R = Me or H). Loss of HN(SiMe₂)₂ or HN(SiHMe₂)₂ and κ⁴C,κ²N-C(Me₂pz)₃ \( \rightarrow \) κ³N-C(Me₂pz)₃ rearrangement subsequently forms 1 or 3, respectively. As mentioned in the Introduction (Section 2.2), structurally authenticated examples of C-metallated pyrazolylmethylidene have been reported previously (2.0 and 2.5, Figure 2.1).\(^{11, 17}\) The compound Cd{C(Me₂pz)₃}{κ⁻¹C, κ²N-C(pz)₃},

\[\text{Int}_C\text{–H (R = H or Me)}\]
synthesised by collaborators, is shown by crystallography and NOESY spectra to contain a \( \kappa^1C, \kappa^2N \)-bound pyrazolylmethylamide ligand. Previous DFT calculations for model compounds \( M\{\kappa^1C-C(Me_2pz)_3\}Me \) (2-coordinate; \( M = \text{Mg or Zn} \)) and \( M\{\kappa^3N-C(Me_2pz)_3\}Me \) (4-coordinate) predicted a substantial thermodynamic preference for the conversion of \( M\{\kappa^1C-C(Me_2pz)_3\}Me \) to \( M\{\kappa^3N-C(Me_2pz)_3\}Me \) (199.2 and 111.3 kJ mol\(^{-1}\) for \( M = \text{Mg and Zn, respectively} \)). The experimental observations that only 1 or 3, rather than Int\(_C\)–H or its amine-free analogue, are obtained from 2.21 or 2 are consistent with these previous calculations.

As shown in Scheme 2.0, both \( \text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}((\text{SiMe}_3)_2)\} \) (1) and \( \text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}((\text{SiHMe}_2)_2)\} \) (3) reacted slowly with further \( \text{HC}(\text{Me}_2\text{pz})_3 \) at 70 °C in \( \text{C}_6\text{D}_6 \) to form \( \text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}_2 \). Under identical conditions of temperature and concentration, the reaction time for 1 (ca. 3 days) was noticeably longer than for 3 (ca. 2 days). Since the formation of 1 from the intermediate adduct 2.21 was faster than for the less sterically encumbered system (i.e. 2 → 3), the slower reaction of 1 with additional \( \text{HC}(\text{Me}_2\text{pz})_3 \) can be attributed to a more effective steric shielding of the magnesium centre in 1 by the bulky amide (this is consistent with the faster rates of reaction of the calcium congener, see below). We were not able to detect any pre-coordination of \( \text{HC}(\text{Me}_2\text{pz}) \) to \( \text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}\{\text{N}((\text{SiRMe}_2)_2)\} \) (\( R = \text{H or Me} \)) when the reactions were followed on the NMR tube scale, either at low or high temperature.

As shown in Figure 2.11, the reaction between 3 and 10 equivalents of either \( \text{HC}(\text{Me}_2\text{pz})_3 \) or \( \text{DC}(\text{Me}_2\text{pz})_3 \) at 50 °C in \( \text{C}_6\text{D}_6 \) follows pseudo first order kinetics with observed rate constants \( k_{\text{obs}}(\text{H}) = 6.75(2) \times 10^{-5} \text{ s}^{-1} \) and \( k_{\text{obs}}(\text{D}) = 4.50(2) \times 10^{-5} \text{ s}^{-1} \), respectively, for the consumption of 3. The \( k_{\text{obs}}(\text{H})/k_{\text{obs}}(\text{D}) \) value of 1.51(4) indicates a slightly reduced primary KIE for \( 3 \rightarrow \text{Mg}\{\text{C}(\text{Me}_2\text{pz})_3\}_2 \) compared with that for \( 2 \rightarrow 3 \) (Figure 2.9), but the two KIEs are nonetheless broadly similar.
Figure 2.11. Pseudo first order plots for the reaction of Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3) with an excess (10 equivalents.) of HC(Me₂pz)₃ (red circles, $R^2 = 0.998$) or DC(Me₂pz)₃ (blue squares, $R^2 = 0.997$) at 50 °C to form Mg{C(Me₂pz)₃}₂. I and I₀ refer to the normalized concentration of 3 at the given time and at time = 0, respectively. $k_{obs}(H) = 6.75(2) \times 10^{-5}$ s⁻¹; $k_{obs}(D) = 4.50(2) \times 10^{-5}$ s⁻¹; $k_{obs}(H) / k_{obs}(D) = 1.51(4)$.

The reactions of the heavier congener Ca{N(SiMe₃)₂}₂(THF)₂ with HC(Me₂pz)₃ are summarized in Scheme 2.1. Reaction with 1 or 2 equivalents of tris(dimethylpyrazolyl)methane afforded the 5-coordinate half-sandwich compound Ca{C(Me₂pz)₃}{N(SiMe₃)₂}(THF) (4) or the homoleptic analogue Ca{C(Me₂pz)₃}₂ (5) in 85% and 61% isolated yield, respectively. These are the first tris(pyrazolyl)methanide complexes of calcium. Both reactions were significantly faster than for those of Mg{N(SiRMe₂)₂}₂ (R = H or Me, Scheme 2.0). Compound 4 reacted readily with HC(Me₂pz)₃ in C₆D₆ to form 5 quantitatively after 2 hours at room temperature. As mentioned above, the corresponding reaction for magnesium (i.e., 1 → Mg{C(Me₂pz)₃}₂) required 3 days at 70 °C under otherwise identical conditions. These observations may be attributed, at least in part, to the reduced steric effects for the larger metal. The carbanion carbon resonance $\text{C}(\text{Me₂pz})₃$ for 4 appears at 72.4 ppm in the $^{13}$C NMR spectrum, which is very similar to the corresponding values for 1 and 3 (72.5 and 71.9 ppm, respectively) and typical for tris(pyrazolyl)methanide complexes featuring “free” carbanions. Unfortunately, compound 5 was too insoluble to obtain a satisfactory $^{13}$C NMR spectrum.
Scheme 2.1. Reactions of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ with HC(Me$_2$pz)$_3$.

The solid state structures of Ca{C(Me$_2$pz)$_3$}[N(SiMe$_3$)$_2$](THF) (4) and Ca{C(Me$_2$pz)$_3$}$_2$ (5) are shown in Figure 2.12. Together with the NMR and other data, these confirm the presence of cationic calcium centers with one or two carbanionic moieties, respectively. Compound 4 has a distorted trigonal bipyramidal geometry at Ca(1). The N(SiMe$_3$)$_2$ ligand occupies one of the equatorial coordination sites, and the THF donor and N(1) of the C(Me$_2$pz)$_3$ ligand are in the axial positions. An analogous geometry was reported by Chisholm for the tris(pyrazolyl)hydroborate compound Ca{HB(iPrpz)$_3$}{N(SiMe$_3$)$_2$}(THF). The distances and angles around calcium in this complex are comparable to those in 4. The aforementioned Mg{C(Me$_2$pz)$_3$}Ph(THF) (11) also has an approximately trigonal bipyramidal geometry at magnesium with the Ph and THF ligands in equatorial and axial positions, respectively. Compound 5 possesses an almost ideal $D_{3d}$ symmetric structure and is the analogue of both Mg{C(Me$_2$pz)$_3$}$_2$ and the bis(hydroborate) compound Ca{HB(Me$_2$pz)$_3$}$_2$. The average Ca-N$_{pz}$ distance in 5 (avg. 2.448 Å, range 2.437(2) – 2.459(2) Å) is experimentally identical to that in Ca{HB(Me$_2$pz)$_3$}$_2$ (2.454(2) Å) as expected based on previous comparisons of homoleptic complexes of the two types of ligand (e.g., for Mg{C(Me$_2$pz)$_3$}$_2$ and Mg{HB(Me$_2$pz)$_3$}$_2$ average Mg-N$_{pz}$ distances of 2.189 and 2.186 Å were found).
Figure 2.12. Displacement ellipsoid plots (20% probability) of 
Ca\{C(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiMe\textsubscript{3})\textsubscript{2}\}(THF) (4, left) and Ca\{C(Me\textsubscript{2}pz\textsubscript{3})\}\textsubscript{2} (5, right). H atoms omitted.

Table 2.2. Selected bond distances (Å) and angles (°) for Ca\{C(Me\textsubscript{2}pz\textsubscript{3})\}\{N(SiMe\textsubscript{3})\textsubscript{2}\}-
(THF) (4).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
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<tbody>
<tr>
<td>Ca(1)-N(1)</td>
<td>2.436(7)</td>
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<td>Ca(1)-N(3)</td>
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<td>Ca(1)-N(5)</td>
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<td>N(5)-Ca(1)-N(7) 155.9(2)</td>
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<td>Ca(1)-N(7)</td>
<td>2.322(6)</td>
<td>O(1)-Ca(1)-N(7) 96.8(2)</td>
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</table>

Table 2.3. Selected bond distances (Å) and angles (°) for Ca\{C(Me\textsubscript{2}pz\textsubscript{3})\}\textsubscript{2} (5).

<table>
<thead>
<tr>
<th>Bond</th>
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<td>Ca(1)-N(1)</td>
<td>2.4370(18)</td>
<td>N(1)-Ca(1)-N(3) 77.81(6)</td>
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<td>Ca(1)-N(3)</td>
<td>2.4591(16)</td>
<td>N(1)-Ca(1)-N(5) 77.43(6)</td>
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<tr>
<td>Ca(1)-N(5)</td>
<td>2.448(2)</td>
<td>N(3)-Ca(1)-N(5) 75.48(6)</td>
</tr>
</tbody>
</table>
2.3 Synthesis of Group 12 tris(pyrazolyl)methanide complexes

In order to develop further the chemistry of Group 12 tris(pyrazolyl)methanide complexes, the only previous example being Zn{C(Me$_2$pz)$_3$}Me (2.11, Figure 2.1), attention was turned to the synthesis and structures of new zinc (Scheme 2.2) complexes. As stated in the Introduction, HC(Me$_2$pz)$_3$ reacts rapidly with MgR$_2$ (R = Bu or Ph) at room temperature to form homoleptic Mg{C(Me$_2$pz)$_3$}$_2$. In contrast, even on heating with an excess of ZnMe$_2$, it takes several days for the half-sandwich derivative Zn{C(Me$_2$pz)$_3$}Me (2.11) to form, and a homoleptic zinc analogue of Mg{C(Me$_2$pz)$_3$}$_2$ could not be obtained. Unsurprisingly, therefore, the reactions of Zn{N(SiMe$_3$)$_2$}$_2$ with HC(Me$_2$pz)$_3$ yielded only trace amounts of product, even after extended periods of time (ca. 3 weeks) under thermally forcing conditions in refluxing hexanes. However, heating a solution of Li{C(Me$_2$pz)$_3$}(THF) (2.2) with anhydrous ZnCl$_2$ in THF for 24 h gave the sparingly soluble, half-sandwich complex Zn{C(Me$_2$pz)$_3$}Cl (6) in 40% yield after extraction into hot benzene. Subsequent reaction of 6 with NaN(SiMe$_3$)$_2$ or LiN(SiHMe)$_2$$_2$ formed Zn{C(Me$_2$pz)$_3$}{N(SiRMe)$_2$}$_2$ (R = Me (7) or H (8)) in ca. 70% yield. The EI mass spectra of the three compounds 6 – 8 showed molecular ions with the expected isotope distributions, and the $^{13}$C NMR spectra revealed resonances for the carbanion carbons C(Me$_2$pz)$_3$ in the range 71.3 – 73.0 ppm, as expected. Neither 7 nor 8 reacted with HC(Me$_2$pz)$_3$ on heating at 70 °C for 1 week in C$_6$D$_6$. Nonetheless, the homoleptic compound Zn{C(Me$_2$pz)$_3$}$_2$ (9) could be alternatively prepared by salt metathesis from ZnCl$_2$ and 2 equivalents of 2.2 after heating at 70 °C for 3 days. The NMR and other data for 9 are comparable to those for the magnesium and calcium analogues Mg{C(Me$_2$pz)$_3$}$_2$ and 5.
Scheme 2.2. Synthesis of sandwich and half-sandwich zinc complexes.

Figure 2.13 shows the solid state structures of Zn{C(Me₂pz)₃}Cl (6, left) and Zn{C(Me₂pz)₃}{N(SiMe₃)₂} (7, right); that of Zn{C(Me₂pz)₃}₂ (9) is given in Figure 2.14. The geometries around Zn(1) in 7 and 9 are analogous to those around magnesium in the analogous Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1) and Mg{C(Me₂pz)₃}₂ respectively. The M-N distances for the zinc complexes are systematically shorter as expected based on atomic radius trends.⁴³

Although these are the first structurally characterized tris(pyrazolyl)methanide complexes of zinc, the structures of a large number of tris(pyrazolyl)hydroborate complexes of this element have been reported.³³ In general, the Zn-Cl, Zn-N₉ and Zn-N(SiMe₃)₂ distances for 6 – 9 lie within the expected literature ranges.³³ The Zn-Cl and average Zn-N₉ bond lengths in 6 are comparable to those of Zn{HB(Me₂pz)₃}Cl⁴⁴ (2.152(3) vs. 2.170(5), and 2.009 vs. 2.015 Å). Likewise, the structural data for 9 are similar to those of Zn{HB(Me₂pz)₃}₂⁴⁵ with average Zn-N₉ distances of 2.162 and 2.177 Å, respectively. The dication [Zn{HC(Me₃pz)₃}₂]²⁺ (Me₃pz = 3,4,5-trimethylpyrazolyl) has also been structurally characterized⁴⁶ and has an average Zn-N₉ distance (2.166 Å) that is very similar to that of
Although this is at first sight surprising, it was previously found that the magnesium sandwich dication \([\text{Mg}\{\text{HC(Me}_2\text{pz)}_3\}_2]^{2+}\) has an average \(\text{Mg–N}_\text{pz}\) bond distance of 2.168 Å that is slightly shorter than in \(\text{Mg}\{\text{C(Me}_2\text{pz)}_3\}_2\), despite the negative charge of the tris(pyrazolyl)methanide ligands in the latter.\(^{21}\)

No tris(pyrazolyl)hydroborate analogue of \(7\) has been structurally characterized, but the \(\text{Zn–N(SiMe}_3\text{)}_2\) distance of 1.913(5) Å is identical within error to the average distance (1.918 Å) for this bond in several 4-coordinate compounds containing a monoanionic \(\text{N}_3\) donor ligand (or ligand set).\(^{33, 47, 48}\) Compound \(7\) possesses a cationic \(\{\text{Zn–N(SiMe}_3\text{)}_2\}^+\) moiety and two related (but non-zwitterionic) systems have been structurally characterized recently.\(^{49, 50}\) The \(\text{Zn–N(SiMe}_3\text{)}_2\) bond distance in \(7\) is identical within error to that in 4-coordinate \([\text{Zn}\{\text{N(SiMe}_3\text{)}_2\}\{\text{OEt}_2\}_3]^+\) (\(\text{Zn–N} = 1.907(3)\) Å) but longer than in \([\text{Zn}\{\text{N(SiMe}_3\text{)}_2\}\{\text{ArNC(Me)(Me)NAr}\}]^+\) (\(\text{Zn–N} = 1.852(4)\) Å; \(\text{Ar} = 2,6-\text{C}_6\text{H}_3\text{Ph}_2\)) which possesses a 3-coordinate zinc cation.

**Figure 2.13.** Displacement ellipsoid plots (20 %) of one of the two crystallographically independent molecules of \(\text{Zn}\{\text{C(Me}_2\text{pz)}_3\}\text{Cl}\ (6, \text{left})\) and \(\text{Zn}\{\text{C(Me}_2\text{pz)}_3\}\{\text{N(SiMe}_3\text{)}_2\} \quad \text{(7, right)}\. H atoms omitted.
Table 2.4. Selected bond distances (Å) and angles (°) for Zn{C(Me$_2$pz)$_3$}Cl (6).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
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<tbody>
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<td>Zn(1)-N(1)</td>
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<td>N(1)-Zn(1)-Cl(1) 124.6(2)</td>
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<tr>
<td>Zn(1)-N(3)</td>
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<td>N(3)-Zn(1)-Cl(1) 124.9(2)</td>
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<tr>
<td>Zn(1)-N(5)</td>
<td>2.016(7)</td>
<td>N(5)-Zn(1)-Cl(1) 122.9(2)</td>
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<tr>
<td>Zn(1)-Cl(1)</td>
<td>2.152(3)</td>
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</tbody>
</table>

Table 2.5. Selected bond distances (Å) and angles (°) for Zn{C(Me$_2$pz)$_3$}{N(SiMe$_3$)$_2$} (7).

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<td>N(2)-Zn(1)-N(7) 123.7(2)</td>
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<td>Zn(1)-N(4)</td>
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<td>N(4)-Zn(1)-N(7) 136.4(2)</td>
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<tr>
<td>Zn(1)-N(6)</td>
<td>2.039(5)</td>
<td>N(6)-Zn(1)-N(7) 115.7(2)</td>
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<tr>
<td>Zn(1)-N(7)</td>
<td>1.913(5)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.14. Displacement ellipsoid plot (20 %) of Zn{C(Me$_2$pz)$_3$}$_2$ (23).
Table 2.6. Selected bond distances (Å) and angles (°) for Zn{C(Me₂pz)₃}₂ (9).

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<td>N(2)-Zn(1)-N(4)</td>
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</tr>
<tr>
<td>Zn(1)-N(4)</td>
<td>2.180(2)</td>
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<tr>
<td>N(2)-Zn(1)-N(6)</td>
<td>84.40(6)</td>
<td></td>
</tr>
<tr>
<td>Zn(1)-N(6)</td>
<td>2.163(2)</td>
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<tr>
<td>N(4)-Zn(1)-N(6)</td>
<td>85.58(6)</td>
<td></td>
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</tbody>
</table>

2.4 Synthesis of heteroleptic zwitterionic sandwich complexes

In contrast to the successful synthesis of Mg{C(Me₂pz)₃}₂, attempts to prepare a homoleptic complex Mg{C(pz)₃}₂ from MgBu₂ and the “parent” HC(pz)₃ gave only poorly soluble materials.²¹ This may be due to the several different potential coordination modes available to a sterically unconstrained tris(pyrazolyl)methanide ligand. Indeed, Stone’s trimetallic compound 2.0 (Figure 2.1)¹¹ and Ru{C(pz)₃}Cp²⁰ are the only examples of unsubstituted tris(pyrazolyl)methanide complexes. It was therefore hoped that the already-introduced C(Me₂pz)₃ co-ligand in 1 or 4 would provide a sterically stabilising influence and allow the introduction of an unsubstituted tris(pyrazolyl)methanide ligand.

Equation 2.0 summarises the reactions of 1 and 4 with HC(pz)₃ which formed the target complexes of the composition M{C(Me₂pz)₃}{C(pz)₃} (M = Mg (10) or Ca (11)) in ca. 55 – 75% yield. As for the corresponding reactions with HC(Me₂pz)₃ described above, more forcing conditions were needed for making 10 compared to 11. The ¹H and ¹³C NMR spectra of 10 and 11 are consistent with C₃ᵥ molecular symmetry and the EI mass spectra showed the expected molecular ions. Furthermore, the ¹³C{¹H} NMR spectra of each showed resonances (assigned using the corresponding HMBC spectra) for two carbanionic carbons, namely C(Me₂pz)₃ (72.1 and 72.8 ppm) and C(pz)₃ (89.1 and 89.0 ppm) for 10 and 11 respectively. The difference in chemical shift between the tris(pyrazolyl)methanide C(Me₂pz)₃ and C(pz)₃ resonances (Δδ = ca. 16.6 ppm) is somewhat larger than that between the tris(pyrazolyl)methane protio-ligands themselves (Δδ = 2.3 ppm; δ HC(Me₂pz)₃ = 81.2 ppm; δ HC(pz)₃ = 83.5 ppm). The nitrogen chemical shifts of both tris(pyrazolyl)methanide ligands C(Me₂pz)₃ and C(pz)₃ in complex 10 (indirectly measured from the ¹H,¹⁵N gHMQC spectrum) slightly differ from each other. Closer examination of the the ¹⁵N NMR cross-peaks allowed observation of the expected four nitrogen chemical shifts (δ = 232, 270 ppm (C(Me₂pz)₃) and 240, 278 ppm (C(pz)₃)), which is a priori consistent with the formulation of two κ³N-coordinated ligands.
Equation 2.0

The solid state structure of \(10\) is shown in Figure 2.15 and confirms that proposed in Equation 2.0. Given the similarity of the spectroscopic data for \(10\) and \(11\) it is reasonable to assume that the two congeners have similar molecular structures. The Mg-N\(_{pz}\) distances for the C(Me\(_2\)pz\(_3\)) ligand (avg. 2.169 Å) are on average shorter than for C(pz\(_3\)) (avg. 2.184 Å). This is reflected in the Mg(1)···C(11) and Mg(1)···C(17) separations of 3.196(3) and 3.267(3) Å, and would be consistent with C(Me\(_2\)pz\(_3\)) being the better donor (in accordance with previous studies of the donor abilities of different HB(R\(_4\)pz\(_3\)) ligands).\(^{51,52}\)

**Figure 2.15.** Displacement ellipsoid plot (20% probability) of Mg{C(Me\(_2\)pz\(_3\))}{C(pz\(_3\))} (10). H atoms omitted.
Table 2.7. Selected bond distances (Å) and angles (°) for Mg\{C(Me₂pz)₃\}\{C(pz)₃\} (10).

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<td>N(5)-Mg(1)-N(7)</td>
<td>82.52(8)</td>
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<td>N(7)-Mg(1)-N(7A)</td>
<td>83.3(1)</td>
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Due to the relatively poor solubility of M\{C(Me₂pz)₃\}\{C(pz)₃\} (M = Mg (10), Ca (11)) and the subsequent negative consequences in polymerisation studies (e.g. inaccurate catalyst loadings and potentially reduced activity), the requirement for a \{C(pz)₃\} moiety with increased solubility became apparent. Therefore, the ligand HC(4-Etpz)₃ was designed and synthesised (Equation 2.1) by an analogous method used by Reger et al. in the synthesis of HC(Me₂pz)₃. The solid state structure of 12 is shown in Figure 2.16 and confirms that proposed in Equation 2.1. The average Nₚz-C-Nₚz angle of 110.8 ° shows the near perfect tetrahedral geometry around the apical C(16) atom.

\[ 	ext{Equation 2.1} \]
**Figure 2.16.** Displacement ellipsoid plot (20% probability) of HC(4-Etpz)$_3$ (12). H atoms omitted.

![Displacement ellipsoid plot](image)

**Table 2.8.** Selected bond distances (Å) and angles (°) for HC(4-Etpz)$_3$ (12).

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<tr>
<td>C(16)-N(6)</td>
<td>1.449(2)</td>
</tr>
<tr>
<td>N(4)-Mg(1)-N(6)</td>
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</tbody>
</table>

Equation 2.2 summarises the reactions of 1 and 4 with HC4-Et(pz)$_3$ which formed the target complexes of the composition M{C(Me$_2$pz)$_3$} {C(4-Etpz)$_3$} (M = Mg (13) or Ca (14)) in ca. 46 – 68% yield. As for the corresponding reactions with HC(Me$_2$pz)$_3$ described above, more forcing conditions were needed for making 13 compared to 14. The $^1$H and $^{13}$C NMR spectra of 13 and 14 are consistent with $C_3v$ molecular symmetry and the EI mass spectra showed the expected molecular ions. Furthermore, the $^{13}$C[$^1$H] NMR spectra of each showed resonances (assigned using the corresponding HMBC spectra) for two carbanionic carbons, namely C(Me$_2$pz)$_3$ (73.1 and 73.3 ppm) and C(pz)$_3$ (90.0 and 90.8 ppm) for 13 and 14 respectively. The difference in chemical shift between the tris(pyrazolyl)methanide C(Me$_2$pz)$_3$ and C(4-Etpz)$_3$ resonances ($\Delta\delta = ca. 17.2$ ppm) is somewhat larger than that between the tris(pyrazolyl)methane protio-ligands themselves ($\Delta\delta = 2.4$ ppm; $\delta$ HC(Me$_2$pz)$_3$ = 81.2 ppm; $\delta$ HC(4-Etpz)$_3$ = 83.6 ppm).
Equation 2.2

2.5 Synthesis of Group 2 heteroscorpionate complexes

Equation 2.3 summarises the reactions of HC('Bu$_2$pz)$_2$SiMe$_2$NPh with Mg[N(SiMe$_3$)$_2$]$_2$ and the sterically less demanding Mg[N(SiHMe$_2$)$_2$]$_2$. The reactions with Mg[N(SiMe$_3$)$_2$]$_2$/Mg[N(SiHMe$_2$)$_2$]$_2$ proceeded smoothly at 60 °C over 6 h and 24 h to afford the half-sandwich compounds Mg[HC('Bu$_2$pz)$_2$SiMe$_2$NPh]N(SiMe$_3$)$_2$ (15) and Mg[HC('Bu$_2$pz)$_2$SiMe$_2$NPh]N(SiHMe$_2$)$_2$ (16) in 49% and 53% recrystallised yields respectively. As with the reactions of HC(Me$_2$pz)$_3$ and Mg[N(SiMe$_3$)$_2$]$_2$ or Mg[N(SiHMe$_2$)$_2$]$_2$ (Scheme 2.0) there was no evidence of sandwich complex (Mg[HC('Bu$_2$pz)$_2$SiMe$_2$NPh]$_2$) formation. In fact, compounds (15) and (16) were the only products of 2:1 NMR scale reactions between HC('Bu$_2$pz)$_2$SiMe$_2$NPh and Mg[N(SiMe$_3$)$_2$]$_2$ or Mg[N(SiHMe$_2$)$_2$]$_2$ under identical conditions.

Equation 2.3

The NMR spectra of 15 and 16 are consistent with the structures proposed in Equation 2.3, assuming fast rotation about the Mg-N(SiRM$_2$)$_2$ bonds. The solid state structures of 15 and 16 are shown in Figure 2.17. The approximately tetrahedral magnesium atoms are $\kappa^2N$
bound to a bis(pyrazolyl)methane ligand. The Mg-Nₚz bond lengths (avg. 2.230 Å in 15 and 2.192 Å in 16) are longer than those in Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1) (avg. 2.115 Å) consistent with various steric factors in the three compounds. The Mg-N(SiRMe₃)₂ distances are within the expected ranges. The largest N-Mg-N(SiMe₃)₂ angle and longest Mg-Nₚz bond in both 15 and 16 is associated with N(5) due to steric repulsions between the methyl groups attached to Si(2) and the phenyl group attached to N(5). The Si(3)Me group has less steric impact as it is able to lodge into the cleft between the pyrazolyl rings. The smaller average Nₚz-Mg-N(SiMe₃)₂ angle in 16 (114.2 °) compared to that in 15 (120.4 °) is consistent with the presence of the less bulky SiHMe₂ group in 16 compared to the more bulky SiMe₃ group in 15.

**Figure 2.17.** Displacement ellipsoid plot (20% probability) of Mg{HC(tBu₂pz)₂SiMe₂NPh}N(SiMe₃)₂ (15, left) Mg{HC(tBu₂pz)₂SiMe₂NPh}-N(SiHMe₂)₂ (16, right). C-bound H atoms omitted and remaining H atoms drawn as spheres of an arbitrary radius.

**Table 2.9.** Selected bond distances (Å) and angles (°) for Mg{HC(tBu₂pz)₂SiMe₂NPh}N(SiMe₃)₂ (15).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(1)-N(1)</td>
<td>2.254(2)</td>
<td></td>
</tr>
<tr>
<td>Mg(1)-N(3)</td>
<td>2.206(2)</td>
<td>123.88(8)</td>
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<tr>
<td>Mg(1)-N(5)</td>
<td>2.023(2)</td>
<td>116.93(8)</td>
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<tr>
<td>Mg(1)-N(6)</td>
<td>2.023(2)</td>
<td>129.76(8)</td>
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</tbody>
</table>
Table 2.10. Selected bond distances (Å) and angles (°) for 
Mg[{HC(tBu2pz)2SiMe2NPh}N(SiHMe2)2 (16).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(1)-N(1)</td>
<td>2.167(4)</td>
<td>N(1)-Mg(1)-N(6)</td>
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<tr>
<td>Mg(1)-N(3)</td>
<td>2.217(4)</td>
<td>N(3)-Mg(1)-N(6)</td>
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<tr>
<td>Mg(1)-N(5)</td>
<td>2.027(4)</td>
<td>N(5)-Mg(1)-N(6)</td>
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<tr>
<td>Mg(1)-N(6)</td>
<td>2.002(4)</td>
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</table>

2.6 Polymerisation studies: ROP of ε-CL

One of the aims of this work was to assess the performance of the heteroleptic homo- and hetero-scorpionate amide complexes 1, 3, 4, 7, 8, 15 and 16 for the catalytic ROP of ε-CL and rac-LA, in light of the success of related complexes previously discussed for similar purposes.40, 54-57 An initial study using the seven compounds was undertaken using ε-CL owing to the relative ease of its polymerisation (compared to LA) due to the favourable release of 7-membered ring strain.

Initial studies at room temperature in THF or toluene showed the amide complexes 1, 3, 4, 7, 8, 15 and 16 to be highly active for the ROP of ε-CL, in some cases reaching full conversion in less than one minute in either solvent. The results are summarised in table 2.11. The calculated $M_n$ values are those expected for one polymer chain growing per metal centre. All of the complexes gave a higher than expected observed $M_n$ value by GPC, consistent with a much greater rate of propagation than rate of initiation in a coordination-insertion mechanism.58 The observed $M_n$ values are also for the most part in better agreement with calculated $M_n$ for polymerisations performed in THF. This is likely to be due to the effect of THF competing with the monomer for coordination to the metal centre, thus reducing the relative rate of propagation (compared to that present in non-coordinating toluene solvent).

The PDI values for polymerisations performed in THF are also generally narrower than corresponding polymerisations performed in toluene (although these are collectively all in the moderate to very poor range). This is also likely to be a direct consequence of the coordinative nature of THF compared to toluene. Broad PDI values are well documented to be the result of intra- and intermolecular transesterification reactions.58 It is reasonable to
assume that the presence of THF molecule bound to a metal coordination site would reduce the likelihood of ‘backbiting’ by a growing polymer chain at the metal centre.

Due to the viscous nature of the polymer formed and the short times involved, it was not possible to acquire full kinetic data over the course of each polymerisation, nor was it possible to collect MALDI-ToF analysis of polymer samples due to the high observed $M_n$ values. However, the polymerisation inactivity of the complexes Mg{C(Me$_2$pz)$_3$}$_2$ (2.8), Ca{C(Me$_2$pz)$_3$}$_2$ (5) and Zn{C(Me$_2$pz)$_3$}$_2$ (9) under identical conditions rules out the possibility of ROP initiated by the carbanion present in the C(Me$_2$pz)$_3$ moiety of the amide catalysts. Therefore coordination-insertion has been deduced to be the most likely mechanism of polymerisation with these complexes.
**Table 2.11. Solution polymerisation of ε-CL by Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1), Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3), Ca{C(Me₂pz)₃}{N(SiMe₃)₂}(THF) (4), Zn{C(Me₂pz)₃}{N(SiMe₃)₂} (7), Zn{C(Me₂pz)₃}{N(SiHMe₂)₂} (8), Mg{HC(′Bu₂pz)₂SiMe₂NPh}N(SiMe₂)₂ (15), Mg{HC(′Bu₂pz)₂SiMe₂NPh}N(SiHMe₂)₂ (16).**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>Time (mins)</th>
<th>Mₙ(GPC)</th>
<th>Mₙ (calcd)</th>
<th>Mₘ/Mₙ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1)</td>
<td>THF</td>
<td>72</td>
<td>&lt; 1</td>
<td>16,130</td>
<td>11,414</td>
<td>2.64</td>
</tr>
<tr>
<td>Mg{C(Me₂pz)₃}{N(SiMe₃)₂} (1)</td>
<td>Toluene</td>
<td>72</td>
<td>&lt; 1</td>
<td>72,650</td>
<td>11,414</td>
<td>1.65</td>
</tr>
<tr>
<td>Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3)</td>
<td>THF</td>
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<td>&lt; 1</td>
<td>17,230</td>
<td>11,414</td>
<td>2.94</td>
</tr>
<tr>
<td>Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3)</td>
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<td>85,970</td>
<td>11,414</td>
<td>1.71</td>
</tr>
<tr>
<td>Ca{C(Me₂pz)₃}{N(SiMe₃)₂}(THF) (4)</td>
<td>THF</td>
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<td>17,720</td>
<td>11,414</td>
<td>2.65</td>
</tr>
<tr>
<td>Ca{C(Me₂pz)₃}{N(SiMe₃)₂}(THF) (4)</td>
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<tr>
<td>Zn{C(Me₂pz)₃}{N(SiMe₃)₂} (7)</td>
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<td>Zn{C(Me₂pz)₃}{N(SiMe₃)₂} (7)</td>
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<td>3.09</td>
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<td>Zn{C(Me₂pz)₃}{N(SiHMe₂)₂} (8)</td>
<td>THF</td>
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<td>16,460</td>
<td>11,414</td>
<td>5.33</td>
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<td>Zn{C(Me₂pz)₃}{N(SiHMe₂)₂} (8)</td>
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<td>3.32</td>
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<tr>
<td>Mg{HC(′Bu₂pz)₂SiMe₂NPh}N(SiMe₃)₂ (15)</td>
<td>THF</td>
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<td>30</td>
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<td>Mg{HC(′Bu₂pz)₂SiMe₂NPh}N(SiHMe₂)₂ (16)</td>
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<td>71,450</td>
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<td>Mg{HC(′Bu₂pz)₂SiMe₂NPh}N(SiHMe₂)₂ (16)</td>
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<td>25</td>
<td>89,740</td>
<td>11,414</td>
<td>3.17</td>
</tr>
</tbody>
</table>

* Conditions: [ε-CL]:[catalyst] = 100:1, 3.4 mL solvent at 23 °C. See Experimental section for other details. * Isolated yield at 100 % NMR conversion. * Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark-Houwink corrections. * Expected Mₙ (g mol⁻¹) for 1 chain growing per metal centre at 100% conversion, ignoring end groups.
2.7 Polymerisation studies: ROP of rac-LA

Polymerisation studies were next extended to the more challenging monomer, rac-LA. Due to the more encouraging results with ε-CL observed using THF as a solvent, and solubility issues with some of the complexes, it was decided to focus solely on THF mediated polymerisations. The results are summarised in Table 2.12.

One of the several interesting contrasts with the ε-CL polymerisation results is that the rac-LA polymerisations all required elevated temperatures and extended reaction times, largely due to the unfavourable release of the stable 6-membered ring strain in rac-LA when compared to the less thermodynamically stable 7-membered ring strain in ε-CL. The observed $M_n$ values are also generally in much closer agreement to the expected values for the amide catalysts (for one growing polymer chain per metal centre). However, the relatively broad PDI values are also evident in rac-LA polymerisations, no doubt due in part to the increased tendency of transesterification side reactions at elevated temperatures. Disappointingly, no stereochemical enrichment in the PLA polymer produced was observed.

As was the case with ε-CL polymerisations, the complexes Mg{C(Me$_2$pz)$_3$}$_2$ (2.8), Ca{C(Me$_2$pz)$_3$}$_2$ (5) and Zn{C(Me$_2$pz)$_3$}$_2$ (9) were all inactive for the ROP of rac-LA under identical polymerisation conditions, again ruling out the possibility of initiation by the carbanion present in the C(Me$_2$pz)$_3$ moiety of the amide catalysts (the activity of complexes Mg{C(Me$_2$pz)$_3$} {C(pz)$_3$} (10), Ca{C(Me$_2$pz)$_3$} {C(pz)$_3$} (11), Mg{C(Me$_2$pz)$_3$} {C(4-Etpz)$_3$} (13) and Ca{C(Me$_2$pz)$_3$} {C(4-Etpz)$_3$} (14) are discussed below).

Unfortunately, quenching the polymerisations resulted mostly in hydrolysis of any potential amide end-groups that would have been formed through a coordination-insertion mechanism, and therefore it was not possible to identify these by $^1$H NMR. However, the MALDI-ToF spectrum (Figure 2.18) obtained by analysis of a polymer produced by Mg{C(Me$_2$pz)$_3$} {N(SiHMe$_2$)$_2$} (3) did provide some useful information. The spectrum shows a primary distribution of integer polymer units († in Figure 2.15) with a separation of 72 m/z (half a lactide unit), strong evidence (along with broad PDI values) for transesterification side reactions leading to cyclic whole and half LA units. Also present is a minor secondary distribution (⋆ in Figure 2.18), again with a separation of 72 m/z, corresponding to polymer chains with N(SiHMe$_2$)$_2$ end groups. This is consistent with the work reported by Okuda et al. investigating the use of rare earth bis(phenolate) amide complexes for the ROP of rac-lactide.\textsuperscript{59}
Table 2.12. Solution polymerisation of rac-LA by Mg\{C(Me\textsubscript{2}pz)\}_3\{N(SiMe\textsubscript{3})\}_2 \textit{(1)}, Mg\{C(Me\textsubscript{2}pz)\}_3\{N(SiHMe\textsubscript{3})\}_2 \textit{(3)}, Ca\{C(Me\textsubscript{2}pz)\}_3\{N(SiMe\textsubscript{3})\}_2(THF) \textit{(4)}, Zn\{C(Me\textsubscript{2}pz)\}_3\{N(SiMe\textsubscript{3})\}_2 \textit{(7)}, Zn\{C(Me\textsubscript{2}pz)\}_3\{N(SiHMe\textsubscript{3})\}_2 \textit{(8)}, Mg\{HC(\textsubscript{t}Bu\textsubscript{2}pz)\}_2SiMe\textsubscript{2}NPh-N(SiMe\textsubscript{3})\}_2 \textit{(15)}, Mg\{HC(\textsubscript{t}Bu\textsubscript{2}pz)\}_2SiMe\textsubscript{2}NPh\}N(SiHMe\textsubscript{3})\}_2(16), Mg\{C(Me\textsubscript{2}pz)\}_3\{C(pz)\}_3 \textit{(10)}, Ca\{C(Me\textsubscript{2}pz)\}_3\{C(pz)\}_3 \textit{(11)}, Mg\{C(Me\textsubscript{2}pz)\}_3-{C(4-Etpz)}\}_3 \textit{(13)} and Ca\{C(Me\textsubscript{2}pz)\}_3\{C(4-Etpz)\}_3 \textit{(14)}.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Time (hours)\textsuperscript{b}</th>
<th>$M_n$(GPC)\textsuperscript{c}</th>
<th>$M_n$(calcd)\textsuperscript{d}</th>
<th>$M_n/M_m$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg{C(Me\textsubscript{2}pz)}_3{N(SiMe\textsubscript{3})}_2 \textit{(1)}</td>
<td>86</td>
<td>2</td>
<td>32,700</td>
<td>12,400</td>
<td>1.57</td>
</tr>
<tr>
<td>Mg{C(Me\textsubscript{2}pz)}_3{N(SiHMe\textsubscript{3})}_2 \textit{(3)}</td>
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<td>2</td>
<td>22,760</td>
<td>12,400</td>
<td>2.19</td>
</tr>
<tr>
<td>Ca{C(Me\textsubscript{2}pz)}_3{N(SiMe\textsubscript{3})}_2(THF) \textit{(4)}</td>
<td>81</td>
<td>2</td>
<td>16,520</td>
<td>10,590</td>
<td>1.21</td>
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<tr>
<td>Zn{C(Me\textsubscript{2}pz)}_3{N(SiMe\textsubscript{3})}_2 \textit{(7)}</td>
<td>94</td>
<td>4</td>
<td>18,820</td>
<td>13,550</td>
<td>1.77</td>
</tr>
<tr>
<td>Zn{C(Me\textsubscript{2}pz)}_3{N(SiHMe\textsubscript{3})}_2 \textit{(8)}</td>
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<td>4</td>
<td>31,860</td>
<td>13,120</td>
<td>1.37</td>
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<tr>
<td>Mg{HC(\textsubscript{t}Bu\textsubscript{2}pz)}_2SiMe\textsubscript{2}NPh}N(SiMe\textsubscript{3})}_2 \textit{(15)}</td>
<td>89</td>
<td>0.75</td>
<td>51,480</td>
<td>12,799</td>
<td>1.45</td>
</tr>
<tr>
<td>Mg{HC(\textsubscript{t}Bu\textsubscript{2}pz)}_2SiMe\textsubscript{2}NPh}N(SiHMe\textsubscript{3})}_2(16)</td>
<td>90</td>
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<td>55,080</td>
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</tr>
<tr>
<td>Mg{C(Me\textsubscript{2}pz)}_3{C(pz)}_3 \textit{(10)}</td>
<td>91</td>
<td>6</td>
<td>9,370</td>
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<td>Ca{C(Me\textsubscript{2}pz)}_3{C(pz)}_3 \textit{(11)}</td>
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<td>6</td>
<td>8,460</td>
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<td>2.90</td>
</tr>
<tr>
<td>Mg{C(Me\textsubscript{2}pz)}_3{C(4-Etpz)}_3 \textit{(13)}</td>
<td>90</td>
<td>8</td>
<td>17,420</td>
<td>12,972</td>
<td>4.08</td>
</tr>
<tr>
<td>Ca{C(Me\textsubscript{2}pz)}_3{C(4-Etpz)}_3 \textit{(14)}</td>
<td>92</td>
<td>12</td>
<td>12,590</td>
<td>13,260</td>
<td>3.94</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Conditions: \textit{rac-LA}:[catalyst] = 100:1, 6.0 mL THF at 70 °C. See Experimental section for other details. \textsuperscript{b} % conversion by $^1$H NMR. \textsuperscript{c} Molecular weights (g mol\textsuperscript{-1}) determined from GPC using the appropriate Mark-Houwink corrections. \textsuperscript{d} Expected Mn (g mol\textsuperscript{-1}) for 1 chain growing per metal centre at the % conversion by $^1$H NMR.
Figure 2.18. MALDI-ToF MS of poly(rac-LA) synthesised using 
Mg{C(Me₂pz)₃}{N(SiHMe₂)₂} (3). \( M_n \) by GPC analysis was 4,520 g mol\(^{-1}\) (from a [rac-LA]₀:[catalyst]₀ = 20:1 polymerisation). † = cyclic PLA units, * = N(SiHMe₂)-capped polymer.

The most closely related complexes studied for the ROP of rac-lactide are Chisholm’s (Tp\(^\mathrm{Bu}\)Ca(X)(THF) \( X = \text{N(SiMe₃)₂} \) or O-2,6-C₆H₄Pr₂\(^4\))\(^{40,57}\) These two complexes showed > 90% polymerisation in ~1 min at room temperature, giving polymer with ca. 80% heterotactic enrichment. The fact that stereochemical control was observed with Chisholm’s catalysts, and not with the catalyst Ca{C(Me₂pz)₃}{N(SiMe₃)₂}(THF) \( \) (4) is most likely due to the presence of tert-butyl groups present around the metal centre in the former case promoting chain end control.

Despite the relatively poor polymerisation control shown by the complexes tested, detailed kinetics studies were carried out in some cases to investigate further the polymerisation process. Gratifyingly, despite the overall poor \( M_n \) and PDI values observed, all of the catalysts tested showed first order consumption of rac-LA, albeit after an initial induction period (up to approximately 20 minutes). Similar induction periods have also been observed in the ROP of cyclic esters using aluminium alkoxides\(^60,61\) or yttrium isopropoxides\(^62\). In these instances the induction period was thought to correspond to a period of ligand rearrangement around the metal centre, in order to allow the monomer access to the coordination sphere.\(^63\) It is thought that a similar process occurs in this instance. An example plot is shown in Figure 2.19 for the catalyst Mg{HC(Bu₂pz)₂SiMe₂NPh}N(SiHMe₂)₂ (16). The measured rate constant for the
polymerisation, $k_{\text{obs}}$ was 0.03(2) min$^{-1}$. This compares with a $k_{\text{obs}}$ value of 0.04(3) min$^{-1}$ for the related catalyst Mg{HC(tBu$_2$pz)$_2$SiMe$_2$NPh}N(SiMe$_3$)$_2$ (15).

**Figure 2.19.** First order plot for rac-LA consumption using Mg{HC(tBu$_2$pz)$_2$SiMe$_2$NPh}N(SiHMe$_2$)$_2$ (16).$^a$

$^a$Conditions [rac-LA]:[16] = 100:1, 6 mL THF, 70 °C, 0.1 mL aliquots taken at the given intervals. See Experimental section for other details.

The final point of interest is the polymerisation activity shown by the heteroleptic sandwich complexes Mg{C(Me$_2$pz)$_3$} {C(pz)$_3$} (10), Ca{C(Me$_2$pz)$_3$} {C(pz)$_3$} (11), Mg{C(Me$_2$pz)$_3$}-{C(4-Etpz)$_3$} (13) and Ca{C(Me$_2$pz)$_3$} {C(4-Etpz)$_3$} (14). Whilst it was previously noted that the complexes Mg{C(Me$_2$pz)$_3$}$_2$, Ca{C(Me$_2$pz)$_3$}$_2$ (5) and Zn{C(Me$_2$pz)$_3$}$_2$ (9) were all inactive for the ROP of rac-LA under identical polymerisation conditions, the difference between the two groups of complexes is the presence of a C(pz)$_3$ or C(4-Etpz)$_3$ moiety in the former compared to {C(Me$_2$pz)$_3$} moieties in the latter.

It is likely that C(pz)$_3$ or C(4-Etpz)$_3$ is able to initiate ROP due to the lack of sterically hindering groups around the carbanion, compared to the degree of steric protection afforded by methyl groups in C(Me$_2$pz)$_3$. Also due to the absence of an amide initiating group in these catalysts a coordination-insertion mechanism centred on the metal ion cannot be envisaged. Therefore initiation through interaction with the carbanion in the C(pz)$_3$ or C(4-Etpz)$_3$ moiety and the rac-LA monomer is the likely possible mechanism. Further evidence supporting initiation by the carbanion, rather than by a group directly attached to the metal
centre, is the fact that in a family of related $\text{Tp}^{\text{Bu}}$ calcium, magnesium and zinc aryloxide complexes, the observed order of rac-LA polymerisation activity was $\text{Ca} > \text{Mg} > \text{Zn}$.\textsuperscript{40} It was postulated that this order was defined by the polarity of the initiating metal-oxygen bond. No such trend can be seen in Table 2.13 listing the data for $\text{Mg\{C(Me_2 pz)_3\}\{C(pz)_3\}}$ (10), $\text{Ca\{C(Me_2 pz)_3\}\{C(pz)_3\}}$ (11), $\text{Mg\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (13) and $\text{Ca\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (14).

Similarly to the amide complexes tested, polymerisations with $\text{Mg\{C(Me_2 pz)_3\}\{C(pz)_3\}}$ (10), $\text{Ca\{C(Me_2 pz)_3\}\{C(pz)_3\}}$ (11), $\text{Mg\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (13) and $\text{Ca\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (14) all showed first order consumption of LA (after an initial induction period). The first order rate constants for these polymerisations are shown in Table 2.13.

**Table 2.13.** First order rate constants ($k_{\text{obs}}$) for rac-LA polymerisation by $\text{Mg\{C(Me_2 pz)_3\}\{C(pz)_3\}}$ (10), $\text{Ca\{C(Me_2 pz)_3\}\{C(pz)_3\}}$ (11), $\text{Mg\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (13) and $\text{Ca\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (14).\textsuperscript{a}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_{\text{obs}}$ (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Mg{C(Me_2 pz)_3}{C(pz)_3}}$ (10)</td>
<td>0.003(2)</td>
</tr>
<tr>
<td>$\text{Ca{C(Me_2 pz)_3}{C(pz)_3}}$ (11)</td>
<td>0.005(4)</td>
</tr>
<tr>
<td>$\text{Mg{C(Me_2 pz)_3}{C(4-Etpz)_3}}$ (13)</td>
<td>0.004(3)</td>
</tr>
<tr>
<td>$\text{Ca{C(Me_2 pz)_3}{C(4-Etpz)_3}}$ (14)</td>
<td>0.002(1)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Conditions: [rac-LA$_0$]:[Catalyst] = 100:1, 6.0 mL THF, 70 °C.

Whilst the polymerisations all showed first order kinetics, the control of $M_n$ with conversion was poor, i.e. non-linear growth was observed (even for the more soluble complexes $\text{Mg\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (13) and $\text{Ca\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (14). Also, MALDI-ToF spectra showed only cyclic (whole and half) PLA units. It would be expected that a nucleophilic polymerisation mechanism would show C(4-Etpz)$_3$ and C(pz)$_3$ capped PLA in MALDI-ToF spectra. However these groups would come in a very similar region to those of cyclic PLA units, therefore MALDI-ToF proved an inconclusive method.

In order to gain more insight into the polymerisation mechanism, an NMR scale experiment was carried out in which ten equivalents of rac-lactide were dissolved in THF-$d_8$ and added to one equivalent of $\text{Mg\{C(Me_2 pz)_3\}\{C(4-Etpz)_3\}}$ (13). The mixture was heated to 70 °C for two hours, after which time the products were analysed by $^1$H NMR. This showed PLA,
a small amount of residual catalyst and, disappointingly, quantitative formation of HC(4-Etpz)₃. Therefore it is likely that the C(4-Etpz)₃ moiety merely acts as a base (and not a nucleophile), deprotonating a lactide monomer unit, forming an enolate and allowing for subsequent polymerisation of monomer units. The same mechanism is implied for the remaining heteroleptic sandwich complexes, although similarly conclusive evidence for the complexes Mg{C(Me₂pz)₃}{C(pz)₃} (10) and Ca{C(Me₂pz)₃}{C(pz)₃} (11) could not be obtained due to the relatively poor solubility of these complexes. The polymerisation mechanism for these four catalysts is therefore thought to be anionic and not nucleophilic. An anionic mechanism was also found for the ROP of LA using potassium tert-butoxide, as well as primary and secondary lithium alkoxides.

### 2.8 Summary and Conclusions

The work presented in this chapter has significantly extended the range of reported Group 2 and 12 tris(pyrazolyl)methanide complexes, primarily through the use of bulky amide metal precursors (except for in the case of zinc). By adjustment of the amide (SiMe₃ vs SiHMe₂) or pyrazolyl (Me₂pz vs pz) substituents, and/or the metal centres themselves new coordination modes, intermediates and fluxional processes have been observed. The diminished rates of reaction of the Group 12 amides with HC(Me₂pz)₃ parallel the results reported previously for ZnMe₂ and are consistent with lower bond polarities and higher metal effective nuclear charge, as analyzed previously using DFT. Additional studies have shown primary kinetic isotope effects that are consistent with H/D−C(Me₂pz)₃ bond-breaking being important in the rate-determining step leading to zwitterion formation. The magnitudes of these KIEs are comparable for both sandwich and half-sandwich formation.

The amide complexes were found to be highly active for the ROP of ε-CL, although poor polymerisation control was observed, this is attributed to a much greater rate of propagation than rate of initiation in a coordination-insertion mechanism. However improved control was shown using THF rather than toluene as a solvent. For the ROP of rac-LA elevated temperatures were required. However, relatively poor control was again observed. The heteroleptic sandwich complexes Mg{C(Me₂pz)₃}{C(pz)₃} (10), Ca{C(Me₂pz)₃}{C(pz)₃} (11), Mg{C(Me₂pz)₃}{C(4-Etpz)₃} (13) and Ca{C(Me₂pz)₃}{C(4-Etpz)₃} (14) were also active for the ROP of rac-LA. However the polymerisation mechanism was shown to be more likely to be base-initiated rather than nucleophilic.
2.9 References


Chapter Three

Cationic and charge-neutral Main Group tetrahydroborate complexes and their use in the controlled ROP of ε-caprolactone and rac-lactide
3.0 Overview

This Chapter will provide an introduction into main group borohydride catalysed ROP, with an overview of the synthesis and characterisation of borohydride complexes. Their solid state structures and solution behaviour will be discussed in conjunction with their application to the ring opening polymerisation of cyclic esters. Comparison of the newly reported complexes and previously reported related complexes will be undertaken within the context of the solid state structures and the ROP activity and selectivity observed. Some of this work has recently been published.1

3.1 Introduction

The last decade has witnessed an exponential increase in activity of the synthesis, structures, reactivity and catalytic applications of compounds of the heavier alkaline earth (Ae) metals.2 Most of this research has centred on calcium, the ionic radius of which lies between those of yttrium and lanthanum, and which is abundant, non-toxic and inexpensive. Nonetheless, both the general solution chemistry and catalytic applications of this element remain considerably underdeveloped in relation to those of the lanthanides to which the heavier Ae elements have been compared.

The ring-opening polymerization (ROP) of cyclic esters such as \(\varepsilon\)-CL and LA to biocompatible and biodegradable polymers, viewed as potential alternatives to petroleum-derived plastics, is an area of considerable current interest.2 Although calcium’s lighter congener, magnesium, and the lanthanides have been extensively studied for ROP, only a handful of well-defined, heteroleptic initiators of the type (L)Ca–X (X = amide or aryloxide) have been reported.3-10 Even so, these few reports indicate superior activity of (L)Ca–X in comparison with the respective Mg analogues, signposting the considerable potential of new Ca complexes in this area.

In the last 5-8 years lanthanide tetrahydroborates,11-15 either as “ligand-free” Ln(BH4)3(THF)x16-20 or heteroleptic (L)Ln(BH4) systems,21-26 have become well-established as effective initiators for the polymerisation of a range of cyclic esters and other monomers. However, no main group borohydride has been established in this regard.11 Furthermore, in terms of both initiating efficiency and molecular weight control, (L)Ln–BH4 systems are better controlled than the corresponding amides, (L)Ln–NR2,21 and comparable to alkoxides, (L)Ln–OR.18 Drawing upon the potential parallels with the lanthanides, it was set out to develop main group tetrahydroborate complexes as a new class of main group initiator for the ROP of rac-LA.
Generally, borohydride complexes comprise at least one BH$_4$ anionic ligand (alkylborohydride complexes are also known but will not be discussed in this thesis); covalent borohydride complexes are well established for the transition metals, lanthanides and to a lesser extent the main group elements. One of the advantages of BH$_4$ ligands is their versatility, both in their coordination mode and their reactivity. Borohydrides can adapt their hapticity to satisfy the size of the coordination sphere around a metal, adopting (most commonly) $\kappa^3$, $\kappa^2$ and $\kappa^1$ (rare) binding modes through the M(µ-H)B bridges (see Figure 3.0). In addition, a borohydride group may be connected to one metal (terminal), or up to three metal atoms (bridging). In relation to their reactivity, borohydrides can be considered as pseudo halides (being monoanionic and readily substituted for other groups), and can also be considered as extended hydrides, showing reactivity associated with a hydridic moiety, e.g. protonolysis and reductive polymerisations. Since little is known about Ae borohydride complexes, the remainder of this introduction will focus on the preparation and characterisation of lanthanide borohydride complexes, given the similarities between the lanthanides and Ae elements.

**Figure 3.0.** Coordination modes of tetrahydroborate ligands in monomeric and dimeric complexes

\[ \begin{array}{ccc}
M - H_b - B - H_t & M - H_b - B - H_t & M - H_b - H_t \cr
\kappa^1 & \kappa^2 & \kappa^3 \cr
\text{Bridging} & \end{array} \]

Several methods are known for the preparation of simple borohydride complexes, however in the context of this thesis the two most relevant are (as shown in Equations 3.0 and 3.1):

i) Substitution of a ligand (most commonly a halide) by a borohydrido anionic reagent MBH$_4$ (M = alkaline metal), in the final step of a synthesis, generally from a lanthanide trihalide.

\[
\text{LnX}_3 + n\text{MZ} \xrightarrow{\text{n MX}} Z_n\text{LnX}_{3-n} \xrightarrow{M'\text{BH}_4} Z_n\text{Ln(BH}_4\text{)}_{3-n} \xrightarrow{-M'\text{X}}
\]

\[ X = \text{halide}; n = 1, 2; Z = \text{anionic ligand}; M, M' = \text{alkali metal} \]

**Equation 3.0**
ii) Salt metathesis – replacing the trihalide with a tris(borohydride) as the starting material

\[
\text{Ln(BH}_4\text{)}_3(\text{THF})_x \quad + \quad n \text{ MZ} \quad \rightarrow \quad Z_n\text{Ln(BH}_4\text{)}_{3-n} - n \text{ MBH}_4
\]

\[n = 1, 2; \ Z = \text{anionic ligand}\]
\[M = \text{alkali metal}\]

**Equation 3.1**

The trivalent lanthanide metalloocene half-sandwich analogues 3.0 and 3.1 (Figure 3.1) were synthesised very recently by Bonnet and Visseaux through salt metathesis from the corresponding tris(borohydrides).\(^{29, 30}\) Ephritikhine *et al.* had previously synthesised 3.2 using the same methodology.\(^{31}\) Experimental evidence suggests that 3.2 possesses both tridentate and bidendate borohydride ligands in solution, supporting a monomeric structure. It was also shown in this work that heating 3.2 under vacuum resulted in the loss of bound THF, forming Cp*Nd(BH\(_4\))\(_2\), which gave a simple IR absorption at 2291 cm\(^{-1}\) (typical of bridging borohydride groups, see Table 3.0), indicating a polymeric structure in the solid state. The lanthanum analogue 3.1 behaved in a very similar fashion to 3.2. It was observed that the synthesis of 3.0 was accompanied by two by-products, the sandwich complex Cp\(^*\)\(_2\)Sc(BH\(_4\)) and the alkoxide half-sandwich \([\text{Cp}\(^*\)\(_2\)Sc(BH\(_4\)}\{\mu-O(\text{CH}_2)\text{CH}_3\}\]\(_2\), the latter resulting from the ring opening of a THF molecule. Structural analysis of 3.0 and IR data showed both borohydride ligands to be tridentate.

The trivalent yttrium and samarium borohydrides 3.3 and 3.4 were synthesised recently by Cui\(^{32}\) and Mountford\(^{21}\) respectively. Complex 3.3 was synthesised using a one-pot method; lithiation of the β-diketimine using \(^{n}\)BuLi was followed by *in situ* salt metathesis with yttrium tris(borohydride). Structural analysis showed that both borohydride ligands were tridentate. Similarly, reaction of the sodium diaminobis(phenoxide) \(\text{Na}_2\text{O}_2\text{N}_p\text{y} [\text{H}_2\text{O}_2\text{N}_p\text{y} = (2-\text{C}_3\text{H}_4\text{N})\text{CH}_2\text{NCH}_2\{2-\text{HO-3,5-}C_6\text{H}_2^t\text{Bu}_2\}_2]\) with samarium tris(borohydride) afforded the complex 3.4, which was shown to be a very good initiator for the ROP of ε-CL and *rac*-LA, producing polymers with narrow PDI and a high degree of heterotactic enrichment with the latter. Under reduced pressure it was shown that 3.4 loses the bound THF molecule, forming a phenolate-bridged species. Both this species and 3.4 were found to possess tridentate borohydride ligands.
Figure 3.1. Examples of rare earth and lanthanide borohydride complexes.

A large family of peralkylsubstituted cyclopentadienyl borohydride metallocenes \((\text{C}_5\text{Me}_4\text{R})_2\text{M(BH}_4\text{)}(\text{THF})\) \((\text{M} = \text{Y (3.5)}, \text{Sm (3.6)} \text{or Lu (3.7)}, \text{R} = \text{H, Me, Et, }^{t}\text{Pr, }^{t}\text{Bu})\) was prepared in 1998 by Schumann et al. through reaction of the sodium salts of the cyclopentadienyl ligands with the trivalent metal chloride, followed by in situ reaction with sodium borohydride. A mixture of tridentate and bidentate borohydride ligands were found to be present, depending on the size of the metal and the steric bulk around the cyclopentadienyl ligand.

In addition to the growing number of trivalent lanthanide borohydride complexes known, a few examples of divalent borohydride species have also been synthesised very recently. Complex 3.8 was synthesised from a salt metathesis reaction between \((\text{Tp}^{\text{Bu,Me}})\text{Yb(I)}(\text{THF})\) and \(\text{NaBH}_4\) in THF. Structural analysis and IR spectroscopy revealed the borohydride ligand to be tridentate. The base free analogue of 3.8, \((\text{Tp}^{\text{Bu,Me}})\text{Yb(BH}_4\text{)}\) was also synthesised by simply performing the reaction in acetonitrile rather than THF. Additionally
the deuterated analogue of 3.8, (Tp^Bu,Me)Yb(BD_4), was also synthesised, and this showed isotopically shifted IR frequencies when compared to 3.8.

A series of compounds Ln(BH_4)_2(THF)_2 (Ln = Sm, Eu, Yb) and their non solvated analogues Ln(BH_4)_2 were prepared in 1999 by thermal reduction of the Na(DME)_4[Ln(BH_4)_4] precursors (Equation 3.0).^{35} However, these compounds were only characterized by IR and elemental analysis.

\[
\text{Na(DME)_4[Ln(BH_4)_4]} \xrightarrow{i) 140-200 \degree C \quad \text{in vacuo} \quad \text{ii) THF} \quad \text{in vacuo} \xrightarrow{200 \degree C} \text{Ln(BH_4)_2(THF)_2} \xrightarrow{\text{Ln(BH_4)_2}}
\]

**Equation 3.2**

In 2010 Bonnet and Visseaux improved the synthesis of Sm(BH_4)_2(THF)_2 through a high yielding comproportionation reaction between Sm(BH_4)_3(THF)_3 and samarium metal.^{36} Structural analysis showed this complex to be polymeric with bidentate borohydride ligands bridging between adjacent metal centres. The subsequent reaction between Sm(BH_4)_2(THF)_2 and KCp^* yielded the complex Cp^*Sm(BH_4)(THF)_2 (3.9), which possesses two bridging borohydrides coordinated to each samarium centre in a tridentate manner. This complex has also been shown to be highly active for the ROP of \( \varepsilon \)-CL, yielding polymers with narrow PDI values.

In 2008 Okuda et al. synthesised the family of cationic borohydride complexes [M(BH_4)_2(THF)_3][BPh_4] (M = Y (3.10), La (3.11), Nd (3.12) and Sm (3.13), by protonolysis reactions between the trivalent borohydrides and [NEt_3H][BPh_4],^{27} producing triethylamine, hydrogen and diborane as the side products. These complexes were also shown to be highly active for the ROP of \( \varepsilon \)-CL. However, in this instance polymers with moderate PDI values and featuring poor control of molecular weight were obtained.

As mentioned, the two foremost techniques in deciphering borohydride hapticity are single crystal X-ray diffraction and IR spectroscopy, although it should be mentioned that both \(^1\)H and \(^11\)B NMR spectroscopy are useful methods in at least detecting the presence of a borohydride. Whilst the difficulties associated with locating H atoms by X-ray diffraction are well known,^{37} the location of hydrides (and borohydrides) can be reliably found using Fourier difference maps. In most cases the hapticity of the borohydride ligand in the solid state can be determined. Neutron diffraction can give more precise data. However, large single crystals are required and the facilities required are not widely available.
IR spectroscopy is used extensively in conjunction with (and solely in the absence of) X-ray diffraction to determine the hapticity of borohydride ligands. For mononuclear complexes the diagnostic bands are generally found in the region 2500-1000 cm\(^{-1}\) region (Table 3.0). Both the terminal and bridging B-H stretches are found in this region for all binding modes, however the number and position of bands leave a precise fingerprint of the binding mode.

**Table 3.0.** IR active fundamental vibrational transitions commonly observed for mononuclear MBH\(_4\) configurations.\(^{14}\)

<table>
<thead>
<tr>
<th>Structure</th>
<th>Freq, cm(^{-1})</th>
<th>Normal Mode</th>
<th>Symmetry</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodentate (I)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>~ 2000</td>
<td>B-H(_t) stretching</td>
<td>A(_1)</td>
<td></td>
<td>Strong</td>
</tr>
<tr>
<td>~ 2000 – 1700</td>
<td>M-H(_b) stretching</td>
<td>A(_1)</td>
<td></td>
<td>Often broad</td>
</tr>
<tr>
<td>1150 – 1000</td>
<td>BH(_3) deformation</td>
<td>A(_1), E</td>
<td></td>
<td>Strong band</td>
</tr>
<tr>
<td>2450 – 2300</td>
<td>B-H(_t) stretching</td>
<td>A(_1), E</td>
<td></td>
<td>Strong doublet</td>
</tr>
<tr>
<td>2600 – 2400</td>
<td>B-H(_t) stretching</td>
<td>A(_1), B(_1)</td>
<td></td>
<td>Strong doublet (50 – 80 cm(^{-1}))</td>
</tr>
<tr>
<td>Bidentate (II)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2150 – 1650</td>
<td>B-H(_b) stretching</td>
<td>A(_1), B(_2)</td>
<td></td>
<td>Strong band possible shoulder</td>
</tr>
<tr>
<td>1500 – 1300</td>
<td>Bridge stretching</td>
<td>A(_1)</td>
<td></td>
<td>Strong band</td>
</tr>
<tr>
<td>1200 – 1100</td>
<td>BH(_2) deformation</td>
<td>B(_2)</td>
<td></td>
<td>Strong</td>
</tr>
<tr>
<td>2600 – 2450</td>
<td>B-H(_t) stretching</td>
<td>A(_1)</td>
<td></td>
<td>Strong singlet</td>
</tr>
<tr>
<td>Tridentate (III)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2200 – 2100</td>
<td>B-H(_b) stretching</td>
<td>A(_1), E</td>
<td></td>
<td>Doublet (50 – 80 cm(^{-1}))</td>
</tr>
<tr>
<td>1250 – 1150</td>
<td>Bridge deformation</td>
<td>E</td>
<td></td>
<td>Strong</td>
</tr>
</tbody>
</table>

As shown in Table 3.0, tridentate borohydrides give a characteristic strong singlet between 2600-2450 cm\(^{-1}\) (A\(_1\) B-H\(_t\) stretching mode, see Figure 3.2) and a doublet between 2200-2100 cm\(^{-1}\) (A\(_1\) and E B-H\(_b\) stretching modes). Bidentate borohydrides give a strong doublet in the range 2600-2400 cm\(^{-1}\) (A\(_1\) and B\(_1\) B-H\(_t\) stretching modes) and a strong band in the...
range 2150-1650 cm\(^{-1}\) (\(A_1\) and \(B_2\) B-H\(_b\) stretching modes), as well as a strong band in the range 1500-1300 cm\(^{-1}\) (\(A_1\) bridge stretching mode). It can also be seen that monodentate borohydrides give unique IR bands.

The initial pioneering work in the area of ROP catalysed by rare earth borohydrides was carried out by Guilleaume and co-workers focusing on \(\text{Ln(BH}_4\text{)}_3(\text{THF})_3\) (\(\text{Ln} = \text{La, Nd, Sm}\)) and \(\text{Cp}^*\text{Sm(BH}_4\text{)}(\text{THF})(3.6)\) for the ROP of \(\varepsilon\text{-CL}\).\(^{19,20,38}\) The ROP was shown to proceed in a living fashion with \textit{ca.} one PCL chain forming per \(\text{Ln–BH}_4\) group. One study has shown that the performance of these systems matches that of “\(\text{La(O}^\dagger\text{Pr})_3\)” under comparable experimental conditions,\(^{19}\) although this is to date the sole “head to head” performance study undertaken for borohydride \textit{versus} more classical initiators.

**Scheme 3.0.** Mechanism for the borohydride-initiated ROP of \(\varepsilon\text{-CL}\) leading to \(\alpha,\omega\)-dihydroxytelechelic PCL.\(^{19,24}\)

An important aspect of the ROP of \(\varepsilon\text{-CL}\) with \((\text{L})\text{Ln–BH}_4\) complexes is the formation of \(\alpha,\omega\)-dihydroxytelechelic PCL, which is a material of importance to polyurethane chemistry. Guillaume and coworkers have established the mechanism shown in Scheme 3.0 by a combination of experimental and computational studies.\(^{19,24}\) Coordination of \(\varepsilon\text{-CL}\) to \((\text{L})\text{Ln–BH}_4\) (forming I) is followed by hydride transfer to the carbonyl carbon and BH\(_3\) transfer to the formally anionic oxygen (II). Crucially, species II is unable to lose BH\(_3\) and so ring-opening only takes place \textit{via} a further hydride transfer event which forms III with a fully reduced carbonyl moiety. Subsequent monomer enchainment \textit{via} a coordination-insertion mechanism, and finally termination by protonolysis, affords the \(\alpha,\omega\)-
dihydroxytelechelic PCL. It is important to contrast this process with the usual one (Scheme 3.1) for metal-amide, alkoxide, alkyl or hydride species of the type (L)M–X. In this case, after migration of the metal-bound initiating group “X” of the adduct V to the carbonyl carbon of ε-CL, spontaneous ring-opening of VI to form VII occurs.18, 19, 24, 38 The polymer subsequently formed is of the type H-[PCL]-X in which the “-X” end group arises from the (L)M-X initiator.

**Scheme 3.1.** Coordination-insertion mechanism for the initial ring-opening of ε-CL with metal-amide, alkoxide, alkyl or hydride species.39-41

\[
\begin{align*}
\text{VI} & \\
\text{X} & = \text{NR}_2, \text{OR}, \text{alkyl}, \text{H} \\
\end{align*}
\]

However, the ROP of other cyclic esters with (L)Ln–BH₄ does not necessarily lead to α,ω-dihydroxy polymers. Guillaume has shown that the poly(TMC) formed with Sm(BH₄)₃(THF)₃ contains both –CH₂OH and –CHO end groups,24 while Nakayama and Shiono found that several lanthanide tris(borohydride) complexes polymerize δ-valerolactone to α,ω-dihydroxy poly(δ-VL).42 The same authors reported that rac- or L-LA also gives α,ω-dihydroxy terminated polyesters with these initiators,16, 24 whereas Carpentier and Trifonov, in addition to work in this Chapter,1 found that ligand-supported borohydride initiators produce poly(rac-LA) with a mixture of –CH₂OH and –CHO end groups.23, 25

3.2 Synthesis of cationic and charge-neutral main group tetrahydroborate complexes

In light of the extensive work carried out in the preparation of lanthanide borohydride complexes and their application towards ROP,11, 14 as well as the growing interest in the development of the chemistry of the Ae elements,2 it was decided to investigate the synthesis and ROP applications of Ae borohydride complexes. At the time of writing, the only Ae borohydride initiators for the ROP of cyclic esters are those presented in this Chapter.1

Scheme 3.2 summarizes the reactions of commercially-available Ca(BH₄)₂(THF)₂ with [NEt₃H][BPh₄] and KTP^{Bu,Me}, as well as the reaction of [Ca(BH₄)(THF)₃][BPh₄] (17-BPh₄) with HC(Me₂pz)₃ to give [Ca{HC(Me₂pz)₃}(BH₄)(THF)₂][BPh₄] (18-BPh₄). The reaction of
Ca(BH₄)₂(THF)₂ with [NET₃][BPh₄] in THF proceeded smoothly over 2 h at -78 °C, giving 17-BPh₄ in 51% recrystallised yield.

Scheme 3.2. Synthesis of new calcium tetrahydroborate complexes. BPh₄ anions are omitted for 17-BPh₄⁺ and 18-BPh₄⁺.

Using these carefully controlled temperature conditions, no formation of the dication [Ca(THF)₆][BPh₄]₂ was observed (as would be expected from a Schlenk-type redistribution also leading to the formation of Ca(BH₄)₂(THF)₂). The ¹H NMR spectrum of 17-BPh₄ in CD₂Cl₂ shows a 1:1:1:1 quartet at -0.19 ppm for the BH₄ ligand (¹J_H₁B = 82 Hz) which appears at -36.1 ppm in the ¹¹B{¹H} NMR spectrum. The THF solution IR spectrum of 17-BPh₄ (Figure 3.2) is consistent with a κ³ bound BH₄ ligand, showing bands at 2406 (B–Hₚ stretch), 2260 cm⁻¹ and 2208 cm⁻¹ (B–Hₚ stretches). Interestingly, the ¹H NMR of Ca(BH₄)₂(THF)₂ in CD₂Cl₂ showed a 1:1:1:1 quartet at -0.21 ppm for the BH₄ ligand (¹J_H₁B = 82 Hz), which appears at -35.6 ppm in the ¹¹B{¹H} NMR spectrum. These shifts are almost identical to those of 17-BPh₄. However, the THF solution IR spectrum of Ca(BH₄)₂(THF)₂ showed a broad multiplet centred at 2280 cm⁻¹, presumably encompassing both the B–Hₚ and B–Hₚ stretches of the BH₄ ligands. Therefore, whilst the comparison of NMR data for 17-BPh₄ and Ca(BH₄)₂(THF)₂ does not provide any insight into the potential occurrence of redistribution, the difference between the solution IR data of the two species rules out this possibility.
Figure 3.2. Borohydride region of solution (THF) IR spectrum of \([\text{Ca(BH}_4](\text{THF})_3][\text{BPh}_4]\) (17-BPh\(_4\)). The background has been subtracted.

Reaction of 17-BPh\(_4\) with HC(Me\(_2\)pz)\(_3\) in dichloromethane at -78 °C gave 18-BPh\(_4\) in 74 % yield. The cation 18-BPh\(_4^+\) also possesses a \(\kappa^3\) bound BH\(_4\) ligand (\(\delta(\text{H}) = 0.15\) ppm (\(^{1}J_{\text{H-B}} = 82\) Hz); \(\delta(\text{\^{11}B}) = -35.6\) ppm in CD\(_2\)Cl\(_2\)). Again the THF solution IR spectrum is also consistent with a \(\kappa^3\) bound BH\(_4\) ligand, showing bands at 2410 (B–H\(_t\) stretch), 2270 cm\(^{-1}\) and 2210 cm\(^{-1}\) (B–H\(_b\) stretches). Once again these data are different to that shown in the solution IR spectrum of Ca(BH\(_4\))\(_2\)(THF)\(_2\), ruling out the possibility of redistribution to [Ca\{HC(Me\(_2\)pz)\(_3\)\}\(_2\)]\(^{2+}\) and Ca(BH\(_4\))\(_2\)(THF)\(_2\).

The solid state structures of the 17\(^+\) and 18\(^+\) are shown in Figure 3.3. The H atoms of the \(\kappa^3\)-BH\(_4\) ligands were located from Fourier difference maps and positionally and isotropically refined. The only previously structurally characterized calcium tetrahydroborate compounds are Ca(BH\(_4\))\(_2\)(DME)\(_2\) (two \(\kappa^3\) bound BH\(_4\) ligands, avg. Ca⋅⋅⋅B = 2.654 Å) and Ca\(_2\)(BH\(_4\))\(_2\)(diglyme)\(_2\) (mixture of \(\kappa^3\) and \(\kappa^2\) bound BH\(_4\) and diglyme ligands (avg. Ca⋅⋅⋅B = 2.714 and 2.878 Å)).\(^{43,44}\) The Ca⋅⋅⋅B distances of 2.610(3) and 2.581(2) Å in 17-BPh\(_4\) and 18-BPh\(_4\) are comparable to those of the \(\kappa^3\) bound BH\(_4\) ligands found in both of these reported complexes.
Figure 3.3. Molecular structures of $[\text{Ca}(\text{BH}_4)(\text{THF})_3]^+$ (17$, \text{left}$) and $[\text{HC}(\text{Me}_2\text{pz})\text{Ca}(\text{BH}_4)(\text{THF})_2]^+$ (18$, \text{right}$). BPh$_4$ anions omitted. The H atoms of the $\kappa^3$-$\text{BH}_4$ ligands were located from Fourier difference maps and positionally and isotropically refined.

Table 3.1. Selected bond distances ($\AA$) and angles ($^\circ$) for $[\text{Ca}(\text{BH}_4)(\text{THF})_3][\text{BPh}_4]$ (17-BPh$_4$).

<table>
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<tr>
<th>Bond/Distance</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
</tr>
</thead>
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<td>O(1)-Ca(1)-O(3)</td>
<td>161.31(9)</td>
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<td>Ca(1)-O(5)</td>
<td>2.3987(19)</td>
<td>O(1)-Ca(1)-O(4)</td>
<td>84.20(10)</td>
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<tr>
<td>Ca(1)$\cdots$B(1)</td>
<td>2.601(3)</td>
<td>O(1)-Ca(1)-O(5)</td>
<td>81.40(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(1)-B(1)-H(2)</td>
<td>111.2(8)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H(2)-B(1)-H(4)</td>
<td>108(3)</td>
</tr>
</tbody>
</table>
**Table 3.2.** Selected bond distances (Å) and angles (°) for [Ca{HC(Me2pz)3}-(BH4)(THF)2][BPh4] (18-BPh4).

<table>
<thead>
<tr>
<th>Bond/Interaction</th>
<th>Distance or Angle</th>
</tr>
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<tr>
<td>Ca(1)-N(1)</td>
<td>2.5046(15)</td>
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<tr>
<td>N(1)-Ca(1)-O(1)</td>
<td>155.72(5)</td>
</tr>
<tr>
<td>Ca(1)-N(3)</td>
<td>2.5025(14)</td>
</tr>
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<td>N(3)-Ca(1)-O(1)</td>
<td>94.82(5)</td>
</tr>
<tr>
<td>Ca(1)-N(5)</td>
<td>2.5335(15)</td>
</tr>
<tr>
<td>N(5)-Ca(1)-O(1)</td>
<td>82.08(5)</td>
</tr>
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<td>Ca(1)-O(1)</td>
<td>2.3643(13)</td>
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<td>N(1)-Ca(1)-O(2)</td>
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<td>Ca(1)-O(2)</td>
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<td>N(3)-Ca(1)-O(2)</td>
<td>151.27(5)</td>
</tr>
<tr>
<td>Ca(1)···B(1)</td>
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</tr>
<tr>
<td>N(5)-Ca(1)-O(2)</td>
<td>80.70(5)</td>
</tr>
<tr>
<td>H(1)-B(1)-H(2)</td>
<td>113.20(18)</td>
</tr>
<tr>
<td>H(2)-B(1)-H(4)</td>
<td>104.60(17)</td>
</tr>
</tbody>
</table>

Interestingly, performing the reaction of 17-BPh4 with HC(Me2pz)3 in THF at room temperature led to isolation of the redistribution product, [Ca{HC(Me2pz)3}]2[BPh4]2 (19-BPh4), in 52 % yield. Presumably the higher temperature and presence of excess THF favours the redistribution of 18-BPh4 to 19-[BPh4]2 and Ca(BH4)2(THF)2. This was indeed evident by monitoring both the low temperature reaction in CH2Cl2 and the room temperature reaction in THF. The reaction solution in CH2Cl2 remained transparent in appearance whereas the reaction in THF led to precipitation of the less soluble (due to its dicationic nature) 19-[BPh4]2. In fact the precipitation of the latter is likely to be an additional driving force in the formation of 19-[BPh4]2 in THF. It is noteworthy that the CH2Cl2 reaction led to the sole formation of 18-BPh4, with no evidence of the presence of 19-[BPh4]2 as a potentially competing redistribution side product. This further highlights the need for careful reaction control when synthesising organocalcium compounds in order to prevent redistribution reactions. However, this case serves to show that with care such difficulties may be overcome.

Sterically demanding tris(pyrazolyl)hydroborate ligands have been used successfully elsewhere for the preparation of heteroleptic Ae complexes. The most studied derivatives of these ligands possess a tert-butyl group in the 3-position of the ligand (i.e. close to the metal centre in a complex). The presence of these bulky groups serves to suppress unwanted redistribution reactions. For example, in the early 1990s Parkin et al.
reported the synthesis and solid state structures of (Tp\(^{\text{Bu}}\))Be(X) (X = Br, H or Me)\(^{46,52}\) and (Tp\(^{\text{Bu}}\))Mg(X) (X = Cl, Me and \(^{1}\)Pr)\(^{47,49,54}\). As mentioned in previous Chapters, Chisholm \textit{et al.} later reported the complexes (Tp\(^{\text{Bu}}\))Ca(X) (X = N(SiMe\(_3\))\(_2\) or O-2,6-C\(_6\)H\(_4\)-iPr)\(^3,4\) which were found to be extremely active initiators for the ROP of LA at room temperature. Interestingly, the attempted synthesis of (Tp\(^{\text{Bu}}\))Ca(I)(THF) from KTp\(^{\text{Bu}}\) and CaI\(_2\) was unsuccessful,\(^3\) presumably the bulk of the ligand was insufficient to stabilise this heteroleptic complex for the relatively large Ca\(^{2+}\) ion.

Recent work by Chisholm \textit{et al.} led to the development of tris(pyrazolyl)hydroborate ligands with pendant methoxy substituted hemi-labile donor arms (in place of the tert-butyl groups seen in Tp\(^{\text{Bu}}\)).\(^{45,51}\) For example, the heteroleptic complexes (Tp\(^{\text{C}^*}\))M(I) (M = Mg, Zn, Ca, Sr and Ba, Tp\(^{\text{C}^*}\) = tris[3-(2-methoxy-1,1-dimethyl)pyrazolyl]hydroborate)\(^{51}\) were synthesised, as well as (Tp\(^{\text{C}^*}\))Ca(X) (X = N(SiMe\(_3\))\(_2\) or O-4-C\(_6\)H\(_4\)-Me).\(^{45}\) Despite the steric bulk imposed by the Tp\(^{\text{C}^*}\) ligand, the homoleptic compounds (Tp\(^{\text{C}^*}\))\(_2\)M (M = Mg or Ca)\(^{45}\) were also synthesised, although these species were shown to exist both in solution and the solid state as separated ion pairs, i.e. [Tp\(^{\text{C}^*}\)Ca][Tp\(^{\text{C}^*}\)]. Interestingly, Harder \textit{et al.} attempted the synthesis of Tp\(^{\text{Bu}}\)Ca(H) and isolated the homoleptic calcium complex (Tp\(^{\text{Bu}}\))\(_2\)Ca\(^{55}\) as a redistribution product. Whilst both of the Tp\(^{\text{Bu}}\) ligands are tridentate in this complex, one is \(\kappa^3\) bound via the pyrazole nitrogen atoms and the other is \(\kappa^2\) bound via the pyrazole nitrogen atoms and a B-H unit.\(^{55}\)

(Tp\(^{\text{Bu,Me}}\))Ca(BH\(_4\))(THF) (20, Scheme 3.2) was readily prepared at room temperature directly from Ca(BH\(_4\))\(_2\)(THF)\(_2\) and KTp\(^{\text{Bu,Me}}\) in 65% recrystallised yield. The IR and NMR data for formally zwitterionic 20 are consistent with the structure proposed in Scheme 3.2 which is analogous to that of cationic \(18-\text{BPh}_4\) and Sella and Takats’ recently reported (Tp\(^{\text{Bu,Me}}\))Yb(BH\(_4\))(THF) (3.8).\(^{34}\) Interestingly, the fact that the unit cell parameters of the solid state structures of 20 are identical to that of 3.8 provide further evidence for the documented similarities between the Ae and lanthanide elements.\(^2\)

\(^1\)H and \(^{11}\)B NMR spectroscopy showed that 20 does not undergo redistribution to (Tp\(^{\text{Bu,Me}}\))\(_2\)Ca and Ca(BH\(_4\))\(_2\)(THF)\(_2\) in THF-\(d_8\) at room temperature or 70 \(^\circ\)C. The stability of 20 compared to the lower temperatures required in the formation of \(18-\text{BPh}_4\) is most likely due to the increased bulk of the tert-butyl group of the former in the 3-position of the Tp\(^{\text{Bu,Me}}\) ligand, providing additional steric stabilisation around the metal centre. The solid state structures of 19-[\text{BPh}_4]_2 and 21 are shown in Figure 3.4.
Figure 3.4. Molecular structures of Ca\{HC(Me_{2}pz)_{3}\}_{2}^{2+} (19^{2+}, left) and (Tp^{Bu,Me})Ca(BH_{4})(THF) (20, right). BPh\textsubscript{4} anions for 19^{2+} omitted. The H atoms of the \kappa\textsuperscript{3}-BH\textsubscript{4} ligand were located from Fourier difference maps and positionally and isotropically refined.

Table 3.3. Selected bond distances (Å) and angles (°) for [Ca\{HC(Me_{2}pz)_{3}\}_{2}[BPh_{4}]_{2} (19-[BPh_{4}]_{2}).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Dist./Angle</th>
</tr>
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<tbody>
<tr>
<td>Ca(1)-N(1)</td>
<td>2.4224(16)</td>
</tr>
<tr>
<td>N(1)-Ca(1)-N(3)</td>
<td>75.46(5)</td>
</tr>
<tr>
<td>Ca(1)-N(3)</td>
<td>2.4471(16)</td>
</tr>
<tr>
<td>N(1)-Ca(1)-N(5)</td>
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</tr>
<tr>
<td>Ca(1)-N(5)</td>
<td>2.4510(16)</td>
</tr>
<tr>
<td>N(3)-Ca(1)-N(5)</td>
<td>76.12(5)</td>
</tr>
</tbody>
</table>

Table 3.4. Selected bond distances (Å) and angles (°) for (Tp^{Bu,Me})Ca(BH_{4})(THF) (20).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Dist./Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(1)-N(1)</td>
<td>2.5053(16)</td>
</tr>
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<td>N(1)-Ca(1)-O(1)</td>
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<tr>
<td>Ca(1)-N(3)</td>
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</tr>
<tr>
<td>N(3)-Ca(1)-O(1)</td>
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</tr>
<tr>
<td>Ca(1)-N(5)</td>
<td>2.4307(16)</td>
</tr>
<tr>
<td>N(5)-Ca(1)-O(1)</td>
<td>81.75(5)</td>
</tr>
<tr>
<td>Ca(1)-O(1)</td>
<td>2.4291(14)</td>
</tr>
<tr>
<td>H(1)-B(1)-H(2)</td>
<td>112(3)</td>
</tr>
<tr>
<td>Ca(1)-..B(1)</td>
<td>2.567(3)</td>
</tr>
<tr>
<td>H(2)-B(1)-H(4)</td>
<td>108(3)</td>
</tr>
</tbody>
</table>
Chapter 3

The Ca···B distance of 2.654(3) Å in 20 is consistent with a κ^3-BH^4 ligand and is very similar to that observed in 17-BPh^4 and 18-BPh^4 (2.610(3) and 2.581(2) Å respectively). This distance is also very close to that (2.596(5) Å) seen in the isostructural (Tp^Bu,Me)Yb(BH^4)(THF) (3.8). The Ca-O distance (2.4291(14) Å) is also strikingly similar to the analogous Yb-O bond distance (2.463(2) Å) in 3.8. The solid state structure of 20 has only one coordinated THF molecule, whereas the related complex 18-BPh^4 has two. This is a consequence of the bulky tert-butyl groups around the metal centre in 20 compared to the less bulky methyl groups in the same position in 18-BPh^4. The Ca-Npz bond lengths in 20 (2.5053(16), 2.4256(17) and 2.4307(16) Å) are also shorter than those in 18-BPh^4 (2.5046(15), 2.5025(14) and 2.5335(15) Å). This is due to the monoanionic ligand in 20 compared to the neutral ligand in 18-BPh^4. The Ca-Npz bond lengths of 20 are longer than those of (Tp^Bu)Ca(O-2,6-C_6H_3iPr) (average 2.381 Å)^4 and slightly shorter than those in (Tp^Bu)_2Ca (average 2.497 Å)^55, consistent with the various steric factors and coordination number effects in the three compounds.

The Ca-Npz bond lengths in 19-[BPh^4]_2 (2.4224(16), 2.4471(16) and 2.4510(16) Å) are almost identical within error to the zwitterionic Ca{C(Me_2pz)_3}^2 (5, where the corresponding bond lengths are 2.4370(18), 2.4591(16) and 2.448(2) Å). This highlights the localised negative charge focused around the C(Me_2pz)_3 carbanion in the anionic tris(pyrazolyl)methanide ligand in the zwitterionic 5. The Ca-Npz bond lengths are also shorter than those in (Tp^Bu)_2Ca (average 2.497 Å)^55, due to the presence of less sterically demanding methyl groups in the 3-position of the ligand compared to the tert-butyl groups in (Tp^Bu)_2Ca.

The magnesium analogue of 20, (Tp^Bu,Me)Mg(BH^4) (22) was synthesised by an identical method (Equation 3.3) in 57% isolated yield. The IR and NMR data for formally zwitterionic 20 are consistent with the structure proposed (with a κ^3 bound BH^4 ligand) in Equation 3.2, although unfortunately it has not yet been possible to obtain diffraction-quality crystals. The absence of bound THF in 22 is a reflection of the smaller size of magnesium compared to calcium.
Unfortunately the reaction between Mg(BH$_4$)$_2$ and [NEt$_3$H][BPh$_4$] at -78 °C in THF led to [Mg(THF)$_6$][BPh$_4$]$_2$ (via a Schlenk equilibrium also producing Mg(BH$_4$)$_2$) rather than the desired heteroleptic analogue of 17-BPh$_4$, [Mg(BH$_4$)(THF)$_2$][BPh$_4$]. This was a surprising result: it was postulated that the smaller size of magnesium should make a half sandwich complex a more favoured product. The synthesis of [Mg{HC(Me$_2$pz)$_3$}-(BH$_4$)(THF)$_2$][BPh$_4$], the analogue of 18-BPh$_4$, was attempted by the addition of [NEt$_3$H][BPh$_4$] to a mixture of HC(Me$_2$pz)$_3$ and Mg(BH$_4$)$_2$ at -78 °C in THF. However, this again resulted in the redistribution product [Mg{HC(Me$_2$pz)$_3$}$_2$][BPh$_4$]$_2$. It was noted that prior to the formation of the insoluble dication, a brief period (following gas evolution) was observed where the contents of the reaction mixture remained in solution before the precipitation of [Mg(THF)$_6$][BPh$_4$]$_2$. It is thought that this may be attributed to the formation of the desired heteroleptic cation, and indeed it may be possible that use of a bulkier tris(pyrazolyl)methane ligand may result in the isolation of a desired heteroleptic cationic magnesium borohydride complex.

3.3 Polymerisation studies: ROP of ε-CL

The borohydride complexes [Ca(BH$_4$)(THF)$_3$][BPh$_4$] (17-BPh$_4$), [Ca{HC(Me$_2$pz)$_3$}$_2$][BPh$_4$]$_2$ (18-[BPh$_4$]$_2$), (Tp$^{Bu,Me}$)Ca(BH$_4$)(THF) (20) and (Tp$^{Bu,Me}$)Mg(BH$_4$) (22) were all highly active for the ROP of ε-CL in THF at room temperature, producing α,ω–dihydroxy telechelic PCL of the form HO(CH$_2$)$_5$C(O)–[PCL]-O(CH$_2$)$_6$OH in a matter of minutes. The formation of α,ω–dihydroxy telechelic PCL is a particular characteristic of (L)Ln(BH$_4$)-initiated ε-CL ROP and the mechanism of formation has been studied in detail experimentally and computationally (see also Scheme 3.0).$^{19, 24}$ Due to the rapid completion it was not possible to investigate the kinetic profiles of the polymerisations. Taking into consideration the aforementioned similarities between the Ae and lanthanide elements, (Tp$^{Bu,Me}$)Yb(BH$_4$)(THF) (3.8) was synthesised by published
methods and also tested, alongside Ca(BH₄)₂(THF)₂ as a control test. Similarly, these catalysts produced polymer within a number of minutes. The polymerisation results for all catalysts are summarised in Table 3.5. The time given for a particular catalyst is that taken to reach 100 % monomer conversion, as determined by ¹H NMR.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield(%)</th>
<th>Time(mins)</th>
<th>Mₙ(GPC)</th>
<th>Mₙ(calcld)</th>
<th>Mₙ/Mₙ</th>
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<tbody>
<tr>
<td>17-BPh₄</td>
<td>84</td>
<td>2</td>
<td>39,100</td>
<td>22,820</td>
<td>1.32</td>
</tr>
<tr>
<td>18-BPh₄</td>
<td>79</td>
<td>2</td>
<td>41,820</td>
<td>22,820</td>
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<td>20</td>
<td>81</td>
<td>10</td>
<td>17,600</td>
<td>22,820</td>
<td>1.28</td>
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<tr>
<td>22</td>
<td>72</td>
<td>10</td>
<td>32,240</td>
<td>22,820</td>
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<td>3.8</td>
<td>76</td>
<td>10</td>
<td>20,600</td>
<td>22,820</td>
<td>1.30</td>
</tr>
<tr>
<td>Ca(BH₄)₂(THF)₂</td>
<td>77</td>
<td>2</td>
<td>11,560</td>
<td>22,820</td>
<td>1.28</td>
</tr>
</tbody>
</table>

*Conditions: [ε-CL]:[catalyst] = 200:1, 3.4 mL solvent at 23 °C. See Experimental section for other details. * Isolated yield at 100 % NMR conversion. * Molecular weights (g mol⁻¹) determined from GPC using the appropriate Mark-Houwink corrections. * Expected Mₙ (g mol⁻¹) for 1 chain growing per metal centre at 100% conversion.

All catalysts produced polymers with narrow PDI values of approximately 1.3 and a fair agreement between measured and calculated Mₙ values was observed, although in most cases the measured Mₙ was higher than expected for the growth of one polymer chain per metal centre. This can be attributed to a fast rate of propagation relative to the rate of initiation. The similarities in the nature of the polymers produced by (Tp²Bu,Me)Ca(BH₄)(THF) (20) and (Tp²Bu,Me)Yb(BH₄)(THF) (3.8) can also be seen. Additionally, Ca(BH₄)₂(THF)₂ produced PCL with an Mₙ (11,560 g mol⁻¹) in very close agreement to that expected from two growing polymer chains per metal centre (11,410 g mol⁻¹). This result appears to rule out redistribution of either 17-BPh₄ or 18-BPh₄ under the polymerisation conditions.

No comparisons can be made with other main group borohydride complexes (since these are the first to be used in ROP studies). However, comparisons with related lanthanide borohydride complexes can be made. The most closely related complexes to [Ca(BH₄)(THF)₃][BPh₄] (17-BPh₄) and [Ca{HC(Me₂pz)₃}(BH₄)(THF)₂][BPh₄] (18-BPh₄)
are Okuda’s lanthanide borohydride cations \([\text{M(BH}_4\text{)}_2\text{(THF)}_3]\text{[BPh}_4\text{]}\) (\(\text{M} = \text{Y} (3.10), \text{La} (3.11), \text{Nd} (3.12)\) and \(\text{Sm} (3.13)\)). Similarly, these complexes also gave rapid gel formation for the ROP of \(\varepsilon\)-CL, giving polymers with comparable PDI values (1.3-1.4).\(^{27}\) The observed \(M_n\) values of the polymers produced were also slightly higher than expected; for these catalysts two growing polymer chains per metal centre was expected and generally three to four chains were found. The most closely related catalysts to 20, 22 and 3.8 and Chisholm’s \((\text{Tp}^{\text{BH}})\text{M(X)(THF)}_n\) (\(\text{M} = \text{Ca} (n = 1)\) or \(\text{Mg} (n = 2)\), \(\text{X} = \text{N(SiMe}_3)_2\) or \(\text{O-2,6-C}_6\text{H}_3\text{Pr}_2\)).\(^3,4\) However, these were not tested for \(\varepsilon\)-CL ROP.

The complex \(\text{Cp}^*\text{Sm(BH}_4\text{)(THF)}_2\) (3.9) also showed fast gel formation in the ROP of \(\varepsilon\)-CL and gave polymers with PDI values in the range 1.3-1.5 with \(M_n\) values generally in very good agreement to that expected for one chain per metal centre.\(^{36}\) For example a 234:1 ratio of \(\varepsilon\)-CL:3.9 polymerisation gave polymer with a PDI of 1.36 and an observed \(M_n\) of 20,400 (expected 22,400). The complex \(\text{Sm(O}_2\text{Npy})(\text{BH}_4\text{(THF)} (3.4) \text{[H}_2\text{O}_2\text{Npy} = (2-\text{C}_3\text{H}_4\text{N})\text{CH}_2\text{NCH}_2[2-\text{HO-3,5-C}_6\text{H}_2\text{Bu}_2)]_2\) gave \(\text{PCL}\) with a PDI of 1.8 and an observed \(M_n\) of 20,400 (expected 31,381). The broad PDI and lower than expected \(M_n\) was attributed to chain transfer events.\(^{21}\) It can be seen from these comparisons that the borohydride complexes prepared in this chapter show similar activity and control (and in some cases superior) to related lanthanide borohydride initiators. MALDI-ToF-MS analysis showed \(\alpha,\omega\)-dihydroxy telechelic polymers (an example is shown in Figure 3.5), consistent with the coordination-insertion mechanism proposed for lanthanide borohydride systems outlined in Scheme 3.0.\(^{19,20,38}\) For example, the peak at 1754.4 \(m/z\) (\(\dagger\) in Figure 3.5) corresponds to \(\text{HO(CH}_2\text{)}_3\text{C(O)[PCL]_13-O(CH}_2\text{)}_n\text{OH}\) (the calculated value is 1754.6).

**Figure 3.5.** MALDI-ToF MS of \(\alpha,\omega\)-dihydroxy telechelic PCL synthesised using \([\text{Ca(BH}_4\text{(THF)}_3]\text{[BPh}_4\text{]}\) (17-BPh_4). \(M_n\) by GPC analysis was 8,310 g mol\(^{-1}\) (from a \(\varepsilon\)-CL:[catalyst] = 20:1 polymerisation).
Additional evidence for the formation of $\alpha,\omega$-dihydroxy telechelic PCL was found in the $^1$H NMR spectra of the polymers formed, showing the two CH$_2$CH$_2$OH end groups (right hand region in Figure 3.6). It can be seen that the number of CH$_2$OH protons in the central repeating unit of $\alpha,\omega$-dihydroxy telechelic PCL is dependent on the length of a polymer chain, whilst the number of terminal CH$_2$ protons (4) is independent. Therefore integration of the two regions in a $^1$H NMR spectrum provides a measure of the $M_n$ value of a polymer sample. This was measured to be 6,740 g mol$^{-1}$ for the polymer sample shown in Figure 3.5 and in reasonable agreement with the value measured by GPC analysis (8,310 g mol$^{-1}$).

**Figure 3.6.** $^1$H NMR spectrum (CDCl$_3$) of $\alpha,\omega$-dihydroxy telechelic PCL synthesised using [Ca(BH$_4$)(THF)$_5$][BPh$_4$] (17-BPh$_4$). $M_n$ by GPC analysis was 8,310 g mol$^{-1}$ ([ε -CL]$_0$: [17-BPh$_4$]$_0$ = 20). The relative ratio of integrals = 29.

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### 3.4 Polymerisation studies: ROP of rac-LA

[Ca(BH$_4$)(THF)$_5$][BPh$_4$] (17-BPh$_4$) was active for the ROP of rac-LA at 70 °C in THF, consumption of rac-LA followed well-behaved first order kinetics (with a measured $k_{obs}$ value of 0.0084(2) min$^{-1}$) and gave a linear $M_n$ (GPC) vs. % conversion plot (Figure 3.7). The PLAs formed with this catalyst were all atactic as expected due to the absence of a supporting ligand, but had fairly narrow PDI values in the range 1.2-1.5. The gradient of the line of best fit for the $M_n$ vs. rac-LA converted plot is 135(6) g mol$^{-1}$ (% conversion)$^{-1}$ ($R^2 = 0.983$), very close to the expected value of 144.1. This, together with the narrow PDIs of the polymers formed, is evidence for a well controlled polymerisation process.
Figure 3.7. Data for the ROP of rac-LA using [Ca(BH₄)(THF)₅][BPh₄] (17-BPh₄). Top: first order plot for rac-LA consumption; \( R^2 = 0.987, k_{\text{obs}} = 0.0084(2) \text{ min}^{-1} \). Bottom: \( M_n \) (as measured by GPC) vs. rac-LA converted. The dotted line is that expected for one PLA chain per metal centre. Conditions: 6 mL THF, 70 °C, 4.5 hours, \([\text{rac-LA}]_0:\[\text{17-BPh}_4]_0 = 100\). PDI values are given in parentheses.

Figure 3.8 shows a plot of \( M_n \) vs equivalents rac-LA converted for \([\text{rac-LA}]_0:\[\text{17-BPh}_4]_0 \) ratios between 50 and 300. The gradient of the best-fit line was 152(3) g mol\(^{-1}\) (equivalents converted\(^{-1}\) \( R^2 = 0.998 \)) in excellent agreement with that predicted (144.1) for one PLA chain growing per Ca-BH₄ group in a living-type fashion.
Figure 3.8. $M_n$ (as measured by GPC) vs. equivalents rac-LA converted using $[\text{Ca(BH}_4\text{)(THF)}_2][\text{BPh}_4]$ ($17-\text{BPh}_4$). The dotted line is that expected for one PLA chain per BH$_4$ group. Conditions: 6 mL THF, 70 °C, 3 or 5 h, $[\text{rac-LA}]_0:[17-\text{BPh}_4]_0 = 50, 100, 150, 200, 250, 300$. PDI values are given in parentheses.

As previously discussed, it was shown by solution IR that $17-\text{BPh}_4$ does not undergo redistribution at room temperature in THF. In order to rule out the possibility of redistribution of $17-\text{BPh}_4$ under the polymerisation conditions (and subsequent polymerisation by $\text{Ca(BH}_4\text{)}_2(\text{THF})_2$), the polymerisation behaviour of $\text{Ca(BH}_4\text{)}_2(\text{THF})_2$ was studied under identical conditions to those used in the testing of $17-\text{BPh}_4$.

Figure 3.9 shows a plot of $M_n$ vs. equivalents rac-LA converted for $[\text{rac-LA}]_0:[\text{Ca(BH}_4\text{)}_2(\text{THF})_2]_0$ ratios between 50 and 300. The gradient of the best-fit line was 55(10) g mol$^{-1}$ (equivalents converted)$^{-1}$ ($R^2 = 0.906$), slightly lower than that predicted (72) for two PLA chains growing per borohydride group in a living-type fashion. The PDI values (1.6-1.8) of the polymers formed using $\text{Ca(BH}_4\text{)}_2(\text{THF})_2$ are broader than those formed using $17-\text{BPh}_4$ (1.3-1.5). Also, it has been shown that $17-\text{BPh}_4$ produces PLA with $M_n$ values consistent with one growing chain per metal centre, which is markedly different to the results obtained using $\text{Ca(BH}_4\text{)}_2(\text{THF})_2$. This is strong evidence that $17-\text{BPh}_4$ does not undergo redistribution under the polymerisation conditions. Unsurprisingly, the PLA formed using $\text{Ca(BH}_4\text{)}_2(\text{THF})_2$ was atactic.
**Figure 3.9.** $M_n$ (as measured by GPC) vs. equivalents $rac$-LA converted using 
Ca(BH$_4$)$_2$(THF)$_2$, $R^2 = 0.906$. The dotted line is that expected for two PLA chains per BH$_4$ group. Conditions: 6 mL THF, 70 °C, 3 or 5 h, $[rac$-LA]$_0$:[Ca(BH$_4$)$_2$(THF)$_2$]$_0$ = 50, 100, 150, 200, 250, 300. PDI values are given in parentheses.

The MALDI-ToF mass spectrum of a PLA sample obtained using [Ca(BH$_4$)(THF)$_5$][BPh$_4$] (17-BPh$_4$) is shown in Figure 3.10. The separation of integer polymer units is 72 m/z, consistent with transesterification side reactions. As mentioned in the introduction, the ROP of cyclic esters with borohydride initiators can lead to $\alpha,\omega$-dihydroxy terminated polyesters. In the case of LA, literature reports have suggested that poly$(rac$-LA) with either $-\text{CH(Me)CH}_2\text{OH}$ or $-\text{CH(Me)CHO}$ end groups may be formed.$^{16,23,25}$ The latter end group arises from protonolysis of the metal-bound “end” of the growing polymeryl chain (i.e. from the last enchained $rac$-LA), whereas the former end group arises from single reduction of one of the carbonyl groups of the first enchained $rac$-LA monomer by the initiating M$-$BH$_4$ group. A recent comprehensive experimental and theoretical study was carried out by Dyer et al.,$^{21}$ confirming this to be the case for a family of bis(phenolate)amine-supported samarium borohydride initiators.

However in the study by Dyer et al. high resolution MALDI-ToF MS techniques superior to those used for the purposes of this thesis were applied. This enabled the absolute determination of polymer end groups. The difficulty with standard MALDI-ToF MS techniques in the context of this thesis is the very similar m/z values predicted for polymer end groups, and their coincidence with cyclic PLA units. For example a linear polymer ($n$ = six) chain with a $-\text{CH(Me)CH}_2\text{OH}$ end group has a calculated m/z of 1050, very similar to
the calculated m/z of 1052 for a linear polymer chain with the same number of repeating units with a –CH(Me)CHO end group. Further complication arises when noting the calculated m/z of 1048 for a cyclic polymer unit consisting of seven monomer units, hence the need for higher resolution techniques when absolutely assigning polymer end groups in this case. Attempted methods to rectify this situation are discussed later in this chapter.

Figure 3.10. MALDI-ToF MS of PLA synthesised using [Ca(BH₄)(THF)₅][BPh₄] (17-BPh₄). Mₙ by GPC analysis was 2,240 g mol⁻¹ (from a [rac-LA]:[17-BPh₄]₀ = 20:1 polymerisation).

The slow ROP of rac-LA with 17-BPh₄ was alleviated by using 18-BPh₄, the HC(Me₂pz)₃ ligand providing a better-defined coordination environment, and perhaps guarding against binuclear or extensively LA chain chelated resting states. Thus up to 250 equivalents of rac-LA could be converted at room temperature within two hours with PDI values generally between 1.2 and 1.4. The consumption of rac-LA followed first order kinetics (with a measured kobs value of 0.037(1) min⁻¹) and gave a linear Mₙ (GPC) vs. % conversion plot (Figure 3.11).

Interestingly, the rate plot in Figure 3.11 appears to have two linear stages (the first ending after approximately five minutes). This effect has been observed elsewhere⁵⁶, ⁵⁷ and is thought to be a result of the equilibrium between aggregated and monomeric polymeryl species.⁵⁷ It is assumed that propagation only occurs from the latter and that monomeric active species are stabilised by an excess amount of monomer. Therefore, at low conversions the concentration of such species is high, accordingly the apparent rate
of polymerisation is high also. At higher conversions the equilibrium is shifted in the favour of aggregated species and therefore the apparent rate of polymerisation decreases. Such behaviour may also explain the higher than expected $M_n$ values seen throughout the polymerisation. Generally the experimental $M_n$ values are twice the expected value for one growing polymer chain per metal centre. This is consistent with a small proportion of the catalyst becoming active species, as would be the case for an equilibrium between aggregated and monomeric polymeryl species. This poor control is reflected in the fact that the gradient of the line of best fit for the $M_n$ vs. rac-LA converted plot is $304(7) \text{ g mol}^{-1} \text{ (% conversion)}^{-1}$ ($R^2 = 0.992$, see also Figure 3.11), approximately twice the expected value of 144.1.

**Figure 3.11.** Data for the ROP of rac-LA using $[\text{Ca}(\text{HC(Me}_2\text{pz})_3)(\text{BH}_4)(\text{THF})_2][\text{BPh}_4] - (18-\text{BPh}_4)$. Top: first order plot for rac-LA consumption; $R^2 = 0.994$, $k_{obs} = 0.037(1)$ min$^{-1}$. Bottom: $M_n$ (as measured by GPC) vs. rac-LA converted. The dotted line is that expected for one PLA chain per metal centre. Conditions: 6 mL THF, RT, 1 hour, $[\text{rac-LA}]_0:[18-\text{BPh}_4]_0 = 100$. PDI values are given in parentheses.
Figure 3.12 shows a plot of $M_n$ vs. equivalents rac-LA converted for $[\text{rac-LA}]_0:[18\text{-BPh}_4]_0$ ratios between 50 and 250. The gradient of the best-fit line was 157(11) g mol$^{-1}$ (equivalents converted)$^{-1}$ ($R^2 = 0.982$), in excellent agreement with that predicted (144.1) for one PLA chain, but in general the $M_n$ values were once again higher (1.5 to 2 times) than expected. Nonetheless, it is clear that the slow rac-LA ROP rates typically associated with cationic initiators$^7, 58$ can be alleviated with the appropriate supporting ligand, thus offering considerable potential for further development. In fact the only other example of a cationic initiator for the ROP of rac-LA was introduced very recently by Wheaton and Hayes.$^59$ The MALDI-ToF mass spectrum of a PLA sample obtained using 18-BPh$_4$ is very similar to that obtained using 17-BPh$_4$, showing a separation of integer polymer units of 72 m/z. Similarly, all of the polymers produced using 18-BPh$_4$ were atactic.

**Figure 3.12.** $M_n$ (as measured by GPC) vs. equivalents rac-LA converted using $[\text{Ca}\{\text{HC(Me}_2\text{pz)}_3\}\{(\text{BH}_4)(\text{THF})_2\}][\text{BPh}_4]$ (18-BPh$_4$). The dotted line is that expected for one PLA chain per BH$_4$ group. Conditions: 6 mL THF, RT, 2 hours, $[\text{rac-LA}]_0:[18\text{-BPh}_4]_0 = 50, 100, 150, 200, 250$. PDI values are given in parentheses.

Gratifyingly, $([\text{Tp}^{\text{Bu,Me}}]\text{Ca}(\text{BH}_4)(\text{THF})$ (20) is also a very efficient initiator for the ROP of rac-LA either at room temperature or -20 °C. For example, with $[\text{rac-LA}]_0:[20]_0 = 200$, >90% conversion was achieved within 5 mins at both temperatures. Figure 3.13 shows a plot of experimental $M_n$ vs. equivalents rac-LA converted for $[\text{rac-LA}]_0:[3]_0$ ratios between 50 and 200 at -20 °C.
**Figure 3.13.** $M_n$ (as measured by GPC) vs. equivalents rac-LA converted using (Tp$_{Bu,Me}$)Ca(BH$_4$)(THF) (20). The dotted line is that expected for one PLA chain per BH$_4$ group. Conditions: 6 mL THF, -20 °C, 5 minutes, [rac-LA]$_0$:[20]$_0$ = 40, 100, 120, 160, 200. PDI values are given in parentheses.

The gradient of the best-fit line is 162(4) g mol$^{-1}$ (equivalents converted)$^{-1}$ ($R^2 = 0.998$), in very good agreement with that predicted (144.1 g mol$^{-1}$ (equivalents converted)$^{-1}$) for one PLA chain growing per Ca–BH$_4$ group of 20 in a living-type fashion. The corresponding plot for ROP at RT was also linear (Figure 3.14) but the gradient of the best-fit line was 239(7) g mol$^{-1}$ (equivalents converted)$^{-1}$ ($R^2 = 0.996$), indicating less optimal control of the relative rates of initiation and propagation for this very active system.

Tetrad analysis of the CH(Me)O region of the selectively homonuclear decoupled $^1$H NMR spectra of the PLA samples formed with 20 revealed heterotactically-enriched polymer with high $P_r$ values of 0.88-0.90 at -20 °C (ca. 0.80 at RT), an example spectrum is shown in Figure 3.15. The stereochemical enrichment present in the polymer samples arises from a chain-end control process (rather than enatiomorphic site control typically seen with chiral catalysts). The bulk of the tert-butyl groups in the 3- position of the ligand clearly favour the addition of consecutive monomer units with opposite chirality (i.e. D-LA followed by L-LA), especially at low temperature where the lowered thermal motion reduces the probability of steroerrors.

The degree of heterotactic enrichment is similar to that found by Chisholm et al. when using (Tp$_{Bu}$)Ca(X) (X = N(SiMe$_3$)$_2$ or O-2,6-C$_6$H$_5$Pr$_2$) ($P_r = 0.9$).$^3,4$ and in contrast to the atactic PLA formed with the bulky calcium $\beta$-diketiminate complex.
The moderate to broad PDI values of the PLA formed using 20 both at -20 °C and room temperature (1.5-1.9) are also comparable to those found using the aforementioned tris(pyrazolyl)borate complexes prepared by Chisholm et al. (1.7, 1.6). The MALDI-ToF mass spectrum of a PLA sample obtained using 20 is very similar to that obtained using 17-BPh₄ and 18-BPh₄, showing a separation of integer polymer units of 72 m/z.

**Figure 3.14.** $M_n$ (as measured by GPC) vs. equivalents rac-LA converted using $(\text{Tp}^{\text{Bu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$ (20). Conditions: 6 mL THF, RT, 5 minutes, $[\text{rac-LA}]_0:[20]_0 = 40, 80, 100, 120, 160, 200$. PDI values are given in parentheses.

**Figure 3.15.** CH(Me)O region of the homonuclear decoupled $^1$H NMR spectrum of PLA formed using 20 ($P_r = 0.90$) at -20 °C.
In order to gain more information on the PLA end groups seen for polymers prepared using 17-BPh₄, 18-BPh₄ and 20, the deuterated analogue of the latter was prepared, (Tp^{1Bu,Me})Ca(BD₄)(THF) (20-\textit{d₄}). Through the use of a BD₄ initiator in place of a BH₄ initiator, the PLA end groups CH(Me)CD₂OH or –CH(Me)CDO, instead of CH(Me)CH₂OH or –CH(Me)CHO would be expected. It was postulated that the increased polymer mass would result in easier interpretation of MALDI-ToF spectra (with the previously mentioned difficulties of overlapping peaks in mind). ²H NMR would also be used as a polymer analysis tool.

Initially it was intended to synthesise all three deuterated analogues from Ca(BD₄)₂(THF)₂. However, the attempted synthesis of this precursor from CaI₂ and NaBD₄ proved non-trivial, resulting in only the monosubstituted product Ca(BD₄)I(THF)₂ regardless of stoichiometry and temperature. The complex (Tp^{1Bu,Me})Yb(BD₄)(THF)\textsuperscript{34} had previously been prepared by reaction of (Tp^{1Bu,Me})Yb(I)(THF) with NaBD₄. Following this approach the synthesis of 20-\textit{d₄} from (Tp^{1Bu,Me})Ca(I)(THF) (21) was similarly successful.

**Scheme 3.3.** Synthesis of (Tp^{1Bu,Me})Ca(I)(THF) (21) and (Tp^{1Bu,Me})Ca(BD₄)(THF) (20-\textit{d₄}).
(Tp^{Bu,Me})Ca(I)(THF) (21) was readily prepared at room temperature directly from CaI₂ and KTp^{Bu,Me} in 71% recrystallised yield. The IR and NMR data for formally zwitterionic 21 are consistent with the structure proposed in Scheme 3.3 which is analogous to that of Takats’ reported (Tp^{Bu,Me})Yb(I)(THF).60 Unlike the identical unit cell parameters seen between 20 and 3.8, in this case the unit cell parameters of 21 are not identical to that of (Tp^{Bu,Me})Yb(I)(THF).

**Figure 3.16.** Molecular structure of (Tp^{Bu,Me})Ca(I)(THF) (21). C-bound H atoms omitted and remaining H atoms drawn as spheres of an arbitrary radius.

**Table 3.6.** Selected bond distances (Å) and angles (°) for (Tp^{Bu,Me})Ca(I)(THF) (21).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(1)-N(1)</td>
<td>2.413(3)</td>
<td></td>
</tr>
<tr>
<td>Ca(1)-N(3)</td>
<td>2.440(3)</td>
<td>82.10(10)</td>
</tr>
<tr>
<td>Ca(1)-N(5)</td>
<td>2.471(3)</td>
<td>85.09(9)</td>
</tr>
<tr>
<td>Ca(1)-O(1)</td>
<td>2.402(2)</td>
<td>152.62(10)</td>
</tr>
<tr>
<td>Ca(1)-I(1)</td>
<td>3.0281(7)</td>
<td>134.70(8)</td>
</tr>
<tr>
<td>N(1)-Ca(1)-O(1)</td>
<td></td>
<td>117.26(7)</td>
</tr>
<tr>
<td>N(3)-Ca(1)-O(1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(5)-Ca(1)-I(1)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The Ca-I distance of 3.0281(7) Å is very close to that of 3.0536(8) Å seen in the isostructural (Tp^{Bu,Me})Yb(I)(THF).60 The Ca-O distance (2.402(2) Å) is also very similar to the analogous Yb-O bond distance (2.447(6) Å) seen in (Tp^{Bu,Me})Yb(I)(THF), as are the average Ca-Nₚₚₚ bond lengths (2.44 Å, c.f. 2.45 Å in (Tp^{Bu,Me})Yb(I)(THF)). The Ca-O
distance is slightly shorter in 21 than 20 (2.4291(14) Å). This is a consequence of the borohydride ligand in 20 possessing greater steric bulk than the iodide ligand in 21. The average Ca-Npz bond lengths in 21 are nonetheless comparable to those in 20 (2.45 Å).

(TpBuMe)Ca(BD4)(THF) (20-d4) was readily prepared at room temperature directly from 20 and NaBD4 in 58% recrystallised yield. The solution IR spectrum (THF) of 20-d4 is shown along with that of 20 in Figure 3.17.

Figure 3.17. Borohydride region of solution (THF) IR spectra of (TpBuMe)Ca(BH4)(THF) (20, red trace) and (TpBuMe)Ca(BD4)(THF) (20-d4, blue trace). The background has been subtracted.

The BH4 stretching region of the IR spectrum of 20 shows bands at 2416, 2223 cm⁻¹ and 2174 cm⁻¹. The first band corresponds to the B–Ht stretch of the BH4 ligand while the other two correspond to the B–Hb stretches. The corresponding 20-d4 isotopomer showed the expected isotope shifts in the IR spectrum, 1807 (s, B–Dt of BD4, νH/νD = 1.34) and 1543 (s, B–Db of BD4); νH/νD = 1.41, the other B–Hb stretch was hidden under the subtraction artefact. The 1H and 11B NMR spectra of 20 and 20-d4 are identical (the BH4 ligand of 20 was not visible by 1H NMR spectroscopy). Whilst the 2H NMR spectrum showed the presence of CD2OH protons of α,ω-dihydroxytelechelic PCL prepared using 20-d4 in an identical position to that seen in the 1H NMR spectrum of polymer prepared using 20, the MALDI-ToF spectra of both polymers were apparently identical. Unfortunately the resolution of the MALDI-ToF spectra were not
good enough to resolve deuterium and proton capped polymers. This was unfortunately also the case for PLA samples as it was not possible to resolve CH(Me)CH₃OH or CH(Me)CHO end groups from cyclic PLA units. Despite this it is likely that rac-LA and ε-CL are polymerised by the same coordination-insertion mechanism for this family of catalysts, as evidenced by generally good levels of control over the $M_n$ and PDIs of the polymers formed.

Despite the similarities observed between $(\text{Tp}^{\text{Bu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$ (20) and $(\text{Tp}^{\text{Bu,Me}})\text{Yb}(\text{BH}_4)(\text{THF})$ (3.8) for the ROP of ε-CL, 3.8 was a much slower initiator for the ROP of rac-LA than 20, and in fact required a temperature of 70 °C. The polymerisation followed first order monomer consumption (Figure 3.18) and took 75 minutes to reach 90% conversion (with a measured $k_{\text{obs}}$ value of 0.032(2) min⁻¹).

**Figure 3.18.** Data for the ROP of rac-LA using $(\text{Tp}^{\text{Bu,Me}})\text{Yb}(\text{BH}_4)(\text{THF})$ (3.8). Top: first order plot for rac-LA consumption; $R^2 = 0.990$, $k_{\text{obs}} = 0.032(2)$ min⁻¹. Bottom: $M_n$ (as measured by GPC) vs. rac-LA converted. The dotted line is that expected for one PLA chain per metal centre. Conditions: 6 mL THF, 70 °C, 75 mins, [rac-LA]₀:[3.8]₀ = 100. PDI values are given in parentheses.
The $M_n$ vs. rac-LA converted plot in Figure 3.18 shows initially higher than expected $M_n$ values, followed by a levelling off period. At high conversions, the $M_n$ values are slightly lower than expected. This trend is most likely due to the increasing degree of transesterification as the polymerisation proceeds. This poor behaviour is reflected in the fact that the gradient of the line of best fit for the $M_n$ vs. rac-LA converted plot is 56(4) g mol$^{-1}$ (% conversion)$^{-1}$ ($R^2 = 0.970$), less than half of the expected value (144.1) for one PLA chain growing per Yb–BH$_4$ group of 3.8 in a living-type fashion. Despite this poor control of $M_n$, the PDIs of the PLA formed were moderate (1.3-1.5).

Figure 3.19 shows a plot of experimental $M_n$ vs. equivalents rac-LA converted for [rac-LA]$_0$:[3.8]$_0$ ratios between 50 and 250. The gradient of the best-fit line is 78(3) g mol$^{-1}$ (equivalents converted)$^{-1}$ ($R^2 = 0.994$), approximately half of that predicted (144.1). For low equivalent polymerisations, the $M_n$ values are fairly close to the expected values for one chain growing per metal centre. Using higher equivalents of monomer, the $M_n$ values fall below the expected values. This is a similar trend to that observed in Figure 3.18 for the $M_n$ vs. rac-LA converted plot. For the PLA samples discussed in Figure 3.19, a slight degree of heterotactic enrichment was found ($P_t$ average = 0.70). This is lower than that seen in PLA prepared using 20 and can be attributed the higher temperature polymerisation conditions required using 3.8.

**Figure 3.19.** $M_n$ (as measured by GPC) vs. equivalents rac-LA converted using (Tp$^{1}$Bu,Me)$\text{Yb(BH}_4)(\text{THF})$ (3.8). Conditions: 6 mL THF, 70 °C, 60 minutes, [rac-LA]$_0$:[3.8]$_0$ = 40, 80, 120, 160, 200, 250. PDI values are given in parentheses.

The MALDI-ToF mass spectrum of a PLA sample obtained using 3.8 is very similar to that seen previously showing a separation of integer polymer units of 72 m/z. It was surprising that 3.8 behaved so differently to 20 given the aforementioned similarities between the two
complexes. However, such differences are not unprecedented.\textsuperscript{2,61} For example, Harder \textit{et al.} recently reported the different stereoselectivity shown towards the polymerisation of styrene by otherwise isomorphous calcium and ytterbium benzyl complexes.\textsuperscript{61} It was shown that the ytterbium centre remained divalent throughout the polymerisation process, i.e. an oxidative mechanism was ruled out. The differences in the results shown were credited to small changes of metal-ligand bonding between the calcium and ytterbium complexes.\textsuperscript{2, 61} However, generally the most obvious difference between calcium and ytterbium is the viable trivalent oxidation state for the latter.

Evans \textit{et al.} showed that a series of samarium(II) compounds initiated the ROP of \( \varepsilon \)-CL by an oxidative pathway involving samarium(III).\textsuperscript{62} More recently, Bonnet and co-workers speculated that the ROP of \( \varepsilon \)-CL using \( \text{Sm(BH}_4)_2(\text{THF})_2 \) proceeded by two competing pathways:\textsuperscript{36} the established coordination-insertion mechanism shown in Scheme 3.0 and an oxidative process involving trivalent samarium (Scheme 3.4).

\textbf{Scheme 3.4.} The oxidative mechanism of polymerisation of \( \varepsilon \)-CL proposed by Bonnet \textit{et al.}\textsuperscript{36}

\[
\begin{align*}
2 \text{Sm(BH}_4)_2(\text{THF})_2 & \rightarrow (\text{BH}_4)_2\text{Sm} - O - (\text{CH}_2)_5\text{C} - \text{C} - (\text{CH}_2)_5\text{O} - \text{Sm(BH}_4)_2 \\
& \downarrow 2n \\
(BH}_4)_2\text{Sm} - O - (\text{CH}_2)_5\text{C} - \text{C} - (\text{CH}_2)_5\text{O} - [O - (\text{CH}_2)_5\text{C} - \text{C} - (\text{CH}_2)_5\text{O}] - \text{Sm(BH}_4)_2 \\
& \downarrow H^+(\text{aq}) \\
H\{O - (\text{CH}_2)_5\text{C} - \text{C} - (\text{CH}_2)_5\text{O} - [O - (\text{CH}_2)_5\text{C} - \text{C} - (\text{CH}_2)_5\text{O}]\}_{n}
\end{align*}
\]

It was argued that the mechanism in operation depended on the \([\varepsilon \text{-CL}]:[\text{catalyst}]\) ratio; at low monomer to catalyst ratios (e.g. 116:1) the observed \( M_n \) values were consistent with one polymer chain growing per two metal centres, i.e. the observed \( M_n \) values were twice that
expected for one growing polymer chain per metal centre. In such situations it was argued that an oxidation pathway became prominent. At moderate monomer to catalyst ratios (e.g. 232:1) $M_n$ values were consistent with one chain per metal centre, and therefore coordination-insertion (with initiation by only one of the borohydride groups) was thought to be the prominent mechanism. At larger monomer to catalyst ratios (e.g. 464:1) the growth of three polymer chains per metal centre was observed and it was argued that both mechanisms could be in operation. However no DFT study was carried out in parallel to the experimental work, and therefore the feasibility of an oxidative mechanism was not determined.

Presumably, if true, a similar oxidative mechanism with ytterbium catalysts is also possible, and also may apply to rac-LA as well as $\varepsilon$-CL. However, it has been shown that PLA prepared using 3.8 generally has a lower than expected $M_n$ value, whereas $M_n$ values twice that expected would be shown by a similar oxidative mechanism. Additionally, the PCL prepared using 3.8 had an $M_n$ (20,600 g mol$^{-1}$), very close to the predicted value for one growing polymer chain per metal centre (22,820).

In order to probe further the likelihood of an oxidative mechanism in the case of 3.8, Takats’ previously reported complex, (Tp$^{tBu,Me}$)Yb(I)(THF) was synthesised by published methods.$^{60}$ With no initiating group available for coordination-insertion, any activity shown by this complex could be argued to be due to an oxidative mechanism. However, under identical polymerisation conditions used in the testing of 3.8 (and in fact for extended time periods), (Tp$^{tBu,Me}$)Yb(I)(THF) was shown to be inactive for the polymerisation of either $\varepsilon$-CL or rac-LA. It is also noteworthy that Sm(I)$_2$(THF)$_2$ was shown to be active for the ROP of $\varepsilon$-CL in THF by Evans et al.$^{62}$ The polymerisation conditions used in this case (refluxing THF), are very similar to those used in the testing of (Tp$^{tBu,Me}$)Yb(I)(THF) for rac-LA. Therefore an oxidative pathway seems to be highly unlikely in the case of polymerisations with 3.8.

(Tp$^{tBu,Me}$)Mg(BH$_4$) (22) was also a much slower initiator for the ROP of rac-LA than 20, and also required a temperature of 70 °C, although heterotactically enriched polymer with $P_r$ values averaging 0.65 were seen. The decreased enrichment when compared to polymers prepared using 20 is once more attributed to the higher temperature polymerisation conditions. The polymerisation followed first order monomer consumption and took 60 minutes to reach 88 % conversion (with a measured $k_{obs}$ value of 0.0039(6) min$^{-1}$, Figure 3.20). The first order rate plot shows an induction period up to 10 minutes. As mentioned in Chapter 2, induction periods have been observed
It is thought that an induction period occurs due to a period of ligand rearrangement around the metal centre, in order to allow the monomer access to the coordination sphere. The $M_n$ of the PLA formed during the polymerisation process is slightly below that expected for one growing polymer chain per metal centre at low conversions. At higher conversions the $M_n$ of the PLA formed is significantly lower, most likely due to transesterification side reactions. This poor control is reflected in the fact that the gradient of the line of best fit for the $M_n$ vs. rac-LA converted plot is $40(4) \text{ g mol}^{-1} (\% \text{ conversion})^{-1}$ ($R^2 = 0.945$), less than a third of the expected value (144.1) for one PLA chain growing per Mg–BH$_4$ group of 22 in a living-type fashion. Despite this poor control of $M_n$, the PDIs of the PLA formed were quite narrow (1.1–1.3).

**Figure 3.20.** Data for the ROP of rac-LA using (Tp$^{\text{Bu,Me}}$)$\text{Mg(BH}_4)$ (22). Top: first order plot for rac-LA consumption; $R^2 = 0.999$, $k_{\text{obs}} = 0.039(6) \text{ min}^{-1}$. Bottom: $M_n$ (as measured by GPC) vs. rac-LA converted. The dotted line is that expected for one PLA chain per metal centre. Conditions: 6 mL THF, 70 $^\circ$C, 60 mins, [rac-LA]$_0$:[22]$_0 = 100$. PDI values are given in parentheses.
Figure 3.21 shows a plot of experimental $M_n$ vs. equivalents rac-LA converted for $[\text{rac-LA}]_0:[3.8]_0$ ratios between 50 and 250. The gradient of the best-fit line is $92(15)$ g mol$^{-1}$ (equivalents converted)$^{-1}$ ($R^2 = 0.927$) lower than that predicted ($144.1$ g mol$^{-1}$ (equiv. converted)$^{-1}$) for one PLA chain growing per Mg–BH$_4$ group of 22 in a living-type fashion. This is consistent with the $M_n$ vs. rac-LA converted plot shown in Figure 3.20 and is most likely due to the occurrence of extensive transesterification.

**Figure 3.21.** $M_n$ (as measured by GPC) vs. equivalents rac-LA converted using $(\text{Tp}^{\text{Bu,Me}})\text{Mg(BH}_4\text{)}$ (22). Conditions: 6 mL THF, 70 °C, 60 minutes, $[\text{rac-LA}]_0:[3.8]_0 = 40, 80, 120, 160, 200$. PDI values are given in parentheses.

The reduced activity of 22 compared to 20 is a consequence of the reduced size of magnesium compared to calcium. Clearly the rate of initiation is slower for 22 than 20, therefore the relative ratio with the rate of propagation would be expected to be higher for 22 than 20. This could also explain similar behaviour shown by 3.8. The MALDI-ToF mass spectrum of a PLA sample obtained using 22 is very similar to that seen previously showing a separation of integer polymer units of 72 $m/z$. This is also strong evidence for transesterification.

The overall performance of 22 is disappointing when compared to related heteroleptic magnesium complexes used for the ROP of LA. For example, the complex (BDI)$\text{MgN}^{(\text{PrO})}(\text{THF})$ (BDI = CH-[CMeN-(2,6-$^{\text{Pr}_2}$C$_6$H$_3$)$_2$]), prepared by Coates in 2001, polymerised 200 equivalents of rac-LA at room temperature within 2 minutes. The PLA formed was atactic, and had a higher than expected $M_n$ ($64,000$ g mol$^{-1}$ compared to the expected value of 28,800$)$. Interestingly, the complex (BDI)$\text{MgN}[\text{N(SiMe}_3\text{)}_2](\text{THF})$ (BDI = CH-[CMeN-(2,6-$^{\text{Pr}_2}$C$_6$H$_3$)$_2$]) gave highly heterotactic PLA ($P_r = 0.90$) in just 5 minutes.
at room temperature.\textsuperscript{3} The closely related complex (Tp^{Bu})Mg(OEt), originally prepared by Parkin\textsuperscript{54}, was shown by Chisholm to polymerise 200 equivalents of \textit{rac}-LA at room temperature in 1 hour, although further details were not given.\textsuperscript{4} One possible explanation for the contrastingly poor activity and control shown by 22 is the possible formation of aggregated species.

The activity of and selectivity of the boroxydride complexes 17-BPh$_4$, 18-BPh$_4$ and 20 is comparable to the best lanthanide systems reported (although the first report by Mountford and co-workers was only published in 2005).\textsuperscript{26} For example, the complex Sm(O$_2$N$_{py}$)(BH$_4$)(THF) (3.4) [H$_2$O$_2$N$_{py}$ = (2-C$_5$H$_4$N)CH$_2$NCH$_2${2-HO-3,5-C$_6$H$_2$Bu$_2$}] polymerised 200 equivalents of \textit{rac}-LA at room temperature in THF, giving heterotactic PLA ($P_t = 0.84$), an $M_n$ of 14,400 (expected 18,160) and a PDI of 1.51.\textsuperscript{21}

### 3.5 Summary and Conclusions

The work presented in this chapter has developed cationic and charge neutral tetrahydroborates as a new type of ROP initiator for the Ae elements. Compounds 17-BPh$_4$ and 18-BPh$_4$ are also the first reported cationic main group tetrahydroborates. The new tetrahydroborates were readily prepared using protonolysis-substitution or salt elimination protocols and extensions to different ancillary ligands and the other Ae elements (e.g. strontium) should be readily achieved. The ROP performance for 17-BPh$_4$, 18-BPh$_4$ and 20 equals or exceeds that found previously for initiators based on the heavier Ae elements. The heterotactic enrichment and molecular weight control achieved with 20 surpasses those of the best (L)Ln(BH$_4$) systems so far reported. These catalysts also show vast improvement compared to those presented in Chapter 2.

Additionally the first comparison between calcium and ytterbium for ROP has been made. Continuing work in the Mountford group is underway to further explain the differences in activity observed. Whilst it was not possible to conclusively prove a coordination-insertion mechanism in the case of the ROP of \textit{rac}-LA, extended work with high resolution MALDI-ToF MS and DFT studies should provide further insight. These synthetic and ROP advances are expected to provide the impetus and basis for further progress in these areas.
3.6 References

Chapter Four

Cationic Rare Earth alkyl and alkoxide complexes and their use in the immortal ROP of rac-lactide
4.0 Overview

This Chapter will provide an introduction into rare earth complexes (with an emphasis on cationic complexes) and their application towards polymerisation. An overview of the synthesis and characterisation of rare earth complexes will be presented. Their solid state structures and solution behaviour will be discussed, in conjunction with their application to the ring opening polymerisation of cyclic esters. An introduction to immortal ROP will also be given. Comparison of the newly reported complexes and related complexes will be undertaken within the context of the solid state structures and the ROP activity and selectivity observed. Some of this work has recently been published.\(^1\)

4.1 Introduction

Until recently the organometallic chemistry of the rare earth metals has been underdeveloped in comparison to the later transition metals, and has been largely dominated by the ubiquitous cyclopentadienyl ligand. The recent renewal in interest in post-metallocene organometallic complexes of the rare earth metals is in part related to recent reports describing their use as pre-catalysts for olefin polymerisation\(^2\)-\(^5\) and well defined initiators for the polymerisation of cyclic esters.\(^6\)-\(^13\)

One of the major contributing factors to the relative lack of organometallic rare earth chemistry is the synthetic challenge associated with the preparation of monomeric, well-defined complexes. Rare earth metals are highly Lewis acidic and therefore have a tendency to form bridged, oligomeric structures.\(^14\) It is not a coincidence that this Lewis acidity is also the driving force behind growing interest in the use of rare earth complexes in polymerisation catalysis. Additionally rare earth metal complexes are prone to ligand redistribution reactions and also have a tendency to form ‘ate’ complexes in the presence of alkali metal halides.\(^11\)

A successful supporting ligand must fulfil a number of criteria. Firstly, the ligand must possess a degree of steric bulk sufficient to stabilise the formation of monomeric complexes, whilst the remaining coordination sphere of the metal must be large enough to conduct substrate coordination and subsequent transformations necessary for catalytic activity. Furthermore, the supporting ligand should not present any competing sites of reactivity. Aside from the cyclopentadienyl ligand and its substituted derivatives, the most commonly used ligands in post-metallocene rare earth chemistry possess ‘hard’ O or N based polydentate ligands.
4.1.1 Neutral Rare Earth Complexes

As mentioned, early organometallic rare earth chemistry was largely focussed around the cyclopentadienyl ligand framework. The first organometallic rare earth complexes, Cp₃M (M = Sc or Y) were prepared by Wilkinson and Birmingham in 1956 by the reaction between the trivalent metal chloride and NaCp in THF. Despite this early discovery, organometallic rare earth chemistry remained relatively unexplored until the 1970s, by this time the necessary advances in analytical techniques and experimental methods had been made to prepare and study a wider range of these extremely air and moisture sensitive complexes. The subsequent fast expansion of the preparation of bis(cyclopentadienyl) rare earth complexes has been the subject of excellent reviews and will not be extensively discussed here, other than highlighting a few key examples.

In 1970 Coutts and co-workers reported the first example of a scandium bis(cyclopentadienyl) complex, [Cp₂Sc(µ-Cl)]₂, prepared by the reaction between the ScCl₃ and NaCp. In subsequent work by Atwood and Smith the solid state structure was obtained showing this complex to be dimeric. Manzer later reported the solid state structure of the monomeric Cp₂ScCl(THF), presumably the presence of a bound THF molecule stabilises the monomeric structure. Later work reported the preparation of the yttrium analogues [Cp₂Y(µ-Cl)]₂ and Cp₂YCl(THF) by similar synthetic methods. Reaction of these complexes with alkali metal and Grignard reagents has led to a large number of scandium and yttrium bis(cyclopentadienyl) derivatives including alkyls, aluminates, alkoxides and borohydrides.

In comparison to the extensive research carried out on bis(cyclopentadienyl) rare earth complexes and their derivatives, there has been relatively little reported work on mono(cyclopentadienyl) rare earth complexes. This area has been a subject of an extensive recent review and this thesis only serves to highlight noteworthy examples. The main reason for the relatively few known mono(cyclopentadienyl) rare earth complexes is the increased difficulty in their handling and preparation, owing much to a more exposed metal centre prone to Lewis base complexation and increased air and moisture sensitivity.

Piers et al. showed that mono(cyclopentadienyl) such as Cp*Sc(OP'tBu₃)Cl₂ (4.0 in Figure 4.0) can be synthesised with the incorporation of another bulky ligand. Alkylation of 4.0 with MeLi yields the compounds Cp*Sc(OP'tBu₃)Me₂ which, when treated with BAr₃F, gave the ion pair [Cp*Sc(OP'tBu₃)Me][MeBAR₃F]. The dimeric hydride complex [Cp*Y(OAr)(µ-H)]₂ (4.1) was prepared by hydrogenation of the parent alkyl complex.
Cp*Y(OAr)(CH$_2$SiMe$_3$) and demonstrated reactivity with a range of unsaturated substrates.$^{27}$

**Figure 4.0.** Rare earth complexes supported by cyclopentadienyl and post-metallocene ligands

Another approach used to saturate the metal coordination sphere is the use of linked donor-cyclopentadienyl ligands. The most commonly used donor arms are amide groups,$^{25}$ and these constrained geometry systems were originally developed for Group 4 metals. The first rare earth constrained geometry systems were prepared by Bercaw$^{28}$ in 1994 and subsequent work by Okuda focused on the preparation of a family of related catalysts.$^{29-32}$ An example is the complex (C$_5$Me$_4$SiMe$_2$NCMe$_2$NCBu)Y(CH$_2$SiMe$_3$)(THF) (4.2) which was shown to be a good catalyst for the polymerisation of ethylene and styrene as well as hydrosilylation.$^{29-32}$ Further work by Piers *et al.* led to the development of {C$_5$H$_3$(3-
CH₂CH₂NMe₂)SiMe₂N₂Bu)Sc(CH₂SiMe₃) (4.3), which is also an active ethylene polymerisation catalyst.

The past 10-15 years have seen a rapid increase in the number and variety of non-cyclopentadienyl based ligands used to support rare earth metals. This area has been the subject of a number of recent reviews. Good examples are the β-diketiminate scandium complex (4.4) and Y{O-2,6-C₆H₃(tBu)CHNPh}₂(CH₂SiMe₃) (4.5), both prepared by Piers et al. The former was shown be highly active in the polymerisation of ethylene and the latter was active for the ROP of ε-CL.

In 1997 Bercaw et al. reported the synthesis of the organoscandium and organoyttrium complexes M(Me₃[9]aneN₃)Me₃ (M = Sc (4.6) or Y(4.7)). The reactivity of these complexes towards small, unsaturated molecules was investigated and the scandium complex was found to be proficient for the polymerisation of ethylene in the presence of a co-catalyst. Recently in the Mountford group the bulky neosilyl homologues M(Me₃[9]aneN₃)(CH₂SiMe₃)₃ (M = Sc or Y) were prepared and the scandium complex was found to be a highly active precatalyst for ethylene polymerisation. The solid state structure of the yttrium catalyst was subsequently reported by Hessen. The first rare earth organometallic complex supported by an all-sulfur donor ligand, Sc([9]aneS₃)(CH₂SiMe₃)₃ (4.8), was recently prepared by Mountford et al. This is the sulfur analogue of the Me₃[9]aneN₃ complex 4.6 and was also a highly active precatalyst for the polymerisation of ethylene. The neutral ‘tris-ox’ scandium alkyl complex (4.9) was recently reported by Gade et al. and was shown to be a highly active pre-catalyst for the stereospecific polymerisation of 1-hexene.

### 4.1.2 Cationic Rare Earth Complexes

The chemistry of the rare earth metals is dominated by neutral and anionic species. More recently, however, thanks to the development of post-metallocene rare earth precatalysts for the polymerisation of olefins, cationic species have been receiving increasing interest. In general, when used as catalysts for the polymerisation of olefins, cationic rare earth complexes are generated in situ and are not isolated. Due to the high Lewis acidity of the cationic rare earth metal centres, coupled with the presence of nucleophilic alkyl groups these complexes are synthetically challenging to prepare and isolate.

Cationic rare earth alkyl complexes are most commonly prepared via one of three main synthetic methods (Equation 4.0): i) alkyl group abstraction by strong Lewis acids; ii) alkyl
group abstraction by trityl cation; iii) alkyl group protonation by Brønsted acids, the conjugate bases of which are usually poor Lewis bases.

\[
\begin{align*}
\text{i)} & \quad \text{LnR}_3 + \text{LA} \quad \rightarrow \quad [\text{LnR}_2][\text{LAR}] \\
\text{ii)} & \quad \text{LnR}_3 + [\text{CPh}_3][\text{A}] \quad \rightarrow \quad [\text{LnR}_2][\text{A}] \\
& \quad \quad \quad \text{-Ph}_3\text{CR} \\
\text{iii)} & \quad \text{LnR}_3 + [\text{NHR'}_3][\text{A}] \quad \rightarrow \quad [\text{LnR}_2][\text{A}] \\
& \quad \quad \quad \text{-NR'}_3 \quad \quad \text{- HR}
\end{align*}
\]

\(\text{Ln} = \text{rare earth metal; LA = Lewis Acid; A = anion, R = hydrocarbyl}\)

**Equation 4.0**

The first example of a cationic rare earth complex, \([\text{Cp}^*\text{La}\{\text{CH(SiMe}_3\}_2}]\{\mu-\text{Ph}\}_2\text{BPh}_2\]1, was reported by Schaverien in 1992.\(^{44}\) This was synthesised by the protonolysis reaction between \([\text{Cp}^*\text{La}\{\text{CH(SiMe}_3\}_2}\]2 and \([\text{NHMe}_2\text{Ph}][\text{BPh}_4]\] in good yield. The addition of three equivalents of THF to a toluene solution of this complex led to irreversible displacement of the \(\text{BPh}_4\) anion and the formation of \([\text{Cp}^*\text{La}\{\text{CH(SiMe}_3\}_2}\](\text{THF})_3][\text{BPh}_4]\] (4.10 in Figure 4.1).\(^{44}\) Okuda et al. later reported the in situ synthesis of the furyl-substituted cyclopentadienyl complexes \(\{[\eta^5:\eta^1-\text{C}_5\text{Me}_4\text{SiMe}_3(\text{C}_4\text{H}_3\text{O-2})]\text{Ln(THF)}_3][\text{BPh}_3(\text{CH}_2\text{SiMe}_3)]\} (\text{Ln} = \text{Y (4.11) or Lu (4.12)}).\(^{45}\) As mentioned previously Piers et al. prepared the complex \([\text{Cp}^*\text{Sc}(\text{OP}^\text{tBu}_3)\text{Me}][\text{MeBAr}_3^\text{F}_2]\] (4.13) by the reaction of \(\text{Cp}^*\text{Sc}(\text{OP}^\text{tBu}_3)\text{Me}_2\) with \(\text{BAr}_3^\text{F}_3\).\(^{26}\)

Evans reported in 1990 that oxidation of the divalent complex \(\text{Cp}^*\text{Sm(THF)}_2\) with \(\text{AgBPh}_4\) in THF led to the formation of the trivalent samarium cationic complex \(\text{[Cp}^*\text{Sm(THF)}_2][\text{BPh}_4]\] (4.14)\(^{46}\) whilst performing the reaction in toluene formed \(\text{[Cp}^*\text{Sm}](\mu-\text{Ph})_2\text{BPh}_2\).\(^{47}\) A unique example of an yttrium mono(cyclopentadienyl) dication, \(\text{[Y(\eta^5-\text{C}_5\text{Me}_4\text{SiMe}_3)}(\text{THF})_4][\text{BPh}_4]\] (4.15), was synthesised by Okuda et al. by reaction of \(\text{Y(\eta^5-\text{C}_5\text{Me}_4\text{SiMe}_3)}_4(\mu-\text{H})_4(\mu_3-\text{H})_4(\text{THF})_2\) with an excess of \([\text{NEt}_3\text{H}][\text{BPh}_4]\] in THF.\(^{48}\) Additionally, Arnold and co-workers have recently reported the in situ generation of the cationic Sm ion pair \(\text{[Cp}^*\text{Sm(\eta^5-\text{ArNC(Me)CHC(Me)NAr})}(\mu-\text{Me})\text{BAr}_3^\text{F}_3]\] (4.16)\(^{49}\) and Berg et al. generated the yttrium complex, \(\text{[Y(MAC)(CH}_2\text{SiMe}_3)]}[\text{BAr}_3^\text{F}_3(\text{CH}_2\text{SiMe}_3)]\) (MAC = deprotonated aza-18-crown-6) (4.17) in situ.\(^{50}\)
Figure 4.1. Cationic rare earth complexes supported by cyclopentadienyl and post-metallocene ligands (anion(s) = BPh$_4^-$ unless otherwise specified).

Bercaw et al. prepared the scandium monocationic complex [Sc(Me$_3$[9]aneN$_3$)Me$_2$(THF)][BAr$_4^-$F] (4.18) by reaction of Sc(Me$_3$[9]aneN$_3$)Me$_3$ with [PhNMe$_2$H][BPh$_4$] in THF, however the Sc-Me resonance of the cation was not detected and in the absence of a solid state structure it was postulated that a liquid lattice had formed. Okuda et al. also reported that treatment of a THF solution of the yttrium tris(alkyl)complex [Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$] with 2 equivalents of [NEt$_3$H][BPh$_4$] or [PhNMe$_2$H][BPh$_4$] gave the dicationic alkyl complex [Y(CH$_2$SiMe$_3$)(THF)$_5$]$_2$[BPh$_4$] (4.19).
4.1.3 Cationic ROP Catalysts

Rare earth mono- and di-cationic alkyl complexes are well-known Ziegler-type catalysts for olefin polymerisation.\textsuperscript{43} However, despite extensive studies of neutral rare earth complexes for the ROP of LA,\textsuperscript{11,52} there are only a handful of reported cationic ROP catalysts (for any metal)\textsuperscript{1,53-58}, although this is a rapidly expanding field. The cationic zinc lactate complex \textbf{4.20} (Figure 4.2) was reported by Hayes and Wheaton in 2010.\textsuperscript{58} \textbf{4.20} is a highly active initiator for the ROP of rac-LA at ambient temperature in CH\textsubscript{2}Cl\textsubscript{2}, giving 90\% conversion of 200 equivalents in 50 minutes and slightly heterotactically enriched polymer (\(P_r = 0.63\)).\textsuperscript{58}

\textbf{Figure 4.2.} Cationic ROP catalysts (anion(s) = BPh\textsubscript{4} unless otherwise specified).

In 2011 Otero \textit{et al.} prepared the heteroscorpionate complex \([\text{HC(Me}_{2}\text{pz})\text{HCCSN(Ph)Al-Me}][\text{BPh}_4]\) (\textbf{4.21}),\textsuperscript{56} which proved to be a very well controlled (but low activity) initiator for the ROP of \(\varepsilon\)-CL. PCL with an observed \(M_n\) of 19,950 g mol\(^{-1}\) (expected 24,900) and a narrow PDI of 1.26 was produced.\textsuperscript{56}

The complex \([\text{Ca}\{\text{HC(Me}_{2}\text{pz})_3\}][\text{BH}_4][\text{BPh}_4]\) (\textbf{18-BPh\textsubscript{4}})\textsuperscript{55} was discussed in the previous chapter and was shown to be a good initiator for the ROP of \(\varepsilon\)-CL and rac-LA.
Very recently Carpentier et al. reported a family of base-free cationic Ae complexes \([2-[(1,4,7,10-tetraoxa-13-azacyclohexadecan-13-yl)methyl]-4,6-di-tert-butylphenol]M][X] (M = Zn (4.22); Mg (4.23); Ca (4.24); Sr (4.25) or Ba, (4.26) and X = H_2N[BAr_3^F_2]).^{53, 59}

These were shown to be very active in the presence of chain transfer reagents (PrOH, BnOH and in some cases BnNH_2) for the immortal ROP of \(L\)-LA, producing polymers with narrow to moderate PDIs and \(M_n\) values close to those expected.\(^{53, 59}\)

In principle, two ROP mechanisms for cationic complexes can be envisaged: classical coordination-insertion and activated chain end (ACE).\(^{53, 60}\) ACE differs from coordination-insertion in that the nucleophilic group attached to the metal centre (the initiating group in coordination-insertion) is not transferred to the monomer. Instead, propagation occurs through an activated (cationic) ring-opened monomer unit bound to the metal centre.\(^{60}\) The complexes 4.20 and 18-BPh_4 are both thought to facilitate the ROP of LA by a coordination-insertion mechanism,\(^{55, 58}\) whereas 4.21 has been postulated to operate by an ACE mechanism.\(^{56}\) The complexes 4.22-4.26 (with no nucleophilic metal-bound group available for coordination-insertion) were reported to operate by an activated monomer mechanism (this is described in Section 4.1.4).\(^{53, 59}\)

### 4.1.4 Immortal ROP

ROP reactions catalysed by metal complexes usually proceed in a ‘living’ fashion (as outlined in the introduction); there are ideally as many growing polymer chains as there are initiating groups. Whilst often successful, living polymerisation does have disadvantages, namely low catalytic productivity and potentially large contamination of the polymer with catalyst residues.\(^{54}\)

The so-called ‘immortal’ ROP (i-ROP) provides an alternative to classical living ROP. This process involves a two component system, a catalyst and an external nucleophile that acts both as an initiator and a chain transfer agent (CTA). In i-ROP the number of growing polymer chains exceeds the number of initiating groups presented by the catalyst. This technique was first introduced by Inoue et al. in the 1980s for the ROP of epoxides and cyclic esters with aluminium porphyrin alkoxide catalysts in conjunction with alcohol CTAs.\(^{61}\) Since then catalyst systems based on other metals (e.g. Mg, Ca, Fe, Zn, Sn and Y) have been successfully studied for i-ROP.\(^{1, 53, 59, 62-66}\)

As is necessary for classical living polymerisation, for i-ROP to occur the rate of initiation must proceed faster than the rate of propagation and irreversible termination reactions (i.e. the formation of cyclic polymer units) must be minimal. Additionally, the rate of reversible
Chapter 4

chain transfer reactions must be greater than the rate of propagation, leading to polymers with narrow PDIs. Two mechanisms have been documented in metal initiated i-ROP: one based on coordination-insertion (Scheme 4.0) and a second known as an activated monomer mechanism (Scheme 4.1).

In the coordination-insertion mechanism, most typically involving a catalyst of the type (L)M-Nu (Nu = initiating group such as alkoxide, amide or borohydride), a preliminary step exists resulting in the in situ formation of the initiating species (L)M-OR (except where Nu and OR are homologous) occurs. This newly formed species undergoes coordination-insertion of the first monomer unit, leading to the propagating species (L)M-[PLA]-OR.

The growing polymer chain undergoes rapid exchange with other protic species, initially CTA molecules, introduced in excess in the reaction medium that rapidly convert to “dormant” (metal free) polymer chains. Thus, species active for propagation for some time do reversibly convert back and forth to inactive species. This rapid growing/dormant interconversion cycle continues over the entire course of the polymerisation process. Any active species bearing a (L)M–O(alkoxide) bond can bring about the propagation and any HO-terminated polymer can behave as the CTA. The rate of this transfer process is the decisive factor in molecular weight control. Finally, termination of living (L)M-[PLA]-OR species gives the H-[PLA]-OR polymer.
Scheme 4.0. The coordination-insertion mechanism for the \( i \)-ROP of LA.\(^5\)

\[
\begin{align*}
\text{[M]} \rightarrow & \quad \text{OR} \\
\text{OR' + } & \quad \text{[M]} \rightarrow \quad \text{[LA]}_n \rightarrow \quad \text{OR} \\
\text{[M]} \rightarrow & \quad \text{OR'} \\
\text{R'OH} & \quad \text{fast} \\
\text{RO[LA]}_m \rightarrow & \quad \text{fast} \\
\text{[M]} \rightarrow & \quad \text{[LA]}_n \rightarrow \quad \text{RO[LA]}_m \rightarrow \quad \text{OR} \\
\end{align*}
\]

\[R'OH = \text{alcohol or another growing chain RO[LA]}_m \text{H}\]
On the other hand, \(i\)-ROP systems commonly based on simple Lewis acidic metal salts (e.g. triflates) usually proceed by the aforementioned activated monomer mechanism (depicted in Scheme 4.1). The Lewis acidic metal center first activates the monomer upon coordination to its carbonyl oxygen. The external protic nucleophilic additive, commonly an alcohol, then initiates the polymerisation upon attack of the electrophilic carbon atom of the carbonyl group, which results in the ring-opening of the monomer via oxygen-acyl bond cleavage.

**Scheme 4.1.** The activated monomer mechanism for the \(i\)-ROP of LA.\(^{54}\)

The CTA and hydroxy end-capped macromolecules H-[PLA]-OR eventually produced during the process all behave as external nucleophiles. These hydroxy end-capped polymers are involved in exchange and/or transfer reaction equilibria as “active” (coordinated to the metal center) and “dormant” species. Again, as long as these transfer equilibria are rapid enough compared to the initiation and subsequent propagation steps, the \(i\)-ROP remains controlled. This implies that all the aforementioned end-capped polymer chains exhibit the same reactivity, so that they are all progressively transformed into higher molar weight products by iterative incorporation of monomer units.
This activated monomer mechanism differs from the coordination-insertion mechanism in that the nucleophile involved in the first ring-opening event is an external molecule, independent from the catalyst, whilst in coordination-insertion the nucleophile is inherent to the active catalyst (starting as a bound initiating group).54 Accordingly, in both mechanisms the \( M_n \) is directly proportional to the monomer-to-CTA ratio. Despite the existence of the previously mentioned neutral systems for \( \epsilon \)-ROP, to date only a handful of examples for cationic systems have been reported.1, 53, 59

4.2 Synthesis of mono- and di-cationic yttrium alkyl and alkoxide complexes.

The monocationic complexes \( Y\{HC(Me_2pz)_3\}(CH_2SiMe_3)_2(THF)[BAR^F_4], \), \( [Y\{HC(Me_2pz)_3\}(O^3Pr)_2(THF)][BAR^F_4] \), \( [Y\{Me_3[9]aneN_3\}(CH_2SiMe_3)_2(THF)][BAR^F_4] \) were previously synthesised in the Mountford group.67, 68 These were all shown to be active catalysts for the ROP of \( \epsilon \)-CL in THF at RT, producing PCL with moderate-to-broad PDIs and \( M_n \) values reasonably close to that expected.67 Inspired by this and the relatively small number of cationic ROP catalysts, it was decided to synthesise a related family of cationic yttrium catalysts and assess any potential activity towards the ROP of LA.

Scheme 4.2 summarises the reactions of \( Y\{(CH_2SiMe_3)_3(THF)_2 \) with one or two equivalents of \( [NET_3H][BPh_4] \) and \( HC(Me_2pz)_3 \) and subsequent reactions with \(^3\)PrOH. The reaction of \( Y\{(CH_2SiMe_3)_3(THF)_2 \) with one or two equivalents of \( [NET_3H][BPh_4] \) followed by the addition of \( HC(Me_2pz)_3 \) in THF at -78 °C proceeded smoothly, giving the alkyl cations \( Y\{HC(Me_2pz)_3\}(CH_2SiMe_3)_2(THF)[BAR^F_4] \) (23-BPh\(_4\)) and \( Y\{HC(Me_2pz)_3\}- \) \( (CH_2SiMe_3)(THF)_3\)[BAR^F_4] \) (25-[BPh\(_4\)]\(_2\)) in 78 and 77 % recrystallised yields respectively. 23-BPh\(_4\) and 25-[BPh\(_4\)]\(_2\) reacted with two and one equivalents of \(^3\)PrOH respectively at room temperature in \( CH_2Cl_2 \) to give the isopropoxide cations \( Y\{HC(Me_2pz)_3\}(O^3Pr)_2(THF)[BAR^F_4] \) (24-BPh\(_4\)) and \( Y\{HC(Me_2pz)_3\}(O^3Pr)(THF)_3\)-[BPh\(_4\)]\(_2\) (26-[BPh\(_4\)]\(_2\)) in 79 and 67 % recrystallised yields.

The NMR spectra of 23-BPh\(_4\), 24-BPh\(_4\), 25-[BPh\(_4\)]\(_2\) and 26-[BPh\(_4\)]\(_2\) are consistent with the structures proposed in Scheme 4.2. The monocationic complexes 23-BPh\(_4\) and 24-BPh\(_4\) have an approximate octahedral geometry around the yttrium centre, whereas the dicationic complexes 25-[BPh\(_4\)]\(_2\) and 26-[BPh\(_4\)]\(_2\) have an approximate pentagonal bipyramidal geometry around the yttrium centre (this can also be seen in the solid state structure of 26\(^{2+}\) shown in Figure 4.3). In all cases, two sets of resonances (relative ratio 1:1) for Me\(_2pz\) groups were observed, consistent with a \( \kappa^3N \)-HC(Me\(_2pz\))\(_3\) ligand.

The alkyl complexes 23-BPh\(_4\) and 25-[BPh\(_4\)]\(_2\) both showed a sharp singlet (\( \delta^1H = -0.15; \delta^{13C} = 4.1 \) and \( \delta^1H = -0.19; \delta^{13C} = 3.9 \) ppm respectively) and a doublet (\( \delta^1H = -0.43 \) and \( \delta^{13C} = 6.9 \) ppm) consistent with the \( \kappa^1 \)-alkyl and \( \kappa^3N \)-HC(Me\(_2pz\))\(_3\) ligand respectively.
(\(J_{\text{HY}} = 2.8\) Hz); \(\delta^{(13)}(\text{C}) = 38.7\) \((J_{\text{CY}} = 49\) Hz) and \(\delta^{(1)}(\text{H}) = -0.19\) \((J_{\text{HY}} = 2.9\) Hz); \(\delta^{(13)}(\text{C}) = 47.8\) \((J_{\text{CY}} = 40\) Hz) ppm) in \(\text{CD}_2\text{Cl}_2\), corresponding to the \(\text{SiMe}_3\) and \(\text{CH}_2\) resonances respectively. The other notable differences between the NMR spectra of the two complexes are the difference in relative intensities for the bound THF molecules and non-coordinating \(\text{BPh}_4^-\) anions. Similar differences can be seen between the NMR spectra of the mono- and di-cationic alkoxide complexes 23-\(\text{BPh}_4\) and 25-\([\text{BPh}_4]_2\).

**Scheme 4.2.** Synthesis of new \(\text{HC(Me}_2\text{pz})_3\) supported mono- and di-cationic yttrium alkyl and alkoxide complexes. \(\text{BPh}_4^-\) anions are omitted.
Figure 4.3. Molecular structure of \([Y\{HC(Me_2pz)_3\}(O^iPr)(THF)_3]^{2+} (26^{2+})\). BPh_4^- anions omitted.

Table 3.0. Selected bond distances (Å) and angles (°) for \([Y\{HC(Me_2pz)_3\}(O^iPr)(THF)_3][BPh_4]_2 (26-[BPh_4]_2)\).

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y(1)-O(1)</td>
<td>1.998(3)</td>
<td>O(1)-Y(1)-N(1)</td>
</tr>
<tr>
<td>Y(1)-O(2)</td>
<td>2.391(3)</td>
<td>O(1)-Y(1)-N(3)</td>
</tr>
<tr>
<td>Y(1)-O(3)</td>
<td>2.438(3)</td>
<td>O(1)-Y(1)-N(5)</td>
</tr>
<tr>
<td>Y(1)-O(4)</td>
<td>2.416(3)</td>
<td>O(1)-Y(1)-O(2)</td>
</tr>
<tr>
<td>Y(1)-N(1)</td>
<td>2.519(3)</td>
<td>O(1)-Y(1)-O(3)</td>
</tr>
<tr>
<td>Y(1)-N(3)</td>
<td>2.500(3)</td>
<td>O(1)-Y(1)-O(4)</td>
</tr>
<tr>
<td>Y(1)-N(5)</td>
<td>2.501(3)</td>
<td></td>
</tr>
</tbody>
</table>

\([Y\{HC(Me_2pz)_3\}(O^iPr)(THF)_3][BPh_4]_2 (26-[BPh_4]_2)\) has a distorted pentagonal bipyramidal geometry with the central 7-coordinate yttrium dication supported by a $\kappa^3N$ bound HC(Me_2pz)_3 ligand. The Y-N(1) and Y-O(1) bonds occupy apical positions, with all other Y-bonded groups occupying equatorial positions. This is evident from the Y-N(1) bond length (2.519(3) Å), which is notably longer than the Y-N(3) or Y-N(5) bond lengths (2.500(3) and 2.501(3) Å respectively). The Y-O(1) bond distance of 1.998(3) Å is very close to the Y-alkoxide bond length of 1.9990(16) Å found in Okuda’s
[Y(OCMePh$_2$)(THF)$_3$][BPh$_4$]$_2$. In addition the Y-O(1) distance is similar (though a little shorter) to the Y siloxide distance (2.0705(15) Å) found in [Y{OSi(O'Bu)$_3$}](THF)$_6$][BPh$_4$]$_2$. The Y-O(THF) distances in 26-[BPh$_4$]$_2$ are also comparable to those found in the complex [Y(Cl)(OCMe$_3$)(THF)$_3$][BPh$_4$] (2.391(5)–2.422(5) Å) reported by Evans. The Y-N$_{pz}$ bond distances found in 26-[BPh$_4$]$_2$ are substantially shorter than those found in the neutral Y(HClMe)$_2$(CH$_2$SiMe$_3$)$_3$ (2.601(2), 2.563(2) and 2.596(2) Å), most likely a consequence of the dicationic nature of 26$^{2+}$.

Scheme 4.3 summarises the reactions of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with one or two equivalents of [NEt$_3$H][BPh$_4$] and Me$_3$[9]aneN$_3$ and subsequent reactions with iPrOH. The reaction of Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ with one or two equivalents of [NEt$_3$H][BPh$_4$] followed by the addition of Me$_3$[9]aneN$_3$ in THF at -78 °C proceeded smoothly, giving the alkyl cations [Y(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)$_2$(THF)][BPh$_4$] (27-BPh$_4$) and [Y(Me$_3$[9]aneN$_3$)(CH$_2$SiMe$_3$)-(THF)$_3$][BPh$_4$]$_2$ (29-[BPh$_4$]$_2$) in 71 and 68 % recrystallised yields respectively. 27-BPh$_4$ and 29-[BPh$_4$]$_2$ reacted with two and one equivalents of iPrOH respectively at room temperature in CH$_2$Cl$_2$ to give the isopropoxide cations [Y(Me$_3$[9]aneN$_3$)(O'Pr)$_2$(THF)][BPh$_4$] (28-BPh$_4$) and [Y(Me$_3$[9]aneN$_3$)(O'Pr)-(THF)$_3$][BPh$_4$]$_2$ (30-[BPh$_4$]$_2$) in 62 and 63 % recrystallised yields.

The NMR spectra of 27-BPh$_4$, 28-BPh$_4$, 29-[BPh$_4$]$_2$ and 30-[BPh$_4$]$_2$ are consistent with the structures proposed in Scheme 4.3. Similarly to the HC(Me$_2$pz)$_3$ supported cations, the monocationic complexes 27-BPh$_4$ and 28-BPh$_4$ have an approximate octahedral geometry around the yttrium centre, whereas the dicationic complexes 29-[BPh$_4$]$_2$ and 30-[BPh$_4$]$_2$ have an approximate pentagonal bipyramidal geometry around the yttrium centre. Unfortunately repeated attempts to grow diffraction-quality crystals were unsuccessful.

In all cases, the NMR spectra were consistent with a $\kappa^3N$-(Me$_3$[9]aneN$_3$) ligand. Two sets of resonances (relative ratio 1:2) for the NMe$_2$ groups were observed, the first set corresponding to an NMe$_2$ group trans to bound THF molecule(s) and the second corresponding to NMe$_2$ groups trans to CH$_2$SiMe$_3$ group(s). The “up” and “down” (with respect to the metal) ring methylene protons appear as mutually coupled second-order multiplets consistent with the macrocycle being $\kappa^3$ bound to the MR (R = (O'Pr)$_n$ or (CH$_2$SiMe$_3$)$_n$, n = 1 or 2) fragment. The relative intensities of the R groups, bound THF molecules and BPh$_4$ anions were consistent with the mono- or di-cationic nature of the complexes.
Scheme 4.3. Synthesis of new Me$_3$[9]aneN$_3$ supported mono- and di-cationic yttrium alkyl and alkoxide complexes. BPh$_4^-$ anions are omitted.

4.3 Polymerisation studies: ROP of rac-LA.

4.3.1 ROP of rac-LA using 24-BPh₄ and 30-[BPh₄]₂.

The consumption of rac-LA followed first order kinetics with both the monocationic complex [Y{HC(Me₂pz)₃}[(O')Pr]₂(THF)][BPh₄] (24-BPh₄) and the dicationic complex [Y(Me₃[9]aneN₃)(O')Pr](THF)₃][BPh₄]₂ (30-[BPh₄]₂), taking 3-4 hours for the polymerisation to approach 90 % in both cases. The first order rate constants ($k_{obs}$) were similar for both catalysts (0.012(9) and 0.010(3) min⁻¹ for 24-BPh₄ and 30-[BPh₄]₂ respectively). The gradients of the lines of best fit for the polymerisations in both cases (75(3) and 138(4) g mol⁻¹ (equivalents converted)⁻¹ for 24-BPh₄ and 30-[BPh₄]₂ respectively), were close to the expected values (72 and 144 g mol⁻¹ (equivalents converted)⁻¹). Additionally the polymers had $M_n$ values close to those expected (see Figures 4.4 and 4.5), and moderate PDI values (1.2-1.4), although there was no stereochemical enrichment obtained.

Both 24-BPh₄ and 30-[BPh₄]₂ also showed first order consumption of rac-LA in the presence of 5 equivalents of tPrOH (see also Figures 4.4 and 4.5), showing evidence of the growth of multiple chains per metal centre (7 in the case of 24-BPh₄ and 6 in the case of 30-[BPh₄]₂). The gradients of the lines of best fit for the polymerisations in both cases (19(1) and 29(2) g mol⁻¹ (equivalents converted)⁻¹ for 24-BPh₄ and 30-[BPh₄]₂ respectively), were close to the expected values (20.6 and 24.0 g mol⁻¹ (equivalents converted)⁻¹). Once more the $M_n$ values observed were in excellent agreement to those expected, and the PDIs were narrow (1.2-1.4). Interestingly, the first order rate constants for both sets of polymerisations were identical within error (0.011(4) and 0.012(3) min⁻¹ for 24-BPh₄ and 30-[BPh₄]₂ respectively) to those measured for polymerisations in the absence of tPrOH (0.012(9) and 0.010(3) min⁻¹), implying a zero order dependence on [tPrOH] of the rate of polymerisation. The implications of this are discussed in detail later in this chapter for polymerisations using [Y{HC(Me₂pz)₃}(CH₂SiMe₃)(THF)₃][BPh₄]₂ (25-[BPh₄]₂) and [Y{HC(Me₂pz)₃}(O'Pr)(THF)₃][BPh₄]₂ (26-[BPh₄]₂).
Figure 4.4. $M_n$ vs. conversion for the ROP of rac-LA using 24-BPh$_4$ (i) without $^3$PrOH (black diamonds) and (ii) with 5 equiv. $^3$PrOH (red squares). The upper dotted line is that predicted for 2 PLA chains per 24$^+$, the lower for 7 chains per 24$^{2+}$. Conditions: 6 mL THF, 70 °C, 3 hours, $[rac\text{-LA}]_0:[24\text{-BPh}_4]_0 = 100$.

Figure 4.5. $M_n$ vs. conversion for the ROP of rac-LA using 30-[BPh$_4$]$_2$ (i) without $^3$PrOH (black diamonds) and (ii) with 5 equiv. $^3$PrOH (red squares). The upper dotted line is that predicted for 1 PLA chain per 30$^{2+}$, the lower for 6 chains per 30$^{2+}$. Conditions: 6 mL THF, 70 °C, 4 hours, $[rac\text{-LA}]_0:[30\text{-BPh}_4]_2]_0 = 100$. 
4.3.2 ROP of rac-LA using 25-[BPh₄]₂ and 26-[BPh₄]₂.

Building upon these initial results, polymerisation studies were extended to the HC(Me₂pz)₃ dicationic complexes \[Y{HC(Me₂pz)₃}(CH₂SiMe₃)(THF)₃][BPh₄]₂ \ (25-[BPh₄]₂) \ and \ [Y{HC(Me₂pz)₃}(O'Pr)(THF)₃][BPh₄]₂ \ (26-[BPh₄]₂).\]

The consumption of rac-LA followed first order kinetics with both 25-[BPh₄]₂ and 26-[BPh₄]₂, taking approximately 12 hours for the polymerisation to approach 90% conversion. The first order rate constants \(k_{obs}\) were identical within error for both catalysts (0.0027(4) \ (25-[BPh₄]₂) \ and \ 0.0027(2) \ (26-[BPh₄]₂)). The identical rate constants suggest the presence of the same propagating species in both cases. Despite the extended times required (most likely due to the dicationic nature of the catalysts and subsequent propagating species), the polymerisations were well controlled. It is notable that polymerisations using 25-[BPh₄]₂ and 26-[BPh₄]₂ are both significantly slower than those using 30-[BPh₄]₂. This is most likely due to the difference between the face capping ligand used (HC(Me₂pz)₃ \ vs. \ Me₃[9]aneN₃) and is discussed further towards the end of this Chapter. Figures 4.6 and 4.7 show that chain growth proceeded in a linear manner with the observed \(M_n\) values being very close to those predicted with either one or six (in the presence of \(^3\)PrOH or BnNH₂ CTAs) polymer chains per metal.

The gradient of the line of best fit for the polymerisation with no CTA using 25-[BPh₄]₂ was 170(10) g mol⁻¹ (equivalents converted)⁻¹, in reasonable agreement with the expected value of 144 g mol⁻¹ (equivalents converted)⁻¹. Together with the good agreement between expected and observed \(M_n\) values and the fairly narrow (average 1.40) PDI values this indicates a well controlled, living polymerisation process. Additionally it can be seen that the agreement between expected and observed \(M_n\) values using both \(^3\)PrOH and BnNH₂ as CTAs is very good. The gradients of the lines of best fit are 30(1) and 31(1) g mol⁻¹ (equivs. converted)⁻¹ respectively, very close to the expected value of 29 g mol⁻¹ (equivs. converted)⁻¹. The average PDI values of the polymers obtained using both CTAs were quite narrow (1.30). It also noteworthy that the first order rate constants \(k_{obs}\) for polymerisations with both CTAs (0.0028(6) \ (\(^3\)PrOH) \ and \ 0.003(1) \ (BnNH₂) \ min⁻¹) were identical within error to the first order rate constant for the polymerisation with no added CTA (0.0027(4) \ min⁻¹).
Figure 4.6. $M_n$ vs. conversion for the ROP of rac-LA using 25-[BPh$_4$]$_2$ (i) without $^1$PrOH or BnNH$_2$ (black diamonds); (ii) with 5 equiv. $^1$PrOH (red squares); (iii) with 5 equiv. BnNH$_2$ (blue triangles). The upper dotted line is that predicted for 1 PLA chain per 25$^{2+}$, the lower for 6 chains per 25$^{2+}$. Conditions: 6 mL THF, 70 °C, 12 hours, $[\text{rac-LA}]_0:[25-[\text{BPh}_4]_2]_0 = 100$.

Similarly, the gradient of the line of best fit for the polymerisation with no CTA using 26-[BPh$_4$]$_2$ was 152(10) g mol$^{-1}$ (equivs. converted)$^{-1}$, in very good agreement with the expected value of 144 g mol$^{-1}$ (equivs. converted)$^{-1}$ and in closer agreement than that observed with 25-[BPh$_4$]$_2$ (170(10) g mol$^{-1}$ (equivs. converted)$^{-1}$ Excellent agreement between expected and observed $M_n$ values was found and the PDI values (1.2-1.3) were very narrow. Once more it can be seen that the agreement between expected and observed $M_n$ values using both $^1$PrOH and BnNH$_2$ as CTAs is very good. The gradients of the lines of best fit are 29(1) and 28(1) g mol$^{-1}$ (equivs. converted)$^{-1}$ respectively, identical within error to the expected value of 29 g mol$^{-1}$ (equivs. converted)$^{-1}$. The average PDI values of the polymers obtained using both CTAs were also narrow (1.2-1.3). As was the case with 25-[BPh$_4$]$_2$, the first order rate constants ($k_{\text{obs}}$) for polymerisations with both CTAs (0.0029(5) ($^1$PrOH) and 0.0028(4) (BnNH$_2$) min$^{-1}$) were identical within error to the first order rate constant for the polymerisation with no CTA (0.0027(2) min$^{-1}$).
Figure 4.7. $M_n$ vs. conversion for the ROP of rac-LA using 26-[BPh$_4$]$_2$ (i) without iPrOH or BnNH$_2$ (black diamonds); (ii) with 5 equiv. iPrOH (red squares); (iii) with 5 equiv. BnNH$_2$ (blue triangles). The upper dotted line is that predicted for 1 PLA chain per 26$^{2+}$, the lower for 6 chains per 26$^{2+}$. Conditions: 6 mL THF, 70 °C, 12 hours, [rac-LA]:[26-[BPh$_4$]$_2$]$_0$ = 100.

The MALDI-ToF MS and $^1$H NMR spectra of polymers formed using 25-[BPh$_4$]$_2$ and 26-[BPh$_4$]$_2$ with iPrOH as a CTA showed the expected iPrO-chain end groups (an example MALDI-ToF mass spectrum is shown in Figure 4.8). As seen with the previous systems described in chapters two and three, the separation of peaks was 72 m/z units, consistent with a degree of transesterification in the polymerisation process. This is not surprising given the extended reaction times and elevated temperatures required. However, the good control and close $M_n$ agreement between observed and expected values are a good indication of the probable minor extent of the occurrence of these processes. The major distribution in the MALDI-ToF spectrum shown in Figure 4.8 corresponds to iPrO-chain end groups, whilst the minor distribution corresponds to cyclic PLA units formed by intramolecular transesterification. Whilst the intensity of the two distributions appears very similar, this is due to the fact that the formation of lower molecular weight cyclic units is probably favoured over larger cyclic units, and therefore a low molecular weight sample would contain a higher concentration of them than a higher molecular weight sample. This is evident by the ‘tailing off’ of the secondary distribution at higher m/z values.
Figure 4.8. MALDI-ToF MS of iPrO-chain end capped PLA synthesised using [Y(HC(Me2pz)3)(OiPr)(THF)3][BPh4]2 (26-[BPh4]2) and iPrOH as a CTA. $M_n$ by GPC analysis was 3,100 g mol$^{-1}$ (from an aliquot taken at 60 minutes). * = iPrO-capped polymer, † = cyclic PLA units.

Similarly the MALDI-ToF MS and $^1$H NMR spectra of polymers formed using 25-[BPh4]2 and 26-[BPh4]2 with BnNH2 as a CTA showed the expected BnNH-chain end groups (an example MALDI-ToF spectrum is shown in Figure 4.9). The spectrum shown corresponds to polymer prepared using 26-[BPh4]2 and shows a major distribution corresponding to BnNH-capped polymer units alongside a minor cyclic unit distribution and a second minor distribution corresponding to iPrO-terminated chains, arising from the iPrO end groups originally attached to 26-[BPh4]2. Once again there is a peak separation of 72 m/z consistent with transesterification side reactions.
Figure 4.9. MALDI-ToF MS of BnNH-chain end capped PLA synthesised using
\([Y\{HC(\text{Me}2\text{pz})3\}(\text{O}i\text{Pr})(\text{THF})3][\text{BPh}_4]_2\) and BnNH\textsubscript{2} as a CTA. \(M_n\) by GPC analysis was 1,520 g mol\(^{-1}\) (from an aliquot taken at 60 minutes). \(* = \text{^iPrO-capped polymer,}\n\n† = cyclic PLA units, ♀ = BnNH-capped polymer.

4.3.3 Mechanistic Studies.

Holding the \([\text{rac-LA}]:[\text{BnNH}_2]\) constant at 100:3 and varying the equivalents of 26-[BPh\textsubscript{4}]\textsubscript{2} from 1 to 4 allowed the order in \([Y]_0\) to be determined (Figure 4.10). The rate constants for \([\text{rac-LA}]:[\text{BnNH}_2]:[Y]_0\) ([\([Y]_0 = 1, 2, 3\) or 4) were measured to be 0.0027(2), 0.006(1), 0.009(2) and 0.013(2) min\(^{-1}\) respectively, consistent with a first order dependence in \([Y]_0\). Furthermore, the plot of -ln\((k_{\text{obs}})\) against -ln(equivalents \(Y\)) (Figure 4.11) had a gradient of 1.02(2), confirming the first order dependence of \(k_{\text{obs}}\) on \([Y]_0\). Additionally, the end point \(M_n\) values for the polymerisations were measured to be 3170, 3140, 3210 and 3270 (for \([Y]_0 = 1, 2, 3\) or 4 respectively), showing that the \(M_n\) of the resultant polymer is independent of \([Y]_0\) and dependent on \([\text{rac-LA}]:[\text{BnNH}_2]\) only. This indicates that the rate of propagation is slower than the rate of chain transfer and therefore the rate of chain transfer is not involved in the rate determining step.
Figure 4.10. First order rate plots for the ROP of 100 equivalents of rac-LA in the presence of 3 equivalents of BnNH$_2$ and 4 (red squares), 3 (blue triangles), 2 (green circles) and 1 (black squares) equivalents of 26-[BPh$_4$]$_2$. Observed first order rate constants are 0.0027(2), 0.006(1), 0.009(2) and 0.013(2) min$^{-1}$ respectively. Conditions: 6 mL THF, 70 °C, 3-12 hours, [rac-LA]$_0$:[26-[BPh$_4$]$_2$]$_0$ = 100.

Figure 4.11. A plot of -$\ln(k_{obs})$ against -$\ln$(equivalents Y) for the ROP of 100 equivalents of rac-LA in the presence of 3 equivalents of BnNH$_2$ and 1-4 equivalents of 26-[BPh$_4$]$_2$. The gradient of the line of best fit was 1.02(2), $R^2 = 0.999$. 
In order to determine the order in LA, a second series of kinetics experiments were carried out. Holding the $[Y]_0: [BnNH_2]$ constant at 1:3 and varying the equivalents of rac-LA from 100 to 250 allowed the order in $[\text{rac-LA}]$ to be determined (Figure 4.12). The rate constants for $[\text{rac-LA}]:[BnNH_2]:[Y]_0$ ($[\text{rac-LA}] = 100, 150, 200$ or 250) were measured to be 0.0027(2), 0.004(1), 0.006(3) and 0.008(2) min$^{-1}$ respectively, consistent with a first order dependence in $[\text{rac-LA}]$. Additionally, the plot of $-\ln(k_{\text{obs}})$ against $-\ln(\text{equivalents rac-LA})$ (Figure 4.13) had a gradient of 1.04(1), confirming the first order dependence of $k_{\text{obs}}$ on $[\text{rac-LA}]$.

**Figure 4.12.** First order rate plots for the ROP of different equivalents of rac-LA (250 (red squares), 200 (blue triangles), 150 (green circles) and 100 (black squares)) using one equivalent of 26-$[\text{BPh}_4]$ and three equivalents of BnNH$_2$. Observed first order rate constants are 0.0027(2), 0.004(1), 0.006(3) and 0.008(2) min$^{-1}$ respectively. Conditions: 6mL THF, 70°C, 3-12 hours.
Figure 4.13. A plot of $-\ln(k_{\text{obs}})$ against $-\ln($equivalents rac-LA$)$ using 1 equivalent of 26-[BPh$_4$]$_2$ in the presence of 3 equivalents of BnNH$_2$. The gradient of the line of best fit was $1.04(1)$, $R^2 = 0.978$.

In a complementary set of experiments, holding the [rac-LA]:[Y]$_0$ value constant and varying the equivalents of BnNH$_2$ from 1 to 5 had no effect on the rate of polymerisation (Figure 4.14). The measured rate constants were 0.0026(3), 0.0028(7) and 0.0029(6) min$^{-1}$ for 1, 3 and 5 equivalents of BnNH$_2$ respectively. Furthermore, whilst the rate of polymerisation was shown to be zero order in [BnNH$_2$], the resulting $M_n$ of the polymer was also shown to have a dependence on [BnNH$_2$] (Figure 4.15). The gradients of the lines of best fit of $M_n$ vs. conversion using 1, 3 and 5 equivalents of BnNH$_2$ were measured to be 74(2), 42(2) and 23(1) g mol$^{-1}$ (equivs. converted)$^{-1}$. These compare well with the calculated gradients of 72, 36 and 24 g mol$^{-1}$ (equivs. converted)$^{-1}$ respectively.

These data, together with the MALDI-ToF mass spectrum in Figure 4.9 showing PLA with predominantly amine end groups (with only a small proportion with alcohol end groups arising from classical coordination-insertion by the bound $^1$PrO ligand in 26-[BPh$_4$]$_2$), suggest that in the presence of Lewis acidic 26$^{2+}$, BnNH$_2$ rapidly (with respect to propagation) ring-opens a molecule of rac-LA to form BnNH-C(O)CH(Me)OC(O)CH(Me)O-H (I) via an activated monomer mechanism (Scheme 4.4). This is then followed by metal-mediated immortal chain extension of the so-formed macromolecules by coordination-insertion. Thereafter, I acts as a CTA in an analogous manner to $^1$PrOH, ultimately forming amine-terminated PLA in an immortal fashion. The overall rate law has been shown to be $\text{Rate} = k_{\text{obs}}[Y][\text{rac-LA}][\text{RNH}_2]^{\theta}$. It is noteworthy that BnNH$_2$ alone does not polymerise rac-LA under these conditions.
Figure 4.14. First order rate plots for the ROP of 100 equivalents of rac-LA using one equivalent of 26-[BPh₄]₂ and 1 (red squares), 3 (blue triangles) and 5 (black squares) equivalents of BnNH₂. Observed first order rate constants are 0.0026(3), 0.0028(7), and 0.0029(6) min⁻¹ respectively. Conditions: 6mL THF, 70°C, 12 hours.

Figure 4.15. Mₙ (as measured by GPC) vs. equivalents % conversion (as measured by ¹H NMR) for the ROP of 100 equivalents of rac-LA using 1 equivalent of 26-[BPh₄]₂ in the presence of 1 (red squares), 3 (blue triangles) and 5 (black squares) equivalents of BnNH₂. Conditions: 6mL THF, 70°C, 12 hours.
The fact that there is a zero order dependence on \([\text{BnNH}_2]\) is consistent with the proposed mechanism and implies fast rates of initiation and chain transfer with respect to the rate of propagation (which is independent of \([\text{BnNH}_2]\) and is therefore likely to be a part of the rate determining step). This has also been observed in related work in the Mountford group using the zwitterionic complex \(\text{Y(O}_2\text{NN') (HO}_2\text{NN') (H}_2\text{O}_2\text{NN')} = \text{Me}_2\text{NCH}_2\text{C}_2\text{N(CH}_2\text{2-HO-3,5-C}_6\text{H}_2\text{tBu}_2)_2}\) for the \(i\)-ROP of \(\text{rac-LA}\) in the presence of \(\text{BnNH}_2\). It is assumed that an analogous mechanism operates for the \(i\)-ROP of \(\text{rac-LA}\) using \(26-\text{[BPh}_4\text{]}_2\) in the presence of \(\text{iPrOH}\). This is consistent with the fact that the rate constants using both CTAs are very similar (0.0029(5) and 0.0028(4) min\(^{-1}\) for \(\text{iPrOH}\) and \(\text{BnNH}_2\) respectively).

Whilst analogous kinetics experiments with \([\text{Y}\{\text{HC(Me}_2\text{pz})_3\}(\text{CH}_2\text{SiMe}_3\text{)(THF)}_3]\text{[BPh}_4\text{]}_2\) (25-\([\text{BPh}_4\text{]}_2\)) were inconclusive (for example a partial order in \([\text{Y}]\) was shown), it is likely that the \(\text{CH}_2\text{SiMe}_3\) group undergoes protonolysis with either \(\text{iPrOH}\) or \(\text{BnNH}_2\) to form an amide or alkoxide complex respectively. However the fact that the rate constants for polymerisations using 25-\([\text{BPh}_4\text{]}_2\) are nearly identical (0.0028(6) and 0.003(1) min\(^{-1}\) for \(\text{iPrOH}\) and \(\text{BnNH}_2\) respectively) and close to that with no CTA (0.0027(4) min\(^{-1}\)) suggest that a similar mechanism may operate also.

NMR scale experiments were carried out in \(\text{THF-d}_8\) at 70 °C with 10 equivalents of \(\text{rac-LA}\), 5 equivalents of \(\text{BnNH}_2\) and one equivalent of either 25-\([\text{BPh}_4\text{]}_2\) or 26-\([\text{BPh}_4\text{]}_2\). \(^1\text{H NMR}\) analysis of the mixture after 12 h showed PLA, a small amount of residual catalyst and almost quantitative formation of uncomplexed \(\text{HC(Me}_2\text{pz})_3\). Despite this, it is thought that \(\text{HC(Me}_2\text{pz})_3\) is likely more than merely a spectator ligand. A dicationic yttrium alkoxide species in the absence of a supporting ligand would likely be polymeric and not give the
same degree of excellent $M_n$ control observed in the PLA’s formed. It is more likely that HC(Me$_2$pz)$_3$ is gradually displaced by chelating LA macromolecules in the progression of the polymerisation process. An analogous experiment was carried out with 30-[BPh$_4$]$_2$. Interestingly, in this case heating in THF-$d_8$ at 70 °C after 4 h showed the presence of PLA and residual catalyst with no uncomplexed Me$_3$[9]-aneN$_3$. This suggests that Me$_3$[9]aneN$_3$ remains bound to the yttrium metal centre throughout the polymerisation process (unlike HC(Me$_2$pz)$_3$). This most likely accounts for the superior activity of 30-[BPh$_4$]$_2$ compared to either 25-[BPh$_4$]$_2$ or 26-[BPh$_4$]$_2$ under the conditions used.

With the aim of developing an improved (higher activity) system, it was attempted to prepare cationic yttrium alkyl and alkoxide species with the monoanionic ligand Tp$^{Bu,Me}$, which was successfully used in Chapter 3. It was reasoned that a monoanionic ligand should remain more tightly bound to the metal centre and the tert-butyl groups in the 3-position of the ligand may also provide a degree of stereochemical control over the PLA formed. However, such attempts unfortunately led to C-H activation of the tert-butyl group in the ligand.

In related work, the complex [Y(O'Bu)(Cl)(THF)$_5$][BPh$_4$] was prepared using the method published by Evans et al.$^{71}$ However, the attempted preparation of [Tp$^{Bu,Me}$] Y(O'Bu)(THF)$_5$][BPh$_4$] by metathesis between [Y(O'Bu)(Cl)(THF)$_5$][BPh$_4$] and KTp$^{Bu,Me}$ proved unsuccessful: no reaction occurred either at RT or 70 °C in THF. Although a surprising result, this is consistent with the lack of reactivity of [Y(O'Bu)(Cl)(THF)$_5$][BPh$_4$] reported by Evans et al., which was attributed to the halophilicity of the yttrium cation.$^{71}$ Perhaps more surprisingly, [Y(O'Bu)(Cl)(THF)$_5$][BPh$_4$] was also found to be inactive towards the ROP of rac-LA, either at room temperature or 70 °C in THF over a period of 12 h.

4.4 Summary and Conclusions

The work presented in this chapter has developed cationic yttrium alkyl and alkoxide complexes as initiators for the ROP of rac-LA. Additionally, 26-[BPh$_4$]$_2$ was the first reported cationic initiator for the ROP of rac-LA at the time of publication, and this area is the subject of growing interest. The catalysts presented in this chapter show excellent $M_n$ control of the polymers formed both in the absence of, and together with, $^1$PrOH and BnNH$_2$ acting as chain transfer reagents in the $i$-ROP of rac-LA, also a subject of growing interest.

The mechanism of $i$-ROP was shown to be coordination-insertion (after an initial activated monomer step to generate amine-capped PLA), as supported by the zero order dependence
on $[\text{BnNH}_2]$ of the rate of polymerisation and the fact that $M_n$ was shown to be independent of $[Y]_0$ but dependent on $[\text{BnNH}_2]$, attributed to the fast rate of chain transfer with respect to the rate of propagation.

4.5 References


Chapter Five

Experimental and Characterising Data
5.0. General methods and instrumentation. All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents were degassed by sparging with dinitrogen and dried by passing through a column of the appropriate drying agent. Toluene was refluxed over sodium and distilled. Deuterated solvents were dried over potassium (C₆H₆, Toluene-d₅ or THF-d₅) or P₂O₅ (CDCl₃ and CD₂Cl₂), distilled under reduced pressure and stored under dinitrogen in Teflon valve ampoules. NMR samples were prepared under dinitrogen in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. ¹H, ¹³C{¹H} and ¹¹B{¹H} NMR spectra were recorded on Varian Mercury-VX 300 and Varian Unity Plus 500 spectrometers at ambient temperature unless stated otherwise and referenced internally to residual protio-solvent (¹H) or solvent (¹³C) resonances, and are reported relative to tetramethylsilane (δ = 0 ppm). Assignments were confirmed using two dimensional ¹H-¹H and ¹³C-¹H NMR correlation experiments. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. IR spectra were recorded on a Nicolet Magna 560 E.S.P. FTIR spectrometer. Samples were prepared in a dry-box either as Nujol mulls between NaCl plates or as solution samples (10 mg per 0.5 mL in the required solvent) and the data are quoted in wavenumbers (cm⁻¹). Elemental analyses were carried out by the Elemental Analysis Service at the London Metropolitan University and Elemental Microanalysis Ltd, Okehampton, Devon.

MALDI-ToF-MS analysis was performed on a Waters MALDI micro equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. The polymer samples were dissolved in THF at a concentration of 1 mg mL⁻¹. The cationization agent used was potassium trifluoroacetate (Fluka, >99%) dissolved in THF at a concentration of 5 mg mL⁻¹. The matrix used was trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in THF at a concentration of 40 mg mL⁻¹. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflectron mode.

Polymer molecular weights (Mₙ, Mₚ) were determined by GPC using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PL-GPC50 Plus instrument equipped with a refractive index detector. THF (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min⁻¹. Linear polystyrenes were used as primary calibration standards, and Mark-Houwink corrections for poly(ε -CL) or poly(rac-LA) in THF were applied for the experimental samples.
5.1. Literature Preparations.

The compounds Mg\{N(SiMe\text{3})\text{2}\}\text{2}, Mg\{N(SiHMe\text{2})\text{2}\}, Ca\{N(SiMe\text{3})\text{2}\}(THF)\text{2}, Zn\{N(SiMe\text{3})\text{2}\}, Li\{C(Me\text{2}pz)\} (THF), HC(Me\text{2}pz)\text{3}, HCpz, 4-Etpz, (3-tBu,5-Mepz), KTp\text{Bu}Me, Li\{SiHMe\text{2}\}, Yb(BH\text{4})(THF) were prepared according to published procedures. DC(Me\text{2}pz)\text{3} was synthesised by another student in the Mountford group. All other compounds and reagents were purchased from commercial suppliers and used without further purification. ε-CL was dried over freshly ground CaH\text{2} and distilled before use. Rac-LA was recrystallised twice from toluene and then sublimed twice prior to use. Other reagents were obtained commercially and used as received.

5.2. Experimental details and characterising data for Chapter Two

Mg\{C(Me\text{2}pz)\}\{N(SiMe\text{3})\text{2}\} (1). A solution of Mg\{N(SiMe\text{3})\text{2}\}\text{2} (1.04 g, 3.02 mmol) in benzene (20 mL) was added to a solution of HC(Me\text{2}pz)\text{3} (0.60 g, 2.0 mmol) in benzene (20 mL) at RT. The resulting yellow solution was stirred for 24 h and the volatiles were removed under reduced pressure, leaving an orange solid. This was extracted into pentane (3 x 15mL) and the solution concentrated and cooled to -30 °C, yielding 1 as a microcrystalline orange solid. Yield: 0.54 g (50%). Diffraction quality crystals were grown from a saturated pentane solution at -30 °C. \text{1}H NMR (C\text{6}D\text{6}, 299.9 MHz, 293 K): 5.42 (3H, s, N\text{2}C\text{3}Me\text{2}H), 2.28 (9H, s, 3-N\text{2}C\text{3}Me\text{2}H), 2.25 (9H, s, 5-N\text{2}C\text{3}Me\text{2}H) 0.47 (18H, s, SiMe\text{3}) ppm. \text{13}C\{\text{1}H\} NMR (C\text{6}D\text{6}, 299.9 MHz, 293 K): 149.3 (3-N\text{2}C\text{3}Me\text{2}H), 147.9 (5-N\text{2}C\text{3}Me\text{2}H), 104.8 (4-N\text{2}C\text{3}Me\text{2}H), 72.5 (C(Me\text{2}pz)\text{3}), 15.1 (3-N\text{2}C\text{3}Me\text{2}H), 13.3 (5-N\text{2}C\text{3}Me\text{2}H), 7.3 (SiMe\text{3}) ppm. IR (KBr plates, Nujol mull, cm\text{1}): 1570(s), 1259(m), 1004(m), 987 (m), 670(m), 631(m), 550(m), 492(m), 430(s). EI-MS: m/z = 481, (6 %), \text{[M]+}; 312 (100%), \text{[M] – N(SiMe\text{3})\text{2}]+}. Anal. found (calcd. for C\text{22}H\text{39}MgN\text{7}Si\text{2}): C, 54.75 (54.81); H, 8.11 (8.15); N, 20.29 (20.34) %.

Mg(κ\text{2}N-HC(Me\text{2}pz)\text{3})\{N(SiHMe\text{2})\text{2}\} (2). A solution of Mg\{N(SiHMe\text{2})\text{2}\}\text{2} (0.27 g, 1.0 mmol) in toluene (20 mL) was added to a solution of HC(Me\text{2}pz)\text{3} (0.200 g, 0.67 mmol) in toluene (20 mL) at -78 °C, which was then allowed to warm to RT and stirred for 2 h. Volatiles were removed under reduced pressure from the resulting yellow solution, leaving a yellow solid. This was washed with cold pentane (0 °C, 3 x 10 mL) and dried in vacuo, yielding 2 as a microcrystalline, pale yellow solid. Yield: 0.26 g (65%). Diffraction-quality crystals were grown from a saturated toluene solution at -30 °C. \text{1}H NMR (CD\text{2}Cl\text{2}, 499.9 MHz, 208 K): 7.57 (1H, s, HC(N\text{2}C\text{3}Me\text{2}H)\text{3}), 6.15 (2H, s,
N$_2$C$_3$Me$_2$H (bound)), 5.85 (1H, s, N$_2$C$_3$Me$_2$H (pendant)), 4.60 (1H, br m, SiMe$_2$H(3)), 4.29 (2H, br m, SiMe$_2$H(1,2)), 3.05 (1H, br m, SiMe$_2$H(4)) 2.49 (6H, s, 3-N$_2$C$_3$Me$_2$H (bound)), 2.43 (6H, s, 5-N$_2$C$_3$Me$_2$H (bound)), 1.97 (3H, s, 3-N$_2$C$_3$Me$_2$H (pendant)), 1.38 (3H, s, 5-N$_2$C$_3$Me$_2$H (pendant)), -0.01 (6H, br d, Si(3)Me$_2$H), -0.30 (12H, br d, Si(1,2)HMe$_2$), -0.48 (6H, br d, Si(4)Me$_2$H) ppm (atom labels refer to the X-ray structure of 2). IR (KBr plates, Nujol mull, cm$^{-1}$): 1548 (s), 1422 (s), 1318 (s), 1222 (s), 1069 (s), 998 (s), 867 (s), 813 (s), 701 (s), 426 (m). EI-MS: $m/z$ = 586, (8%), $[M]^+$. Anal. found (calcd. for C$_{30}$H$_{50}$N$_7$Si$_4$): Found (Calculated): C, 49.65 (49.10); H, 8.10 (8.58); N, 19.55 (19.10) %. A satisfactory $^{13}$C spectrum could not be obtained in the slow exchange limit.

**Mg[κ$^3$N-D(Me$_2$pz)$_3$]{N(SiHMe$_2$)$_2$}$_2$ (2-d).** A solution of Mg{N(SiHMe$_2$)$_2$}$_2$ (0.27 g, 1.0 mmol) in toluene (20 mL) was added to a solution of DC(Me$_2$pz)$_3$ (0.20 g, 0.67 mmol) in toluene (20 mL) at -78 °C, which was then allowed to warm up to RT and stirred for 2 h. The volatiles were then removed under reduced pressure from the resulting yellow solution, leaving a yellow solid. This was washed with cold pentane (0 °C, 3 x 10 mL) and dried in vacuo, yielding 2-d as a microcrystalline pale yellow solid. Yield: 0.26 g (71 %). $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): Identical to that for 2 except for the absence of the H(Me$_2$pz)$_3$ resonance. $^2$H NMR (C$_6$H$_6$, 46.0 MHz, 293 K): 7.49 (s, 2DC(Me$_2$pz)$_3$).

**Mg[C(Me$_2$pz)$_3$]{N(SiHMe$_2$)$_2$} (3).** A solution of Mg{N(SiHMe$_2$)$_2$}$_2$ (0.27 g, 1.0 mmol) in toluene (20 mL) was added to a solution of HC(Me$_2$pz)$_3$ (0.20 g, 0.67 mmol) in toluene (20 mL) at RT. The resulting yellow solution was stirred at 50 °C for 3 d, after which time the solution became orange. Volatiles were removed under reduced pressure, leaving an orange solid. This was extracted into pentane (3 x 15 mL) and the solution concentrated and cooled to -30 °C, yielding 3 as a microcrystalline orange solid. Yield: 0.15 g (49%). $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.43 (2H, sept, $^3$J = 2.7 Hz, SiMe$_2$H), 5.38 (3H, s, N$_2$C$_3$Me$_2$H), 2.30 (9H, s, 3-N$_2$C$_3$Me$_2$H), 2.26 (9H, s, 5-N$_2$C$_3$Me$_2$H), 0.56 (12H, d, $^3$J = 2.7 Hz, SiMe$_2$H) ppm. $^{13}$C{ $^1$H} NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 148.8 (3-N$_2$C$_3$Me$_2$H), 147.1 (5-N$_2$C$_3$Me$_2$H), 104.0 (4-N$_2$C$_3$Me$_2$H), 71.9 (C(Me$_2$pz)$_3$), 14.4 (3-N$_2$C$_3$Me$_2$H), 12.9 (5-N$_2$C$_3$Me$_2$H), 4.6 (SiMe$_2$H) ppm. IR (KBr plates, Nujol mull, cm$^{-1}$): 2726(s), 2362(s), 2065(s), 1556(s), 1457(s), 1307(s), 1260(s), 1050(m), 949(s), 890(s), 806(s), 666(s), 475(m). EI-MS: $m/z$ = 453 (5%), $[M]^+$; 312 (100 %), $[M – N(SiHMe$_2$)$_2$]^{+}$. Anal. found (calcd. for C$_{30}$H$_{35}$MgN$_7$Si$_4$): C, 52.91 (52.91); H, 7.64 (7.77); N, 21.44 (21.60) %.
NMR Tube Scale Synthesis of Mg{C(Me$_2$pz)$_3$)$_2$. From Mg{N(SiMe$_3$)$_2$}$_2$: A solution of Mg{N(SiMe$_3$)$_2$}$_2$ (11.5 mg, 33.6 μmol) and HC(Me$_2$pz)$_3$ (20.0 mg, 67.1 μmol) in C$_6$D$_6$ (0.8 mL) was heated at 70 °C for 4 d to quantitatively form Mg{C(Me$_2$pz)$_3$}$_2$. From Mg{C(Me$_2$pz)$_3$}{N(SiRMe$_2$)$_2$}: A solution of Mg{C(Me$_2$pz)$_3$}{N(SiRMe$_2$)$_2$} (R = Me (1) or H (3), 67.1 μmol) and HC(Me$_2$pz)$_3$ (20.0 mg, 67.1 μmol) in C$_6$D$_6$ (0.8 mL) was heated at 70 °C for 2 d (R = H) or 3 d (R = Me) to quantitatively form Mg{C(Me$_2$pz)$_3$}$_2$. The $^1$H NMR resonances for Mg{C(Me$_2$pz)$_3$}$_2$ were identical to those previously reported.$^{19}$

Ca{C(Me$_2$pz)$_3$}{N(SiMe$_3$)$_2$}(THF) (4). THF (20 mL) at -78 °C was added to a solid mixture of Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (0.25 g, 0.50 mmol) and HC(Me$_2$pz)$_3$ (0.15 g, 0.50 mmol) at -78 °C which was then allowed to warm to RT and stirred for 2 h. The volatiles were removed under reduced pressure and the residue extracted into benzene (2 x 20 mL) leaving an insoluble beige solid (presumed to be Ca{C(Me$_2$pz)$_3$}$_2$). Volatiles were removed under reduced pressure to yield 4 as a yellow solid which was washed with benzene (2 x 10 mL) and dried in vacuo. Yield: 0.24 g (85%). Diffraction-quality crystals were grown from a saturated toluene solution at -30 °C. $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.58 (3H, s, N$_2$C$_3$Me$_2$H), 3.54 (4H, br m, OCH$_2$CH$_2$), 2.43 (9H, s, 3-N$_2$C$_3$Me$_2$H), 2.26 (9H, s, 5-N$_2$C$_3$Me$_2$H), 1.22 (4H, br m, OCH$_2$CH$_2$) 0.41 (18H, s, SiMe$_3$) ppm. $^{13}$C (C$_6$D$_6$, 299.9 MHz, 293 K): 147.0 (3-N$_2$C$_3$Me$_2$H), 146.8 (5-N$_2$C$_3$Me$_2$H), 103.2 (4-N$_2$C$_3$Me$_2$H), 72.4 (C(Me$_2$pz)$_3$)$_2$, 69.5 (OCH$_2$CH$_2$), 25.0 (OCH$_2$CH$_2$), 14.8 (3-N$_2$C$_3$Me$_2$H), 13.1 (5-N$_2$C$_3$Me$_2$H), 5.9 (SiMe$_3$) ppm. IR (KBr plates, Nujol mull, cm$^{-1}$): 1553(m), 1423(m), 1391(m), 1246(m), 1236(m), 1217(w), 1155(w), 1057(s), 1037(s), 967(s), 876(m), 829(m), 788(m), 770(m), 745(m), 660(m), 607(m), 590(m). EI-MS: m/z = 569, (8 %), [M]$^+$. Anal. found (calcd. for C$_{26}$H$_{47}$CaN$_7$O$_{12}$): C, 54.92 (54.79); H, 8.18 (8.31); N, 17.12 (17.20) %.

Ca{C(Me$_2$pz)$_3$}$_2$ (5). Ca{N(SiMe$_3$)$_2$}$_2$(THF)$_2$ (0.20 g, 0.40 mmol) and HC(Me$_2$pz)$_3$ (0.25 g, 0.84 mmol) were stirred together in benzene (20 mL) at RT for 16 h, giving a pale yellow solution and a sparingly soluble beige solid. This was filtered and washed with benzene (2 x 10 mL) and dried in vacuo to afford 5. Yield: 0.16 g (61 %). Diffraction-quality crystals were grown from a saturated benzene solution at RT. $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.65 (6H, s, N$_2$C$_3$Me$_2$H)$_2$, 2.49 (18H, s, 3- or 5-N$_2$C$_3$Me$_2$H), 1.95 (18H, s, 3- or 5-N$_2$C$_3$Me$_2$H) ppm. IR (NaCl plates, Nujol mull, cm$^{-1}$): 1548(m), 1450(m), 1427(m), 1393(m), 1351(m), 1214(m), 1151(w), 1095(m), 1039(m), 975(w), 872(m), 792(m), 661(m). EI-MS: m/z = 634 (6 %), [M]$^+$. Anal. found (calcd. for C$_{32}$H$_{42}$CaN$_{12}$): C,
60.51 (60.54); H, 6.53 (6.67); N, 26.46 (26.48) %. The compound was too insoluble to obtain a $^{13}$C NMR spectrum.

**Alternative NMR Tube Scale Synthesis of Ca{C(Me$_2$pz)$_3$}$_2$ (5).**

Ca{C(Me$_2$pz)$_3$}{N(SiMe$_3$)$_2$}(THF) (18, 38.2 mg, 67.1μmol) and HC(Me$_2$pz)$_3$ (20.0 mg, 67.1 μmol) were dissolved in C$_6$D$_6$ (0.8 mL). After 2 h at RT the $^1$H NMR spectrum showed quantitative formation of Ca{C(Me$_2$pz)$_3$}$_2$ (5), the resonances for which were identical to those reported above.

**Zn{C(Me$_2$pz)$_3$}Cl (6).** A solution of Li{C(Me$_2$pz)$_3$}(THF) in THF (20 mL) was added to a solution of ZnCl$_2$ (3.52 mL of a 1.0 M solution in Et$_2$O, 3.52 mmol) in THF (20 mL), giving a pale suspension. The mixture was heated at 70 °C for 24 h, after which time the volatiles were removed under reduced pressure to leave an orange solid. This was extracted into hot benzene (65 °C, 3 x 30 mL) and the volatiles were removed under reduced pressure to give 6 as an analytically pure, yellow powder. Yield: 0.51 g (40 %).

Diffraction-quality crystals were grown from a pentane-layered THF solution. $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.32 (3H, s, N$_2$C$_3$Me$_2$H), 2.26 (9H, s, 3-N$_2$C$_3$Me$_2$H), 2.18 (9H, s, 5-N$_2$C$_3$Me$_2$H). $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 148.9 (3-N$_2$C$_3$Me$_2$H), 146.8 (5-N$_2$C$_3$Me$_2$H), 104.1 (4-N$_2$C$_3$Me$_2$H), 73.0 (C(Me$_2$pz)$_3$), 13.6 (3-N$_2$C$_3$Me$_2$H), 12.5 (5-N$_2$C$_3$Me$_2$H) ppm. IR (KBr plates, Nujol mull, cm$^{-1}$): 1700 (s), 1260 (s), 1093 (m), 987 (m), 802 (s), 666(s), 472(m). EI-MS: m/z = 396 (5 %), [M$^+$]; 361 (100 %), [M - Cl]$^+$. Anal. found (calcd. for C$_{14}$H$_{21}$ClN$_6$Zn): C, 48.16 (48.26); H, 5.30 (5.32); N, 20.93 (21.10) %.

**Zn{C(Me$_2$pz)$_3$}{N(SiMe$_3$)$_2$} (7).** Na$_2$N(SiMe$_3$)$_2$ (0.75 mL of a 1.0 M solution in THF, 0.75 mmol), was added to a solution of Zn{C(Me$_2$pz)$_3$}Cl (0.28 g, 0.70 mmol) in benzene (20 mL). The resulting yellow suspension was stirred at RT for 4 h, after which time the volatiles were removed under reduced pressure, leaving a yellow solid. This was extracted into hot hexanes (70 °C, 3 x 15 mL) and the solution was concentrated and cooled to -30 °C, giving 7 as an analytically pure, yellow powder. Yield: 0.25 g (68 %).

Diffraction-quality crystals were grown from hexanes at RT. $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.59 (3H, s, N$_2$C$_3$Me$_2$H), 2.29 (18H, br, s, overlapping 3- and 5- N$_2$C$_3$Me$_2$H), 0.47 (18H, s, SiMe$_3$) ppm. $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 148.8 (3-N$_2$C$_3$Me$_2$H), 147.0 (5-N$_2$C$_3$Me$_2$H), 104.6 (4-N$_2$C$_3$Me$_2$H), 72.8 (C(Me$_2$pz)$_3$), 15.4 (3-N$_2$C$_3$Me$_2$H), 13.2 (5-N$_2$C$_3$Me$_2$H), 7.4 (SiMe$_3$) ppm. IR (KBr plates, Nujol mull, cm$^{-1}$): 1558(s), 1250 (s), 1093 (s), 987 (s), 802 (s), 666(s), 472(m). EI-MS: m/z = 521 (100 %), [M$^+$]; 361 (10 %). [M -
N(SiMe$_3$)$_2]^+$. Anal. found (calcd. for C$_{22}$H$_{39}$N$_2$Si$_2$Zn): C, 50.64 (50.51); H, 7.58 (7.51); N, 18.92 (18.74) %.

**Zn{C(Me$_2$pz)$_3$}[N(SiHMe)$_2$]$_2$** (8). Benzene (30 mL) was added to a solid mixture of LiN(SiHMe)$_2$ (0.11 g, 0.80 mmol) and Zn{C(Me$_2$pz)$_3$}Cl (0.30 g, 0.75 mmol). The resulting yellow suspension was stirred at RT for 4 h and the volatiles were removed under reduced pressure to give a yellow solid. This was extracted into hot hexanes (70 °C, 3 x 15 mL), filtered, and the solution concentrated and cooled to -30 °C, giving 8 as an analytically pure, yellow powder. Yield: 0.28 g (75 %). $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.44 (2H, sept, $^3$$J$ = 2.7 Hz, SiMe$_3$H), 5.38 (3H, s, N$_2$C$_3$Me$_2$H), 2.29 (18H, br, s, overlapping 3- and 5- N$_2$C$_3$Me$_2$H), 0.57 (12H, d, $^3$$J$ = 2.7 Hz, SiMe$_3$H) ppm. $^{13}$C($^1$H) NMR (C$_6$D$_6$, 125.7 MHz, 293 K): 148.0 (3-N$_2$C$_3$Me$_2$H), 146.1 (5-N$_2$C$_3$Me$_2$H), 103.8 (4-N$_2$C$_3$Me$_2$H), 71.3 (C(Me$_2$pz)$_3$), 14.3 (3-N$_2$C$_3$Me$_2$H), 12.3 (5-N$_2$C$_3$Me$_2$H), 4.2 (SiMe$_3$H) ppm. IR (KBr plates, Nujol mull, cm$^{-1}$): 1559 (s), 1269 (s), 1100 (s), 883 (m), 802 (s), 666 (s), 469 (m). EI-MS: \text{m/z} = 493 (6 %), \left[ M^+ \right]; 361 (100 %), \left[ M - N(SiHMe)_2 \right]^+$. Anal. found (calcd. for C$_{22}$H$_{39}$N$_2$Si$_2$Zn): C, 48.43 (48.52); H, 7.17 (7.13); N, 19.75 (19.80) %.

**Zn{C(Me$_2$pz)$_3$}$_2$** (9). A solution of Li{C(Me$_2$pz)$_3$}(THF) (1.20 g, 3.20 mmol) in THF (30 mL) was added to a solution of ZnCl$_2$ (1.59 mL of a 1.0 M solution in Et$_2$O, 1.59 mmol) in THF (20 mL) and the mixture was heated at 70 °C for 3 d, forming a dark orange suspension. Volatiles were removed under reduced pressure to leave an orange solid. This was extracted into hot toluene (80 °C, 3 x 30 mL), filtered, concentrated and cooled to -30 °C. Compound 9 was isolated as an analytically pure, white powder. Yield: 0.10 g (9 %). Diffraction-quality crystals were grown from hexanes at RT. $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.63 (6H, s, N$_2$C$_3$Me$_2$H), 2.52 (18H, s, 3-N$_2$C$_3$Me$_2$H), 1.68 (18H, s, 5-N$_2$C$_3$Me$_2$H) ppm. $^{13}$C($^1$H) NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 147.5 (3-N$_2$C$_3$Me$_2$H), 145.1 (5-N$_2$C$_3$Me$_2$H), 102.5 (4-N$_2$C$_3$Me$_2$H), 72.9 (C(Me$_2$pz)$_3$), 13.1 (3-N$_2$C$_3$Me$_2$H), 12.8 (5-N$_2$C$_3$Me$_2$H) ppm. IR (NaCl plates, Nujol mull, cm$^{-1}$): 1636 (s), 1260 (s), 1100 (s), 1057 (m), 809 (m), 665 (w). EI-MS: \text{m/z} = 658 (8 %), \left[ M^+ \right]. Anal. found (calcd. for C$_{32}$H$_{42}$N$_2$Zn): C, 58.12 (58.22); H, 6.31 (6.41); N, 25.48 (25.46) %.

**Mg{C(Me$_2$pz)$_3$}{C(pz)$_3$}** (10). A solution of HC(pz)$_3$ (0.13 g, 0.61 mmol) in benzene (20 mL) was added dropwise to a solution of 1 (0.30 g, 0.61 mmol) in benzene (20 mL). The resulting dark red suspension was heated to 70 °C for 24 h. Volatiles were removed under reduced pressure to leave an orange solid. This was extracted into hot hexanes (70 °C, 3 x 15 mL), filtered, concentrated and cooled to -30 °C. Compound 10 was isolated as an off-
white solid. Yield: 0.18 g (55 %). Diffraction-quality crystals were grown from a saturated hexanes solution at RT. $^1$H NMR (CD$_2$D$_6$, 299.9 MHz, 293 K): 7.88 (3H, d, $^3$$J$ = 1.24 Hz, 5-N$_2$C$_3$(H)), 7.18 (3H, d, $^3$$J$ = 1.24 Hz, 3-N$_2$C$_3$(H)), 5.67 (3H, dd, $^3$$J$ = 1.24, 1.81 Hz, 4-N$_2$C$_3$(H)), 5.62 (3H, s, N$_2$C$_3$Me$_2$(H)), 2.58 (9H, s, 3-N$_2$C$_3$Me$_2$(H)), 1.58 (9H, s, 5-N$_2$C$_3$Me$_2$(H)) ppm. $^{13}$C($^1$H) NMR (CD$_2$D$_6$, 75.4 MHz, 293 K): 147.8 (3-N$_2$C$_3$Me$_2$(H)), 145.6 (5-N$_2$C$_3$Me$_2$(H)), 139.6 (3-N$_2$C$_3$(H$_3$)), 137.2 (5-N$_2$C$_3$(H$_3$)), 103.6 (4-N$_2$C$_3$(H$_3$)), 103.3 (4-N$_2$C$_3$Me$_2$(H)), 89.1 (C(pz)$_3$), 72.1 (C(Me$_2$pz)$_3$), 13.4 (3-N$_2$C$_3$Me$_2$(H)), 12.7 (5-N$_2$C$_3$Me$_2$(H)) ppm. IR (KBr plates, Nujol mull, cm$^{-1}$): 3750 (s), 1531 (s), 1418 (s), 1308 (m), 1127 (s), 927 (s), 772 (s), 615 (s), 423 (s). EI-MS: $m/z$ = 550 (20 %), [M$^+$]. Anal. found (calcd. for C$_{26}$H$_{30}$MgN$_{12}$): C, 58.34 (58.40); H, 5.76 (5.66); N, 31.36 (31.45) %.

Ca[C(Me$_2$pz)$_3$]{C(pz)$_3$} (11). A solution of HC(pz)$_3$ (0.13 g, 0.60 mmol) in benzene (20 ml) was added dropwise to a solution of 4 (0.35 g, 0.60 mmol) in benzene (20 mL). The resulting dark red suspension was stirred at RT for 24 h. Volatiles were removed under reduced pressure to leave an orange solid. Recrystallisation from a saturated toluene solution at -30 °C yielded 11 as an analytically pure, beige solid. Yield: 0.24 g, (73 %). $^1$H NMR (CD$_2$D$_6$, 299.9 MHz, 293 K): 7.95 (3H, d, $^3$$J$ = 1.21 Hz, 5-N$_2$C$_3$(H)), 7.21 (3H, s, $^3$$J$ = 1.21 Hz, 3-N$_2$C$_3$(H)), 5.75 (3H, dd, $^3$$J$ = 1.21, 1.82 Hz, 4-N$_2$C$_3$(H)), 5.65 (3H, s, N$_2$C$_3$Me$_2$(H)), 2.55 (9H, s, 3-N$_2$C$_3$Me$_2$(H)), 1.90 (9H, s, 5-N$_2$C$_3$Me$_2$(H)) ppm. $^{13}$C($^1$H) NMR (CD$_2$D$_6$, 75.4 MHz, 293 K): 147.7 (3-N$_2$C$_3$(Me$_2$H)), 145.5 (5-N$_2$C$_3$(Me$_2$H)), 139.6 (3-N$_2$C$_3$(H$_3$)), 137.1 (5-N$_2$C$_3$(EtH)), 103.5 (4-N$_2$C$_3$(H$_3$)), 103.2 (4-N$_2$C$_3$(Me$_2$H)), 89.0 (C(pz)$_3$), 72.8 (C(Me$_2$pz)$_3$), 17.5 (N$_2$C$_3$CH$_2$CH$_3$), 13.2 (3-N$_2$C$_3$(Me$_2$H)), 12.6 (5-N$_2$C$_3$(Me$_2$H)) ppm IR (KBr plates, Nujol mull, cm$^{-1}$): 1531 (s), 1418 (s), 1220 (s), 1127 (s), 927 (m), 772 (s), 615 (s), 423 (s). EI-MS: $m/z$ = 550 (20 %), [M$^+$]. Anal. found (calcd. for C$_{26}$H$_{30}$CaN$_{12}$): C, 56.56 (56.70); H, 5.51 (5.49); N, 30.52 (30.54) %.

HC(4-Etpz)$_3$} (12). Distilled water (200 ml) was added to a 1 L flask containing a mixture of 4-ethyl pyrazole (11.1 g, 0.12 mol) and tetra-n-butylammonium bromide (2.25g, 7.0 mol). With vigorous stirring, sodium carbonate (64 g, 0.60 mol) was added gradually to the reaction mixture. After cooling to RT, chloroform (100mL) was added and the flask equipped with a reflux condenser. The mixture was heated at gentle reflux for 24 h, during which time it became an orange/red emulsion. The mixture was allowed to cool to RT, filtered through a Büchner funnel to remove the excess base, and the organic layer separated from the aqueous layer. The organic layer was washed with distilled water (3 x 25 mL) and dried over sodium sulfate. The drying agent was removed by filtration and the solvent was removed by rotary evaporation. The resulting brown
residue was dissolved in CH₂Cl₂ (50 mL) and passed through a silica plug with CH₂Cl₂ (2 x 200 mL). The solvent was removed by rotary evaporation to afford an analytically pure off-white solid. Yield: 6.20 g (54 %). Diffraction-quality crystals were grown from a saturated benzene solution at RT. 1H NMR (C₆D₆, 299.9 MHz, 293 K): 8.43 (1H, s, HC(4-Etpz)₃), 7.38 (3H, s, 5-N₂C₅EtH₂), 7.29 (3H, s, 3-N₂C₅EtH₂) 2.13 (6H, q, 3J = 8.6 Hz, CH₂), 0.87 (9H, t, 3J = 8.6 Hz, CH₃) ppm. 13C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): 140.5 (3-N₂C₅EtH₂), 126.7 (5-N₂C₅EtH₂), 124.4 (4-N₂C₅EtH₂), 83.6 (HC(4-Etpz)₃), 17.1 (CH₂), 14.5 (CH₃) ppm. IR (KBr plates, Nujol mull, cm⁻¹): 2726 (s), 2641 (s), 147.3 (s), 1143 (s), 851 (s). EI-MS: m/z = 219 (100 %), [M]⁺. Anal. found (calcd. for C₁₆H₂₅N₆): C, 64.30 (64.40); H, 7.28 (7.43); N, 27.94 (28.16) %.

Mg{C(Me₃pz)₃}{C(4-Etpz)₃} (13). A solution of HC(4-Etpz)₃ (12) (0.30 g, 1.01 mmol) in benzene (20 mL) was added dropwise to a solution of 1 (0.49 g, 1.01 mmol) in benzene (20 mL). The resulting dark red suspension was stirred at 70 °C for 24 h. Volatiles were removed under reduced pressure to leave an orange solid. Recrystallisation from a saturated toluene:pentane solution (1:3 v/v) at -30 °C yielded 13 as an analytically pure, beige solid. Yield: 0.29 g (46 %). 1H NMR (C₆D₆, 299.9 MHz, 293 K): 7.82 (3H, s, 5-N₂C₅EtH₂), 6.99 (3H, s, 3-N₂C₅EtH₂), 5.67 (3H, s, N₂C₅Me₂H), 2.60 (9H, s, 5-N₂C₅Me₂H), 2.12 (6H, q, 3J = 7.5 Hz, CH₂CH₃), 1.66 (9H, s, 3-N₂C₅Me₂H), 0.83 (9H, t, 3J = 7.5 Hz, CH₂CH₃) ppm. 13C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): 147.7 (3-N₂C₅Me₂H), 145.4 (5-N₂C₅Me₂H), 138.3 (3-N₂C₅EtH₂), 135.1 (5-N₂C₅EtH₂), 120.5 (4-N₂C₅EtH₂), 103.4 (4-N₂C₅Me₂H), 90.0 (C(4-Etpz)₃), 73.1 (C(Me₃pz)₃), 17.5 (CH₂CH₃), 15.4 (CH₂CH₃), 13.4 (3-N₂C₅Me₂H), 12.6 (5-N₂C₅Me₂H) ppm. IR (KBr plates, Nujol mull, cm⁻¹): 2726 (m), 1703 (s), 1663 (w), 1261 (s), 1143 (s), 851 (s). EI-MS: m/z = 618 (40 %), [M]⁺. Anal. found (calcd. for C₃₂H₄₂MgN₁₂): C, 62.03 (62.10); H, 6.96 (6.85); N, 27.27 (27.18) %.

Ca{C(Me₂pz)₃}{C(4-Etpz)₃} (14). A solution of HC(4-Etpz)₃ (12) (0.13 g, 0.44 mmol) in benzene (20 mL) was added dropwise to a solution of 4 (0.25 g, 0.44 mmol) in benzene (20 mL). The resulting dark red suspension was stirred at RT for 24 h. Volatiles were removed under reduced pressure to leave an orange solid. Recrystallisation from a saturated toluene solution at -30 °C yielded 14 as an analytically pure, beige solid. Yield: 0.19 g (68 %). 1H NMR (C₆D₆, 299.9 MHz, 293 K): 7.97 (3H, s, 5-N₂C₅EtH₂), 7.25 (3H, s, 3-N₂C₅EtH₂), 5.79 (3H, s, N₂C₅Me₂H), 2.69 (9H, s, 5-N₂C₅Me₂H), 2.29 (6H, q, 3J = 7.6 Hz, CH₂CH₃), 2.07 (9H, s, 3-N₂C₅Me₂H), 1.02 (9H, t, 3J = 7.6 Hz, CH₂CH₃) ppm. 13C{¹H} NMR (C₆D₆, 75.4 MHz, 293 K): 147.3 (3-N₂C₅Me₂H), 146.8 (5-N₂C₅Me₂H), 157
olatiles were removed under reduced pressure to give a pale yellow solid.

\[ \text{Mg}[\text{HC}^\text{(Bu}^\text{2}^\text{pz})\text{SiMe}_2^\text{NPh}]\{\text{N(SiMe}_3)\}_2 \] (15). To a solution of Mg\{N(SiMe_3)_2\}_2 (0.30 g, 0.87 mmol) in benzene (15 mL) was added slowly HC\{(Bu_2pz)_2SiMe_2N(H)Ph (0.45 g, 0.87 mmol) in benzene (15 mL). The mixture was heated to 60 °C and stirred for 6 h.

Recrystallisation from a saturated pentane solution at -30 °C yielded 15 as an analytically pure, off-white solid. Yield: 0.30 g (49 %). \(^1\)H NMR (C_6D_6, 299.9 MHz, 293 K): 7.24 (2 H, app. t, app. \(^3\)J = 7.9 Hz, 3-C_6H_5), 6.98 (2 H, d, \(^3\)J = 7.1 Hz, 2-C_6H_5), 6.83 (1 H, app. t, app. \(^3\)J = 7.9 Hz, 4-C_6H_5), 6.21 (1 H, s, HC\{(Bu_2pz)_2\}), 6.05 (2 H, s, N_2C_3H^3Bu_2), 1.61 (18 H, s, 3-N_2C_3H^3Bu_2), 1.07 (18 H, s, 5-N_2C_3H^3Bu_2), 0.36 (18 H, SiMe_3), -0.08 (6 H, s, SiMe_2) ppm. \(^{13}\)C\{\(^1\)H\} NMR (C_6D_6, 75.4 MHz, 293 K): 165.4 (3-N_2C_3H^3Bu_2), 156.8 (1-C_6H_5), 156.3 (5-N_2C_3H^3Bu_2), 128.4 (3-C_6H_5), 126.9 (2-C_6H_5), 118.0 (4-C_6H_5), 104.8 (4-N_2C_3H^3Bu_2), 68.5 (HC\{(Bu_2pz)_2\}), 32.8 (5-N_2C_3H(CMe_3)_2), 32.6 (3-N_2C_3H(CMe_3)_2), 31.4 (5-N_2C_3H(CMe_3)_2), 31.2 (3-N_2C_3H(CMe_3)_2), 6.1 (SiMe_3), 0.2 (SiMe_2) ppm. IR (NaCl plates, Nujol, cm\(^{-1}\)): 2726 (s), 2670 (m), 1589 (w), 1549 (w), 1196 (w), 1167 (w), 1067 (s), 951 (w), 837 (m). Anal. found (calcd. for C_{37}H_{68}MgN_5Si_3): C, 59.07 (62.99); H, 9.19 (9.71); N, 11.21 (11.91) %. This was the best of several attempts.

\[ \text{Mg}[\text{HC}^\text{(Bu}^\text{2}^\text{pz})\text{SiMe}_2^\text{NPh}]\{\text{N(SiHMe}_3)\}_2 \] (16). To a solution of Mg\{N(SiHMe_3)_2\}_2 (0.17 g, 0.59 mmol) in benzene (15 mL) was added slowly HC\{(Bu_2pz)_2SiMe_2N(H)Ph (0.31 g, 0.59 mmol) in benzene (15 mL). The mixture was heated to 60 °C and stirred for 24 h. Volatiles were removed under reduced pressure to give a pale yellow solid.

Recrystallisation from a saturated pentane solution at -30 °C yielded 16 as an analytically pure, off-white solid. Yield: 0.21 g (53 %). Diffraction-quality crystals were grown from a saturated pentane solution at -30 °C. \(^1\)H NMR (C_6D_6, 299.9 MHz, 293 K): 7.26 (2 H, app. t, app. \(^3\)J = 7.9 Hz, 3-C_6H_5), 7.01 (2 H, d, \(^3\)J = 7.1 Hz, 2-C_6H_5), 6.84 (1 H, app. t, app. \(^3\)J = 7.9 Hz, 4-C_6H_5), 6.30 (1 H, s, HC\{(Bu_2pz)_2\}), 6.03 (2 H, s, N_2C_3H^3Bu_2), 5.24 (2H, sept, \(^3\)J = 2.7 Hz, SiMe_3H), 1.59 (18 H, s, 3-N_2C_3H^3Bu_2), 1.11 (18 H, s, 5-N_2C_3H^3Bu_2), 0.38 (12 H, \(^3\)J = 2.7 Hz, SiHMe_2), -0.05 (6 H, s, SiMe_2) ppm. \(^{13}\)C\{\(^1\)H\} NMR (C_6D_6, 75.4 MHz, 293 K): 165.5 (3-N_2C_3H^3Bu_2), 156.8 (1-C_6H_5), 155.9 (5-N_2C_3H^3Bu_2), 128.8 (3-C_6H_5), 126.4
(2-C₆H₅), 117.5 (4-C₆H₅), 104.7 (4-N₂C₆H blades Bu₂), 69.0 (HC(Bu₂pz)₂), 33.1 (5-N₂C₆H(ClC₆H₃)), 33.0 (3-N₂C₆H(ClC₆H₃)), 31.6 (5-N₂C₆H(ClC₆H₃)), 31.4 (3-N₂C₆H(ClC₆H₃)), 3.7 (SiHMe₃), 0.4 (SiMe₃) ppm. IR (NaCl plates, Nujol, cm⁻¹): 2854 (s), 2058 (m), 1586 (w), 1261 (w), 1093 (s), 976 (w), 886 (m), 759 (w). EI-MS: m/z 676 [M- Mg(N(SiHMe₃)₂)-NPh]⁺ (20 %). Anal. found (calcd. for C₃₅H₆₄MgN₅Si₃): C, 62.0 (62.09); H, 9.57 (9.54); N, 12.36 (12.42) %.

5.3. Experimental details and characterising data for Chapter Three

[Ca(BH₄)(THF)]₃[BPh₄] (17-BPh₄). A solution of [Et₃NH][BPh₄] (3.94 g, 9.40 mmol) in THF (20 mL) was added to a solution of Ca(BH₄)₂(THF)₂ (2.00 g, 9.40 mmol) in THF (20 mL) at -78 °C. The resulting white suspension was stirred for 30 min at this temperature, then allowed to warm to RT and stirred for a further 2 h (gas evolution was observed). Volatiles were removed under reduced pressure, leaving a white solid. This was extracted into THF (3 x 15 mL), and the solution concentrated and cooled to -30 °C, yielding 17-BPh₄ as a colourless microcrystalline solid. Yield: 3.50 g (51 %). Diffraction-quality crystals were grown from a saturated THF solution at -30 °C. ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.35 (8 H, m, o-B(C₆H₅)₃), 7.05 (8 H, t, 3J = 7.5 Hz, m-B(C₆H₅)₃), 6.90 (4 H, t, 3J = 7.5 Hz, p-B(C₆H₅)₃), 3.83 (20 H, m, OCH₂CH₂), 1.95 (20 H, m, OCH₂CH₂), -0.19 (4 H, q, BH₄), 1 ⁴JBH = 82 Hz) ppm. ¹³C[¹H] NMR (CD₂Cl₂, 75.5 MHz, 293 K): 164.4 (i-B(C₆H₅)₃), 153.3 (136.3 (o-B(C₆H₅)₃), 125.9 (m-B(C₆H₅)₃), 122.1 (p-B(C₆H₅)₃), 69.2 (OCH₂CH₂), 25.7 (OCH₂CH₂) ppm. ¹¹B[¹H] NMR (CD₂Cl₂, 92.6 MHz, 293 K): -6.6 (BPh₄), -36.1 (BH₄). IR (NaCl plates, Nujol mull, cm⁻¹): 2725 (s), 2670 (s), 2336 (s), 2261 (s), 2217 (s), 1261 (s), 1150 (m), 1092 (s), 1023 (s), 870 (m), 705 (s). IR (NaCl cell, THF, v(B-H), cm⁻¹): 2406 (s, B-H, of BH₄), 2260 and 2208 (s, B-H of BH₄; 52 cm⁻¹ splitting). ES⁺-MS (THF): m/z = 415 [M]⁺. Anal. found (calcd. for C₄₄H₆₄B₂CaO₅): C, 71.75 (71.93); H, 8.72 (8.78) %.

[Ca(HC(Me₂pz)₃)(BH₄)(THF)]₂[BPh₄] (18-BPh₄). A solution of HC(Me₂pz)₃ (0.30 g, 1.00 mmol) in CH₂Cl₂ (20 mL) was added dropwise to a solution of [Ca(BH₄)(THF)]₃[BPh₄] (0.67 g, 1.00 mmol) in CH₂Cl₂ (20 mL) at -78 °C. The resulting pale yellow solution was stirred at this temperature for 2 h, then allowed to warm to RT and stirred for a further 2 h. Volatiles were removed under reduced pressure, leaving a spongy yellow solid. Recrystallisation from CH₂Cl₂:pentane (1:3 v/v) at -30 °C, gave 18-BPh₄ as an off-white microcrystalline solid. Yield: 0.61 g (74 %). Diffraction-quality crystals were grown from a hexane-layered CH₂Cl₂ solution at RT. ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.80 (1 H, s, HC(N₂C₆Me₂H)₃), 7.33 (8 H, m, o-B(C₆H₅)₃), 7.00 (8
suspension was filtered and volatiles were removed under reduced pressure, leaving a white solid. Yield: 0.61 g (52 %). Diffraction-quality crystals were grown from a saturated CH$_2$Cl$_2$ solution at RT. $^1$H NMR (CD$_2$Cl$_2$, 299.9 MHz, 293 K): 7.90 (2 H, t, J = 6.6 Hz, m-B(C$_6$H$_5$)$_4$), 6.31 (8 H, m, o-B(C$_6$H$_5$)$_4$), 6.04 (6 H, s, N$_2$C$_3$Me$_2$H), 2.44 (18 H, s, 3-N$_2$C$_3$Me$_2$H), 1.98 (18 H, s, 5-N$_2$C$_3$Me$_2$H) ppm. $^{13}$C$^{[1]}$H NMR (CD$_2$Cl$_2$, 75.5 MHz, 293 K): 164.4 (i-B(C$_6$H$_5$)$_4$), 153.6 (3-N$_2$C$_3$Me$_2$H), 143.4 (5-N$_2$C$_3$Me$_2$H) 136.5 (o-B(C$_6$H$_5$)$_4$), 126.0 (m-B(C$_6$H$_5$)$_4$), 122.1 (p-B(C$_6$H$_5$)$_4$), 108.7 (4-N$_2$C$_3$Me$_2$H), 68.1 (HC(N$_2$C$_3$Me$_2$H)$_3$), 13.4 (3-N$_2$C$_3$Me$_2$H), 11.7 (5-N$_2$C$_3$Me$_2$H) ppm. $^{11}$B$^{[1]}$H NMR (CD$_2$Cl$_2$, 96.2 MHz, 293 K): -7.3 (BPh$_4$), -36.6 (B$_2$H$_4$). IR (NaCl plates, Nujol mull, cm$^{-1}$): 2725 (s), 2670(s), 2336(s), 2269(s), 2214(s), 1306 (s), 1260(s), 1154(m), 1098(m), 1032(s), 977(s), 858(s). IR (NaCl cell, THF, ν(B-H), cm$^{-1}$): 2410 (s, B{H} 2270 and 2220 (s, B-H of BPh$_4$; 50 cm$^{-1}$ splitting). ES$^+$-MS (THF): m/z = 426 ([M-THF]$^+$), 353 ([M-(THF)$_2$]$^+$). Anal. found (calcd. for Cs$_2$H$_7$B$_2$Ca$_1$N$_6$O$_3$ (18-BPh$_4$-THF): C, 69.98 (70.27); H, 7.93 (7.94); N, 9.43 (9.45) %.

[Ca{HC(Me$_2$pz)$_3$}]$[BPh$_4$]_2$ (19-[BPh$_4$]$_2$). A solution of HC(Me$_2$pz)$_3$ (0.30 g, 1.00 mmol) in THF (20 mL) was added to a solution of [Ca(BH$_4$)(THF)$_3$][BPh$_4$] (0.67 g, 1.00 mmol) in THF (20 mL) at RT. The resulting white suspension was stirred for 2 h. Volatiles were removed under reduced pressure, leaving a white solid. Recrystallisation from THF:pentane (1:2 v/v) at -30 °C, gave 19-[BPh$_4$]$_2$ as a colourless microcrystalline solid. Yield: 0.61 g (52 %). Diffraction-quality crystals were grown from a saturated CH$_2$Cl$_2$ solution at RT. $^1$H NMR (CD$_2$Cl$_2$, 299.9 MHz, 293 K): 7.90 (2 H, s, HC(N$_2$C$_3$Me$_2$H)$_3$), 7.30 (16 H, m, o-B(C$_6$H$_5$)$_4$), 6.96 (16 H, t, J = 6.6 Hz, m-B(C$_6$H$_5$)$_4$), 6.81 (8 H, t, J = 6.6 Hz, p-B(C$_6$H$_5$)$_4$), 6.04 (6 H, s, N$_2$C$_3$Me$_2$H), 2.44 (18 H, s, 3-N$_2$C$_3$Me$_2$H), 1.96 (18 H, s, 5-N$_2$C$_3$Me$_2$H) ppm. $^{13}$C$^{[1]}$H NMR (CD$_2$Cl$_2$, 75.5 MHz, 293 K): 164.4 (i-B(C$_6$H$_5$)$_4$), 153.6 (3-N$_2$C$_3$Me$_2$H), 143.4 (5-N$_2$C$_3$Me$_2$H) 136.5 (o-B(C$_6$H$_5$)$_4$), 126.0 (m-B(C$_6$H$_5$)$_4$), 122.1 (p-B(C$_6$H$_5$)$_4$), 108.7 (4-N$_2$C$_3$Me$_2$H), 68.1 (HC(N$_2$C$_3$Me$_2$H)$_3$), 13.4 (3-N$_2$C$_3$Me$_2$H), 11.7 (5-N$_2$C$_3$Me$_2$H) ppm. $^{11}$B$^{[1]}$H NMR (CD$_2$Cl$_2$, 96.2 MHz, 293 K): -7.3 (BPh$_4$). IR (NaCl plates, Nujol mull, cm$^{-1}$): 1559(s), 1306(s), 1259(s), 1152(s), 1107(s), 1039(m), 977(m), 898(s), 856(s), 812(m), 706(s). Anal. found (calcd. for Cs$_{80}$H$_{85.6}$B$_2$CaCl$_1$$_2$N$_{12}$ (19-[BPh$_4$]$_2$:0.8(CH$_2$Cl$_2$)): C, 72.27 (72.25); H, 6.47 (6.42); N, 12.52 (12.51) %.

(Tp$^{[1}{Bu}Me$)Ca(BH$_4$)(THF) (20). A suspension of KTp$^{[1}{Bu}Me$ (0.50 g, 1.08 mmol) in THF (30 mL) was added dropwise over 30 mins to a solution of Ca(BH$_4$)$_2$(THF)$_2$ (0.23 g, 1.08 mmol) in THF (20 mL) at RT. The resulting suspension was stirred for 3 h. The suspension was filtered and the volatiles removed under reduced pressure, leaving a white
residue. This was extracted into benzene (3 x 10 mL) and the volatiles removed under reduced pressure to give a spongy white solid. This was recrystallised from THF:pentane (1:3 v/v) to give 20 as a colorless microcrystalline solid. Yield: 0.37 g (65 %). $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.68 (3 H, s, N$_2$C$_3$BuMeH), 3.26 (4 H, m, OCH$_2$CH$_2$), 2.19 (9 H, s, N$_2$C$_3$BuMeH), 1.42 (27 H, s, N$_2$C$_3$BuMeH), 1.17 (4 H, m, OCH$_2$CH$_2$), BH of Tp$_{^{18}Bu,Me}$ and BH$_4$ not observed. $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 75.5 MHz, 293 K): 163.4 (3-N$_2$C$_3$BuMeH), 145.3 (5-N$_2$C$_3$BuMeH), 103.1 (4-N$_2$C$_3$BuMeH), 68.6 (OCH$_2$CH$_2$), 32.2 (CMe$_3$), 31.5 (C(Me$_3$)), 25.5 (OCH$_2$CH$_2$), 13.5 (N$_2$C$_3$BuMeH) ppm. $^{11}$B{$^1$H} NMR (C$_6$D$_6$, 96.2 MHz, 293 K): -7.9 (B-H of Tp$_{^{18}Bu,Me}$), -32.1 (BH$_4$). IR (NaCl plates, Nujol mull, cm$^{-1}$): 2558 (s), 2396(m), 2214(s), 1541(s), 1334(s), 1240(s), 1199(s), 1178(s), 1068(s), 1027(s), 705(s). IR (NaCl cell, THF), v(B-H, cm$^{-1}$): 2562 (s, B-H of Tp$_{^{18}Bu,Me}$), 2416 (s, B-H of BH$_4$), 2223 and 2174 (s, B-H$_6$ of BH$_4$; 49 cm$^{-1}$ splitting). EI-MS: m/z = 478 (80 %), [M-THF]$^+$. Anal. found (calcd. for C$_{28}$H$_{52}$B$_2$CaON$_6$): C, 60.67 (61.10); H, 9.35 (9.52); N, 14.56 (15.27) %.

(Tp$_{^{18}Bu,Me}$)Ca(I)(THF) (21). A suspension of KTp$_{^{18}Bu,Me}$ (1.46 g, 3.16 mmol) in THF (40 mL) was added dropwise over 30 mins to a suspension of CaI$_2$ (0.93 g, 3.16 mmol) in THF (20 mL) at RT. The resulting suspension was stirred for 24 h, filtered and the volatiles removed under reduced pressure, leaving a white residue. This was extracted into benzene (3 x 10 mL) and the volatiles were removed under reduced pressure to give a spongy white solid which was recrystallised from THF:pentane (1:3 v/v) to give 21 as a colorless microcrystalline solid. Yield: 1.49 g (71 %). $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.70 (3 H, s, N$_2$C$_3$BuMeH), 3.36 (4 H, m, OCH$_2$CH$_2$), 2.24 (9 H, s, N$_2$C$_3$BuMeH), 1.49 (27 H, s, N$_2$C$_3$BuMeH), 1.19 (4 H, m, OCH$_2$CH$_2$), BH of Tp$_{^{18}Bu,Me}$ not observed. $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 75.5 MHz, 293 K): 163.5 (3-N$_2$C$_3$BuMeH), 145.4 (5-N$_2$C$_3$BuMeH), 102.8 (4-N$_2$C$_3$BuMeH), 69.1 (OCH$_2$CH$_2$), 32.4 (CMe$_3$), 32.0 (C(Me$_3$)), 25.4 (OCH$_2$CH$_2$), 13.4 (N$_2$C$_3$BuMeH) ppm. $^{11}$B{$^1$H} NMR (C$_6$D$_6$, 96.2 MHz, 293 K): -8.1 (B-H of Tp$_{^{18}Bu,Me}$). IR (NaCl plates, Nujol mull, cm$^{-1}$): 2558 (s), 1538(s), 1461(m), 1336(m), 1261(m), 1068(s), 1020(s), 867(s), 767(m). EI-MS: m/z = 590 (20 %), [M-THF]$^+$. Anal. found (calcd. for C$_{28}$H$_{52}$B$_2$CaON$_6$): C, 50.57 (50.76); H, 7.25 (7.30); N, 12.50 (12.69) %.

(Tp$_{^{18}Bu,Me}$)Ca(BD$_4$)(THF) (20-d$_4$). A suspension of NaBD$_4$ (0.19 g, 4.53 mmol) in acetonitrile (10 mL) was added to a solution of 21 (1.00 g, 1.51 mmol) in acetonitrile (20 mL) at RT. The resulting suspension was stirred for 24 h. The suspension was filtered and the volatiles removed under reduced pressure, leaving a white residue. This was extracted
into benzene (3 x 10 mL) and the volatiles were removed under reduced pressure to give a spongy white solid which was recrystallised from THF:pentane (1:3 v/v) to give 20-d as a colourless microcrystalline solid. Yield: 0.58 g (58 %). $^1$H NMR (CD$_6$D$_6$, 299.9 MHz, 293 K): Identical to that for 20. $^2$H NMR (C$_6$H$_6$, 46.0 MHz, 293 K): 0.23 (br, s, BD$_3$). $^{11}$B{$^1$H} NMR (C$_6$D$_6$, 96.2 MHz, 293 K): -7.2 (B-H of Tp$^{\text{Bu,Me}}$), -32.0 (BD$_3$). IR (NaCl cell, THF), ν(B-H or B-D), cm$^{-1}$: 2558 (s, B-H of Tp$^{\text{Bu,Me}}$), 1807 (s, B-D$_3$ of BD$_3$); ν$_H$/ν$_D$ = 1.34, 1543 (s, B-D$_3$ of BD$_3$); ν$_H$/ν$_D$ = 1.41, other stretching frequency hidden under subtraction artefact. EI-MS: m/z = 553 (10 %) [M]$^+$.

(Tp$^{\text{Bu,Me}}$)Mg(BH$_4$) (22). A suspension of KTp$^{\text{Bu,Me}}$ (1.00 g, 2.16 mmol) in THF (30 mL) was added dropwise over 30 mins to a solution of Mg(BH$_4$)$_2$ (0.12 g, 2.16 mmol) in THF (20 mL) at RT. The resulting suspension was stirred for 24 h, and the volatiles removed under reduced pressure, leaving a white residue. This was extracted into benzene (3 x 10 mL) and the volatiles were removed under reduced pressure to give a white solid which was recrystallised from THF:pentane (1:3 v/v) to give 22 as a colourless microcrystalline solid. Yield: 0.57 g (57 %). $^1$H NMR (C$_6$D$_6$, 299.9 MHz, 293 K): 5.62 (3 H, s, N$_2$C$_3$BuMeH), 2.04 (9 H, s, N$_2$C$_3$BuMeH), 1.51 (4 H, q, BH$_4$, $^1$J$_{BH}$ = 83.4 Hz), 1.45 (27 H, s, N$_2$C$_3$BuMeH), BH of Tp$^{\text{Bu,Me}}$ not observed. $^{13}$C{$^1$H} NMR (C$_6$D$_6$, 75.5 MHz, 293 K): 165.3 (3-N$_2$C$_3$BuMeH), 145.0 (5-N$_2$C$_3$BuMeH), 104.1 (4-N$_2$C$_3$BuMeH), 32.1 (C(Me$_3$)), 31.2 (C(Me$_3$)), 13.0 (N$_2$C$_3$BuMeH) ppm. $^{11}$B{$^1$H} NMR (C$_6$D$_6$, 96.2 MHz, 293 K): -8.9 (B-H of Tp$^{\text{Bu,Me}}$), -37.6 (BH$_4$). IR (NaCl cell, THF), ν(B-H), cm$^{-1}$: 2564 (s, B-H of Tp$^{\text{Bu,Me}}$), 2439 (s, B-H of BH$_4$), 2229 and 2174 (s, B-H$_3$ of BH$_4$; 55 cm$^{-1}$ splitting). EI-MS: m/z = 449 (10 %), [M$^-$BH$_3$]$^+$. Anal. found (calcd. for C$_{3}$H$_{44}$B$_2$MgN$_6$): C, 60.67 (62.32); H, 9.35 (9.59); N, 14.56 (18.17) %.

5.4. Experimental details and characterising data for Chapter Four

[Y{HC(Me$_2$pz)$_3$}(CH$_2$SiMe$_3$)$_3$(THF)][BPh$_4$] (23-BPh$_4$). To cold (-78 °C) solid Y(CH$_2$SiMe$_3$)$_3$(THF)$_2$ (0.50 g, 1.01 mmol) and [NEt$_3$H][BPh$_4$] (0.42 g, 1.01 mmol) at -78 °C, THF (15 mL) at -78 °C was added. To this was added a solution of HC(Me$_2$pz)$_3$ (0.30 g, 1.01 mmol) in cold (-78 °C) THF (10 mL). The solution was stirred at -78 °C for 1.5 h after which time it was allowed to warm to RT and stirred for another 2 h. The solution was concentrated to ca. 2 mL and then pentane (10 mL) added. The supernatant was carefully decanted to leave a yellow oil, which upon drying gave 23-BPh$_4$ as a spongy yellow solid. Yield: 0.75 g (78 %). $^1$H NMR (CD$_2$Cl$_2$, 299.9 MHz, 293 K): 7.78 (1 H, s, HC(N$_2$C$_3$Me$_2$H)$_3$), 7.31 (8 H, m, o-B(C$_6$H$_5$)$_4$), 6.99 (8 H, t, $^3$J = 7.4 Hz, m-B(C$_6$H$_5$)$_4$) 6.86
(4 H, t, 3J = 7.4 Hz, p-B(C6H5)4), 6.05 (3 H, s, N2C3Me2H), 3.90 (4 H, m, OCH2CH2), 2.47 (9 H, s, 3-N2C3Me2H), 2.38 (9 H, s, 5-N2C3Me2H), 1.95 (4 H, m, OCH2CH2), -0.15 (18 H, s, SiMe3), -0.43 (2 H, d, JHY = 2.8 Hz, YCH2) ppm. 13C{1H} NMR (CD2Cl2, 75.5 MHz, 293 K): 164.5 (i-B(C6H5)4) 154.7 (3-N2C3Me2H), 143.0 (5-N2C3Me2H), 136.4 (oB(C6H5)4), 126.1 (m-B(C6H5)4), 122.5 (p-B(C6H5)4), 109.2 (4-N2C3Me2H), 70.7 (OCH2CH2), 68.5 (HC(N2C3Me2H)3), 38.7 (d, JCY = 49 Hz, YCH2) 26.0 (OCH2CH2), 15.2 (3-N2C3Me2H), 11.7 (5-N2C3Me2H), 4.1 (SiMe3) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 2670 (m), 2407 (s), 1819 (m), 1566 (m), 1305 (m), 1304 (m), 1034 (m), 980 (m), 861 (s). Anal. found (calcd. for C52H72BN6OSi2Y): C, 65.37 (65.52); H, 7.62 (7.62); N, 8.77 (8.82) %.

[Y{HC(Me2pz)3}(O'Pr)2(THF)][BPh4] (24-BPh4). To a stirring solution of [Y{HC(Me2pz)3}(CH2SiMe3)2(THF)][BPh4] (0.50 g, 0.53 mmol) in CH2Cl2 (20 mL) 1PrOH (80 μL, 1.05 mmol) was added. The solution was stirred at RT for 2 h after which time the volatiles were removed under reduced pressure to leave 24-BPh4 as a spongy pale yellow solid. This was dissolved in the minimum amount of THF and then pentane added dropwise until the solution turned cloudy. The minimum amount of THF was then added dropwise until the solution became transparent. The solution was then cooled to -78 °C, yielding 24-BPh4 as a microcrystalline, off-white solid. Yield: 0.37 g (79 %). 1H NMR (CD2Cl2, 299.9 MHz, 293 K): 7.77 (1 H, s, HC(N2C3Me2H)3), 7.24 (8 H, m, oB(C6H5)4), 6.98 (8 H, t, 3J = 7.5 Hz, m-B(C6H5)4), 6.83 (4 H, t, 3J = 7.5 Hz, p-B(C6H5)4), 6.02 (3 H, s, N2C3Me2H), 4.11 (2 H, sept., 2J = 6.5 Hz, OCH(CH3)2), 3.79 (4 H, m, OCH2CH2), 2.47 (9 H, s, 3-N2C3Me2H), 2.38 (9 H, s, 5-N2C3Me2H), 2.09 (4 H, m, OCH2CH2), 1.14 (12 H, d, 2J = 5.9 Hz, OCH(CH3)2) ppm. 13C{1H} NMR (CD2Cl2, 75.5 MHz, 293 K): 164.8 (i-B(C6H5)4) 154.2 (3-N2C3Me2H), 141.4 (3-N2C3Me2H), 136.0 (oB(C6H5)4), 125.7 (m-B(C6H5)4), 121.8 (p-B(C6H5)4), 108.1 (4-N2C3Me2H), 68.3 (OCH(CH3)2), 67.1 (HC(N2C3Me2H)3), 67.8 (OCH2CH2), 27.5 (OCH(CH3)2), 25.6 (OCH2CH2), 14.4 (3-N2C3Me2H), 11.2 (5-N2C3Me2H). IR (NaCl plates, Nujol Mull, cm⁻¹): 2670 (m), 2410 (s), 1580 (s), 1565 (s), 1099 (m), 1032 (m), 859 (m), 800 (s), 703 (m). Anal. Found (calcd. for C50H64B11N6O3Y1): C, 66.83 (66.93); H, 7.21 (7.20); N, 9.27 (9.37) %.

[Y{HC(Me2pz)3}(CH2SiMe3)(THF)2][BPh4]2 (25-[BPh4]2). To cold (−78 °C) solid Y(CH2SiMe3)3(THF)2 (0.50 g, 1.01 mmol) and [NEt3H][BPh4] (0.85 g, 2.02 mmol), THF (15 mL) was added. To this was added a solution of HC(Me2pz)3 (0.30 g, 1.01 mmol) in cold (−78 °C) THF (10 mL). The solution was stirred at −78 °C for 1.5 h after which time
it was allowed to warm to RT and stirred for another 2 h. The solution was concentrated to ca. 2 mL and then pentane (10 mL) added. The supernatant was carefully decanted to leave a yellow oil which, upon drying, gave 25-[BPh₄]₂ as a spongy yellow solid. Yield: 1.03 g (77 %). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.65 (1 H, s, HC(N₂C₃Me₂H)₃), 7.33 (16 H, m, o-B(C₆H₅)₄), 6.98 (16 H, t, ³J = 7.5 Hz, m-B(C₆H₅)₄), 6.83 (8 H, t ³J = 7.5 Hz, p-B(C₆H₅)₄), 5.96 (3 H, s, N₂C₃Me₂H), 3.75 (12 H, m, OCH₂CH₂), 2.24 (9 H, s, 3-N₂C₃Me₂-H), 2.21 (9 H, s, 5-N₂C₃Me₂H), 1.88 (12 H, m, OCH₂CH₂), -0.11 (9 H, s, SiMe₃), -0.19 (2 H, d, JHY = 2.9 Hz, YCH₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 164.3 (i-B(C₆H₅)₄), 155.1 (3-N₂C₃Me₂H), 145.4 (5-N₂C₃Me₂H), 136.8 (o-B(C₆H₅)₄), 126.2 (m-B(C₆H₅)₄), 122.3 (p-B(C₆H₅)₄), 110.1 (4-N₂C₃Me₂H), 71.3 (OCH₂CH₂), 68.5 (N₂C₃Me₂H)₃), 47.8 (d, JCY = 40 Hz, YCH₂), 26.0 (OCH₂CH₂), 14.6 (3-N₂C₃Me₂H), 11.7 (5-N₂C₃Me₂H), 3.9 (SiMe₃) ppm. IR (NaCl plates, Nujol mull, cm⁻¹): 2727 (m), 1670 (m), 1616 (w), 1563 (m), 1261 (s), 1223 (m), 1093 (m), 1018 (m), 799 (s) ppm.

[Y{HC(Me₂pz)₁}(O¹Pr)(THF)₃][BPh₄]₂ (26-[BPh₄]₂). To a stirring solution of [Y{HC(Me₂pz)₁}(CH₂SiMe₃)(THF)₃][BPh₄]₂ (0.50 g, 0.38 mmol) in CH₂Cl₂ (20 mL), ¹PrOH (30 μL, 0.38 mmol) was added. The solution was stirred at RT for 2 hours, after which time the volatiles were removed under reduced pressure to leave 26-[BPh₄]₂ as a spongy pale yellow solid. This was dissolved in the minimum amount of THF and pentane added dropwise until the solution turned cloudy. The minimum amount of THF was then added dropwise until the solution became transparent. The solution was then cooled to -78 °C, yielding 26-[BPh₄]₂ as a microcrystalline off-white solid. Yield: 0.33 g (67%). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.76 (1 H, s, HC(N₂C₃Me₂H)₃), 7.33 (16 H, m, o-B(C₆H₅)₄), 6.97 (16 H, t, ³J = 7.5 Hz, m-B(C₆H₅)₄), 6.81 (8 H, t ³J = 7.5 Hz, p-B(C₆H₅)₄), 6.02 (3 H, s, N₂C₃Me₂H), 4.07 (1 H, sept., ³J = 6.5 Hz, OCH₂(CH₃)₂), 3.73 (12 H, m, OCH₂CH₂), 2.29 (9 H, s, 3-N₂C₃Me₂H), 2.24 (9 H, s, 5-N₂C₃Me₂H), 1.89 (12 H, m, OCH₂CH₂), 1.16 (6 H, d, ³J = 5.9 Hz, OCH(CH₃)₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 165.2 (i-B(C₆H₅)₄), 163.9 (3-N₂C₃Me₂H), 139.5 (5-N₂C₃Me₂H), 136.8 (o-B(C₆H₅)₄), 129.2 (5-N₂C₃Me₂H), 126.5 (m-B(C₆H₅)₄), 122.7 (p-B(C₆H₅)₄), 70.3 (OCH₂(CH₃)₂), 69.1 (HC(N₂C₃Me₂H)₃), 67.1 (OCH₂CH₂), 27.1 (OCH₂(CH₃)₂), 26.5 (OCH₂CH₂), 14.7 (3-N₂C₃Me₂H), 12.0 (5-N₂C₃Me₂H). IR (NaCl plates, Nujol mull, cm⁻¹): 2726 (m), 1460 (m), 1304 (m), 1261 (s), 1093 (m), 1018 (m), 799 (s). Anal. found (calcd. for C₇₀H₉₃B₂N₆O₄Si): C, 72.83 (72.88); H, 7.09 (7.21); N, 6.51 (6.46) %.
[Y(Me₃[9]aneN₃)(CH₂SiMe₃)₂(THF)][BPh₄] (27-BPh₄). To cold (-78 °C) solid Y(CH₂SiMe₃)₃(THF)₂ (0.40 g, 0.80 mmol) and [NEt₃H][BPh₄] (0.34 g, 0.80 mmol), cold (-78 °C) THF (15 mL) was added. To this was added Me₃[9]aneN₃ (156 μl, 0.800 mmol). The solution was stirred at -78 °C for 1.5 h after which time it was allowed to warm to RT, stirred for another 2 h and concentrated to ca. 2 mL. Pentane (10 mL) was added and the supernatant carefully decanted to leave a yellow oil, which, upon drying gave 27-BPh₄ as a yellow solid. Yield: 0.47 g (71 %). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.36 (8 H, m, o-B(C₆H₅)₃), 7.06 (8 H, t, ³J = 7.5 Hz, m-B(C₆H₅)₃), 6.93 (8 H, t ³J = 7.5 Hz, p-B(C₆H₅)₃), 4.19 (3 H, s, NMe, trans to THF), 3.81 (4 H, m, OCH₂CH₂), 2.53-2.46 (12 H, m, NCH₂), 2.40 (6 H, s, NMe, trans to CH₂SiMe₃), 1.92 (4 H, m, OCH₂CH₂), -0.02 (18 H, s, SiMe₃), -0.76 (4 H, br, s, YCH₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 164.2 (i-B(C₆H₅)₃), 136.3 (o-B(C₆H₅)₃), 126.1 (m-B(C₆H₅)₃), 122.3 (p-B(C₆H₅)₃), 71.2 (OCH₂CH₂), 47.8 (NMe trans to CH₂SiMe₃), 40.9 (d, J_CY = 45 Hz, YCH₂), 41.1 ((NMe, trans to THF), 25.8 (OCH₂CH₂), 3.7 (SiMe₃) ppm. NCH₂ resonances obscured by CD₂Cl₂. IR (NaCl plates, Nujol mull, cm⁻¹): 1580 (m), 1366 (m), 1304 (m), 1237 (s), 1209 (m), 1003 (m), 862 (s). Anal. found (calcd. for C₄₅H₇₁B₄N₁₃O₁₁Si₂Y): C, 65.83 (65.44); H, 8.17 (8.66); N, 5.24 (5.09) %.

[Y(Me₃[9]aneN₃)(O¹Pr)₂(THF)][BPh₄] (28-BPh₄). To a stirring solution of [Y(Me₃[9]aneN₃)(CH₂SiMe₃)₂(THF)][BPh₄] (0.40 g, 0.48 mmol) in CH₂Cl₂ (20 mL), O¹PrOH (74 μL, 0.96 mmol) was added. The solution was stirred at RT for 2 h after which time the volatiles were removed under reduced pressure to leave 28-BPh₄ as a pale yellow solid. This was dissolved in the minimum amount of THF and pentane added dropwise until the solution turned cloudy. The minimum amount of THF was then added dropwise until the solution became transparent. The solution was then cooled to -78 °C, yielding 28-BPh₄ as a microcrystalline yellow solid. Yield: 0.23 g (62 %). ¹H NMR (CD₂Cl₂, 299.9 MHz, 293 K): 7.38 (8 H, m, o-B(C₆H₅)₃), 7.06 (8 H, t, ³J = 7.5 Hz, m-B(C₆H₅)₃), 6.94 (8 H, t ³J = 7.5 Hz, p-B(C₆H₅)₃), 4.07 (2 H, sept., ³J = 6.7 Hz, OCHMe₂), 4.02 (3 H, s, NMe, trans to THF), 3.77 (4 H, m, OCH₂CH₂), 2.56 (6 H, s, NMe, trans to CH₂SiMe₃), 2.28-2.21 (12 H, m, NCH₂), 1.88 (4 H, m, OCH₂CH₂), 1.19 (12 H, d, ³J = 5.9 Hz, OCHMe₂) ppm. ¹³C{¹H} NMR (CD₂Cl₂, 75.5 MHz, 293 K): 163.8 (i-B(C₆H₅)₃), 136.2 (o-B(C₆H₅)₃), 126.3 (m-B(C₆H₅)₃), 121.8 (p-B(C₆H₅)₃), 70.6 (OCH(CH₃)₂), 69.2 (OCH₂CH₂), 54.7 (NCH₃ trans CH₂SiMe₃), 42.6 ((NCH₃, trans THF), 26.2 (OCH(CH₃)₂), 25.8 (OCH₂CH₂) ppm. NCH₂ resonances obscured by CD₂Cl₂. IR (NaCl plates, Nujol mull, cm⁻¹): 2854 (m), 1457 (m), 1419 (m), 1261 (s), 1063 (m), 1022 (m), 816 (s), 668 (s). Anal. found
(calcd. for C\textsubscript{72}H\textsubscript{92}B\textsubscript{2}N\textsubscript{3}O\textsubscript{4}Y): C, 63.56 (67.10); H, 6.88 (8.25); N, 4.79 (5.46) %.

[\text{Y(Me\textsubscript{3}[9]aneN\textsubscript{3})(CH\textsubscript{2}SiMe\textsubscript{3})(THF)}\textsubscript{3}][\text{BPh\textsubscript{4}}\textsubscript{2}] (29-[BPh\textsubscript{4}]\textsubscript{2}). To cold (-78 °C) solid containing Y(CH\textsubscript{2}SiMe\textsubscript{3})\textsubscript{3}(THF)\textsubscript{2} (0.40 g, 0.80 mmol) and [NEt\textsubscript{3}][BPh\textsubscript{4}] (0.68 g, 1.60 mmol), cold (-78 °C) THF (15 mL) was added, followed by Me\textsubscript{3}[9]aneN\textsubscript{3} (156 µl, 0.800 mmol). The solution was stirred at -78 °C for 1.5 h after which time it was allowed to warm to RT, then stirred for another 2 h. The solution was concentrated to ca. 2 mL and then pentane (10 mL) added. The supernatant was carefully decanted to leave a yellow oil, which, upon drying gave 29-[BPh\textsubscript{4}]\textsubscript{2} as an off-white solid. Yield: 0.65 g (68 %). \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 299.9 MHz, 293 K): 7.34 (16 H, m, o-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 7.05 (16 H, t, \textsuperscript{3}J = 7.5 Hz, m-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 6.90 (8 H, t, \textsuperscript{3}J = 7.5 Hz, p-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 4.22 (3 H, s, NMe, trans to THF), 3.73 (12 H, m, OCH\textsubscript{2}CH\textsubscript{2}), 2.58 (6 H, s, NMe, trans to CH\textsubscript{2}SiMe\textsubscript{3}), 2.32-2.18 (12 H, m, NCH\textsubscript{2}), 1.88 (12 H, m, OCH\textsubscript{2}CH\textsubscript{2}), -0.05 (9 H, s, SiMe\textsubscript{3}), -0.78 (4 H, br, s, YCH\textsubscript{2}) ppm.

\textsuperscript{13}C\textsuperscript{([1]H)} NMR (CD\textsubscript{2}Cl\textsubscript{2}, 75.5 MHz, 293 K): 164.4 (i-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 136.3 (o-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 126.0 (m-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 122.3 (p-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 69.1 (OCH\textsubscript{2}CH\textsubscript{2}), 51.1 (NMe trans to CH\textsubscript{2}SiMe\textsubscript{3}), 47.1 (d, \textit{J}_{\text{CV}} = 43 Hz, YCH\textsubscript{2}), 43.1 ((NMe, trans to THF), 25.9 (OCH\textsubscript{2}CH\textsubscript{2}), -0.2 (SiMe\textsubscript{3}) ppm. N\textsubscript{CH}\textsubscript{2} resonances obscured by CD\textsubscript{2}Cl\textsubscript{2}. IR (NaCl plates, Nujol mull, cm\textsuperscript{-1}): 1943 (m), 1581 (m), 1305 (s), 1285 (m), 1265 (m), 1091 (s), 755 (s) ppm. Anal. found (calcd. for C\textsubscript{73}H\textsubscript{98}B\textsubscript{2}N\textsubscript{3}O\textsubscript{4}SiY): C, 72.98 (72.90); H, 8.00 (8.05); N, 3.57 (3.50) %.

[\text{Y(Me\textsubscript{3}[9]aneN\textsubscript{3})(O\textsuperscript{t}Pr)(THF)}\textsubscript{3}][\text{BPh\textsubscript{4}}\textsubscript{2}] (30-[BPh\textsubscript{4}]\textsubscript{2}) To a stirring solution of [\text{Y(Me\textsubscript{3}[9]aneN\textsubscript{3})(CH\textsubscript{2}SiMe\textsubscript{3})(THF)}\textsubscript{3}][\text{BPh\textsubscript{4}}\textsubscript{2} (0.60 g, 0.50 mmol) in CH\textsubscript{2}Cl\textsubscript{2} (20 mL), \textsuperscript{1}PrOH (40 µL), 0.50 mmol) was added. The solution was stirred at RT for 2 h after which time the volatiles were removed under reduced pressure to leave 30-[BPh\textsubscript{4}]\textsubscript{2} as a pale yellow solid. This was dissolved in the minimum amount of THF and pentane added dropwise until the solution turned cloudy. The minimum amount of THF was then added dropwise until the solution became transparent. The solution was then cooled to -80 °C, yielding 30-[BPh\textsubscript{4}]\textsubscript{2} as a microcrystalline off-white solid. Yield: 0.37 g (63 %). \textsuperscript{1}H NMR (CD\textsubscript{2}Cl\textsubscript{2}, 299.9 MHz, 293 K): 7.29 (16 H, m, o-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 6.96 (16 H, t, \textsuperscript{3}J = 7.5 Hz, m-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 6.82 (8 H, t, \textsuperscript{3}J = 7.5 Hz, p-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 4.11 (1 H, br, m, OCHMe\textsubscript{2}), 3.99 (3 H, s, NMe, trans to THF), 3.68 (12 H, m, OCH\textsubscript{2}CH\textsubscript{2}), 2.47 (6 H, s, NMe, trans to CH\textsubscript{2}SiMe\textsubscript{3}), 2.18 (12 H, m, NCH\textsubscript{2}), 1.80 (12 H, m, OCH\textsubscript{2}CH\textsubscript{2}), 1.09 (6 H, br, m, OCHMe\textsubscript{2}) ppm. \textsuperscript{13}C\textsuperscript{([1]H)} NMR (CD\textsubscript{2}Cl\textsubscript{2}, 75.5 MHz, 293 K): 164.2 (i-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 136.9 (o-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 127.7 (m-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 122.8 (p-B(C\textsubscript{6}H\textsubscript{5})\textsubscript{4}), 70.3 (OCHMe\textsubscript{2}), 69.4 (OCH\textsubscript{2}CH\textsubscript{2}), 54.5 (NMe trans to CH\textsubscript{2}SiMe\textsubscript{3}), 43.3 (NMe, trans to THF), 26.3 (OCHMe\textsubscript{2}), 25.9 (OCH\textsubscript{2}CH\textsubscript{2}) ppm.
NCH$_2$ resonances obscured by CD$_2$Cl$_2$. IR (NaCl plates, Nujol mull, cm$^{-1}$): 1942 (m), 1885 (s), 1821 (s), 1650 (s), 1580 (s), 1427 (m), 1286 (s), 1155 (m), 1030 (m), 982 (s), 744 (s), 704 (s). Anal. found (calcd. for C$_7$H$_9$B$_2$N$_3$O$_4$Y$_1$): C, 73.46 (73.62); H, 7.85 (7.90); N, 3.62 (3.58) %.

5.5. Polymerisation procedures for Chapters Two, Three and Four.

**General procedure for the polymerisation of ε-CL.** A solution of ε-CL (3.3 mmol) in solvent (toluene or THF, 2.0 mL, heated to 70 ºC or at RT) was added to a solution of catalyst (0.033 mmol) in solvent (toluene or THF, 1.4 mL, heated to 70 ºC or at RT). Upon completion, the reaction was quenched by addition of wet THF (5 mL) and an aliquot was taken. The percentage conversion was recorded by $^1$H NMR in CDCl$_3$. Isolated yields were obtained by precipitation of polymer from the remaining mixture by addition to hexanes (100 mL) with vigorous stirring. The polymer was filtered and dried to constant weight in vacuo.

**General procedure for the polymerisation of rac-LA.** A solution of rac-LA (3.00 mmol) in solvent (toluene or THF) (3.0 mL, heated to 70 ºC or at RT) was added to a solution of catalyst (0.03 mmol) in solvent (toluene or THF) (3.0 mL, heated to 70 ºC or at RT). The resultant solution was stirred (at 70 ºC or RT) and aliquots were taken at the respective time intervals. Upon completion of the reaction, wet THF (10 mL) was added and the solution evaporated to dryness to give PLA. Conversions were determined by $^1$H NMR integration of the OCHMe resonance relative intensities of the residual rac-LA and PLA.

**Procedure for solution polymerization of rac-LA in the presence of co-initiators (Chapter four).** Rac-LA (3.00 mmol) was dissolved in THF (3.0 mL) and the required amount (e.g. 0.15 mmol for a standard 5 equivalents of co-initiator test) of co-initiator ( $^i$PrOH or BnNH$_2$) was added. This was heated to 70 ºC and was added to a THF solution (3 mL) of catalyst (0.03 mmol) at 70 ºC. The resultant solution was stirred at 70 ºC and aliquots were taken at the respective time intervals. Upon completion of the reaction, wet THF (10 mL) was added and the solution evaporated to dryness to give PLA. Conversions were determined by $^1$H NMR integration of the OCHMe resonance relative intensities of the residual rac-LA and PLA.
5.6. X-ray data collection and processing parameters.

Crystal structure determinations of 1, 2, 4, 5, 6, 7, 9, 10, 12, 15, 16, 17-BPh₄, 18-[BPh₄]₂, 19-BPh₄, 20, 21, and 26-[BPh₄]₂. Crystal data collection and processing parameters are given in Table 5.0. In order to avoid degradation, the single crystals were mounted on glass fibres using perfluoropolyether oil and cooled rapidly in a stream of cold N₂ using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using an Enraf-Nonius KappaCCD and graphite-monochromated MoKα (0.71073 Å) radiation. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged. All calculations were performed using SHELXL-97, SIR92 or the CRYSTALS program suite. The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F). All non-hydrogen atoms were refined anisotropically. The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks.
### Table 5.0. X-ray data collection and processing parameters for Mg\{C(Me₂pz)₃\}\{N(SiMe₃)₂\} (1), Mg\{κ²N-HC(Me₂pz)₃\}\{N(SiHMe₂)₂\} (2), Ca\{C(Me₂pz)₃\}\{N(SiMe₃)₂\}(THF) (4), Ca\{C(Me₂pz)₃\} · 2 C₆H₆ (5 · 2 C₆H₆), Zn\{C(Me₂pz)₃\}Cl (6), Zn\{C(Me₂pz)₃\}\{N(SiMe₃)₂\} (7), Zn\{C(Me₂pz)₃\}₂ (9), Mg\{C(Me₂pz)₃\}\{C(pz)₃\} (10), HC(4-Etpz)₃ (12), Mg\{HC('Bu₂pz)₂SiMe₂NPh\}N(SiMe₃)₂ (15) and Mg\{HC('Bu₂pz)₂SiMe₂NPh\}N(SiHMe₂)₂ (16).

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<td>( C_{16}H_{21}ClN_6Zn )</td>
<td>( C_{22}H_{30}N_7Si_2Zn )</td>
<td>( C_{32}H_{42}N_{12}Zn )</td>
<td>( C_{28}H_{30}MgN_{12} )</td>
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<td>660.15</td>
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<td>150</td>
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<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<td>( P , 2_1/\text{n} )</td>
<td>( P , \bar{1} )</td>
<td>( C , 2/m )</td>
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<td>8.665(2)</td>
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<tr>
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<td>( c ) / Å</td>
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<td>14.2993(6)</td>
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<td>90</td>
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<td>( \beta ) / deg</td>
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<td>86.583</td>
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<td>( \gamma ) / deg</td>
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<td>90</td>
<td>81.813</td>
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<td>0.984</td>
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<td>R indices: ( R_1 = ) &amp; ( R_w ) or ( wR^2 = )</td>
<td>0.0703 [I&gt;3( \sigma(I) )](^a) &amp; 0.0721 [I&gt;3( \sigma(I) )](^b)</td>
<td>0.0748 [I&gt;2( \sigma(I) )](^a) &amp; 0.2077 [all data](^c)</td>
<td>0.0278 [I&gt;2( \sigma(I) )](^a) &amp; 0.0794 [all data](^c)</td>
<td>0.0787 [I&gt;3( \sigma(I) )](^a) &amp; 0.0817 [I&gt;3( \sigma(I) )](^b)</td>
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<td>Compound</td>
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<td>16</td>
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<td>C_{37}H_{68}Mg_{1}N_{6}Si_{3}</td>
<td>C_{35}H_{64}Mg_{1}N_{6}Si_{3}·0.75C_{5}H_{12}</td>
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<tr>
<td>b / Å</td>
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<td>90</td>
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</tr>
<tr>
<td>β / deg</td>
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<td>90</td>
<td>110.253(2)</td>
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<tr>
<td>γ / deg</td>
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<tr>
<td>V / Å³</td>
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<tr>
<td>d (calcd) / Mg·m⁻³</td>
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<td>0.092</td>
<td>1.053</td>
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<tr>
<td>Abs coeff / mm⁻¹</td>
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<td>0.157</td>
<td>0.148</td>
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<tr>
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<td>0.0357 \text{[I&gt;2σ(I)]}^a</td>
<td>0.0619 \text{[I&gt;3σ(I)]}^a</td>
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<tr>
<td>R_w or wR² =</td>
<td>0.0565 \text{I&gt;2σ(I)}^b</td>
<td>0.0372 \text{[all data]}^b</td>
<td>0.0591 \text{[I&gt;3σ(I)]}^b</td>
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\(^{a}R₁ = \frac{\sum |F_o| |F_c|}{\sum |F_o|}; \quad ^{b}R_w = \sqrt{\frac{\sum w(|F_o| |F_c|)^2}{\sum w|F_o|^2}}; \quad ^{c}wR² = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)}}\)
Table 5.1. X-ray data collection and processing parameters for [Ca(BH₄)(THF)₃][BPh₄] (17-BPh₄), [Ca{HC(3,5-Me₂pz)₃}][BPh₄]₂ (18-[BPh₄]₂), [Ca{HC(3,5-Me₂pz)₃}(BH₄)(THF)][BPh₄] (19-BPh₄), (Tp³Bu,Me)Ca(BH₄)(THF) (20), Tp³Bu,Me)Ca(I)(THF) (21) and [Y{HC(3,5-Me₂pz)₃}(OPr)(THF)]₂[BPh₄]₂ (26-[BPh₄]₂).

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<th>19-BPh₄</th>
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<td>C₅₆H₆₂B₁Ca₁N₁₂</td>
<td>C₄₈H₆₂B₂Ca₁N₆O₂</td>
<td>C₂₈H₅₂B₂Ca₁N₆O₁</td>
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<tr>
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<td>0.71073</td>
<td>0.71073</td>
<td>0.71073</td>
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<tr>
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<td>P 2₁/n</td>
<td>P ¹</td>
<td>I 2₁/a</td>
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<td>82.3488(12)</td>
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<td>β / deg</td>
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<td>104.834(1)</td>
<td>82.0004(12)</td>
<td>95.5320(8)</td>
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[^a]: I>3σ(I); [^b]: I>2σ(I); [^c]: all data
Table 5.1 (Continued)

| Compound | 21 | 26-|BPh$_4$|$_2$
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<tr>
<td>Wavelength / Å</td>
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<td>0.71073</td>
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</tr>
<tr>
<td>Space group</td>
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<td>$P \bar{1}$</td>
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<tr>
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<tr>
<td>$b$ / Å</td>
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<td>F_c</td>
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5.7 References


