

# **Alkaline Earth Hydroborate Complexes for the Ring-Opening Polymerisation of Cyclic Esters**

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The work described in this Thesis was carried out in the Chemistry Research Laboratory, University of Oxford from October 2014 to July 2018 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.

A handwritten signature in black ink, reading "N. Diteepeng". The signature is written in a cursive, flowing style with a large initial 'N' and a long, sweeping underline.

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## Abstract

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This Thesis describes the activity and mechanism of alkaline earth organohydroborate, tetrahydroborate and alkoxide catalysts for the ring-opening polymerisation (ROP) of cyclic esters including *rac*-, *L*-, *D*- and *meso*-lactide (LA), and *rac*- $\beta$ -butyrolactone (*rac*-BBL).

**Chapter One** introduces cyclic esters and general mechanisms for their ROP to give polyesters. Living and immortal ROP, an overview of stereocontrolled ROP, and determination of polylactide (PLA) stereosequences are given. Various techniques for polymer characterisations are also described.

**Chapter Two** describes the activity and mechanism of heavy alkaline earth organohydroborate complexes for the ROP of LA. The synthesis and characterisation of alkaline earth alkoxide complexes serving as model species are also described, together with their activities for the ROP of LA.

**Chapter Three** describes the activity and mechanism of a cyclic organohydroborate calcium complex for the ROP of LA. The role of borinic esters as chain transfer agents in the ROP of *rac*-LA is also discussed.

**Chapter Four** describes the activity and mechanism of heavy alkaline earth tetrahydroborate complexes for the ROP of LA. The immortal ROP of *rac*-LA using heavy alkaline earth alkoxide complexes and borate esters as chain transfer agents is discussed.

**Chapter Five** describes the activity and mechanism of alkaline earth organohydroborate, tetrahydroborate and alkoxide complexes for the ROP of *rac*-BBL.

**Chapter Six** presents experimental procedures and characterising data for new complexes reported.

**CD Appendix** contains CIF files for all new crystallographically characterised complexes.

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## CD Appendix

## Abbreviations

### General

|                         |                                          |
|-------------------------|------------------------------------------|
| Å                       | Ångstrom                                 |
| av.                     | Average                                  |
| <i>ca.</i>              | <i>circa</i> , about                     |
| calcd                   | calculated                               |
| cal                     | calories                                 |
| °                       | degrees                                  |
| °C                      | degrees Celsius                          |
| <i>D</i>                | dispersity                               |
| DFT                     | Density Functional Theory                |
| equiv(s).               | equivalent(s)                            |
| g                       | gram(s)                                  |
| GPC                     | gel permeation chromatography            |
| h                       | hour(s)                                  |
| η                       | intrinsic viscosity                      |
| J                       | Joule(s)                                 |
| k                       | kilo                                     |
| kcal mol <sup>-1</sup>  | kilocalorie(s) per mole                  |
| K                       | Kelvin                                   |
| <i>k</i> <sub>app</sub> | apparent rate constant                   |
| <i>k</i> <sub>i</sub>   | rate constant of initiation              |
| <i>k</i> <sub>p</sub>   | rate constant of propagation             |
| <i>k</i> <sub>tr</sub>  | rate constant of chain-transfer reaction |
| L                       | litre(s)                                 |
| mg                      | milligram(s)                             |
| min                     | minute(s)                                |
| mL                      | milliliter(s)                            |
| <i>M</i> <sub>n</sub>   | number average molecular weight          |
| <i>M</i> <sub>p</sub>   | peak molecular weight                    |
| M-OR                    | metal alkoxide                           |
| <i>M</i> <sub>w</sub>   | weight average molecular weight          |
| <i>P</i> <sub>m</sub>   | probability of <i>meso</i> - linkages    |
| <i>P</i> <sub>r</sub>   | probability of racemic linkages          |

|       |                               |
|-------|-------------------------------|
| ROP   | ring-opening polymerisation   |
| RT    | room temperature              |
| s     | second(s)                     |
| SEC   | Size Exclusion Chromatography |
| T     | temperature                   |
| $T_g$ | glass transition temperature  |
| $T_m$ | melting temperature           |
| vs.   | versus                        |

## Chemical

|                                                         |                                                       |
|---------------------------------------------------------|-------------------------------------------------------|
| 9-BBN                                                   | 9-borabicyclo[3.3.1]nonane                            |
| Ar                                                      | aryl group                                            |
| BBL                                                     | $\beta$ -butyrolactone or 4-methyl-2-oxetanone        |
| Bn                                                      | benzyl                                                |
| BnOH                                                    | benzyl alcohol                                        |
| (BC <sub>8</sub> H <sub>14</sub> )(OBn)                 | 9-(benzyloxy)-9-borabicyclo[3.3.1]nonane              |
| (BC <sub>8</sub> H <sub>14</sub> )(OCHPh <sub>2</sub> ) | 9-(benzhydryloxy)-9-borabicyclo[3.3.1]nonane          |
| (BC <sub>8</sub> H <sub>14</sub> )(OCyMe)               | 9-(2-methylcyclohexyloxy)-9-borabicyclo[3.3.1]nonane  |
| B(OBn) <sub>3</sub>                                     | tribenzyl borate                                      |
| B(OCHPh <sub>2</sub> ) <sub>3</sub>                     | tribenzhydryl borate                                  |
| B(OCyMe) <sub>3</sub>                                   | <i>tris</i> (2-methylcyclohexyl) borate               |
| Cp                                                      | C <sub>5</sub> H <sub>5</sub>                         |
| Cp*                                                     | C <sub>5</sub> Me <sub>5</sub>                        |
| CyMeO                                                   | 2-methylcyclohexanone                                 |
| CyMeOH                                                  | 2-methylcyclohexanol                                  |
| $\epsilon$ -CL                                          | $\epsilon$ -caprolactone                              |
| <i>D</i> -lactide                                       | ( <i>R,R</i> )-cis-3,6-dimethyl-1,4-dioxane-2,5-dione |
| DMAP                                                    | 4-dimethylaminopyridine                               |
| <sup>n</sup> Bu                                         | <i>n</i> -butyl                                       |
| <sup>t</sup> Bu                                         | <i>tert</i> -butyl                                    |
| <sup>n</sup> PentOH                                     | <i>n</i> -pentyl alcohol                              |
| <sup>i</sup> Pr                                         | <i>iso</i> -propyl                                    |
| <sup>i</sup> PrOH                                       | isopropyl alcohol                                     |
| L                                                       | a supporting ligand (set)                             |
| LA                                                      | lactide                                               |



|                                   |                                                               |
|-----------------------------------|---------------------------------------------------------------|
| <i>L</i> -lactide                 | ( <i>S,S</i> )-cis-3,6-dimethyl-1,4-dioxane-2,5-dione         |
| Me                                | methyl                                                        |
| <i>meso</i> -lactide              | ( <i>R,S</i> )-cis-3,6-dimethyl-1,4-dioxane-2,5-dione         |
| Ph                                | phenyl                                                        |
| PHA                               | polyhydroxyalkanoate                                          |
| PHB                               | poly(3-hydroxybutyrate)                                       |
| PhCHO                             | benzaldehyde                                                  |
| PhCOPh                            | benzophenone                                                  |
| PLA                               | poly(lactide)                                                 |
| PCL                               | poly(ε-caprolactone)                                          |
| py                                | pyridine                                                      |
| pz                                | pyrazolyl                                                     |
| R                                 | generic aryl or alkyl                                         |
| <i>rac</i> -BBL                   | a racemic mixture of <i>R</i> - and <i>S</i> -β-butyrolactone |
| <i>rac</i> -lactide               | a racemic mixture of <i>D</i> - and <i>L</i> -lactide         |
| ROP                               | ring opening polymerisation                                   |
| Sn(Oct) <sub>2</sub>              | tin octanoate                                                 |
| THF                               | tetrahydrofuran                                               |
| Tp <sup>(<sup>t</sup>Bu,Me)</sup> | 3-methyl, 5- <i>tert</i> -butyl tris(pyrazolyl)hydroborate    |

### Mass Spectrometry

|              |                                                                                |
|--------------|--------------------------------------------------------------------------------|
| Da           | dalton                                                                         |
| EI           | electron impact                                                                |
| ESI-HRMS     | High resolution electrospray ionization mass spectrometry                      |
| FI           | field ionisation                                                               |
| <i>m/z</i>   | mass to charge ratio                                                           |
| MS           | mass spectrometry                                                              |
| MALDI-ToF MS | matrix-assisted laser desorption/ionization - time of flight mass spectroscopy |

### Nuclear Magnetic Resonance Spectroscopy

|                                   |                                  |
|-----------------------------------|----------------------------------|
| <sup>11</sup> B-{ <sup>1</sup> H} | proton-decoupled <sup>11</sup> B |
| <sup>13</sup> C-{ <sup>1</sup> H} | proton-decoupled <sup>13</sup> C |
| app.                              | apparent                         |

|            |                                                                      |
|------------|----------------------------------------------------------------------|
| br         | broad                                                                |
| COSY       | correlation spectroscopy                                             |
| d          | doublet                                                              |
| hept       | heptet                                                               |
| HETCOR     | heteronuclear correlation                                            |
| HMBC       | heteronuclear multiple bond correlation                              |
| HSQC       | heteronuclear single quantum coherence                               |
| HSQC-TOCSY | heteronuclear single quantum coherence-total correlated spectroscopy |
| <i>i</i>   | <i>ipso</i>                                                          |
| <i>J</i>   | coupling constant                                                    |
| <i>m</i>   | <i>meta</i>                                                          |
| m          | multiplet                                                            |
| NMR        | nuclear magnetic resonance                                           |
| nOe        | nuclear Overhauser effect                                            |
| <i>o</i>   | <i>ortho</i>                                                         |
| <i>p</i>   | <i>para</i>                                                          |
| ppm        | parts per million                                                    |
| q          | quartet                                                              |
| ROESY      | rotating-frame nuclear Overhauser effect spectroscopy                |
| s          | singlet                                                              |
| sept       | septet                                                               |
| t          | triplet                                                              |
| TOCSY      | total correlated spectroscopy                                        |
| VT         | variable temperature                                                 |
| $\delta$   | chemical shift in ppm                                                |

### **Infrared Spectroscopy**

|       |                                |
|-------|--------------------------------|
| br    | broad                          |
| FT-IR | fourier transform infrared red |
| IR    | infrared red                   |
| m     | medium                         |
| s     | strong                         |
| w     | weak                           |
| $\nu$ | frequency                      |

## Calculations

|     |                                          |
|-----|------------------------------------------|
| DFT | density functional theory                |
| Q   | charge                                   |
| ‡   | transition state or activation parameter |

### Note about numbering of compounds described in this Thesis

Literature compounds described in this Thesis are numbered **2.x**, **3.x**, **4.x**, **5.x** according to the Chapter in which they first occur. The new compounds described in this Thesis are numbered **1** - **27**.

Mass spectrometry was performed by Dr James Wickens, Colin Sparrow, Dr Ashley Shepherd, Elisabete Pires and Dr Victor Mikhailov. Elemental analysis was performed by Stephen Boyer at London Metropolitan University.

X-ray crystallography data was collected, solved and refined by Dr Matthew Blake. Molecular drawings were produced by Professor Philip Mountford.

DFT calculations were performed by Professor Philip Mountford.

# **Chapter One**

## **Introduction**

## **Chapter One**

### **1.1 Overview**

This Chapter will provide an introduction to the ring-opening polymerisation (ROP) of cyclic esters. General mechanisms in ROP promoted by metal complexes will be discussed, together with concepts of living and immortal polymerisations. A brief account of polymer microstructures and an overview of analytical techniques used for characterisation of polymers will be described.

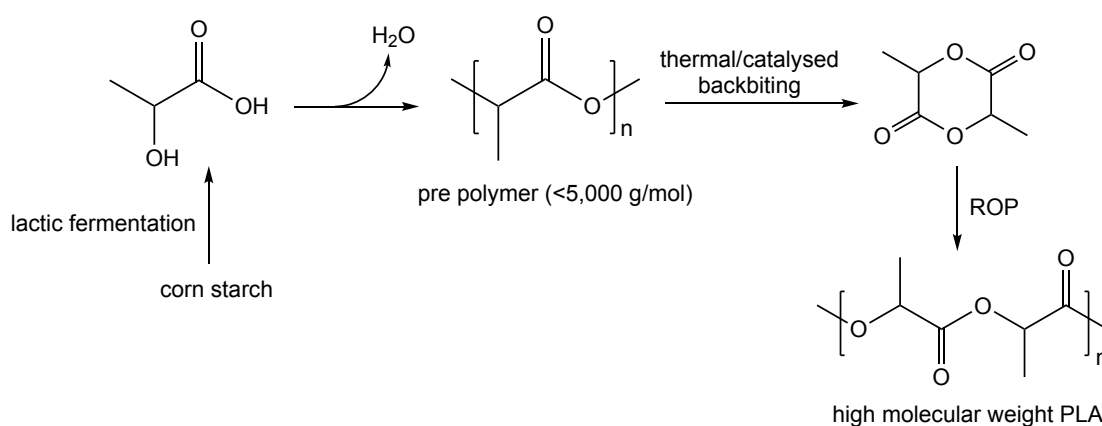
### **1.2 General introduction**

Since the 1950s, the development of petroleum-based plastics has led to a variety of materials whose low cost, processing versatility, and a range of mechanical properties have made them an essential part of our daily lives from clothing, packaging, automotive parts, electronics, healthcare, industrial machinery to building and construction.<sup>1-4</sup> A global analysis of all mass-produced plastics manufactured shows that 8,300 million metric tons (Mt) of virgin plastics were produced between 1950 and 2015.<sup>5</sup> From this, approximately 6,300 Mt of plastic waste was generated, of which only 9% was recycled, 12% was incinerated and 79% was disposed of in landfills. If the current production and waste management trends continue, 12,000 Mt of plastic waste is estimated to be in landfills or the natural environment by 2050. A recent study showed that plastic debris, in particular single-use products, has reached the deepest parts of the ocean (11 km in the Marianas Trench).<sup>6</sup> In order to tackle the environmental effect of conventional products, the development of sustainable polymers as alternatives for current petroleum-based plastics is crucial for modern society.<sup>3, 7-9</sup> Sustainable polymers such as polylactide (PLA), polyhydroxyalkanoates (PHAs), polyethylene carbonate (PEC) or polypropylene carbonate (PPC) from CO<sub>2</sub>, bio-based polybutylene succinate (PBS), starch composites or cellulose acetate are promising materials due to their feedstock renewability and excellent biodegradability.<sup>10, 11</sup> Some commercial examples of sustainable polymers are Ingeo (PLA),<sup>12</sup> Mirel (PHA),<sup>13</sup> BiOH (soy-based PU),<sup>14</sup> Mater-Bi (starch-modified PVA)<sup>15</sup> or Sorona (bio-based PDO).<sup>16</sup>

### **1.3 Polylactide (PLA)**

PLA is a biodegradable, thermoplastic aliphatic polyester derived from renewable resources such as corn starch, tapioca products (roots, chips or starch) or sugar cane, which alleviates our reliance on non-renewable sources (fossil fuels).<sup>17, 18</sup> PLA was

discovered in 1932 by Carothers *et al.*, a low molecular weight PLA was produced by heating lactic acid (120-140 °C) under reduced pressure while removing condensed water.<sup>19</sup> The production of high molecular weight PLA is difficult through direct polycondensation of lactic acid due to equilibrium between lactic acid, water and lactoyl oligomers as well as increasing viscosity during polymerisation, causing difficulty in removing water as a by-product.<sup>20, 21</sup> A polycondensation method with azeotropic distillation with *m*-xylene as a solvent and SnCl<sub>2</sub> catalyst has been reported, giving 30,000 g mol<sup>-1</sup> PLA which is still relatively low.<sup>21</sup> Therefore, high molecular weight PLA is industrially manufactured by the ring-opening polymerisation (ROP) of lactide (LA), a six-membered dimeric cyclic ester of lactic acid. LA monomer can be prepared from lactic acid *via* two pathways. First, lactic acid is converted to low molecular weight PLA (1-5 kDa) by polycondensation. The oligomers are then depolymerised to LA by intramolecular transesterification using a tin-based catalyst, usually tin-octanoate.<sup>22</sup> This step is carried out above 200 °C and 1-80 mbar to distil off LA. The final mixtures of commercial *L*-LA contain 5-12% of *meso*-LA as a result of racemisation caused by severe conditions.<sup>23, 24</sup> Recently, Dusselier *et al.* reported the direct conversion of lactic acid to LA using microporous zeolite catalysts.<sup>25</sup> The shape-selective properties of zeolites lead to higher selectivity for *L*-LA synthesis and reduce racemisation and side-product formation, yielding 79% of *L*-LA at full conversion. Lactic acid is industrially produced by fermentation of carbohydrates by micro-organisms or chemical synthesis from acetaldehyde.<sup>20, 26</sup> The two-step process of PLA preparation is depicted in Scheme 1.1, LA preparation and ROP of LA yielding growing polymer chain in the absence of water.<sup>20, 27</sup> The industrial PLA synthesis was first commercialised by Cargill-Dow (NatureWorks LLC) in 2001.<sup>28</sup>



**Scheme 1.1** Industrial production of PLA.<sup>20, 27</sup>

In terms of its end-of-life options, PLA can be degraded in several ways such as photo-, oxidative- or bio-degradations by microorganisms or enzymes in soil, converting PLA to CO<sub>2</sub>, H<sub>2</sub>O and biomass in a reasonable time frame.<sup>29, 30</sup> CO<sub>2</sub> and H<sub>2</sub>O will re-enter the life cycle through photosynthesis to grow plants that serve as the feedstock of PLA.<sup>1</sup> Total Corbion PLA has developed Luminy® high heat PLA resins ( $T_m = 170\text{--}180\text{ }^{\circ}\text{C}$ ) for various applications including hot food containers with temperature resistance to 120 °C, single-use coffee capsules, automotive, textiles, consumer products and 3D printing.<sup>31</sup> For commercial three-dimensional (3D) printing, PLA has been used to fabricate scaffold structures for tissue engineering.<sup>32</sup>

#### 1.4 Polyhydroxyalkanoates (PHAs)

PHAs are a family of polyhydroxyesters of 3-, 4-, 5-, and 6-hydroxyalkanoic acids, which are produced by bacterial fermentation as intracellular reserve material.<sup>33-38</sup> Depending on the total number of carbons in the repeating units, over 150 different types of PHAs can be categorised into short-chain-length PHAs with 4-5 carbons in one repeating unit, medium-chain-length PHAs with 6-14 carbons in a monomer unit, and long-chain-length PHAs with 15 or more carbons.<sup>36, 39-41</sup> The general formula of PHA is shown in Figure 1.1.<sup>39-41</sup> For example, where R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub> or C<sub>4</sub>H<sub>9</sub> and x = 1, the polymers are called poly-3-hydroxybutyrate (PHB), polyhydroxyvalerate (PHV) or polyhydroxyoctanoate (PHO), respectively.<sup>39</sup>

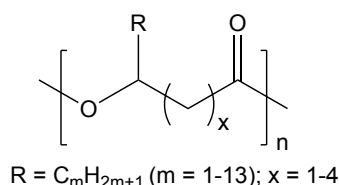


**Figure 1.1** General formula of polyhydroxyalkanoates (PHAs).<sup>39</sup>

Among PHAs, poly-3-hydroxybutyrate (PHB) is the most prominent representative example.<sup>42</sup> PHB has been produced by bacterial fermentation since 1925, or by the ROP of *rac*-β-butyrolactone (*rac*-BBL) in the presence of metal-based catalysts since 1961.<sup>43-47</sup> Biosynthesised isotactic PHB consisting of only *R* stereocentres displays similar mechanical and physical properties to polypropylene (PP), such as high melting point (175 °C) and high tensile strength (30-35 MPa).<sup>37, 48</sup> However, the applications of PHB are limited due to undesirable properties including stiffness and brittleness from secondary crystallisation.<sup>49, 50</sup> A slow crystallisation rate and low nucleation density

also promote large spherulites, leading to crack and fracture evidenced by low elongation at break (capability of PHB to resist changes without crack formation)<sup>51</sup> = 5-7%.<sup>52</sup> In addition, the melting temperature is similar to its thermal decomposition temperature where PHB degrades *via* random chain scission on the ester bond at 170-200 °C leading to the formation of olefinic and carboxylic compounds such as crotonic acid and various oligomers.<sup>37, 53-56</sup> Its poor thermal stability renders PHB incompatible with thermal processing, and susceptible to thermal degradation. The industrial production for PHAs (including PHB) is *via* biosynthesis using large scale microbial fermentation of carbohydrates or lipids, resulting in the considerable quantities of the polymer in the cytoplasm.<sup>3</sup> However, high production costs (at least twice that of PLA) limits its competitiveness in industrial and commercial applications.<sup>50, 57</sup> The efforts in attempting the chemical synthesis of high molecular weight isotactic PHB have so far been limited to the use of *rac*-BBL rather than the more expensive (*R*)-BBL.<sup>58</sup> BBL is carcinogenic,<sup>59</sup> and the competing ROP mechanisms (alkyl vs. acyl cleavages) were also reported.<sup>60, 61</sup> Very recently, the new route to produce PHB was reported *via* the ROP of *rac*-cyclic diolide (*rac*-DL) derived from bio-sourced dimethyl succinate.<sup>58</sup> With stereoselective racemic yttrium catalysts, *rac*-DL was converted under mild conditions to isotactic PHB ( $P_m > 0.99$ ) with high molecular weight and high melting temperature ( $T_m = 164-171$  °C).

Due to its biodegradability, biocompatibility, water-insolubility and good gas barrier performance,<sup>37</sup> PHB has been used for packaging materials, drug delivery or medical implant biomaterials.<sup>10, 62-67</sup> Also, PHB is able to be hydrolysed to form 3-hydroxybutyrate methyl esters used as alternative biofuel.<sup>68, 69</sup>

### 1.5 Ring-opening polymerisation (ROP)

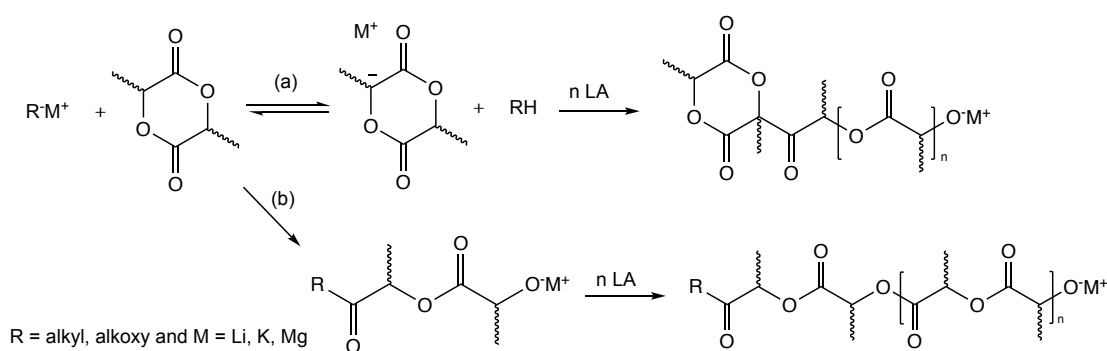
ROP is a form of chain-growth polymerisation in which an initiator is used to ring-open a cyclic monomer, generating a reactive centre where further cyclic monomers are added to produce a longer polymer chain.<sup>70</sup> ROP provides benefits over step-growth polycondensation allowing a fine degree of control over macromolecular parameters including molecular weight, dispersity, the natures of end-groups, stereoselectivity and architecture (block, star, comb or brush).<sup>71, 72</sup> The ability of cyclic monomers to be polymerised by ROP is determined by two factors.<sup>60, 73</sup> First, the conversion of the monomer to polymer must be allowed thermodynamically, which occurs when the free enthalpy (Gibbs free energy) is negative. The thermodynamic driving force for ROP is



dependent on the ring size and degree of substitution.<sup>60, 74-76</sup> For cyclic monomers with ring size < 8, ring-opening is driven by enthalpy from a relief of ring strain. Four-, six- and seven-membered rings are more favourable for ROP (due to their large strains) than five-membered lactones ( $\gamma$ -BL), which shows a less favourable enthalpy of polymerisation.<sup>77</sup> For the large ring size monomers, changes in enthalpy are minimal and polymerisation becomes entropy-driven through an increase of conformational freedom.<sup>78</sup> Secondly, the polymerisation must be allowed kinetically by the use of catalysts, decreasing activation barriers and promoting a mechanistic path.<sup>60, 73</sup> General mechanisms including anionic, cationic, organocatalysed- and metal-mediated ROP are discussed in the following section.

### 1.5.1 Anionic ROP

Anionic ROP uses ionic nucleophilic reagents as initiators, including metal-alkyl complexes, metal amides, alkoxides, phosphines, amines, alcohols and water.<sup>60</sup> Monomers possessing polarised bonds such as ester, carbonate, amide, urethane and phosphate are capable of undergoing anionic ROP, generating polyester, polycarbonate, polyamide, polyurethane and polyphosphate, respectively.<sup>60</sup> Anionic ROP of LA has been proposed to proceed *via* acyl bond cleavage with two initiation steps; either deprotonation of monomer (Scheme 1.2, a) or ring-opening by nucleophilic attack (Scheme 1.2, b).<sup>79</sup>



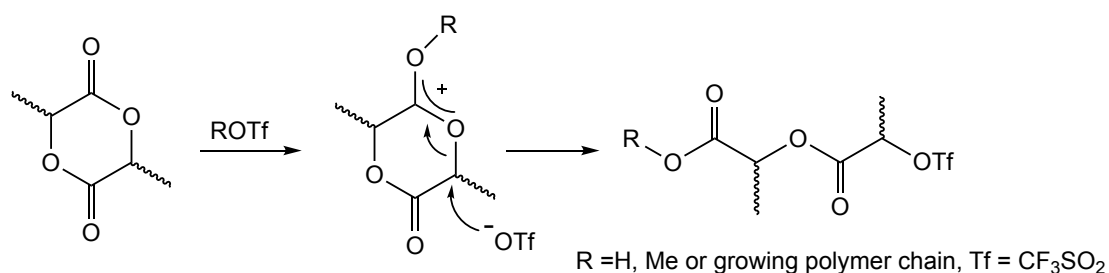
**Scheme 1.2** Anionic ROP of LA mechanism.<sup>60, 79, 80</sup>

The pioneering anionic ROP of *L*-LA with potassium *tert*-butoxide and butyllithium was reported by Kricheldorf *et al.*<sup>81</sup> 54-82% monomer conversion was reached after 24 h in toluene or 1,4-dioxane at variable temperatures. Active anionic chain ends were observed to cause transesterification reactions leading to broad dispersity (*D*), formation of cyclic oligomers, and racemisation as observed from optical rotation

measurements. Jedlinski *et al.* studied the ROP of *L*-LA and *rac*-LA using potassium methoxide in THF at RT.<sup>82</sup> Over 90% conversion was observed after 10-135 min, giving PLA with good agreement between experimental and calculated  $M_n$  values. Moderate  $\bar{D}$  values were observed (1.30-1.38). The microstructure of PLA analysed by  $^{13}\text{C}$  NMR showed racemisation and transesterification reactions which were minimised compared to those reported by Kricheldorf *et al.*<sup>81</sup> possibly due to different reaction conditions such as initiator, temperature or solvent. Occurrence of side reactions was also observed from using lithium diisopropylamide (LDA) mono(THF) complex in the anionic ROP of *meso*-LA in dioxane or toluene.<sup>80</sup> Lithium *tert*-butoxide,<sup>83</sup>  $\text{Bu}_2\text{Mg}$  and  $\text{Bu}_2\text{Li}$ ,<sup>84, 85</sup> or N-heterocyclic molecules<sup>86</sup> have been reported as anionic ROP initiators for LA.

### 1.5.2 Cationic ROP

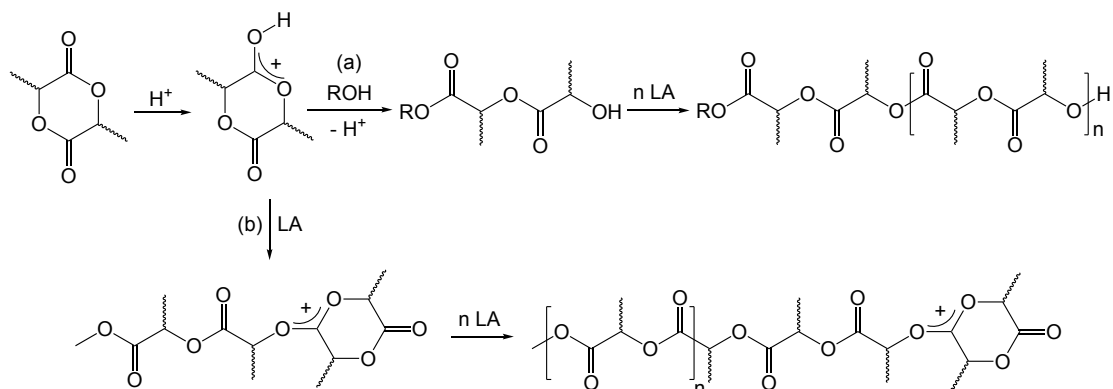
Few studies of cationic ROP have been reported. Kricheldorf *et al.* studied the cationic ROP of *L*-LA using trifluoromethanesulfonic acid (HOTf) and methyl trifluoromethanesulfonate (MeOTf) as initiators, and copolymerisation of glycolide (GA) and *L*-LA initiated by MeOTf in late 1980s.<sup>87, 88</sup> The  $^1\text{H}$  NMR spectrum of the polymer formed using MeOTf showed PLA terminated with methyl ester end groups, indicating the polymerisation occurs *via* alkylation of the exocyclic oxygen and alkyl-oxygen bond cleavage (Scheme 1.3).



**Scheme 1.3** Cationic ROP of LA mechanism with ROTf as initiators.<sup>79, 88</sup>

A series of cationic homo- or co-polymerisations of *L*-LA,  $\epsilon$ -CL,  $\delta$ -VL or cyclic carbonate was reported to operate *via* an activated monomer (AM) mechanism, using acids (in particular  $\text{HCl}\cdot\text{Et}_2\text{O}$ ) as activators in the presence of alcohol or diols as initiators.<sup>89-95</sup> As depicted in Scheme 1.4 (a), The first step is the protonation of the carbonyl oxygen of the monomer to produce an activated species, which reacts with an alcohol (ROH). The ring-opened monomer is produced and then reacts with another

monomer and grows the chain, giving the resultant polymer with –OH and –OR termini.<sup>60</sup>



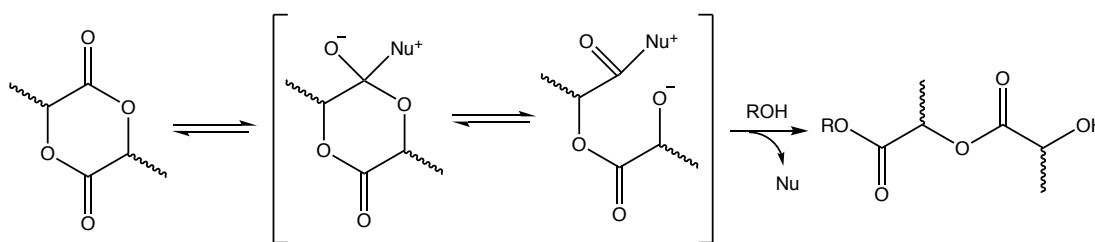
**Scheme 1.4** Activated monomer (AM, a) and active chain end (ACE, b) pathways for cationic ROP of LA.<sup>90, 92, 94</sup>

Compared to the conventional active chain end (ACE) mechanism (Scheme 1.4, b) using only acid as an initiator, the AM mechanism (Scheme 1.4, a) provides better control of  $M_n$  and end group, and suppresses the formation of cyclic polymer caused by back-biting as there is no active centre at the end of growing polymer chain. For instance, Bourissou *et al.* reported the cationic ROP of *rac*-LA using HOTf with protic agents (water, <sup>i</sup>PrOH and <sup>n</sup>PentOH).<sup>92</sup> The polymerisations of 10-125 equiv. of *rac*-LA were carried out in CH<sub>2</sub>Cl<sub>2</sub> at RT, reaching over 96% conversion after 3-28 h. The PLAs showed moderate  $\bar{D}$  values (1.13-1.48) and  $M_n$  values in a good agreement with those calculated. End group analyses showed –OH and –OR end capped PLA and dihydroxy PLA, which were derived from alcohols and water, respectively. No transesterification or epimerisation reactions were observed.

### 1.5.3 Organocatalytic ROP

The replacement of metal catalysts with organocatalysts has emerged particularly for plastics used in biomedical and microelectronic applications.<sup>1</sup> The pioneering work was reported by Hedrick *et al.* for the use of amines, 4-dimethylaminopyridine (DMAP) and 4-pyrrolidinopyridine (PPY), in the ROP of *rac*- and *L*-LA in the presence of EtOH or BnOH as initiators.<sup>96</sup> PLAs with narrow  $\bar{D}$  values and expected molecular weights were synthesised from the bulk or solution polymerisations ( $[\text{monomer}]_0:[\text{ROH}]_0 = 15\text{-}140$ ) from 35-135 °C with the reaction times ranging from 5 min to 96 h. Since then, various organocatalysts such as N-heterocyclic carbenes (NHCs),<sup>97-99</sup> guanidines,<sup>100, 101</sup> thiourea-amines,<sup>102, 103</sup> and DMAP<sup>104-106</sup> were reported to act as activators with protic

agents such as water, lipases or alcohols as initiators. Organocatalysed ROP is proposed to occur through an activated-monomer mechanism involving a transient catalyst-LA species (Scheme 1.5). An activated monomer mechanism has been defined by Penczek as “a chain polymerisation in which propagation involves reaction between a neutral growing chain end and a cationic or anionic species generated reversibly from monomer (activated monomer)”.<sup>107</sup> As illustrated in Scheme 1.5, an external alcohol reacts with the catalyst-LA complex to form the ring-opened adduct. During the propagation step, the hydroxyl group of the ring-opened adduct reacts with an activated monomer.<sup>79</sup>



**Scheme 1.5** Activated monomer mechanism for organocatalytic ROP of LA. “Nu” denotes organocatalysts. “ROH” denotes protic agents or the secondary alcohol function of the growing polymer chain.<sup>79</sup>

While low stereoselectivity at ambient temperature has been a major drawback for organocatalysed ROP, recent studies showed the potential of organocatalysts that are competitive with metal catalysts.<sup>1, 108-110</sup> Satoh and Terada *et al.* reported a high enantiomeric-selective ROP of *rac*-LA using chiral binaphthol (BINOL)-derived monophosphoric acids with 3-phenyl-1-propanol.<sup>110</sup> *D*-LA was preferentially polymerised at 75 °C in toluene *via* kinetic resolution with  $k_D/k_L = 28.3$  at monomer conversion of 49%, generating isotactic PLA ( $P_m = 0.86$ ). Chen *et al.* reported isotactic PLA synthesised by the epimerisation of *meso*-LA into *rac*-LA followed by the ROP using a bifunctional catalyst combining a  $\beta$ -isocupreidine core and thiourea in the presence of BnOH as an initiator.<sup>109</sup> Isotactic PLA ( $P_m = 0.88$ ) was achieved with  $k_L/k_D = 53$  at monomer conversion of 51%. Recently, Cossio and Mecerreyes *et al.* develop co-catalysts consisting of densely substituted amino acid prolines with DBU.<sup>108</sup> The ROP of *rac*-LA at RT by these co-catalysts gave isotactic PLAs with  $P_m = 0.87$ -0.96 at 50-58% conversion.

### 1.5.4 Metal-catalysed ROP

Tin(II) octanoate  $\text{Sn}(\text{Oct})_2$ ,<sup>111-113</sup> aluminium isopropoxides  $\text{Al}(\text{O}^i\text{Pr})_3$ <sup>114-116</sup> and zinc lactate  $\text{Zn}(\text{Lact})_2$ <sup>117-119</sup> are the most widely used ROP catalysts (Figure 1.2).<sup>60</sup>  $\text{Sn}(\text{Oct})_2$  has been used industrially for the bulk polymerisation (140-180 °C) in the presence of an alcohol initiator. A reaction time between a few minutes to several hours is required, providing high molecular weight PLA (up to  $10^5$ - $10^6$  g mol<sup>-1</sup>).  $\text{Al}(\text{O}^i\text{Pr})_3$  is less reactive than  $\text{Sn}(\text{Oct})_2$  as the polymerisation usually requires an induction period attributed to aggregation phenomena.<sup>120</sup> Although  $\text{Sn}(\text{Oct})_2$  is approved by the FDA as a food additive, it is not desirable for some applications.<sup>119</sup> Therefore, less toxic  $\text{Zn}(\text{Lact})_2$  is a preferred alternative for the synthesis of plastics used for biomedical applications as Zn participates in the human metabolism.<sup>121</sup>

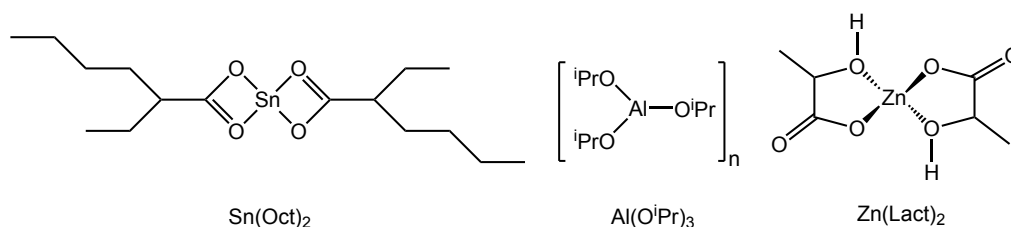
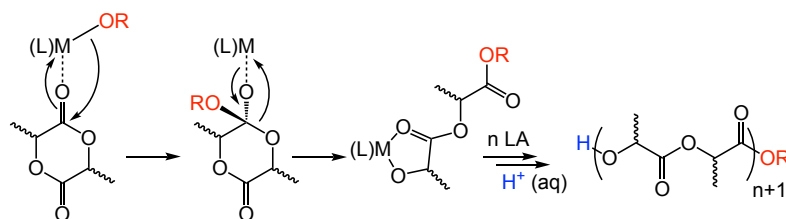


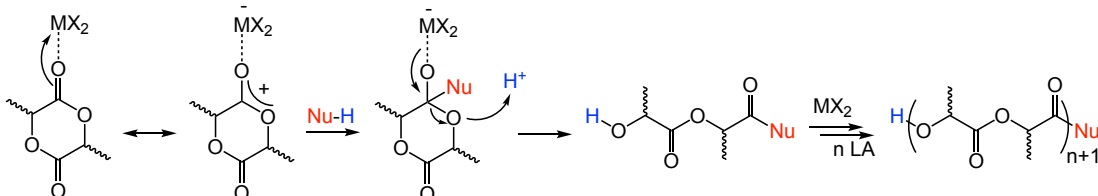
**Figure 1.2** Structures of  $\text{Sn}(\text{Oct})_2$ ,  $\text{Al}(\text{O}^i\text{Pr})_3$  and  $\text{Zn}(\text{Lact})_2$ .<sup>60</sup>

Two distinct mechanisms, coordination-insertion and activated monomer, can be envisaged for the metal-catalysed ROP of cyclic esters (Scheme 1.6).<sup>122</sup> ROP promoted by metal complexes,  $(\text{L})\text{M}-\text{Nu}$  where  $\text{Nu}$  = alkoxide, amide, alkyl or tetrahydroborate, normally involves a coordination-insertion mechanism. The mechanism begins with LA monomer coordinating to the metal centre through its carbonyl oxygen.<sup>123</sup> Attack from the nucleophilic moiety such as an alkoxide group to the activated carbonyl carbon and subsequent ring-opening *via* acyl-oxygen bond cleavage leads to the formation of a new metal alkoxide species acting as the propagating species.

## Coordination-insertion



## Activated monomer

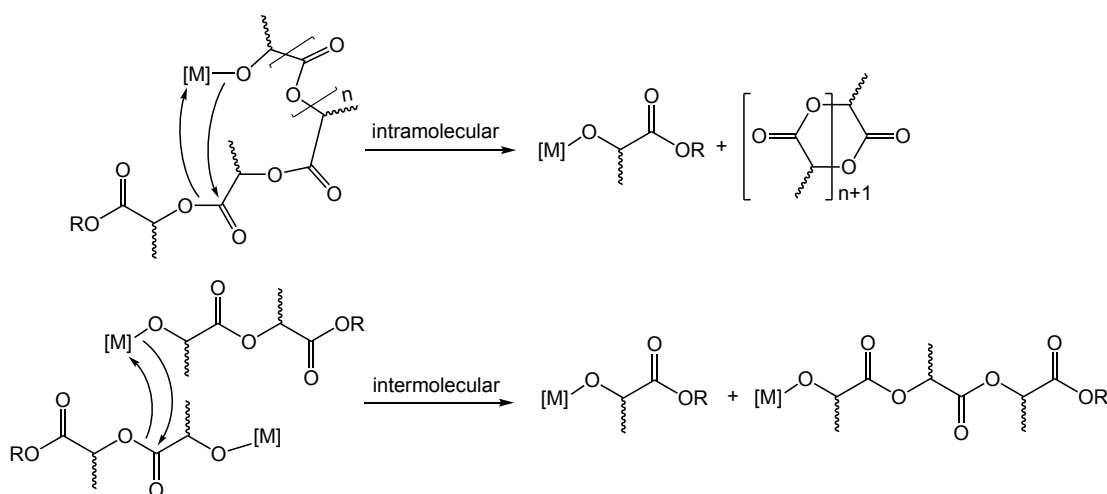


**Scheme 1.6** Coordination-insertion and activated monomer mechanisms for the metal-mediated ROP of LA.<sup>122</sup>

The activated monomer mechanism differs from the coordination-insertion mechanism in that the nucleophile is an external molecule acting as an initiator, independent from the metal catalyst.<sup>122, 124</sup> Upon coordination of the incoming monomer, the Lewis acidic metal centre activates its carbonyl oxygen. The external nucleophile such as alcohol attacks the carbonyl carbon of LA and initiates the polymerisation.

The polymerisation activity can be determined by the propagation rate constant ( $k_p$ ).<sup>125</sup> Most ROP of LA follows a second order rate law, *i.e.* a first order dependence on concentrations of LA and initiator;  $-d[\text{LA}]/dt = k_p[\text{LA}]_0[\text{I}]_0^n$  ( $[\text{LA}]_0$  = initial LA concentration,  $[\text{I}]_0$  = initial initiator concentration and  $n$  = order in initiator concentration). In order to measure  $k_p$ , the pseudo first order experiments at various concentrations of initiator are performed to determine  $k_{\text{app}}$  (pseudo first order rate constant =  $k_p[\text{I}]_0^n$ , or referred as  $k_{\text{obs}}$ ) at each concentration. It is noteworthy that  $k_p$  is independent of  $[\text{I}]_0$ . However, not only first order dependence on monomer concentration but also second<sup>126-131</sup> and zero<sup>132-137</sup> order dependence has been reported in the literature. Second order dependence on monomer concentration is discussed further in Chapter Two (section 2.3.1). For zero-order dependence, Mountford, Hillmyer and Tolman have rationalised this based on the Michaelis-Menten equation for the ROP of  $\epsilon$ -CL;  $-d[\epsilon\text{-CL}]/dt = k_2[\text{I}][\epsilon\text{-CL}]/(K_m + [\epsilon\text{-CL}])$ .<sup>134, 135</sup> Under high  $[\epsilon\text{-CL}]$ , saturation kinetics are expected due to the Michaelis constant ( $K_m$ )  $\ll [\epsilon\text{-CL}]$ , and that the equation would be consistent with the zero-order dependence on  $[\epsilon\text{-CL}]$ ;  $-d[\epsilon\text{-CL}]/dt = k_2[\text{I}]$ .

Common to coordination-insertion polymerisations, transesterification reactions can compete with propagation, undermining the control on molecular weight distribution and microstructure of polymers.<sup>1, 125</sup> As shown in Scheme 1.7, intramolecular transesterification or back-biting of the chain end onto an ester group on the polymer chain results in the formation of macrocyclic structures and shorter chains. While intermolecular transesterification reaction leads to chain scrambling and broadens the molecular weight distributions. These side reactions are generally encountered during later stages of polymerisation, particularly at high temperatures.



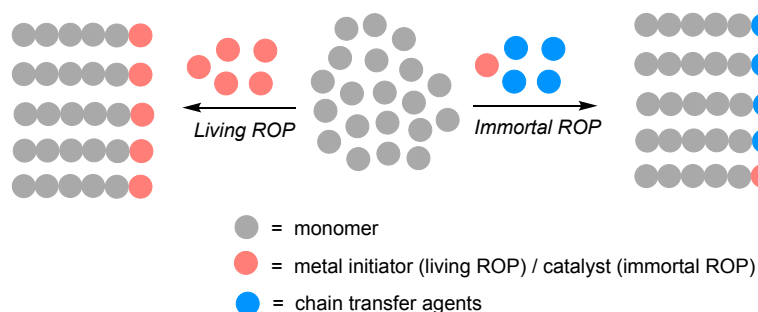
**Scheme 1.7** Intra- and intermolecular transesterification reactions in the ROP of LA.<sup>60</sup>

It is essential that the propagation rate exceeds any transesterification reaction rates for the synthesis of well-defined polymers. The degree of transesterification in the ROP of LA can be determined by GPC (increasing  $D$  values),  $^{13}\text{C}$  NMR spectroscopy ( $mrr$  or  $rrr$  tetrads observed from PLA prepared from *rac*-LA),<sup>138, 139</sup> and MALDI-ToF mass spectrometry showing cyclic polymer and the separation between peak envelopes by  $\Delta m/z = 72.0$  Da (half LA unit).<sup>125</sup>

### 1.5.5 Living ROP vs. immortal ROP

ROP promoted by metal catalysts often proceed in a living controlled fashion. For the classical living ROP, the number of polymer chains generated during polymerisation is determined by the number of active sites available at the initiator (Scheme 1.8).<sup>122, 124</sup> Mostly, a single nucleophilic group is attached to the metal centre, providing one growing polymer chain per metal centre. To achieve a successful controlled living ROP, all metal centres must initiate the polymerisation. The initiation rate must be greater than propagation rate ( $k_i \gg k_p$ , where  $k_i$  = initiation rate constant and  $k_p$  = propagation

rate constant). Irreversible termination and transfer reactions (e.g. elimination, transesterification) must be absent or negligible. A linear increase in  $M_n$  with % conversion together with narrow  $D$  values is also anticipated from well-controlled ROP.<sup>125</sup>

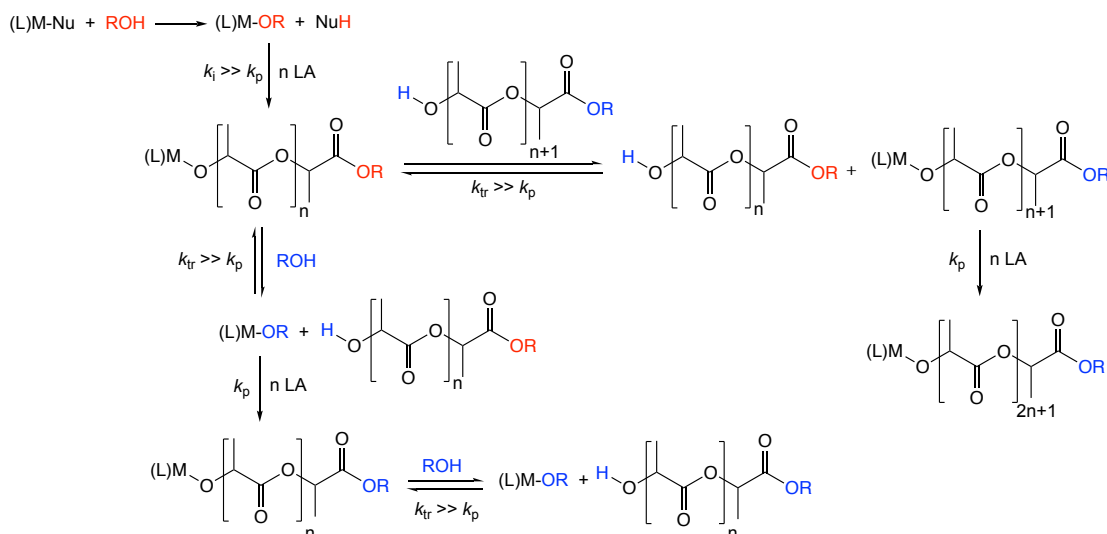


**Scheme 1.8** Illustration of living and immortal ROP processes.<sup>122</sup>

Immortal polymerisation, initially named by Inoue,<sup>140</sup> is a polymerisation in which the rapid and reversible transfer reaction takes place between growing polymer chains and chain transfer agents (commonly protic species such as alcohol, water or amine). Unlike living ROP, the number of polymer chains is equal to the number of equivalents of chain transfer agents and the metal centre (Scheme 1.8). The first reported example of immortal ROP is the ROP of epoxide with (tetraphenylporphinato)aluminium chloride in the presence of MeOH, giving polymer with narrow  $D$  values (1.07-1.17) and number of polymer chains consistent with that of the initiator and equivalents of MeOH.<sup>141</sup> Following this, various metal catalysts (Group 2 metals and Zn,<sup>142-146</sup> Al,<sup>147-149</sup> Sn,<sup>150, 151</sup> Y<sup>152, 153</sup>) and organocatalysts<sup>154, 155</sup> have been used for the immortal ROP. Scheme 1.9 demonstrates the immortal ROP by non-alkoxide species, (L)M–Nu (L = ligand, M = metal and Nu = initiator) in a presence of an alcohol.<sup>124, 152</sup> In the preliminary step, alkoxide species, (L)M–OR, is generated *in situ* by alcoholysis, followed by coordination-insertion of the first monomer leading to the propagating species, (L)M{OCHMeC(O)OCHMeC(O)OR}. The growing polymer chain undergoes fast exchange with chain transfer agents (ROH), generating temporary dormant  $\alpha$ -hydroxy,  $\omega$ -alkoxy end capped polymer (H–pol–OR) and the active alkoxide propagating species (L)M–OR. The dormant macromolecule acting as chain transfer agent and active propagating species reversibly exchange over the entire polymerisation. A greater chain transfer reaction rate than propagation rate ( $k_{tr} \gg k_p$ , where  $k_{tr}$  = chain transfer rate constant) is required to produce polymer with narrow molecular weight distribution.<sup>124,</sup>



<sup>156</sup> In the final step, the deactivation of the propagating species provides  $\alpha$ -hydroxy,  $\omega$ -alkoxy terminated polymer.



**Scheme 1.9** The immortal ROP of LA by  $(L)M-Nu/ROH$  system operated *via* coordination-insertion mechanism.<sup>124</sup>

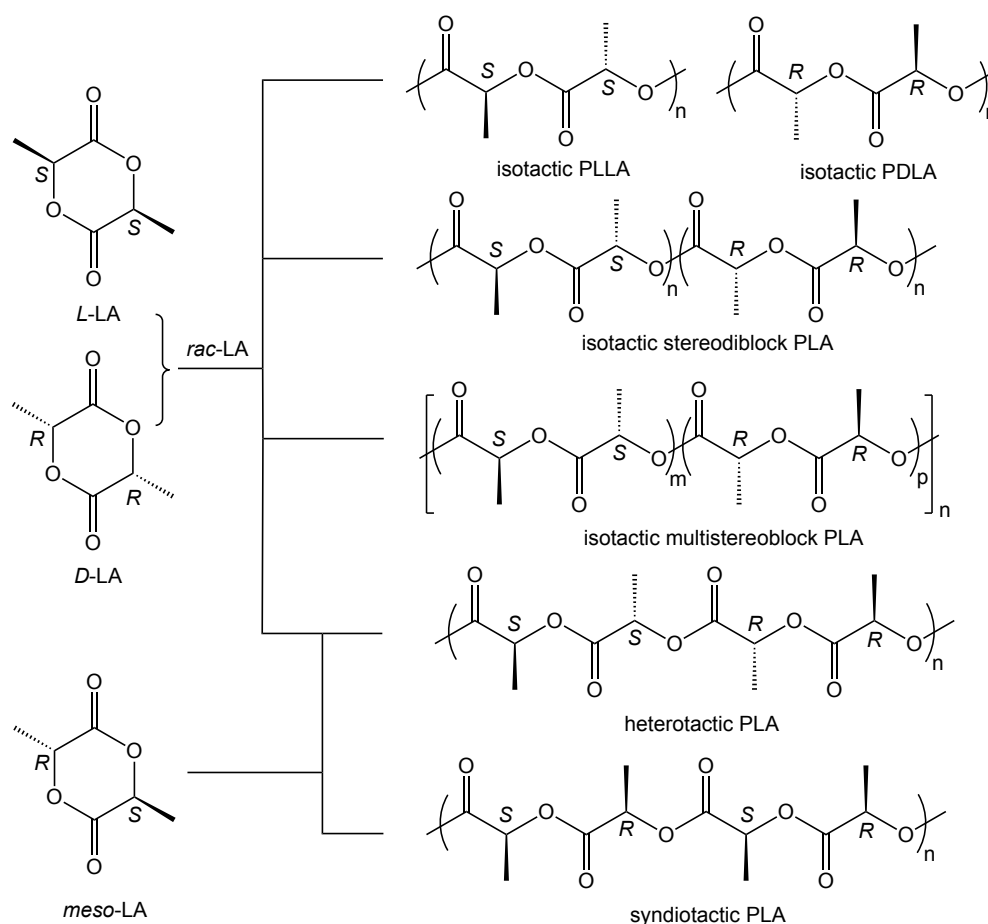
### 1.5.6 Stereocontrolled ROP

As the microstructure of polymer alters their properties, stereoselective polymerisation allows the fine tuning of the parameters such as thermal, mechanical, degradability and other physiochemical properties.<sup>71</sup> LA possesses two stereocentres (*R* and *S*), therefore, three stereoisomers, *L*-LA (*S,S*), *D*-LA (*R,R*) and *meso*-LA (*R,S*), are possible.<sup>123</sup> A 50:50 racemic mixture of *L*- and *D*-LA is referred to as *rac*-LA. In the absence of epimerisation, ROP of either *L*- or *D*-LA produces isotactic PLLA or PDLA. Isotactic PLLA is a crystalline polymer with  $T_m = 173-178$  °C.<sup>71</sup> An increased melting temperature can be obtained from stereocomplex PLA formed by co-crystallisation of PLLA and PDLA as reported by Ikada *et al.*, giving  $T_m = 230$  °C.<sup>157</sup> The stereo diblock copolymer of *L*- and *D*-LA reported by Feijen *et al.* shows  $T_m = 205$  °C.<sup>158</sup> Multiblock stereo-copolymer exhibits  $T_m = 179-210$  °C.<sup>159-161</sup>

As shown in Scheme 1.10, the stereocontrolled ROP of *meso*-LA results in either syndiotactic PLA<sup>162-168</sup> (alternating *R* and *S* stereocentres *i.e.*  $-RSRSRS-$ ) or heterotactic PLA<sup>169-171</sup> in which the stereocentres double alternate *i.e.*  $-RRSSRRSS-$ .<sup>123</sup> Syndiotactic PLA is crystalline, exhibiting  $T_m = 149-153$  °C and  $T_g = 34$  °C.<sup>160, 172</sup>

The ROP of *rac*-LA also leads to heterotactic PLA *via* alternating enchainment of *L*- and *D*-LA monomers. Heterotactic PLA is amorphous,<sup>172</sup> however,  $T_m$  of 120 °C and a

glass transition temperature ( $T_g$ ) of 46 °C were measured from semi-crystalline heterotactic PLA.<sup>173</sup> Isotactic polymers (PLLA or PDLA)<sup>108-110</sup> or isotactic diblock and multiblock copolymer<sup>159-161, 174-176</sup> can be produced from the ROP of *rac*-LA via kinetic resolution. Atactic polymer formed by random insertion of enantiomers of *rac*-LA is amorphous, exhibiting  $T_g = 44-55$  °C.<sup>172</sup>

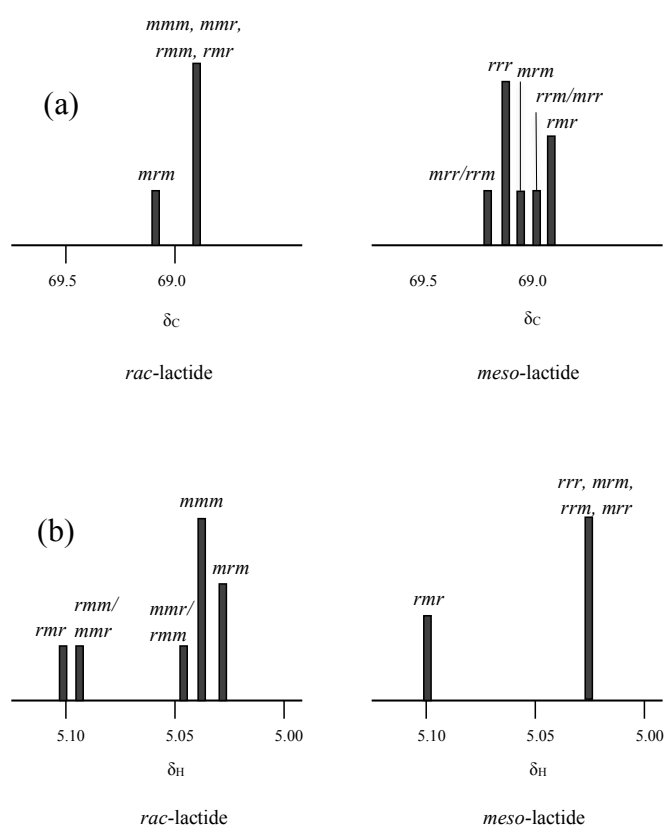


**Scheme 1.10** PLA microstructures from the stereocontrolled ROP of *rac*- and *meso*-LA.<sup>71, 123</sup>

Two mechanisms can be distinguished in the stereocontrolled ROP of *rac*- and *meso*-LA with single site catalysts.<sup>60</sup> First, enantiomorphic site control in which the chirality of the catalyst determines the stereochemistry of the inserted monomer. An alternative pathway is chain end control in which the last inserted unit on the polymer chain influences which enantiomorphic form of the monomer is preferentially incorporated. Chain end control normally leads to an enchainment of the monomer with opposite chirality to the last inserted monomer in order to minimise the steric repulsions in the transition state, resulting in syndiotactic PLA from the ROP of *meso*-LA or heterotactic PLA from the ROP of *rac*-LA.<sup>71</sup>

## 1.6 Determination of PLA stereosequences using NMR spectroscopy

NMR spectroscopy has been the most common technique used to identify the stereosequence distribution of PLA.<sup>83, 138, 177-182</sup> Munson *et al.* have assigned the polymer tacticity at the tetrad level in the  $^1\text{H}\{^1\text{H}\}$  and  $^{13}\text{C}$  NMR spectra (Scheme 1.11) analysed by  $^1\text{H}\{^1\text{H}\}$ ,  $^{13}\text{C}$ , HMBC and HMQC.<sup>178</sup> It is common to designate the assignment of PLA as various combinations of “*i*” isotactic pairwise relationships (-*RR*- and -*SS*-) and “*s*” syndiotactic pairwise relationships (-*RS*- and -*SR*-).<sup>178</sup> These could also be denoted as “*m*” (*meso*) and “*r*” (*racemic*), respectively.<sup>123</sup> For example, the octad stereosequence of PLA containing the *RRSSRRSS* unit can be assigned as *mrmrmrm*.<sup>178</sup> For the tetrad level containing four stereocentres, three letters represent the stereosequence of PLA. Pure PLLA possessing *SSSS* tetrad would be represented by *mmm*, whereas heterotactic PLA containing *SSRR* or *SRRS* would give *mrm* or *rmr*, respectively. Syndiotactic PLA consisting of *SRSR* tetrad would be expressed by *rrr*.



**Scheme 1.11** Tetrad stereosequence assignments in  $^{13}\text{C}\{^1\text{H}\}$  (a) and  $^1\text{H}\{^1\text{H}\}$  (b) of PLA synthesised using *rac*-LA and *meso*-LA.<sup>123, 178, 183</sup>

The degree of stereoregularity in the ROP of LA is expressed as the probability of forming *racemic* (syndiotactic) or *meso* (isotactic) enchainments,  $P_{\text{r}}$  and  $P_{\text{m}}$ ,

respectively.<sup>123</sup> For determining isotacticity of PLAs,  $P_m$  values are calculated from (intensity of *mmm* tetrad)/(total integral in the methine proton region) obtained from  $^1\text{H}\{^1\text{H}\}$  NMR spectra.<sup>184</sup> For heteroselectivity,  $P_r$  values are calculated from (intensities of *rmr* and *mrmm* tetrads)/(total integral in the methine proton region),<sup>185, 186</sup> or by the intensity of *rmr* tetrad against *rmm* tetrad.<sup>187</sup> For syndiospecificity,  $P_r$  values are calculated from intensity of *rrr* tetrad against the total integral in the methine proton peak.<sup>160</sup>

Values of  $P_r$  and  $P_m$  are alternatively analysed from  $^1\text{H}\{^1\text{H}\}$  NMR spectra of PLA which are deconvoluted using the Mestrenova software package. The  $^1\text{H}\{^1\text{H}\}$  NMR spectra of heterotactic PLA and syndiotactic PLA prepared from *rac*-LA and *meso*-LA, respectively (Figure 1.3 and 1.4) show singlet resonances of different tetrads. From the normalised integrals of each tetrad,  $P_r$  and  $P_m$  are calculated by comparison against values determined using Bernoullian statistics as shown in Table 1.1.

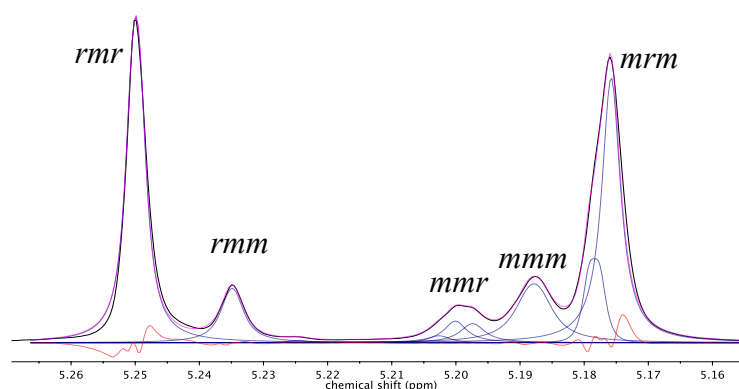


**Figure 1.3**  $^1\text{H}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of the methine region of heterotactically-enriched PLA with tetrad assignments ( $P_r = 0.83$ ).

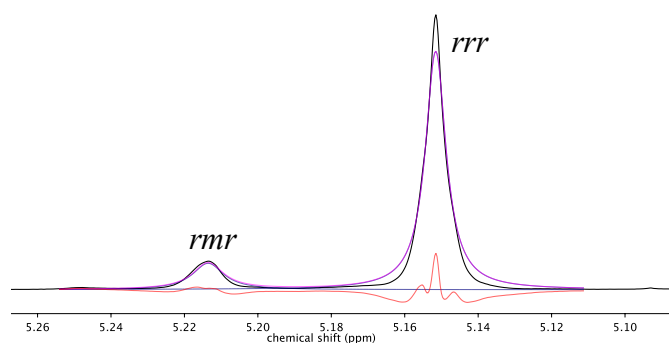


**Figure 1.4**  $^1\text{H}\{^1\text{H}\}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of the methine region of syndiotactically-enriched PLA with tetrad assignments ( $P_r = 0.83$ ).

**Table 1.1** Tetrad probabilities based on Bernoullian statistics.<sup>168</sup>

| Tetrad     | Probability                 |                             |
|------------|-----------------------------|-----------------------------|
|            | <i>rac</i> -LA              | <i>meso</i> -LA             |
| <i>iii</i> | $P_m^2 + \frac{P_r P_m}{2}$ | 0                           |
| <i>iis</i> | $\frac{P_r P_m}{2}$         | 0                           |
| <i>sii</i> | $\frac{P_r P_m}{2}$         | 0                           |
| <i>sis</i> | $\frac{P_r^2}{2}$           | $\frac{P_m^2 + P_r P_m}{2}$ |
| <i>sss</i> | 0                           | $P_r^2 + \frac{P_r P_m}{2}$ |
| <i>ssi</i> | 0                           | $\frac{P_r P_m}{2}$         |
| <i>iss</i> | 0                           | $\frac{P_r P_m}{2}$         |
| <i>isi</i> | $\frac{P_r^2 + P_r P_m}{2}$ | $\frac{P_m^2}{2}$           |

For the ROP of *rac*- and *meso*-LA,  $P_r$  or  $P_m = 0.50$  describes atactic PLA. While  $P_r = 1.00$  ( $P_m = 0.00$ ) and  $P_m = 1.00$  ( $P_r = 0.00$ ) express perfect heterotactic and isotactic PLAs, respectively. For the ROP of *meso*-LA,  $P_r = 1.00$  ( $P_m = 0.00$ ) and  $P_m = 1.00$  ( $P_r = 0.00$ ) describe perfect syndiotactic and heterotactic PLAs, respectively.<sup>123</sup>

## 1.7 Polymer characterisation

### 1.7.1 Polymer molecular weight definitions

Synthetic polymers are polydisperse, consisting of polymer chains with a different number of repeating units, the molecular weight is therefore not a single value.<sup>188-190</sup> The molecular weight of a polymer is normally described as statistically based average molecular weight values such as the molecular averages of the number ( $M_n$ ) or weight ( $M_w$ ) and the dispersity ( $\mathcal{D}$ ).

The number average molecular weight ( $M_n$ ) is the statistical average molecular weight of all polymer chains in the sample, and is calculated by Equation 1.1 (where  $N_i$  = the number of chains of the molecular weight ( $M_i$ )).

$$M_n = \frac{\sum N_i M_i}{\sum N_i}$$

**Equation 1.1**

The weight average molecular weight ( $M_w$ ) is defined by Equation 1.2 (where  $W_i$  = the total molecular weight of polymer chains =  $N_i \times M_i$ ).  $M_w$  is always higher than  $M_n$  unless the polymer is monodispersed.

$$M_w = \frac{\sum W_i M_i}{\sum W_i} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

**Equation 1.2**

The dispersity ( $\mathcal{D}$ ) is used as a measure of broadness of a molecular weight distribution of a polymer, calculated by Equation 1.3.

$$\mathcal{D} = \frac{M_w}{M_n}$$

**Equation 1.3**

A monodisperse polymer possessing all equal chain lengths has a  $\mathcal{D}$  equal to 1.0. However, even extremely well-controlled living ROP of cyclic esters produced polymers with  $\mathcal{D}$  values greater than 1.0. An increase in  $\mathcal{D}$  values is attributed to side reactions such as transesterification reactions, slow initiation rate or chain transfer reaction rate compared to propagation rate, or elimination reaction. Regarding polymers produced by ROP of cyclic esters, polymers are described showing narrow  $\mathcal{D}$  values if  $\mathcal{D} < 1.2$ . Values of  $\mathcal{D}$  in a range of 1.2-2.0 are moderate, whereas broad  $\mathcal{D}$  values are higher than 2.0.<sup>191</sup>

Several techniques available to determine molar mass averages are categorised as fractionating and non-fractionating methods. A single average molecular weight is provided by methods that do not fractionate the polymer such as NMR spectroscopy or small angle X-ray scattering (SAXS).<sup>189, 192, 193</sup> Only fractionating methods allow the determination of various molecular averages  $M_n$ ,  $M_w$  or z-average molecular weight ( $M_z$ ) such as analytical ultracentrifugation,<sup>194</sup> field flow fractionation,<sup>195, 196</sup> and Gel Permeation Chromatography or Size Exclusion Chromatography (GPC/SEC), which is the most commonly used method.

### 1.7.2 Gel Permeation Chromatography (GPC)

As synthetic polymers possess different chain lengths, GPC is a technique for separating out polymer chain lengths on the basis of size, and measuring their relative abundance.<sup>191</sup> A GPC instrument consists of the pump flowing the eluent through the column packed with different sized particles with different pore size such as cross-linked polystyrene/divinylbenzene beads with particle size between 3-20  $\mu\text{m}$  at a constant flow rate, detectors and software to calculate and display the results. The polymer sample is first dissolved in a solvent such as THF or  $\text{CHCl}_3$ , forming a coil conformation in solution. The higher the molecular weight, the larger the coil. These coiled polymers are then introduced to the mobile phase and flow into the column. The large polymer coils that cannot enter the pores elute the column first. Whereas the smaller polymer coils can access the pores through the column and spend more time in those pores, increasing their retention time. The polymer samples are detected by various methods such as differentiating refractive index of mobile phase and pure solvent, comparing viscosity of the mobile phase and pure solvent, or measuring the intensity of light scattered by a polymer in a solution.<sup>197</sup> The elution behaviour displayed in a chromatogram is compared to a calibration of standard polymers with narrow molecular weight distribution such as polystyrene, calculating  $M_n$ ,  $M_w$ , peak molecular weight ( $M_p$ ) and  $D$  values.

The principle of separation by GPC described by Benoit *et al.* shows a correlation between elution volume and hydrodynamic volume.<sup>198</sup> The hydrodynamic volume ( $V_H$ ) is proportional to the product of the molecular weight ( $M$ ) and the intrinsic viscosity ( $[\eta]$ ); *i.e.*  $V_H \propto [\eta]M$ . In order to obtain the molecular weight of polymer sample, the calibration of polymer standards is needed. A series of narrow molecular weight polymer standards with known molecular weight such as polystyrene (PS) is run, providing a linear plot of  $\log(M)$  vs. elution volume. The results of an unknown polymer calibrated by narrow PS standards are reported as “polystyrene equivalent molecular weights”.<sup>199</sup> A drawback of this method is that the calibration is only valid for one particular polymer-solvent-temperature.<sup>199</sup> Reliable standards are also costly and only available for a few, well established polymer classes.<sup>200</sup>

Another calibration method is a universal calibration (UC) which uses hydrodynamic volume or a product of  $[\eta]M$  as the universal calibration parameter.<sup>198</sup> The UC shows

that the semilogarithmic plot of  $\log[\eta]M$  vs. elution volume gives a calibration curve for different polymer samples with various molecular structures. Based on the UC theory, two different polymers are assumed to have same elution volume if they have same hydrodynamic volume under the same solvent and temperature.<sup>201</sup> This theory together with the Mark-Houwink constants ( $K$  and  $\alpha$  values) is extensively used to determine molecular weight of unknown polymer.<sup>202</sup> The Mark-Houwink equation shows a relationship between molecular weight and intrinsic viscosity (Equation 1.4).

$$[\eta] = KM^\alpha$$

#### Equation 1.4

The slope and intercept of the linear plot of  $\log[\eta]$  vs.  $\log(M)$  gives  $\log K$  and  $\alpha$  values which depend on the particular polymer-solvent system. At any retention time, the hydrodynamic volume ( $V_H \propto [\eta]M$ ) of two polymers with molecular weight  $M_1$  and  $M_2$  are assumed to be identical (Equation 1.5).<sup>200</sup>

$$K_1M_1^{1+\alpha_1} = K_2M_2^{1+\alpha_2}$$

#### Equation 1.5

As long as the  $K$  and  $\alpha$  values are known for both standard and unknown polymers, the molecular weight ( $M_2$ ) of unknown polymer can be determined by Equation 1.6.<sup>199</sup>

$$\log M_2 = \frac{\log(K_1/K_2)}{(1 + \alpha_2)} + \frac{(1 + \alpha_1)}{(1 + \alpha_2)} \log M_1$$

#### Equation 1.6

Values of  $\alpha$  relate to the nature of the polymer in solution, where a value of 0 represents a hard sphere, 1 a semi-coil, and 2 an absolute rigid rod.<sup>203</sup> The  $M_n$  and  $\bar{D}$  values of PLA and PHB samples reported in this Thesis were analysed by GPC analysis in THF at 30 °C with the application of appropriate Mark-Houwink corrections as previously determined for PLA<sup>204</sup> and PHB<sup>205</sup> after calibrations against polystyrene standards. Refractive index (RI) detectors do not accurately measure cyclic polymers, therefore, the cyclic polymers as a result of back-biting are taken into account by approximation.<sup>206</sup> In some literature, approximate correction factors have been used in which the experimental  $M_n$  values of PLA samples obtained from GPC using the polystyrene standards have to be multiplied by 0.58 [ $M_n(\text{corr.}) = 0.58M_n(\text{GPC})$ ].<sup>80, 97,</sup>



To confirm the cyclic structure of PLA, triple detection GPC combining light scattering and viscometer detectors with a RI detector is applied.<sup>211</sup> For polymers having exactly the same molecular weight, the cyclic products will elute later due to their smaller hydrodynamic volume than for the linear products.<sup>212</sup> Cyclic structures also have lower intrinsic viscosity ( $[\eta]$ ) than linear structures due to smaller size and no end groups for entanglement.<sup>97, 213, 214</sup> In general, plots of  $\log(M_w)$  vs. elution volume and  $\log([\eta])$  vs.  $\log(M_w)$  show two different trends corresponding to cyclic PLA and linear PLA.<sup>97, 211, 212</sup>

### 1.7.3 Nuclear Magnetic Resonance (NMR) spectroscopy

$^1\text{H}$  NMR spectroscopy is alternative method to determine molecular weight ( $M_n$ ) as the integrals of the resonance peaks in the spectra are proportional to the molar concentration of the analysed species.<sup>215</sup> Therefore, the  $M_n$  value is calculated from equation of  $M_n = \sum A_i / \sum N_i$  (where  $A_i$  = intensity of the  $^1\text{H}$  NMR signal and  $N_i$  = number of protons). However, the determination is limited to polymers with molecular weights less than 25 kDa as the resolution is decreased at higher molecular weight. Also, the kinetic analysis of polymerisation can be determined from the  $^1\text{H}$  NMR, in which the monomer conversion was measured from the intensity of the polymer against the monomer.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectroscopy are pivotal to characterise an isolated novel polymer, and identify end-group from low molecular weight polymers. To characterise the stereosequence of PLA, homodecoupled  $^1\text{H}\{^1\text{H}\}$  NMR spectroscopy is carried out in order to decouple the effect of splitting between the methyl and methine protons, resulting in singlet resonances in the region of  $\delta = 5.15\text{-}5.25$  ppm.<sup>123</sup>

### 1.7.4 Matrix Assisted Laser Desorption/Ionisation Time-of-Flight mass spectrometry (MALDI-ToF MS)

MALDI-ToF MS is another useful technique to characterise a wide range of molecules such as peptides, proteins, biomolecules and synthetic polymers. MALDI-ToF MS provides structural, molecular weight and end group information of the polymer.<sup>216</sup> In mass spectrometry, MALDI is considered a soft desorption/ionisation method. This is due to the co-crystallisation of the sample and the matrix during solvent evaporation which allows matrix assistance during the desorption step.<sup>217</sup> Sample preparation is a crucial point in MALDI MS as it influences the quality of the spectra.<sup>218</sup> The sample for the MALDI is uniformly mixed in a solvent with the matrix such as dithranol or

dihydroxybenzoic acid (DHB) which are commonly used for synthetic polymers, and cationising agents (such as NaCl), forming a [polymer-Na]<sup>+</sup> adduct. The sample within the matrix is then irradiated with a nitrogen laser beam.<sup>219, 220</sup> The matrix absorbs energy from the laser, followed by the desorption of the analytes that are then vaporised and ionised in the gas phase, generating singly charged ions ( $z = 1$ ).<sup>221</sup> The released ions are accelerated by the same voltage through the flight tube, reaching the detector at distinct times. The velocity of the ions depends on the mass-to-charge ratios ( $m/z$ ) with smaller ions travelling faster than larger ones.

### 1.8 Aims and outlook

Metal-based catalysts for the ROP of cyclic esters have been extensively studied. Various types of initiators such as alkoxide, amide, alkyl or tetrahydroborate have been reported to give remarkable activity and selectivity, producing polyesters with good control of molecular weight, molecular weight distribution and tacticity. After two decades of research, the field is slowly reaching maturity.<sup>71</sup> However, challenges remain. For example, although the ROP of cyclic esters using metal complexes with tetrahydroborate ligands has been thoroughly studied, questions remain regarding the mechanism and nature of the polymer end group. In this Thesis, novel heavy alkaline earth (Ca and Sr) metal-based initiators with organohydroborate ligands are introduced as initiators for the ROP of LA, together with proposed ROP mechanisms in Chapters Two and Three. In Chapter Four, performance and mechanism of heavy alkaline earth tetrahydroborate complexes in the ROP of LA are described. Borate esters as chain transfer agents in the ROP of LA are also demonstrated. Finally, Chapter Five describes the study of the ROP of *rac*-BBL initiated by various alkaline earth hydroborate complexes, in conjunction with their mechanistic investigations.

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# **Chapter Two**

**Alkaline earth organohydroborate complexes  
for the ROP of LA and their mechanistic  
investigations**

## Chapter Two

### 2.1 Overview

This Chapter will describe detailed investigations into the ROP of LA using a series of alkaline earth organohydroborate ( $[\text{HBEt}_3]^-$ ) complexes. The polymerisation studies towards ROP of *rac*-, *L*-, *D*- and *meso*-LA using alkaline earth organohydroborate complexes will be presented, in addition to an in-depth mechanistic evaluation of the ROP of LA by NMR spectroscopy. The synthesis and characterisation of analogous alkoxide complexes, serving as models for intermediate species, along with their catalytic activities will be discussed.

### 2.2 Introduction

#### 2.2.1 Alkaline earth metal complexes as ROP catalysts

As discussed in Chapter One, the ring-opening polymerisation (ROP) of cyclic esters is an efficient method for the synthesis of well-controlled aliphatic polyesters in terms of molecular weight, composition and microstructure achieved by suitable initiators.<sup>1-4</sup> Various ROP catalyst systems largely based on Al, Sn, transition metals (especially Fe, Ni, Cu, Zr and Ti), lanthanide metals (in particular La, Nd, Sm, Eu and Yb) and alkali metals (Li, Na and K) have been reported in the literature for the past decades. By contrast, alkaline earth metals have been comparatively less used. For the last 20 years, a variety of Mg and the larger alkaline earth metals (Ca, Sr and Ba) have been disclosed. Development of Mg catalysts in the ROP of cyclic esters such as  $\epsilon$ -CL, GA, LA and TMC have gained attention. However, the organometallic and coordination chemistry of larger alkaline earth metals are much less developed than that of Mg. Due to large ion size, their heteroleptic complexes are more prone to undergo ligand redistribution by the Schlenk equilibrium to generate the corresponding homoleptic complexes.<sup>5-7</sup> Alkaline earth metal complexes have also drawn attention due to their combination of high activity, relatively low toxicity and biocompatibility, which makes them suitable ROP catalysts to produce PLA employed in medical and pharmaceutical applications.<sup>8</sup> Alkaline earth metals are also among the most abundant elements in the Earth's crust, rendering them considerably cheaper and more accessible than transition metals and lanthanides.<sup>9</sup>



### 2.2.2 Magnesium complexes

The initial breakthrough in magnesium ROP catalysts was from Chisholm *et al.* and Coates *et al.* who introduced well-defined magnesium alkoxide and amide complexes supported by tris(pyrazolyl)borate ( $\text{Tp}^{\text{R}}$ ) or  $\beta$ -diketiminato (NacNac) ligands.<sup>10-14</sup> ( $\text{Tp}^{\text{tBu}}$ )Mg(OEt) (**2.1**, Figure 2.1) reported by Chisholm *et al.* was active for the ROP of *L*-LA in  $\text{CH}_2\text{Cl}_2$  at RT, converting 1,000 equiv. of *L*-LA while maintaining a narrow  $\bar{D}$  value (1.2).<sup>10, 11</sup> Chisholm's ( $\text{Dipp}$ NacNac)Mg(O<sup>*t*</sup>Bu)(THF) (**2.2**, Figure 2.1) polymerised 100 equiv. of *rac*-LA in  $\text{CH}_2\text{Cl}_2$  within 2 min, giving atactic PLA.<sup>12, 13</sup> The solvent effect was observed as the ROP catalysed by **2.2** in THF (5 min) was slower than in  $\text{CH}_2\text{Cl}_2$  due to competitive coordination of THF molecules, and produced heterotactically-enriched PLA ( $P_{\text{r}} = 0.90$ ). Similarly, Coates' [ $(\text{Dipp}$ NacNac)Mg(O<sup>*i*</sup>Pr)]<sub>2</sub> (**2.3**, Figure 2.1) converted 200 equiv. of *rac*-LA within 5 min at RT giving atactic PLA with a moderate  $\bar{D}$  value (1.59).<sup>14</sup> The ROP with **2.3** and 1 equiv. of <sup>*i*</sup>PrOH polymerised 50-500 equiv. of *rac*-LA within 1-5 min in  $\text{CH}_2\text{Cl}_2$  at RT.

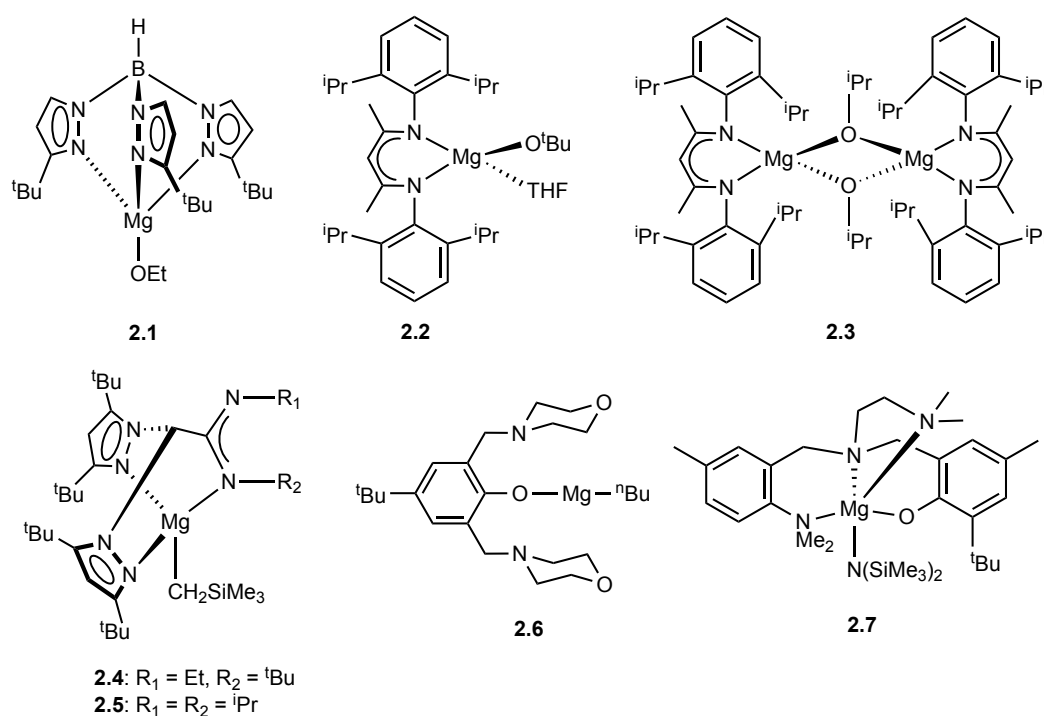


**Figure 2.1** Magnesium complexes for ROP of LA (**2.1-2.7**).<sup>10-17</sup>

Sanchez-Barba *et al.* prepared {tpbamd}Mg( $\text{CH}_2\text{SiMe}_3$ ) (**2.4**) (tpbamd = *N*-ethyl-*N'*-*tert*-butylbis(3,5-di-*tert*-butylpyrazolyl)acetamidinate) and {pbpamd}Mg( $\text{CH}_2\text{SiMe}_3$ ) (**2.5**) (pbpamd = *N,N'*-diisopropylbis(3,5-di-*tert*-butylpyrazolyl)acetamidinate) (Figure 2.1).<sup>15</sup> Complexes **2.4** and **2.5** converted over 80% of 200 equiv. of *rac*-LA within 2

min at RT. Good agreement between measured and calculated  $M_n$  values was observed, and  $\bar{D}$  values were narrow (1.05-1.09). Moderately heterotactic PLAs were obtained with  $P_r = 0.71$ -0.72. End group analysis by NMR spectroscopy showed PLA terminated by  $-\text{OH}$  and  $-\text{CH}_2\text{SiMe}_3$  termini.

Carpentier and Sarazin *et al.* prepared  $\{\text{LO}^{\text{morph}_2}\}\text{Mg}(\text{}^n\text{Bu})$  (**2.6**, Figure 2.1) ( $\text{LO}^{\text{morph}_2} = 4\text{-tert-butyl-2,6-bis(morpholinomethyl)phenoxy}$ ) which was an extremely effective catalyst for the immortal ROP of *L*-LA.<sup>16</sup> The immortal ROP of *L*-LA by **2.6** with 10-100 equiv. of  $^i\text{PrOH}$  polymerised 1,000-5,000 equiv. of *L*-LA within 2-90 min. Close agreement between measured and calculated  $M_n$  values was observed together with narrow  $\bar{D}$  values = 1.11-1.18. Later, Ma and Wang reported a series of magnesium silylamido complexes supported by aminophenolate ligand.<sup>17</sup> As shown in Figure 2.1, complex **2.7** polymerised 10,000 equiv. of *rac*-LA (91% conversion) within 15 min in toluene. The ROP activity was improved by an addition of 1-2 equiv. of  $^i\text{PrOH}$ , converting 200-10,000 equiv. of *rac*-LA within 1-5 min in toluene at RT. Slightly isotactic PLAs ( $P_m = 0.55$ -0.59) with moderate  $\bar{D}$  values (1.23-1.56) were obtained.

### 2.2.3 Homoleptic heavy alkaline earth metal complexes

In 2001, Feijen *et al.* reported the use of commercially available  $\text{Ca}(\text{OMe})_2$  as an initiator for bulk polymerization of 100 equiv. of *L*-LA at 120 °C, reaching 66% conversion after 90 min.<sup>18</sup> A mismatch between measured and calculated  $M_n$  together with a moderate  $\bar{D}$  value (1.43) was observed attributed to aggregation of alkoxide species. PLLA was formed in an absence of epimerisation. Later in the same year, the first example of well-defined calcium based catalysts was reported by Feijen *et al.*<sup>19</sup> the ROP of *L*-LA using the *in situ* generated calcium alkoxide prepared *via* reaction of  $\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$  with 2 equiv. of alcohol ( $\text{MeOH}$ ,  $^i\text{PrOH}$  and PEG2000) in THF. The sterically hindered alcohol ( $^i\text{PrOH}$ ) in THF was introduced to circumvent the aggregation and insolubility of calcium alkoxide derivatives leading to well-controlled ROP and polymer chain end capped with  $-\text{O}^i\text{Pr}$  end groups.

Bochmann *et al.* reported dimeric calcium initiators supported by dianionic multidentate  $\{\text{ONNO}\}^{2-}$  ligands.<sup>20</sup>  $[\{\text{ONNO}\}\text{Ca}]_2$  (**2.8**, Figure 2.2) promoted the ROP of 200 equiv. of  $\varepsilon\text{-CL}$ , reaching 40% conversion after 12 h at 60 °C in toluene. The related complex  $\{\text{ON}\}_2\text{Ca}(\text{THF})_2$  (**2.9**, Figure 2.2) containing two imino-phenolate ligands was inactive in the ROP of  $\varepsilon\text{-CL}$  under analogous conditions.

In 2007, Lin *et al.* used homoleptic  $[\text{Ca}\{\text{DAIP}\}_2]_2$  complex prepared *via* reaction of  $\text{Ca}(\text{OMe})_2$  and 2-((2-dimethylamino-ethylimino)methyl)phenol (DAIP-H) (**2.10**, Figure 2.2) in toluene/THF in the presence of various alcohols for the ROP of *L*-LA.<sup>21</sup> Full conversion was reached after 30-60 min for the ROP of 50-250 equiv. of *L*-LA in toluene at RT. PLLAs with  $M_n(\text{GPC})$  values higher than those calculated and moderate *D* values (1.11-1.28) were obtained.

At the same time, Davidson and O'Hara *et al.* reported a trinuclear barium complex containing three dianionic, tetradentate amino-*bis*(phenolate)  $\{\text{ONNO}\}^{2-}$  ligands (**2.11**, Figure 2.2) as an initiator for ROP of *L*-LA and  $\varepsilon$ -CL.<sup>22</sup> Complex **2.11** polymerised 900 equiv. of *L*-LA (bulk polymerisation, 130 °C) or 300 equiv. of  $\varepsilon$ -CL (toluene, RT). However, broad and bimodal *D* values were found even in the presence of BnOH. First order dependence on monomer concentration was observed. MALDI-ToF and NMR analyses showed two distinct polymers ( $-\text{OBn}$  and  $-\text{OH}$  terminated PCL and  $\alpha,\omega$ -dihydroxytelechelic PCL) suggesting two initiation pathways.

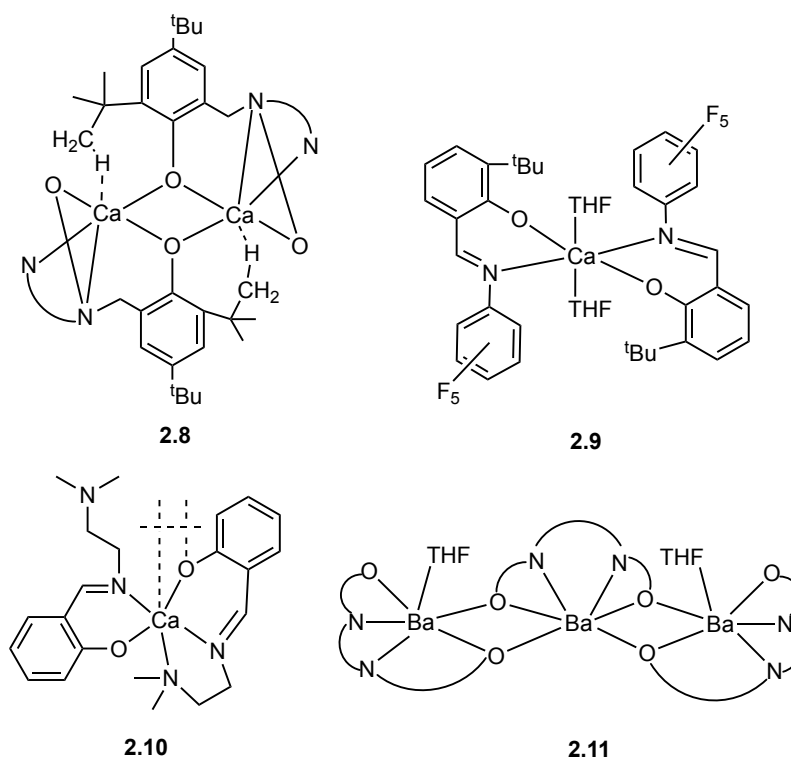


**Figure 2.2** Homoleptic alkaline earth complexes for ROP of cyclic esters (**2.8-2.11**).<sup>20-</sup>

### 2.2.4 Heteroleptic heavy alkaline earth metal complexes

Single-site catalysts have revolutionised polymer synthesis. These homogeneous complexes have a formula  $(L)_nMR$  where  $(L)_n$  is a set of ancillary ligands attached to the metal centre (M) which is Ca, Sr or Ba. R is a reactive nucleophile acting as an initiating group for polymerisation. The main challenge of alkaline earth metal chemistry is the synthesis of complexes that overcomes the Schlenk equilibrium in solution.

The first example was reported in 2003 when Westerhausen *et al.* presented a series of dinuclear complexes prepared *via* reaction of  $\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$  with 2,2,6,6-tetramethylheptane-3,5-dione (H-TMHD) to give  $[\text{Ca}(\text{THF})(\text{TMHD})]_2[\mu\text{-N}(\text{SiMe}_3)_2](\mu\text{-TMHD})$  (**2.12**). Complex **2.12** reacted with 1-phenylethanol to form  $[\text{Ca}(\text{THF})(\text{TMHD})]_2\{\mu\text{-OCH}(\text{Me})\text{Ph}\}(\mu\text{-TMHD})$  (**2.13**) used in the ROP of *L*-LA and  $\epsilon$ -CL in the presence of  $i\text{PrOH}$ .<sup>23, 24</sup> Complex **2.12** polymerised 750 equiv. of  $\epsilon$ -CL within 5 min, or converted 150 equiv. of *L*-LA within 30 min in THF at RT. Broad  $\bar{D}$  values (1.80-2.13) and  $M_n$  values higher than those calculated were observed. Complex **2.13** was less active than **2.12**, polymerised 150 equiv. of  $\epsilon$ -CL in 30 min or 150 equiv. of *L*-LA in 2 h under analogous conditions. However, better agreement between measured and calculated  $M_n$  and narrow  $\bar{D}$  values (1.13-1.19) were observed. Kinetic studies also showed first order dependence on monomer concentration. In the presence of  $i\text{PrOH}$ , the ROP of *L*-LA using **2.12** gave PLA with a moderate  $\bar{D}$  value (1.26), and  $M_n(\text{GPC})$  value consistent with that calculated.

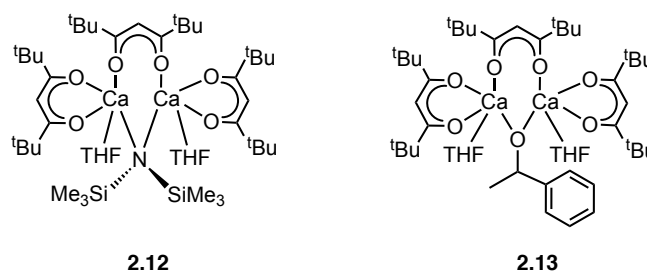


**Figure 2.3** Bimetallic complexes (**2.12** and **2.13**) reported by Westerhausen *et al.*<sup>23, 24</sup>

In the same year, Chisholm *et al.* presented the first class of monomeric calcium complexes supported by sterically demanding tris(pyrazolyl)hydroborate ligands ( $\text{Tp}^R$ ),  $(\text{Tp}^{\text{tBu}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**2.14**),  $(\text{Tp}^{\text{tBu}})\text{Ca}(\text{O}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)$  (**2.15**) and  $(\text{Tp}^{i\text{Pr}})\text{Ca}(\text{O}-2,6\text{-C}_6\text{H}_3^i\text{Pr}_2)(\text{THF})$  (**2.16**).<sup>25, 26</sup> These three complexes were remarkably active for the ROP

of *rac*-LA giving full conversion of 200 equiv. of *rac*-LA within 1 min in THF at RT. Broad  $\bar{D}$  values were obtained ( $\bar{D}$  = 1.74, 1.68 and 1.61 with **2.14**, **2.15** and **2.16**, respectively). Heterotactically-enriched PLAs with  $P_r$  = 0.9 was obtained from **2.14** and **2.15**. Conversely, the less bulky complex **2.16** showed no stereoselectivity, giving atactic PLA. The authors also reported (<sup>Dipp</sup>NacNac)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF) (**2.17**), polymerising 200 equiv. of *rac*-LA in 2 h under analogous conditions to provide atactic PLA. However, the homoleptic form of **2.17** was observed in solution leading to the isolation of (<sup>Dipp</sup>NacNac)<sub>2</sub>Ca. This was attributed to the lack of steric hindrance around the metal centre.

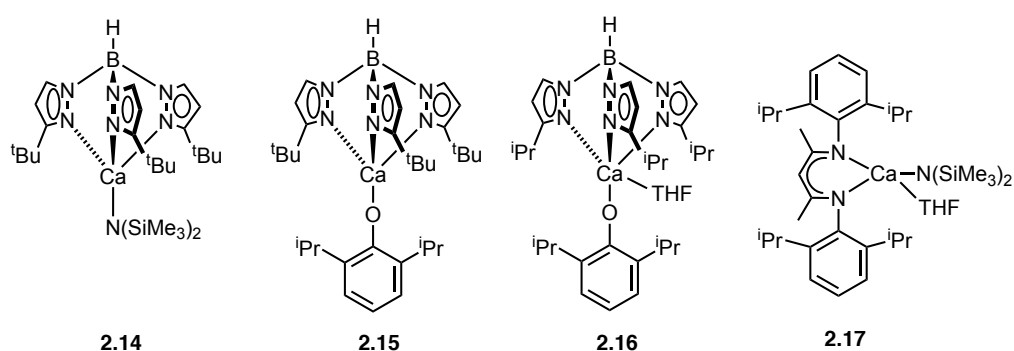


**Figure 2.4** (Tp<sup>R</sup>)Ca(X) and (<sup>Dipp</sup>NacNac)Ca(X) (**2.14-2.17**) reported by Chisholm *et al.*<sup>25, 26</sup>

In 2010, Zou *et al.* reported heteroleptic calcium complex {NNN}Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**2.18**) supported by a diamino-anilide ligand {NNN} (Figure 2.5).<sup>27</sup> The idea was to employ a more flexible pendant arm compared to other diketiminate ligands such as <sup>Ar</sup>NacNac where Ar = C<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>4</sub> or C<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2</sub>OMe.<sup>28, 29</sup> The activity of **2.18** in the ROP of *rac*-LA is relatively high, converting 100 equiv. of *rac*-LA within 30 min (90% conversion) in CH<sub>2</sub>Cl<sub>2</sub> or 66% conversion after 2 h in THF at RT. Atactic PLAs were obtained.

Darensbourg *et al.* prepared several {NNO}Ca(X)(THF) (X = N(SiMe<sub>3</sub>)<sub>2</sub>, OMe) complexes, where the metal is supported by tridentate Schiff base ligands.<sup>30, 31</sup> Among those complexes, **2.19** (Figure 2.5) was the most active initiator, polymerised 350-700 equiv. of *L*-LA (69-80% conversion) within 30 min without solvent at 110 °C. Very narrow  $\bar{D}$  values (1.02-1.04) and higher than calculated  $M_n$  were observed. Kinetic studies showed first order dependence on *L*-LA concentration. The ROP of *rac*-LA using **2.19** in either THF or CHCl<sub>3</sub> at RT produced atactic PLAs.

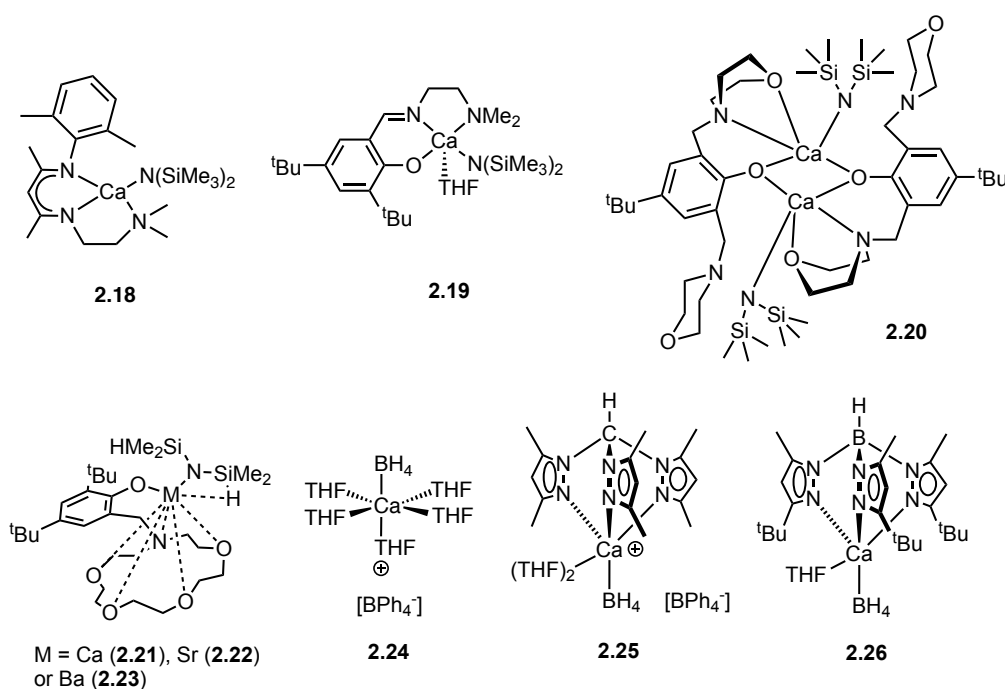


**Figure 2.5** Heteroleptic alkaline earth metal complexes for ROP of cyclic esters (**2.18-2.26**).<sup>16, 27-35</sup>

Carpentier *et al.* synthesised dimeric [ $\{LO^{morph2}\}Ca\{N(SiMe_3)_2\}\}_2$  (**2.20**, Figure 2.5) supported by a mono anionic 4-*tert*-butyl-2,6-bis(morpholinomethyl)phenoxide ligand ( $LO^{morph2}$ ).<sup>16</sup> The polymerisation of 500 equiv. of *L*-LA using **2.20** with 10 equiv. of *i*PrOH in toluene at 60 °C was complete within 1 min, giving PLA with  $\bar{D} = 1.27$  and close agreement between  $M_n$ (GPC) and calculated one.

A different amide ligand  $N(SiMe_2H)_2$  was also developed to preserve the integrity of heteroleptic complexes *via* secondary  $\beta$ -Si-H agostic interactions. The preparation of  $\{LnO\}M\{N(SiMe_2H)_2\}$  where M = Ca, Sr or Ba was also reported by Carpentier *et al.*<sup>32</sup> The reaction of the amino-ether phenol protio ligand  $\{O_4NO^{Aryl}\}$  and  $M\{N(SiMe_2H)_2\}_2(THF)_x$  produced  $\{O_4NO^{Aryl}\}M\{N(SiMe_2H)_2\}_2(THF)_x$  (M = Ca, x = 1, **2.21**; Sr, x = 0.66, **2.22**; Ba, x = 0, **2.23** as illustrated in Figure 2.5). Complex **2.21** with 10-25 equiv. of *i*PrOH as chain transfer agent polymerised 1,000 equiv. of *L*-LA in a controlled fashion and full conversion achieved in 10 min at 30 °C in toluene. Gratifyingly, the ROP of 1,000 equiv. of *rac*-LA under analogous conditions resulted in moderately isotactic PLA ( $P_m = 0.65$ ).

Well-defined cationic complexes  $[(L)_nM]^+$  where a series of alkaline earth metals (Ca, Sr and Ba) stabilised by a bulky ligand and a weakly coordinating counterion  $X^-$  were

reported by Carpentier *et al.*<sup>33,34</sup> A series of zinc and alkaline earth (Zn, Mg, Ca, Sr and Ba) ionic compounds  $[(L)_nM][H_2N\{B(C_6F_5)_3\}_2]$  was studied as ROP catalysts. Moreover, the weakly coordinating anion and the lack of Lewis base on the metal centre strongly enhanced the Lewis acidity of the cations and therefore increased the ROP activities. The polymerisation of *L*-LA using a Mg derivative and <sup>i</sup>PrOH as external initiator (100 °C, toluene) was totally inactive after 3 h. The Sr and Ba analogues in the presence of <sup>i</sup>PrOH rapidly converted 1,000 equiv. of *L*-LA at 30 °C within 1 h. Although moderate *D* values were obtained (*D* = 1.20-1.30), poor agreement between measured and calculated *M<sub>n</sub>* values was observed due to transesterification reactions. The calcium derivative provided well-controlled immortal ROP with <sup>i</sup>PrOH or BnOH. Full conversion of up to 3,000 equiv. of *L*-LA was achieved after 24 h, along with close agreement between observed and calculated *M<sub>n</sub>* values and narrow *D* values (1.06-1.12).

In 2010, Mountford and Cushion reported the first cationic calcium tetrahydroborate complexes  $[Ca(BH_4)(THF)_5][BPh_4]$  (**2.24**) and  $[(Tpm)Ca(BH_4)(THF)_2][BPh_4]$  (**2.25**, Tpm = HB(Me<sub>2</sub>pz)<sub>3</sub>) as shown in Figure 2.5.<sup>35</sup> Complex **2.24** rapidly polymerised 200 equiv. of  $\epsilon$ -CL in THF at RT within 2 min, and polymerised 50-300 equiv. of *rac*-LA in THF at 70 °C within 3-5 h to produce  $\alpha,\omega$ -dihydroxytelechelic polymers. The ROP gave very good agreement between measured and calculated *M<sub>n</sub>*, and moderate *D* values (*ca.* 1.4). The more sterically hindered complex **2.25** was more active, converting 250 equiv. of *rac*-LA after 2 h at RT with *D* = 1.2-1.4. However, **2.24** and **2.25** both produced atactic PLA. The use of bulkier ancillary ligand Tp<sup>tBu,Me</sup> ligand, however, gave good stereoselectivity *via* chain-end control. Thus, (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**2.26**, Figure 2.5) was very active for the ROP of *rac*-LA at 20 °C (full conversion of 50-200 equiv. of *rac*-LA achieved after 5 min). The resulting PLA was heterotactically-enriched with *P<sub>r</sub>* = 0.88-0.90. Tetrahydroborate complexes as ROP catalysts are described in further detail in Chapter Four.

### 2.2.5 Alkaline earth organohydroborate complexes

Organohydroborate ligands have the general formulas as  $[H_xBR_{4-x}]^-$  (*x* = 1-3, R = alkyl or aryl) and are formally anionic. Common examples are  $[HBt_3]^-$ ,  $[HBPh_3]^-$ ,  $[HB(C_6F_5)_3]^-$  and  $[H_2BC_8H_{14}]^-$ . Due to its nucleophilicity and selectivity, the triethylhydroborate anion ( $[HBt_3]^-$ ) has been extensively used in organic,

organometallic and materials chemistry as a reducing agent and hydride source. With the exception of alkali metal (Li, Na, K), the chemistry of metal complexes incorporating  $[\text{HBEt}_3]^-$  is limited because of its high activity and poor coordinating ability.  $\text{Cp}^{\text{tBu}}_2\text{Sm}(\text{HBEt}_3)(\text{THF})_x$  and  $\text{Cp}^{\text{tBu}}_2\text{Nd}(\text{HBEt}_3)$  have been synthesised by salt elimination reaction of  $\text{Na}[\text{HBEt}_3]$  with  $[\text{Cp}^{\text{tBu}}_2\text{SmCl}]_2$  or  $\text{Cp}^{\text{tBu}}_2\text{NdCl}$ , respectively.<sup>36</sup> <sup>37</sup> Despite of the stability of these complexes in solution, attempts to isolate them were unsuccessful. In 2000, Hanusa *et al.* synthesised  $\text{Cp}'''\text{Ca}(\text{HBEt}_3)(\text{THF})_2$  (**2.27**,  $\text{Cp}''' = \text{C}_5\text{H}_2(\text{SiMe}_3)_3$ , Figure 2.6) *via* salt elimination of  $\text{Na}[\text{HBEt}_3]$  with the corresponding calcium iodide-bridged dimer,  $\text{Cp}'''\text{Ca}(\mu\text{-I})(\text{THF})_2$ .<sup>38</sup> Spectroscopic and X-ray diffraction studies showed the first example of  $\text{Ca}-(\mu\text{-H})\text{-BEt}_3$  interaction. Several approaches to remove the  $\text{BEt}_3$  moiety from **2.27** was unsuccessful. The solid structure of **2.27** revealed  $\kappa^2$ -bidentate coordination of  $\text{HBEt}_3$  to calcium through both  $\text{Ca-H-B}$  and  $\text{Ca-H-C}$  (agostic) interactions.

Examples of  $[\text{HBEt}_3]^-$  anion coordinated to metal centre *via*  $\kappa^3$  bonding mode through one hydride and two methylene hydrogens from an ethyl group of  $\text{HBEt}_3$  were reported such as  $(^{\text{Dipp}}\text{NacNac})\text{Sc}(\text{NHAr}')(\text{HBEt}_3)$  ( $\text{Ar}' = 2,6\text{-C}_6\text{H}_3^{\text{iPr}}_2$ ),<sup>39</sup>  $\text{Cp}^*_2\text{La}(\text{HBEt}_3)(\text{THF})_x$  ( $x = 0$  or  $1$ ),<sup>40</sup> and  $\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^{\text{iPr}})\}_2\text{Y}(\text{HBEt}_3)_2(\text{THF})$ .<sup>41</sup>

In 2010, Westerhausen *et al.* reported a rare example of a stable arylcalcium triethylboronate  $\text{Ca}(2,6\text{-C}_6\text{H}_3\text{ToI}_2)(\text{HBEt}_3)(\text{DME})(\text{THF})$  (**2.28**, Figure 2.6) synthesised *via* reaction of  $\text{Ca}(2,6\text{-C}_6\text{H}_3\text{ToI}_2)\text{I}(\text{THF})_3$  with  $\text{K}[\text{HBEt}_3]$  and crystallised in a mixture of THF and DME.<sup>42</sup> The molecular structure of **2.28** showed monodentate coordination  $\text{HBEt}_3$  ( $\text{Ca-H-B}$ ), along with the binding of DME and THF molecules. The saturated coordination sphere prevented oligomerisation, disproportionation and precipitation of the insoluble corresponding calcium hydrides.

In 2009, Sadow *et al.* reported  $\text{Ca}\{\text{HB}(\text{C}_6\text{F}_5)_3\}\{\text{C}(\text{SiHMe}_2)_3\}(\text{THF})_2$  (**2.29**, Figure 2.6) and  $\text{Ca}\{\text{HB}(\text{C}_6\text{F}_5)_3\}_2(\text{THF})_2$  (**2.30**, Figure 2.6) obtained *via*  $\beta\text{-SiH}$  abstraction of  $\text{Ca}\{\text{C}(\text{SiHMe}_2)_3\}_2(\text{THF})_2$  with 1 or 2 equiv. of  $\text{B}(\text{C}_6\text{F}_5)_3$ , respectively.<sup>43</sup> The solid state structures of **2.29** and **2.30** show that two  $\text{HB}(\text{C}_6\text{F}_5)_3$  ligands bond through  $\kappa^3\text{-H, F, F}$  tridentate modes.



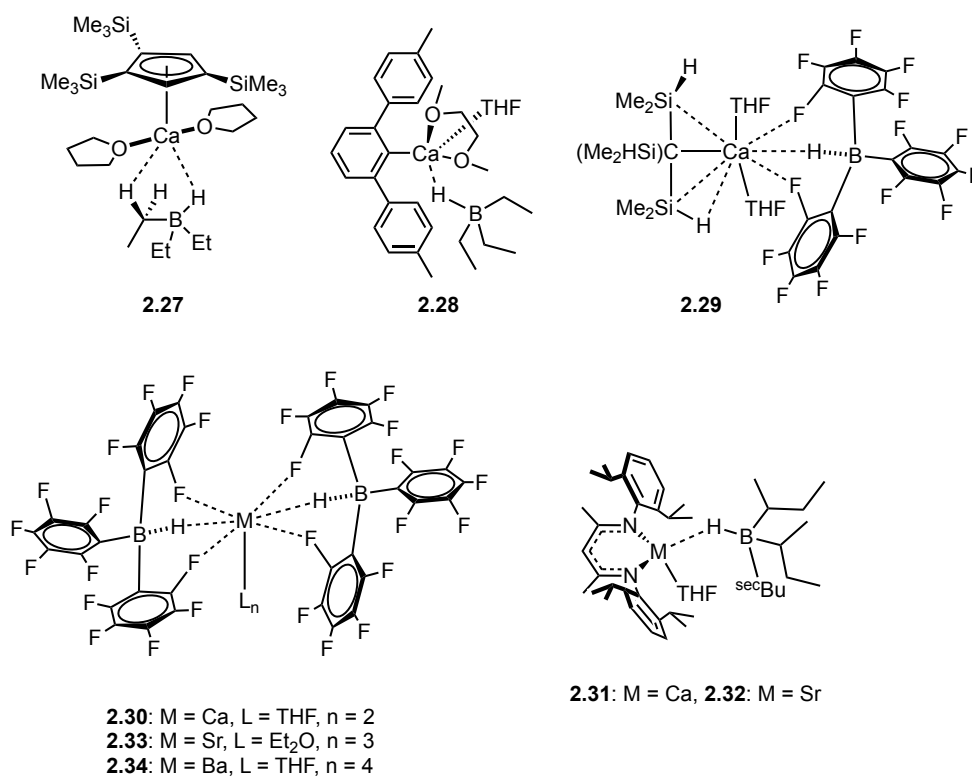


**Figure 2.6** Alkaline earth metal organohydroborate complexes (**2.27-2.34**).<sup>38, 42-45</sup>

In 2010, Roesky *et al.* reported  $(^{\text{Dipp}}\text{NacNac})\text{M}\{\text{HB}(\text{sBu})_3\}(\text{THF})$  (M = Ca (**2.31**); Sr (**2.32**), Figure 2.6).<sup>44</sup> Complexes **2.31** and **2.32** were prepared *via* salt elimination reaction of  $\text{K}[\text{HB}(\text{sBu})_3]$  and  $[(^{\text{Dipp}}\text{NacNac})\text{M}(\mu\text{-I})(\text{THF})]_2$ . The solid state structures of **2.31** and **2.32** showed the bridging hydrides to groups  $\text{M}-(\mu\text{-H})-\text{B}(\text{sBu})_3$ . Upon heating, **2.31** and **2.32** formed the corresponding homoleptic complexes by redistribution reaction.

Very recently, Hill *et al.* described the synthesis of heavier alkaline earth metal bis(hydridoborate) derivatives of  $\text{M}\{\text{HB}(\text{C}_6\text{F}_5)_3\}_2(\text{L})_n$  (**2.33**, M = Sr, L = Et<sub>2</sub>O, n = 3 and **2.34**, M = Ba, L = THF, n = 4 as shown in Figure 2.6).<sup>45</sup> Complexes **2.33** and **2.34** were synthesised *via* two pathways. The first route is *via* reaction of  $\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2(\text{THF})_2$  with  $\text{Me}_2\text{NHBH}_3$  and  $\text{B}(\text{C}_6\text{F}_5)_3$ . The other is *via* the salt elimination reaction of  $\text{MI}_2$  with 2 equiv. of  $\text{K}[\text{HB}(\text{C}_6\text{F}_5)_3]$ . The solid state structures of both complexes (**2.33** and **2.34**) resemble that of **2.30**, possessing  $\text{HB}(\text{C}_6\text{F}_5)_3$  ligand coordinating with the metal *via*  $\kappa^3$  bonding mode through  $\text{M}-(\mu\text{-H})-\text{B}$  units and two fluorine atoms on two  $\text{C}_6\text{F}_5$  rings.

Okuda *et al.* reported  $[\text{Mg}(\text{THF})_6][\text{HBPh}_3]_2$  (**2.35**) and  $[\text{Mg}(\text{THF})_6][\text{HB}(\text{C}_6\text{F}_5)_3]_2$  (**2.36**) and their catalytic hydroboration.<sup>46</sup> These solvent-separated ion pairs, **2.35** and

**2.36** were synthesised from reaction between  $\text{Mg}\{\text{N}(\text{SiHMe}_2)_2\}_2$  with 2 equiv. of  $\text{BPh}_3$  or  $\text{B}(\text{C}_6\text{F}_5)_3$  in THF at RT, respectively. Complex **2.35** was found to be active in the hydroboration of several unsaturated substrates including carbonyls, pyridines, nitriles, imines, esters, amides,  $\text{CO}_2$ , carbodiimides and isocyanates. Whereas **2.36** exhibited much poorer catalytic activity in the hydroboration of benzophenone (2 mol% **2.36**, 70% conversion after 13 h at RT) and was inactive in the hydroboration of pyridine.

### 2.2.6 Alkaline earth organohydroborate complexes for the ROP of *rac*-LA

The catalytic activities of alkaline earth organohydroborate complexes towards the ROP of *rac*-LA have been previously studied by our group.<sup>47</sup> The complexes  $(\text{Tp}^{\text{tBu,Me}}\text{M}(\text{HBEt}_3)(\text{THF})_x$  (**1**: M = Ca, x = 1; **2**: M = Sr, x = 2) were synthesised *via* the salt elimination reaction of  $(\text{Tp}^{\text{tBu,Me}}\text{M}(\text{I})(\text{THF})_x$  (M = Ca, x = 1; M = Sr, x = 2) with  $\text{Na}[\text{HBEt}_3]$ . The solid state structures of **1** and **2** show that the  $\text{HBEt}_3$  ligand bonded to calcium *via*  $\kappa^3$  binding mode through a bridging hydride and two-agostic-type hydrogens on one of the ethyl groups (Figure 2.7).

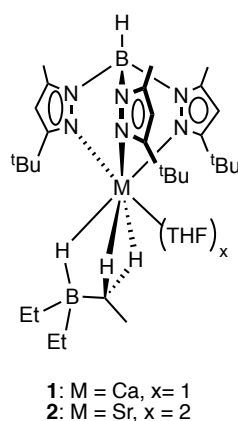
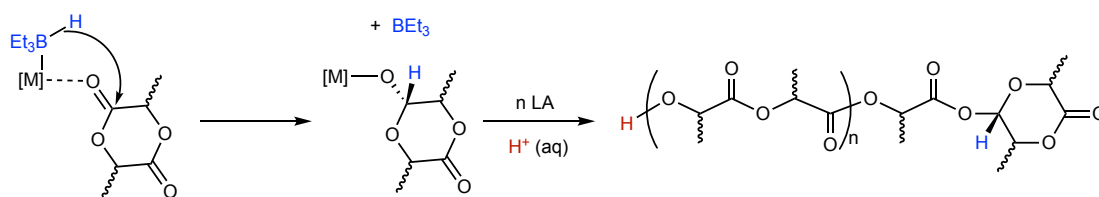


**Figure 2.7** Alkaline earth organohydroborate complexes as ROP of *rac*-LA catalysts (**1** and **2**).<sup>47</sup>

The mechanism in the ROP of LA using **1** or **2** was initially proposed as shown in Scheme 2.1. Hydride transferred from the  $\text{HBEt}_3$  moiety to the carbonyl carbon of the LA monomer leads to the formation of  $(\text{Tp}^{\text{tBu,Me}}\text{M}(\text{LA-H})(\text{THF})_x$  in the presence of a non-opened ring LA (LA-H) alkoxide species and free  $\text{BEt}_3$ .  $(\text{Tp}^{\text{tBu,Me}}\text{M}(\text{LA-H})(\text{THF})_x$  could act as a ROP initiator to give PLA terminated with a non-opened ring LA end group (-LA-H) at one end and a hydroxy group at the other end. The same type of LA-H end group was also found with certain tetrahydroborate initiators of the type  $(\text{L})\text{M}(\text{BH}_4)$ . This is described in full detail in Chapter Four.



**Scheme 2.1** Proposed mechanism for the ROP of LA initiated by **1** and **2** in THF. [M] =  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})$  or  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{THF})_2$ .<sup>47</sup>

Preliminary polymerisation studies highlighted their potential as catalysts for the ROP of *rac*-LA. The ROP of 100 equiv. of *rac*-LA using **1** or **2** was very rapid, over 95% monomer conversion was reached within 1 min giving PLA with considerably lower than expected  $M_n$  values and broad  $D$  values (3.48-4.39). However, an attempt to observe  $(\text{Tp}^{\text{tBu,Me}})\text{M}(\text{LA-H})(\text{THF})_x$  by NMR spectroscopy from a reaction between **1** or **2** with 10 equiv. of *rac*-LA in THF- $d_8$  at RT was unsuccessful.

## 2.3 ROP of LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$ (**1**)

### 2.3.1 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$ (**1**)

Complex **1** was introduced in the previous work in the Mountford group. The preliminary studies revealed high activity of **1** in the ROP of *rac*-LA.<sup>47</sup> However, a mismatch between measured and calculated  $M_n$  of the resultant polymer was reported. A primary aim for the work carried out in this thesis is to investigate the polymerisation activity, stereoselectivity and mechanistic pathway for ROP of LA using **1**. The ROP of *rac*-LA with **1** was performed in THF at RT in a glove-box under an  $\text{N}_2$  atmosphere. The conversion of *rac*-LA monomer was followed by collecting aliquots at regular intervals which were quenched with degassed, wet THF. The polymer samples were analysed by NMR spectroscopy, MALDI-ToF mass spectrometry and Gel Permeation Chromatography (GPC).

Complex **1** was found to be highly active for the ROP of *rac*-LA. At  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 100$  in THF at RT (Table 2.1, entry 5), 96% monomer conversion was reached within 30 s. The polymerisation was too fast to follow the conversion over time to assess a kinetic profile. Therefore, the high loading of  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 800$  was performed (Table 2.1, entry 1), 92% conversion was achieved after 3 min. Kinetic studies showed a second-order dependency on *rac*-LA concentration as judged by linear plot of  $1/[\textit{rac}\text{-LA}]_t$  vs. time, with  $k_{\text{app}} = 0.145(3) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.998$ ) (Figure 2.8, squares). No induction period was observed. A second-order dependence on monomer concentration

is unusual but not unprecedented. A monomer-triggered insertion mechanism was proposed by Ystenes to explain kinetic phenomena when the kinetic order dependence on monomer concentration exceeded 1.<sup>48</sup> The mechanism involves two monomers at the transition state and the insertion of the first monomer will not proceed unless the second monomer enters coordination sphere and triggers the insertion of the first monomer. A few examples have been disclosed for the ROP of *rac*-LA promoted by magnesium,<sup>49</sup> calcium,<sup>50</sup> strontium,<sup>50</sup> zinc,<sup>51</sup> lanthanum,<sup>52</sup> yttrium<sup>53</sup> and neodymium<sup>54</sup> complexes.

In order to determine the kinetic order dependence on the concentration of **1** and propagation rate constant ( $k_p$ ), ROP of *rac*-LA using various concentrations of **1** was carried out under analogous conditions. The *rac*-LA concentration was held constant at 0.5 M while catalyst concentration was varied, providing a ratio of  $[rac\text{-LA}]_0:[\mathbf{1}]_0 = 800, 500, 300$  and 200. The ROP results are summarised in Table 2.1. Second order plots are shown in Figure 2.8, giving a rate law of  $-d[rac\text{-LA}]/dt = k_{app}[rac\text{-LA}]^2$  where  $k_{app} = k_p[\mathbf{1}]^x$ .

**Table 2.1** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**).<sup>a</sup>

| Entry | [ <i>rac</i> -LA] <sub>0</sub> : [ <b>1</b> ] <sub>0</sub> | Conv. <sup>b</sup><br>(%) | Time<br>(s) | <i>M</i> <sub>n</sub> (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>k</i> <sub>app</sub> <sup>f</sup><br>(M <sup>-1</sup> s <sup>-1</sup> ) | <i>R</i> <sup>2f</sup> | <i>P</i> <sub>r</sub> <sup>g</sup> |
|-------|------------------------------------------------------------|---------------------------|-------------|--------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------|----------------------------------------------------------------------------|------------------------|------------------------------------|
| 1     | 800                                                        | 92                        | 180         | 91,940                                                             | 106,059                                                              | 1.40                  | 0.145(3)                                                                   | 0.998                  | 0.82                               |
| 2     | 500                                                        | 93                        | 120         | 74,880                                                             | 67,008                                                               | 1.42                  | 0.239(14)                                                                  | 0.990                  | 0.78                               |
| 3     | 300                                                        | 94                        | 90          | 45,430                                                             | 40,638                                                               | 1.43                  | 0.383(32)                                                                  | 0.979                  | 0.79                               |
| 4     | 200                                                        | 94                        | 60          | 34,870                                                             | 27,093                                                               | 1.40                  | 0.587(27)                                                                  | 0.996                  | 0.82                               |
| 5     | 100                                                        | 96                        | 30          | 15,090                                                             | 13,836                                                               | 1.88                  | <sup>h</sup>                                                               | <sup>h</sup>           | 0.81                               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub> = 0.5 M, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated *M*<sub>n</sub> for –OH and –LA-H end groups (g mol<sup>-1</sup>), *M*<sub>n</sub>(calcd) (entry 1-5) = conv. (%) × [*rac*-LA]<sub>0</sub>: [**1**]<sub>0</sub> × 144.1 + 2. <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> Apparent second order rate constant for consumption of monomer with standard error and *R*<sup>2</sup> determined by linear regression analysis. <sup>g</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>h</sup> Not measured.

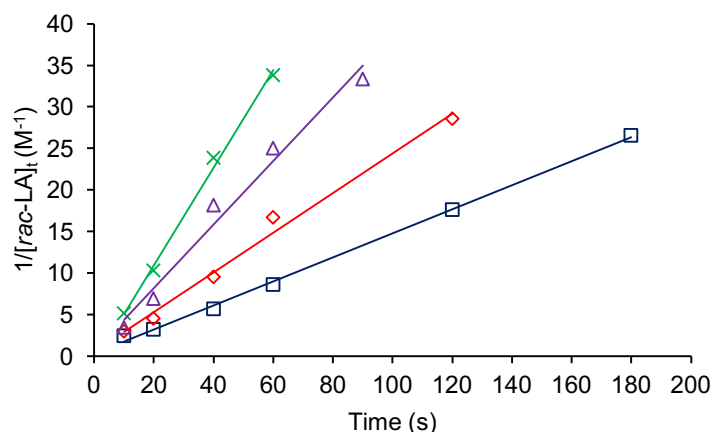


**Figure 2.8** ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**). Plots of  $1/[\text{rac-LA}]_t$  vs. time (s). Conditions: 6 mL THF, RT,  $[\text{rac-LA}]_0 = 0.5$  M. Squares:  $[\text{rac-LA}]_0:[\mathbf{1}]_0 = 800:1$  ( $k_{\text{app}} = 0.145(3) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.998$ ). Diamonds:  $[\text{rac-LA}]_0:[\mathbf{1}]_0 = 500:1$  ( $k_{\text{app}} = 0.239(14) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.990$ ). Triangles:  $[\text{rac-LA}]_0:[\mathbf{1}]_0 = 300:1$  ( $k_{\text{app}} = 0.383(32) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.979$ ). Crosses:  $[\text{rac-LA}]_0:[\mathbf{1}]_0 = 200:1$  ( $k_{\text{app}} = 0.587(27) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.996$ ).

The propagation rate constant ( $k_p$ ) of  $258(14) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.994$ ) was calculated from the gradient of the graph between  $k_{\text{app}}$  vs.  $[\mathbf{1}]_0$  (Figure 2.9, left). The gradient of  $1.01(5)$  ( $R^2 = 0.997$ ) from the plot between  $-\ln(k_{\text{app}})$  vs.  $-\ln[\mathbf{1}]_0$  is indicative of first order dependence on concentration of **1** (Figure 2.9, right). The overall rate law was determined as  $-\text{d}[\text{rac-LA}]/\text{dt} = k_p[\text{rac-LA}]^2[\mathbf{1}]$ ,  $k_p = 258(14) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.994$ ).

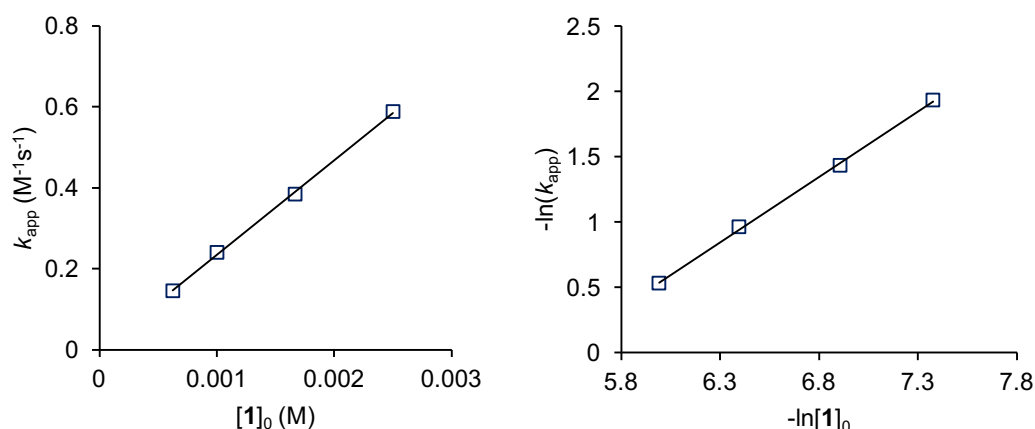


**Figure 2.9** Left, plot of  $k_{\text{app}}$  vs.  $[\mathbf{1}]_0$ , for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) shows  $k_p = 258(14) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.994$ ). Right, plot of  $-\ln(k_{\text{app}})$  vs.  $-\ln[\mathbf{1}]_0$  shows an order in  $[\mathbf{1}]$  equal to  $1.01(5)$  ( $R^2 = 0.997$ ).

As shown in Figure 2.10, ROP of 800 equiv. of *rac*-LA with **1** experienced greater propagation than initiation rate during initial polymerisation stages, resulting in  $M_n(\text{GPC})$  values higher than those calculated for one growing polymer chain per metal centre. At the later stages of polymerisation (>85% conversion), lower than anticipated  $M_n(\text{GPC})$  values were observed due to intratransesterification reaction (back-biting).  $\bar{D}$  values were narrow at low conversion and then become broader at high conversion ( $\bar{D} = 1.06\text{--}1.40$ ). At  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 500, 300$  and  $200$ , the greater propagation than initiation rate was more apparent than at  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 800$ . Therefore, the  $M_n(\text{GPC})$  values were observed to be higher than those calculated over the conversion range (Figure 2.10).

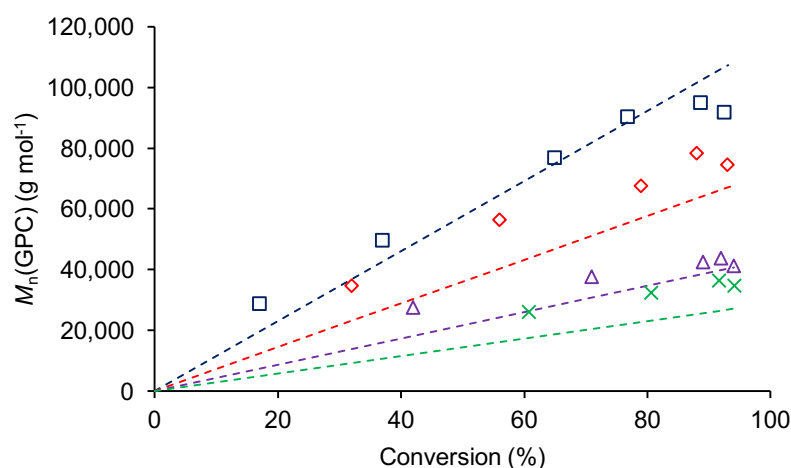


**Figure 2.10** Plots of  $M_n(\text{GPC})$  vs. conversion (%) for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**). Conditions: 6 mL THF, RT,  $[\textit{rac}\text{-LA}]_0 = 0.5$  M. The dashed lines represent  $M_n(\text{calcd})$  for one PLA chain per metal centre. Squares:  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 800:1$ ,  $\bar{D} = 1.06\text{--}1.40$ . Diamonds:  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 500:1$ ,  $\bar{D} = 1.10\text{--}1.42$ . Triangles:  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 300:1$ ,  $\bar{D} = 1.15\text{--}1.43$ . Crosses:  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 200:1$ ,  $\bar{D} = 1.13\text{--}1.40$ .

End groups of PLA formed by using **1** was analysed by MALDI-ToF mass spectrometry. The resultant PLA was prepared from the ROP with  $[\textit{rac}\text{-LA}]_0:[\mathbf{1}]_0 = 20$ . The polymerisation solution was quenched immediately after the addition of the catalyst solution into the *rac*-LA solution in order to suppress the transesterification reactions. MALDI-ToF mass spectrum of the crude PLA sample (Figure 2.11) shows the presence of cyclic PLA as a major contribution resulting from intramolecular transesterification (back-biting). The peak envelopes are separated by  $\Delta m/z = 72.0$  Da

which is half of a LA monomer (*i.e.*, -OCH(Me)CO-) consistent with transesterification reactions. The peaks corresponding to PLA terminated with a non-opened LA ring at one end and hydroxyl group at the other end were observed as a very minor distribution. The polymer end group analysis was consistent with the previous ROP results obtained from  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)^{47}$  and  $(\text{Tpm}^*\text{d})\text{Mg}(\text{BH}_4)^{55}$ . Detailed examination of isotopic peak patterns comparing with theoretical ones in MALDI-ToF MS analysis was conducted to identify the end groups of the polymer chain. The peak envelope centred at  $m/z = 903.5$  Da corresponds to cyclic PLA containing 12 units of half LA and  $\text{K}^+$  (Figure 2.11). The other peak envelope centred at  $m/z = 905.6$  Da is assigned to PLA having 10 units of half LA end capped with non-opened ring LA (-LA-H) and -OH groups and  $\text{K}^+$   $[72.0(10) + 146.1 + 39.1]$  (Figure 2.11). A series of theoretical isotopic distributions of these two polymer adducts ( $m/z(\text{calcd}) = 903.2$  and  $905.2$  Da) were simulated and compared with the measured ones (Figure A1). Good agreement between the theoretical and measured isotopic distributions of two types of polymer adducts was observed, confirming the formation of PLA end capped with -LA-H unit, and cyclic PLA.

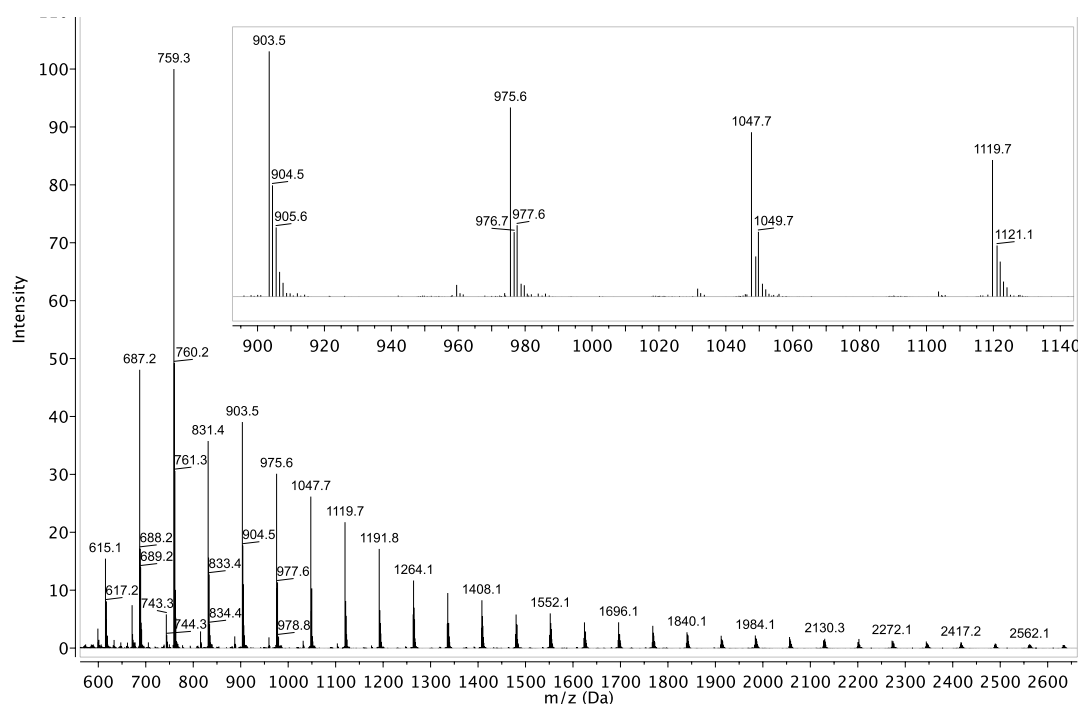


**Figure 2.11** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**).  $M_n(\text{GPC}) = 4,300 \text{ g mol}^{-1}$ ,  $D = 1.46$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{1}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $[\textbf{1}]_0 = 0.025 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0$  Da between peak envelopes.



However, the  $^1\text{H}$  NMR spectra of crude and isolated PLAs (Figure 2.12, b and c) show PLAs with an absence of terminal group either  $-\text{LA-H}$  or  $-\text{OH}$  groups. However, the  $^1\text{H}$  NMR spectrum of the filtrate from polymer precipitation (Figure 2.12, a) shows two doublets in the region of 5.30-5.50 ppm corresponding to  $\text{OCH}$  proton on the non-opened LA chain end ( $-\text{LA-H}$ ), which was consistent with those observed from using  $(\text{Tpm}^*\text{d})\text{Mg}(\text{BH}_4)$ .<sup>55</sup> These results show that a low molecular weight PLA terminated with non-opened LA ring was formed as a minor product and had a higher solubility than cyclic PLA. Further evidence to support the non-opened LA ring end group will be discussed in Chapter Four.

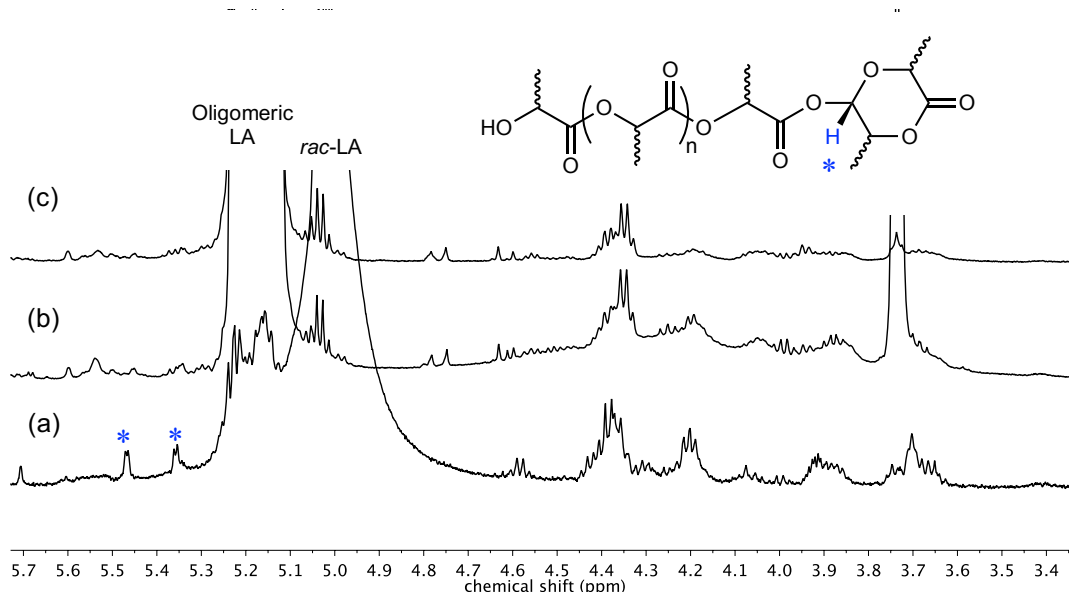


**Figure 2.12**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of the filtrate from polymer precipitation (a), crude PLA sample (b) and isolated PLA sample (c) obtained from the ROP of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**) with 20 equiv. of *rac*-LA in THF at RT. “\*” denotes  $\text{OCH}$  proton of the non-opened LA ring chain end ( $-\text{LA-H}$ ).

Heterotactically-enriched PLAs ( $P_r = 0.79\text{--}0.82$ ) were obtained due to the preference of **1** to form polymer chains *via racemic* linkage ( $-\text{RR-SS-}$  or  $-\text{SS-RR-}$ ) than a *meso* linkage ( $-\text{RR-RR-}$  or  $-\text{SS-SS-}$ ) (Table 2.1). The use of a bulky  $\text{Tp}^{\text{tBu,Me}}$  ligand can induce heterotactic enchainment through a chain-end control. According to Chisholm’s report on  $(\text{Tp}^{\text{tBu}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**2.14**) and  $(\text{Tp}^{\text{tBu}})\text{Ca}(\text{O-2,6-C}_6\text{H}_3\text{iPr}_2)$  (**2.15**), heterotactic-rich PLAs with  $P_r = \text{ca. } 0.9$  were formed.<sup>26</sup> Mountford also reported highly heterotactic PLAs synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**2.26**) with high  $P_r$  values in the range of 0.88–0.90 at  $-20\text{ }^\circ\text{C}$  and *ca.* 0.80 at RT.<sup>35</sup>

### 2.3.2. ROP of *L*-, *D*- and *meso*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$ (**1**)

Following the promising ROP of *rac*-LA using **1**, the ROP of *L*-, *D*- and *meso*-LA was investigated under analogous conditions. The results are summarised in Table 2.2. Complex **1** was found to be considerably less active for the ROP of enantiomerically pure *L*- and *D*-LA than that of *rac*-LA. The kinetic studies of the ROP of *L*- or *D*-LA exhibited two polymerisation stages obtained in each case (Figure 2.13). In the presence of 800 equiv. of monomer, conversion for the ROP of *L*-LA reached approximately 70% after 10 min, the polymerisation of *D*-LA also took place at the same rate as *L*-LA. The plots of  $1/[\text{LA}]_t$  vs. time show the ROP of *L*- or *D*-LA appearing to follow a second order dependence on monomer concentration up to *ca.* 70% conversion. The  $k_{\text{app}}$  values obtained from the ROP of *L*- and *D*-LA in this region are  $0.0085(6) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.982$ ) and  $0.0075(7) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.981$ ), respectively. However, after this stage the monomer conversions in each case increased only slowly from 70% (10 min) up to 80% (30 min). The second stage was found not to follow with either second or first order dependency. The lower catalytic activities in the ROP of *L*- or *D*-LA is indicative of the catalyst preference to insert LA monomers *via* a *racemic* dyad over a *meso* dyad.

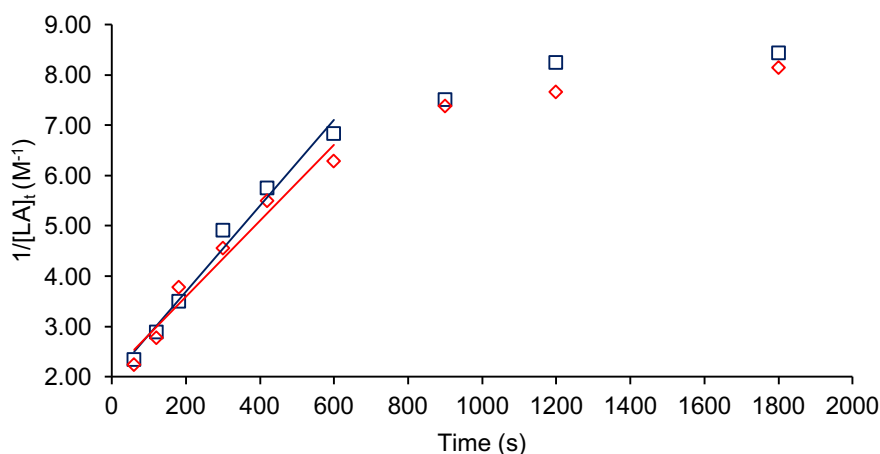


**Figure 2.13** ROP of *L*- and *D*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**). Plots of  $1/[\text{LA}]_t$  vs. time (s). Conditions: 6 mL THF, RT,  $[\text{LA}]_0 = 0.5 \text{ M}$ . Squares:  $[\text{L-LA}]_0:[\textbf{1}]_0 = 800:1$  ( $k_{\text{app}} = 0.0085(6) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.982$ ). Diamonds:  $[\text{D-LA}]_0:[\textbf{1}]_0 = 800:1$  ( $k_{\text{app}} = 0.0075(7) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.981$ ).

**Table 2.2** Selected data for the ROP of *rac*-, *L*-, *D*-, and *meso*-LA using (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**).<sup>a</sup>

| Entry | Monomer         | Conv. <sup>b</sup><br>(%) | Time<br>(min) | <i>M</i> <sub>n</sub> (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>k</i> <sub>app</sub> <sup>f</sup><br>(s <sup>-1</sup> ) | <i>k</i> <sub>app</sub> <sup>g</sup><br>(M <sup>-1</sup> s <sup>-1</sup> ) | <i>R</i> <sup>2</sup> | <i>P</i> <sub>r</sub> <sup>h</sup> |
|-------|-----------------|---------------------------|---------------|--------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------|------------------------------------------------------------|----------------------------------------------------------------------------|-----------------------|------------------------------------|
| 1     | <i>rac</i> -LA  | 92                        | 3             | 91,940                                                             | 106,060                                                              | 1.40                  | -                                                          | 0.145(3)                                                                   | 0.998 <sup>g</sup>    | 0.82                               |
| 2     | <i>L</i> -LA    | 80                        | 30            | 56,890                                                             | 92,226                                                               | 1.31                  | -                                                          | 0.0085(6)                                                                  | 0.982 <sup>g</sup>    | <sup>i</sup>                       |
| 3     | <i>D</i> -LA    | 82                        | 30            | 53,490                                                             | 94,532                                                               | 1.40                  | -                                                          | 0.0075(7)                                                                  | 0.981 <sup>g</sup>    | <sup>i</sup>                       |
| 4     | <i>meso</i> -LA | 96                        | 2             | 68,180                                                             | 110,671                                                              | 1.48                  | 0.026(2)                                                   | -                                                                          | 0.985 <sup>f</sup>    | 0.87                               |

<sup>a</sup> Conditions: [monomer]<sub>0</sub>:**1**<sub>0</sub> = 800:1, [monomer]<sub>0</sub> = 0.5 M, [**1**]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated *M*<sub>n</sub> for –OH and –LA-H end groups (g mol<sup>-1</sup>), *M*<sub>n</sub>(calcd) (entry 1-4) = conv. (%) × [*rac*-LA]<sub>0</sub>:**1**<sub>0</sub> × 144.1 + 2. <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> Apparent first order rate constant for consumption of monomer with standard error and *R*<sup>2</sup> determined by linear regression analysis. <sup>g</sup> Apparent second order rate constant for consumption of monomer with standard error and *R*<sup>2</sup> determined by linear regression analysis. <sup>h</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>i</sup> In the absence of epimerisation, the ROP of *L*- and *D*-LA leads to the formation of pure isotactic PLLA or PDLA, respectively (*P*<sub>m</sub> = 1.00).

As observed previously in the ROP of *rac*-LA with **1**, close agreement between measured (GPC) and calculated  $M_n$  based on one growing polymer chain per metal centre was observed at the beginning of polymerisation (<40% conversion) from the ROP of *L*- or *D*-LA, followed by a deviation of  $M_n$  as a result of transesterification reactions until *ca.* 80% conversion (Figure 2.14). The ROP of 800 equiv. of *L*-LA with **1** gave isotactic poly(*L*-LA) ( $P_m = 1.00$ ) determined by  $^1\text{H}\{^1\text{H}\}$  NMR spectroscopy, indicating the absence of epimerisation of the monomer or polymer usually observed with truly anionic ROP initiators.<sup>56</sup>

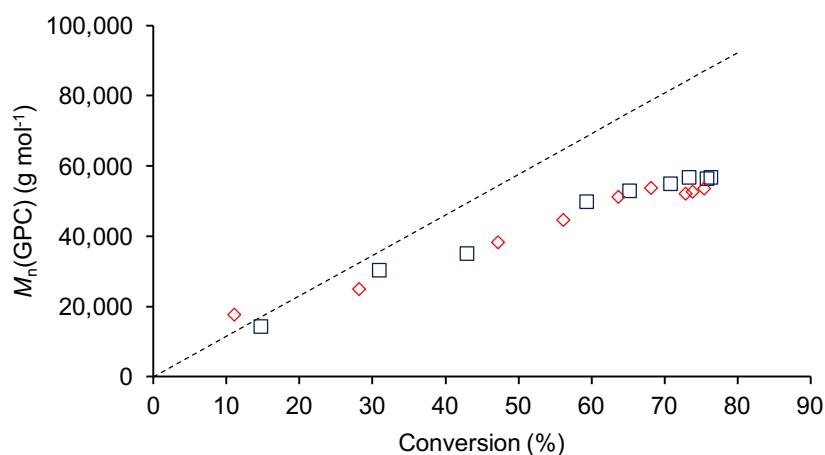


**Figure 2.14** Plots of  $M_n(\text{GPC})$  vs. conversion (%) for ROP of *L*- and *D*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**). Conditions: 6 mL THF, RT,  $[\text{LA}]_0 = 0.5$  M. The dashed line represents  $M_n(\text{calcd})$  for one PLA chain per metal centre. Squares:  $[\text{L-LA}]_0:[\text{1}]_0 = 800:1$ ,  $\bar{D} = 1.07\text{-}1.31$ . Diamonds:  $[\text{D-LA}]_0:[\text{1}]_0 = 800:1$ ,  $\bar{D} = 1.10\text{-}1.40$ .

Complex **1** was found to be more active for the ROP of *meso*-LA than *rac*-LA. The ROP of 800 equiv. of *meso*-LA with **1** in THF at RT revealed 96% monomer conversion after 2 min. The faster polymerisation rate of *meso*-LA than *rac*-LA has been reported.<sup>10, 57-59</sup> It was suggested that *meso*-LA is less stable in the ground state compared with *rac*-LA based on CVFF (consistent valence force field) calculations showing that *rac*-LA is 0.4 kcal mol<sup>-1</sup> more stable than *meso*-LA.<sup>10</sup> The linearity of the plot of  $\ln([\text{meso-LA}]_0/[\text{meso-LA}]_t)$  vs. time shows the ROP rate is in agreement with first order dependence on *meso*-LA concentration, with  $k_{\text{app}} = 0.026(2) \text{ s}^{-1}$  ( $R^2 = 0.985$ ) (Figure 2.15, left).

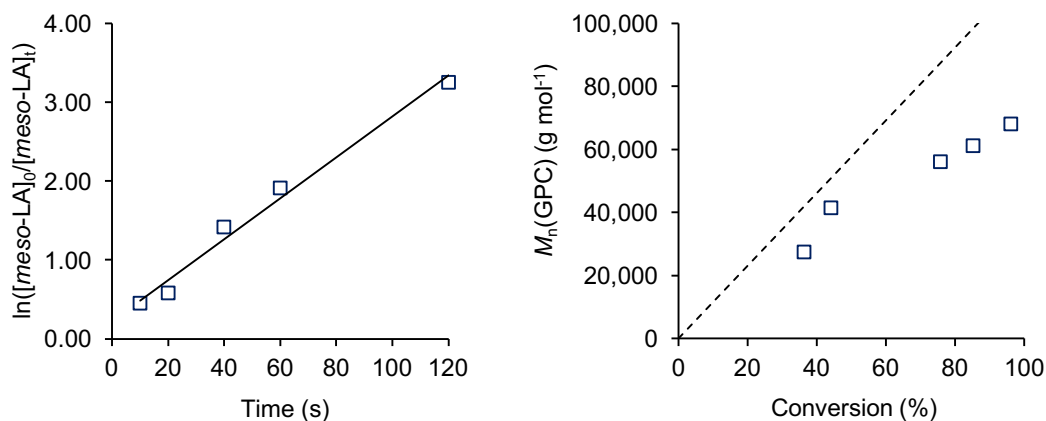


**Figure 2.15** Left, plot of  $\ln([meso-LA]_0/[meso-LA]_t)$  vs. time (s) ( $k_{app} = 0.026(2) \text{ s}^{-1}$ ,  $R^2 = 0.985$ ). Right, plot of  $M_n$ (GPC) vs. conversion (%). The dashed line represents  $M_n$ (calcd) for one PLA chain per metal centre.  $\bar{D} = 1.06$ -1.48. Condition: 6 mL THF, RT,  $[meso-LA]_0:[1]_0 = 800:1$ ,  $[meso-LA]_0 = 0.5 \text{ M}$ .

The plot of  $M_n$ (GPC) vs. conversion (%) (Figure 2.15, right) shows lower experimental  $M_n$  than those calculated for one chain per metal centre due to back-biting which dominates at high monomer conversions. A difference in kinetic behaviour was observed as the ROP of *meso*-LA provided a first order dependency while second order dependency found for the ROP of *rac*-LA, and for *L*- and *D*-LA in the early stages.

Analysis by  $^1\text{H}\{^1\text{H}\}$  NMR spectroscopy showed that highly syndiotactic PLA (-*RS*-*RS*- linkages) was afforded in the ROP of *meso*-LA ( $P_r = 0.87$ ). As the ROP of *rac*-LA using **1** produces heterotactically enriched PLA ( $P_r = 0.79$ -0.82), it is unsurprising that the ROP of *meso*-LA would give syndiotactically-enriched PLA ( $P_r > 0.5$ ).<sup>14, 59-64</sup> This is attributed to the preference of the catalyst to insert monomer *via* *racemic* dyad (-*RS*-*RS*- or -*SR*-*SR*-) instead of *meso* dyad (-*RS*-*SR*- or -*SR*-*RS*-), presumably as a consequence of chain-end control.

## 2.4 Mechanistic investigations of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$ (**1**) for the ROP of LA

### 2.4.1 NMR tube scale studies of the ROP of *rac*-LA with $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$ (**1**)

To study the polymerisation behaviour of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) for the ROP of *rac*-LA,  $^1\text{H}$  and  $^{11}\text{B}$  NMR analyses of an NMR tube scale reaction between **1** and 1 equiv. of *rac*-LA in THF-*d*<sub>8</sub> were undertaken. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra were recorded after 10 min. The  $^1\text{H}$  NMR spectrum of **1** (Figure 2.16, a) shows a triplet at

0.90 ppm and a quartet at 0.43 ppm corresponding to methyl protons and methylene protons of coordinated  $\text{BEt}_3$ , respectively. The  $^{11}\text{B}$  NMR spectrum of **1** (Figure 2.17, a) also shows two signals at -7.6 and -9.7 ppm corresponding to the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  ligand and the coordinated  $\text{BEt}_3$ , respectively.

The  $^1\text{H}$  NMR spectrum of **1** with 1 equiv. of *rac*-LA recorded after 10 min (Figure 2.16, b) shows signals which are reminiscent of those of homoleptic  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**) (Figure 2.16, d).<sup>47</sup> The  $^{11}\text{B}$  NMR spectrum (Figure 2.17, b) also shows signals at -1.7 and -7.6 ppm which are also reminiscent of those of **3** (Figure 2.17, d), which has  $\kappa^2$  and  $\kappa^3$  bond  $\text{Tp}^{\text{tBu,Me}}$  ligand.<sup>47</sup> The presence of signals at -1.7 and -7.6 ppm therefore suggested the possible formation of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) as a redistribution product. A broad singlet was observed at 73.6 ppm corresponding to free  $\text{BEt}_3$  with an absence of a doublet at -9.9 ppm corresponding to  $\text{Ca-HBEt}_3$ . A doublet corresponding to the apical B-H of an unknown  $\text{Tp}^{\text{tBu,Me}}$  containing species also appeared at -6.2 ppm (Figure 2.16, b).

An NMR tube scale reaction of **1** and 5 equiv. of *rac*-LA was performed in  $\text{THF-}d_8$  at RT. The  $^1\text{H}$  NMR spectrum recorded after 10 min (Figure 2.16, c) shows an absence of the signals corresponding to **3**, together with an appearance of a new set of signals corresponding to the unknown  $\text{Tp}^{\text{tBu,Me}}$  species. The free  $\text{BEt}_3$  also appeared as apparent quartet and triplet at 0.97 and 0.87 ppm, respectively (Figure 2.16, c). The  $^{11}\text{B}$  NMR spectrum recorded after 10 min (Figure 2.17, c) shows signals at -5.7 and 71.7 ppm assigned to the unknown  $\text{Tp}^{\text{tBu,Me}}$  species and free  $\text{BEt}_3$ , respectively, with no signals at -1.7 and -7.6 ppm.

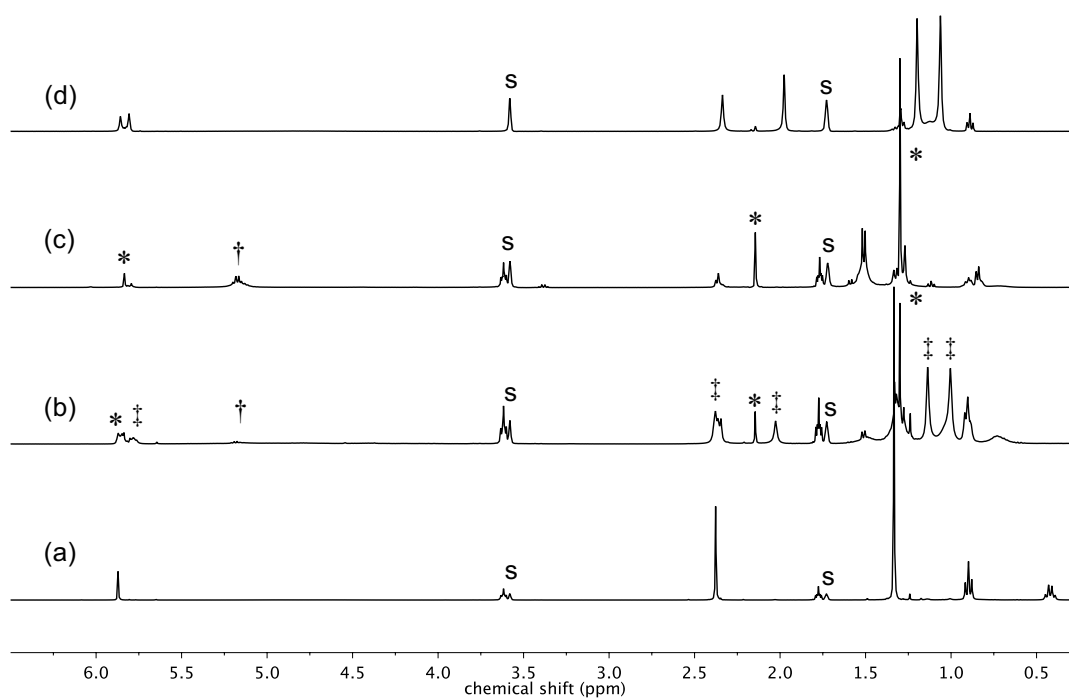


**Figure 2.16**  $^1\text{H}$  NMR spectra ( $\text{THF-}d_8$ , 499.9 MHz, 298 K) of (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**), (b) reaction of **1** with 1 equiv. of *rac*-LA after 10 min, (c) reaction of **1** with 5 equiv. of *rac*-LA after 10 min and (d)  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**). “s” denotes residual protio-solvent. “†” denotes possible homoleptic  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) “\*” denotes the unknown species featuring  $\text{Tp}^{\text{tBu,Me}}$  ligand. “†” denotes oligomeric LA.

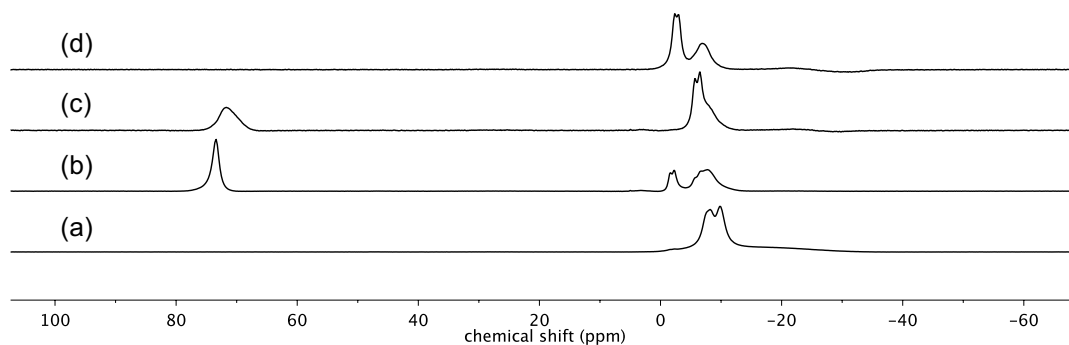


**Figure 2.17**  $^{11}\text{B}$  NMR spectra ( $\text{THF-}d_8$ , 160.4 MHz, 298 K) of (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**), (b) reaction of **1** with 1 equiv. of *rac*-LA after 10 min, (c) reaction of **1** with 5 equiv. of *rac*-LA after 10 min and (d)  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**).

A test of the presumed inertness of  $\text{BEt}_3$  for the ROP of *rac*-LA was carried out. An NMR tube scale reaction of  $\text{BEt}_3$  (1M in THF) and 1 equiv. of *rac*-LA was performed in  $\text{THF-}d_8$ . After 24 h, there was no polymerisation observed from the  $^1\text{H}$  NMR spectrum. Another control experiment was to determine whether  $\text{BEt}_3$  could exchange

with a propagating alkoxide species during polymerisation. *In situ* generated  $\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$ , formed by reaction of  $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$  with 9 equiv. of benzophenone, was used as a model for an alkoxide propagating species. The  $^{11}\text{B}$  NMR spectrum of the reaction between  $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$  and  $\text{BEt}_3$  (as a model of  $\text{BEt}_3$  being released from **1** after addition of *rac*-LA) showed a singlet and quintet at 73.1 and -36.6 ppm corresponding to  $\text{BEt}_3$  and coordinated  $\text{BH}_4$ , respectively. After the addition of 9 equiv. of benzophenone, the  $^1\text{H}$  NMR spectrum was monitored after 18 h. Two singlets appeared at 6.38 and 6.05 ppm corresponding to the methine protons of  $\text{B}(\text{OCHPh}_2)_3$  and  $\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$ , respectively. The  $^{11}\text{B}$  NMR spectrum showed two singlets at 18.4 and 73.1 ppm corresponding to  $\text{B}(\text{OCHPh}_2)_3$  and unreacted  $\text{BEt}_3$ , respectively. Therefore,  $\text{BEt}_3$  does not undergo redistribution with a propagating alkoxide species, or indeed with  $\text{B}(\text{OCHPh}_2)_3$ .

#### 2.4.2 Isolation of $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$ (**4**) and redistribution between $\text{Ca}(\text{OR})_2(\text{THF})_x$ and **4**

Because the  $^{11}\text{B}$  NMR spectrum of the reaction of **1** with 1 equiv. of *rac*-LA in  $\text{THF}-d_8$  shows signals reminiscent of those of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**) (Figure 2.17, b), the formation of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) was therefore anticipated. The attempted synthesis of **4** was unsuccessful even under extreme conditions. Reaction of 3 equiv. of  $\text{K}(\text{Tp}^{\text{tBu,Me}})$  with  $\text{CaI}_2$  in THF at 60 °C for 24 h produced  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{I})(\text{THF})$  as a major product and **4** as a minor product, along with unreacted  $\text{K}(\text{Tp}^{\text{tBu,Me}})$ . A few studies on the synthesis of alkaline earth homoleptic complexes supported by various ligands were reported.<sup>65-71</sup> Harder *et al.* reported the solid state structure of  $(\kappa^2, \kappa^3\text{-Tp}^{\text{tBu}})_2\text{Ca}$  obtained from the reaction of  $(\text{Tp}^{\text{tBu}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  with  $\text{PhSiH}_3$ , *via* the transient hydride species,  $(\text{Tp}^{\text{tBu}})\text{CaH}$ .<sup>72</sup> Takats prepared  $[(\text{Tp}^{\text{tBu,Me}})\text{Yb}(\mu\text{-H})]_2$  by an exposure of a solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Yb}(\text{CH}_2\text{SiMe}_3)(\text{THF})$  to a hydrogen atmosphere.<sup>73</sup> Yaman also reported homoleptic  $(\text{Tp}^{\text{C*}})_2\text{Ca}$  ( $\text{Tp}^{\text{C*}} = 3\text{-(2-methoxy-1,1-dimethyl) tris(pyrazolyl)hydroborate}$  ligand) formed by a redistribution by the Schlenk equilibrium of  $(\text{Tp}^{\text{C*}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  upon heating in benzene solution.<sup>74</sup>

##### 2.4.2.1 Synthesis and characterisation of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$ (**5**)

$(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) was therefore synthesised in order to react with  $\text{PhSiH}_3$  aiming to give  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**). Complex **5** was synthesised by the salt elimination



reaction of  $\text{K}(\text{Tp}^{\text{tBu,Me}})$ ,  $\text{CaI}_2$  and  $\text{K}[\text{N}(\text{SiMe}_3)_2]$  in THF at RT for 18 h (Equation 2.1). It was fully characterised by single crystal X-ray diffraction, and the molecular structure is presented in Figure 2.18. Selected bond and angles are presented in Table 2.3.

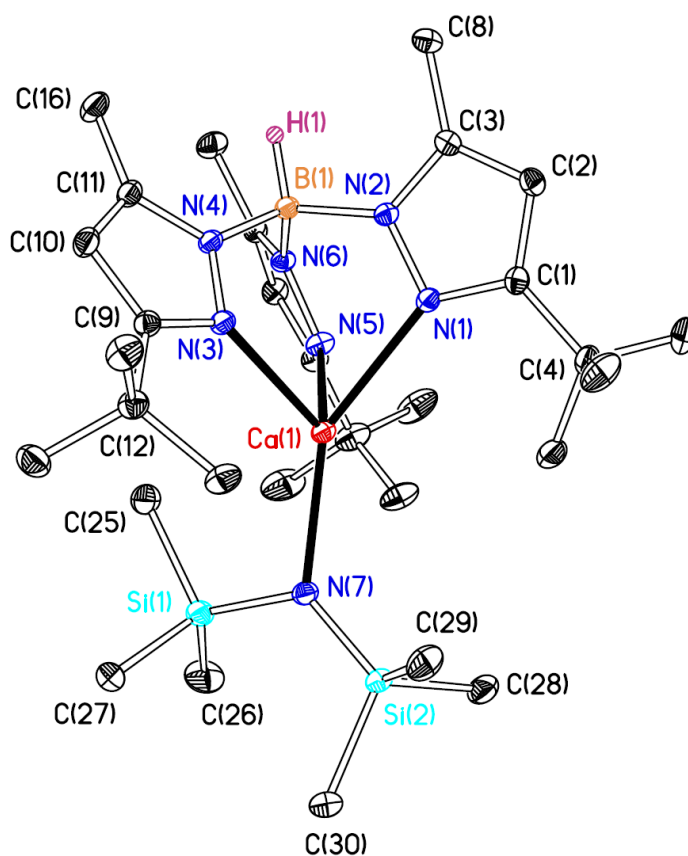
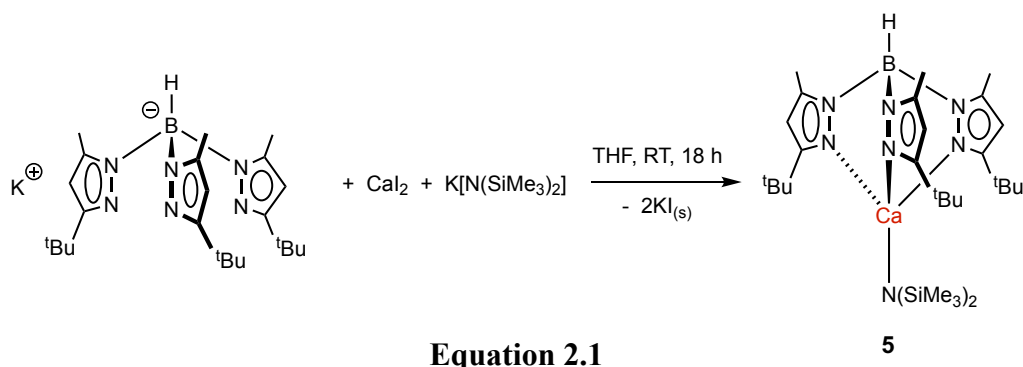


**Figure 2.18** Displacement ellipsoid plot of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**). H atoms are omitted. Ellipsoids are drawn at the 20% probability level.

**Table 2.3** Selected bond lengths (Å) and angles (°) for (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**).

|                  |            |                  |            |
|------------------|------------|------------------|------------|
| Ca(1)-N(1)       | 2.4244(15) | Ca(1)-N(3)       | 2.4422(14) |
| Ca(1)-N(5)       | 2.4206(15) | Ca(1)-N(7)       | 2.3225(14) |
| N(1)-Ca(1)-N(7)  | 145.23(5)  | N(3)-Ca(1)-N(7)  | 121.28(5)  |
| N(5)-Ca(1)-N(7)  | 126.01(5)  | N(1)-Ca(1)-N(3)  | 76.91(5)   |
| N(1)-Ca(1)-N(5)  | 75.24(5)   | N(3)-Ca(1)-N(5)  | 95.86(5)   |
| Ca(1)-N(7)-Si(1) | 105.72(7)  | Ca(1)-N(7)-Si(2) | 130.43(8)  |

Complex **5** is four coordinate in which calcium bonded to the three N donors of the Tp<sup>tBu,Me</sup> ligand and the N donor of a N(SiMe<sub>3</sub>)<sub>2</sub> ligand. The geometry at the calcium centre is distorted tetrahedral, with (Tp<sup>tBu,Me</sup>)N-Ca-N(Tp<sup>tBu,Me</sup>) and (Tp<sup>tBu,Me</sup>)N-Ca-N(SiMe<sub>3</sub>)<sub>2</sub> angles in the range of 121.28(5)-145.23(5)° and 75.24(5)-95.86(5)°, respectively. The bond length of the calcium to the silylamido N atom of **5** is 2.3225(14) Å which is in close agreement with those found from (Tp<sup>iPr</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF) (2.339(3) Å) and (DippNacNac)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF) (**2.17**, 2.370(1) Å).<sup>26</sup> The average distances between Ca to N donors of the Tp<sup>tBu,Me</sup> ligand (2.4291(14) Å) are comparable to that of 2.425(1) Å seen in (Tp<sup>iPr</sup>)Ca(O-2,6-C<sub>6</sub>H<sub>3</sub><sup>iPr</sup>Pr<sub>2</sub>)(THF) (**2.16**). The narrow angle between N(3)-Ca(1)-N(7) of 121.28 (5) and N(5)-Ca(1)-N(7) of 126.01(5) compared to N(1)-Ca(1)-N(7) of 145.23(5) can be attributed to a lack of THF molecules in the structure causing the trimethylsilyl group to distort to complete the coordination sphere. This distortion places two hydrogen atoms in C(25) in close proximity to calcium, with a Ca···H distances of 2.761 and 2.771 Å compared to longer distances of 3.811 Å and 4.006 Å between calcium and a hydrogen atom in C(29) and C(28), respectively. The short Ca···H distances fall within the range for agostic interaction between metal centres and silylamide groups.<sup>32, 75, 76</sup> The <sup>1</sup>H NMR spectrum of **5** in toluene-*d*<sub>8</sub> exhibits only one singlet at 0.28 ppm for the trimethylsilyl groups at RT, indicating fast rotation about the Ca-N(SiMe<sub>3</sub>)<sub>2</sub> bond. Variable temperature <sup>1</sup>H NMR at 273, 233 and 188 K were carried out in an attempt to freeze out this rotation, but a singlet for the equivalent SiMe<sub>3</sub> groups was observed at all temperature suggesting that any possible agostic interaction are only relatively weak.

The reaction of **5** with PhSiH<sub>3</sub> in C<sub>6</sub>D<sub>6</sub> was undertaken. However, no reaction was observed after heating at 60 °C for 24 h. This probably results from the steric hindrance of Tp<sup>tBu,Me</sup> ligand that prevents the calcium centre undergoing σ-bond metathesis with

PhSiH<sub>3</sub>. The result is different from Harder's reaction of PhSiH<sub>3</sub> with (Tp<sup>tBu</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} which reacted quantitatively at 60 °C to form PhH<sub>2</sub>SiN(SiMe<sub>3</sub>)<sub>2</sub>.<sup>72</sup> No further attempts were made to independently synthesise **4**.

#### 2.4.2.2 Isolation and characterisation of (Tp<sup>tBu,Me</sup>)<sub>2</sub>Ca (**4**)

Unexpectedly, diffraction-quality colourless crystals grown from a solution of (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**) in benzene at 4 °C were determined to be (Tp<sup>tBu,Me</sup>)<sub>2</sub>Ca (**4**) by NMR spectroscopy and X-ray diffraction. Complex **4** could be formed *via* the Schlenk equilibrium of **5** during the crystallisation process. Unfortunately, the isolation of **4** could not be reproduced, and so the catalytic activity in the ROP of *rac*-LA with **4** was therefore not determined. The molecular structure and selected distances and angles of **4** are shown in Figure 2.19 and Table 2.4.

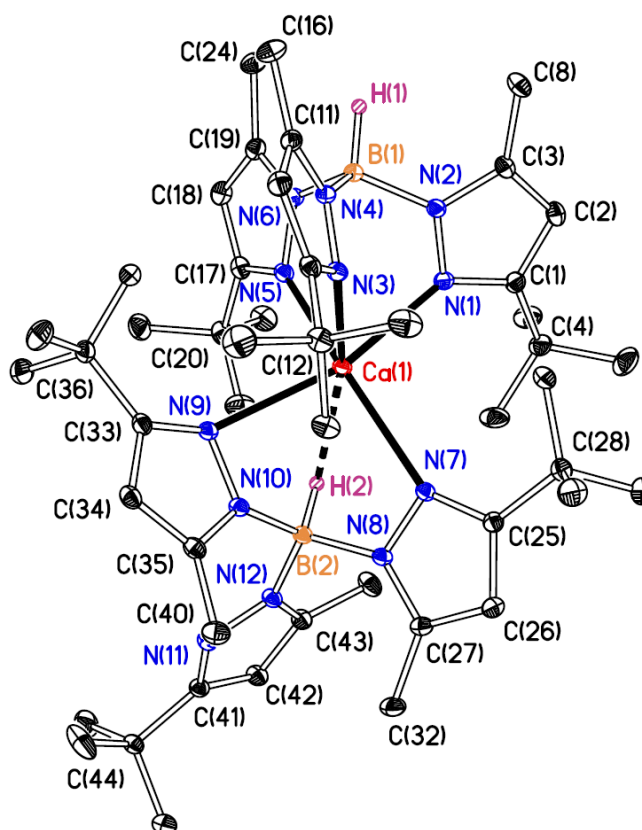


**Figure 2.19** Displacement ellipsoid plot of (Tp<sup>tBu,Me</sup>)<sub>2</sub>Ca (**4**). H atoms are omitted. Ellipsoids are drawn at the 20% probability level.

**Table 2.4** Selected bond lengths (Å) and angles (°) for (Tp<sup>tBu,Me</sup>)<sub>2</sub>Ca (**4**).

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| Ca(1)-N(1)      | 2.4982(14) | Ca(1)-N(3)      | 2.4558(13) |
| Ca(1)-N(5)      | 2.5029(14) | Ca(1)-N(7)      | 2.5995(14) |
| Ca(1)-N(9)      | 2.5174(14) | Ca(1)-H(2)      | 2.3290(18) |
| N(1)-Ca(1)-N(3) | 88.19(5)   | N(1)-Ca(1)-N(5) | 69.02(5)   |
| N(3)-Ca(1)-N(5) | 94.46(5)   | N(1)-Ca(1)-N(7) | 102.36(4)  |
| N(3)-Ca(1)-N(7) | 107.11(4)  | N(5)-Ca(1)-N(7) | 156.72(4)  |
| N(1)-Ca(1)-N(9) | 160.16(5)  | N(3)-Ca(1)-N(9) | 96.14(4)   |
| N(5)-Ca(1)-N(9) | 91.30(5)   | N(7)-Ca(1)-N(9) | 94.88(4)   |
| N(1)-Ca(1)-H(2) | 117.4(4)   | N(3)-Ca(1)-H(2) | 153.4(4)   |
| N(5)-Ca(1)-H(2) | 101.3(4)   | N(7)-Ca(1)-H(2) | 62.5(4)    |
| N(9)-Ca(1)-H(2) | 62.5(4)    |                 |            |

The molecular structure of **4** is consistent with the reported homoleptic sandwich complexes (Tp<sup>tBu,Me</sup>)<sub>2</sub>Sr (**3**),<sup>47</sup> (Tp<sup>tBu,Me</sup>)<sub>2</sub>Sm,<sup>77</sup> (Tp<sup>tBu,Me</sup>)<sub>2</sub>Yb<sup>77</sup> and (Tp<sup>tBu</sup>)<sub>2</sub>Ca.<sup>72</sup> The solid state structure of **4** shows that two Tp<sup>tBu,Me</sup> ligands can coordinate at calcium as tridentate ligands. One of the Tp<sup>tBu,Me</sup> ligands is coordinated with three nitrogen atoms *via*  $\kappa^3$  binding mode *via* N(1), N(3) and N(5). Whereas another is bonded through  $\kappa^2$  fashion with two pyrazolyl nitrogens, N(7) and N(9) in addition to B-H unit due to pyrazolyl ring orientation. The interesting feature of **4** is an agostic Ca $\cdots$ H-B interaction, and this is supported by the short Ca(1)-H(2) distance of 2.329(18) Å. This type of bonding has been observed previously in (Tp<sup>tBu,Me</sup>)<sub>2</sub>Sr<sup>47</sup> and (Tp<sup>tBu</sup>)<sub>2</sub>Ca<sup>72</sup>. The coordination geometry of **4** is described as a capped octahedron. The least-square plane is defined by four equatorial nitrogen atoms N(1), N(5), N(7) and N(9) and the axial position is occupied by N(3) and H(2). The distortion of the molecule is reflected by large deviation from linearity of the N(3)-Ca(1)-H(2) angle (153.4(4) Å). The steric crowding of **4** was emphasised by the comparatively long average bonds of Ca-N (2.5148(14) Å).

Due to the agostic Ca $\cdots$ H-B interaction, the <sup>1</sup>H NMR spectrum of **4** at RT (Figure 2.20, a) shows two sets of signals corresponding to two sets of Tp<sup>tBu,Me</sup> ligands. The <sup>11</sup>B NMR spectrum showed two different environment of boron atoms, doublet at -1.6 ppm and singlet at -7.2 ppm corresponding to Ca $\cdots$ H-B and the apical H-B of Tp<sup>tBu,Me</sup> ligand, respectively. Crucially, the signals corresponding to **4** shown in <sup>1</sup>H NMR (THF-*d*<sub>8</sub>)

(Figure 2.20, a) are consistent with signals of **4** observed from  $^1\text{H}$  NMR spectrum of the reaction between  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) and 1 equiv. of *rac*-LA in  $\text{THF-}d_8$  (Figure 2.20, b).

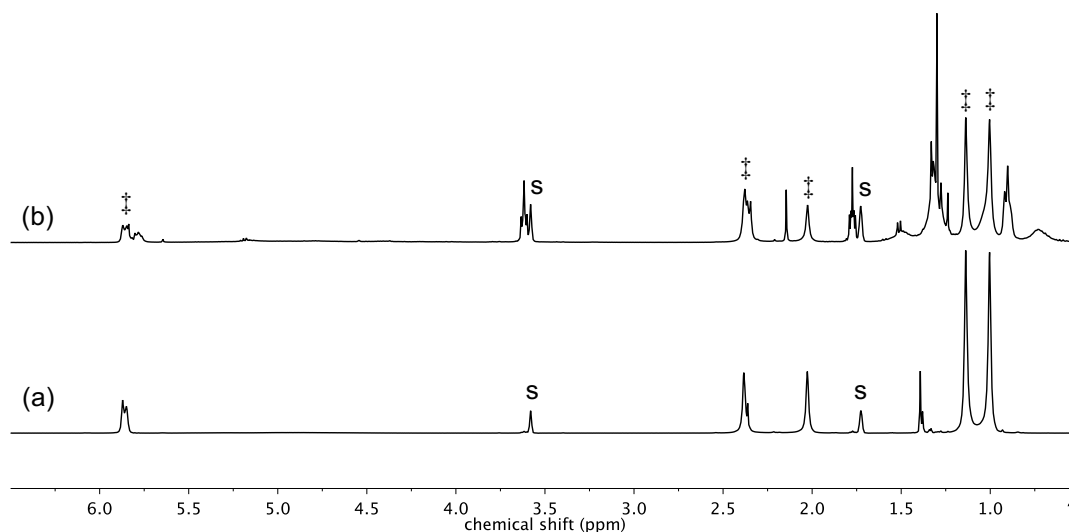


**Figure 2.20**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 298K) of (a)  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) and (b) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) with 1 equiv. of *rac*-LA after 10 min. “s” denotes residual protio-solvent. “‡” denotes  $\text{Tp}^{\text{tBu,Me}}$  of **4**.

#### 2.4.2.3 Redistribution reactions of $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$ (**4**) and $\text{Ca}(\text{OR})_2(\text{THF})_x$

As the reaction of **1** with 1 equiv. of *rac*-LA in  $\text{THF-}d_8$  was further complicated by the Schlenk equilibrium of a presumed labile initiating alkoxide featuring a non-opened ring LA,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  to give **4** and  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$  as a product, two questions arise. First, if **4** and  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$  can be formed during polymerisation, it is important to determine whether  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$  can act as initiator. Second, it is necessary to determine whether  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  could be obtained from a redistribution reaction between **4** and  $\text{Ca}(\text{LA-H})_x(\text{THF})_x$ .

$\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$  (**6**) and 2 equiv. of  $\text{B}(\text{OCHPh}_2)_3$  were generated *in situ* from  $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$  and 9 equiv. of benzophenone in THF and served as a model for  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$ . Polymerisation of 800 equiv. of *rac*-LA with *in situ* generated **6** as a catalyst was found to be significantly slow as only 65% of monomer was polymerised after 264 h to provide atactic PLA ( $P_r = 0.5$ ). The  $M_n(\text{GPC})$  value ( $15,542 \text{ g mol}^{-1}$ ) was lower than that calculated ( $37,650 \text{ g mol}^{-1}$ ) for two growing chains per metal centre due to transesterification reactions. The innocence of  $\text{B}(\text{OCHPh}_2)_3$  as chain transfer agent

will be discussed in Chapter Four. The slow rate of ROP and lack of stereocontrol support the crucial role of  $\text{Tp}^{\text{tBu,Me}}$  ligand on the ROP rate and polymer tacticity and clearly indicate the poor ability of  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$  as ROP initiator.

**6** and 2 equiv. of  $\text{B}(\text{OCHPh}_2)_3$  were generated *in situ* from an NMR tube scale reaction of  $\text{Ca}(\text{BH}_4)_2(\text{THF})_2$  with 9 equiv. of benzophenone in  $\text{THF-}d_8$  at RT after 18 h (Figure 2.21, b and Figure 2.22, b). The  $^1\text{H}$  NMR spectrum monitored after addition of 1 equiv. of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) (Figure 2.21, c) shows the instantaneous formation of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) (*vide infra*) with the disappearance of **4**. The  $^{11}\text{B}$  NMR spectrum (Figure 2.22, c) exhibits two broad singlets at -8.3 and 18.6 ppm corresponding to the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  of **7** and  $\text{B}(\text{OCHPh}_2)_3$ , respectively, instead of characteristic signals for **4** at -1.6 and -7.2 ppm (Figure 2.22, a). These results suggested that ROP of LA with **1** was unlikely to be affected by the presence of **4** since **4** was prone to undergo redistribution reaction with  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$  giving  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})$ .

Complex **7** serving as a model for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})$  was generated *in situ* from NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 4 equiv. of benzophenone in  $\text{THF-}d_8$  at RT after 10 min. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra (Figure 2.21, d and Figure 2.22, d) show signals corresponding to **7** which is consistent with those observed from reaction of **4** and **6** (Figure 2.21, c and Figure 2.22, c). Complex **7** was also independently synthesised and fully characterised, and will be discussed later in the following section 2.5.1.

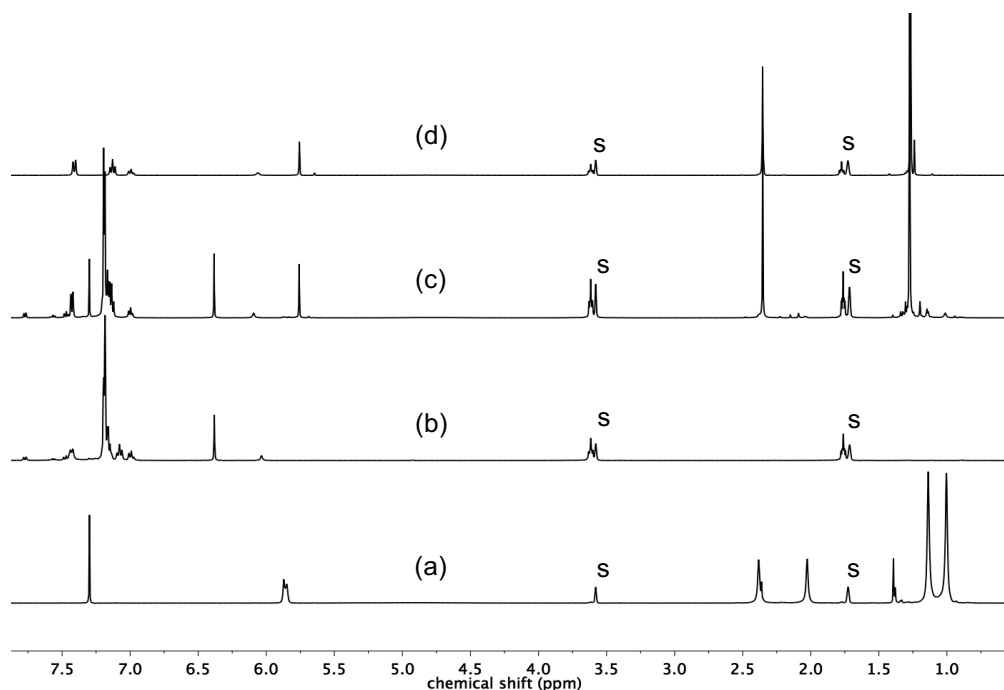


**Figure 2.21**  $^1\text{H}$  NMR spectra (THF- $d_8$ , 499.9 MHz, 298K) of (a)  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**), (b)  $\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$  (**6**) and  $\text{B}(\text{OCHPh}_2)_3$ , (c) reaction of  $\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$  (**6**) and  $\text{B}(\text{OCHPh}_2)_3$  with 1 equiv. of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) and (d)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**). “s” denotes residual protio-solvent.

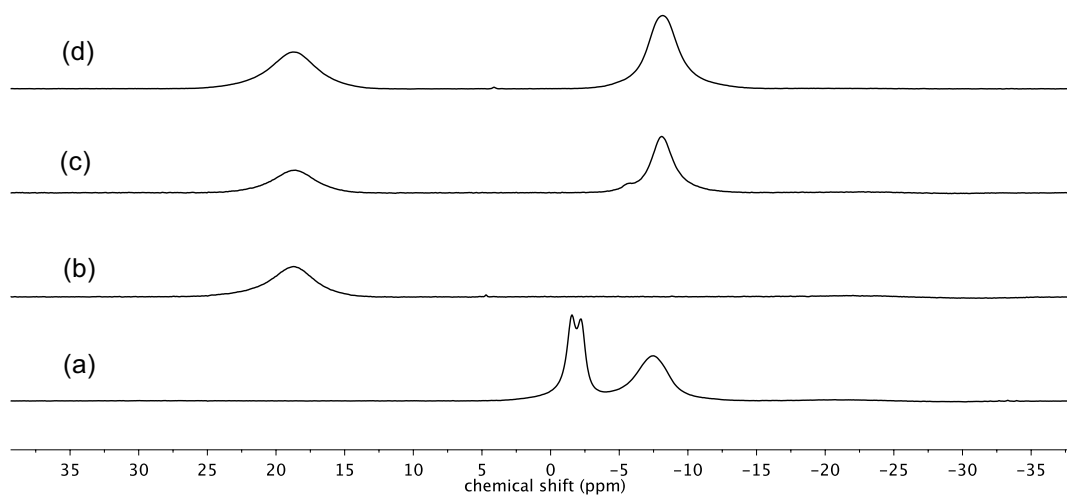


**Figure 2.22**  $^{11}\text{B}$  NMR spectra (THF- $d_8$ , 160.4 MHz, 298K) of (a)  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**), (b)  $\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$  (**6**) and  $\text{B}(\text{OCHPh}_2)_3$ , (c) reaction of  $\text{Ca}(\text{OCHPh}_2)_2(\text{THF})_x$  (**6**) and  $\text{B}(\text{OCHPh}_2)_3$  with 1 equiv. of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) and (d)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**).

### 2.4.3 Identification of first hydride transfer product of *L*-LA with (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**)

As previously mentioned in section 2.2.6, the spectroscopic evidence for the presence of a non-opened ring LA moiety as a product of hydride transfer from **1** to *rac*-LA in THF-*d*<sub>8</sub> prepared at RT was not observed by <sup>1</sup>H NMR. An NMR tube scale reaction of **1** and 5 equiv. of *L*-LA was performed in THF-*d*<sub>8</sub> at 223 K. *L*-LA was therefore employed to give a simpler spectrum (*cf rac*-LA). In addition, due to the slow rate of the ROP of *L*-LA with **1**, the first hydride transfer product would persist for longer. An excess amount of *L*-LA (5 equiv.) was used to guarantee that all hydrides were reacted.

A solution of 5 equiv. of *L*-LA was added into **1** in THF-*d*<sub>8</sub> at 195 K. The <sup>1</sup>H NMR spectrum recorded after 10 min at 223 K (Figure 2.23) shows signals corresponding to (Tp<sup>tBu,Me</sup>)Ca(*L*-LA-H)(THF)<sub>x</sub>. Signals for methine, methyl and *tert*-butyl protons on the pyrazolyl rings of (Tp<sup>tBu,Me</sup>)Ca(*L*-LA-H)(THF)<sub>x</sub> were observed at 5.84, 2.38 and 1.32 ppm, respectively. Three characteristic signals of a non-opened LA ring moiety were assigned in the diagnostic region of 4.0-6.0 ppm based on the characterisation of (Tp<sup>tBu,Me</sup>)Mg(*rac*-LA-H)<sup>47</sup> and (Tp<sup>m\*</sup>)Mg(*L*-LA-H)<sup>55</sup>. The methine proton of CaOCH (H<sub>a</sub>) appeared as a doublet at 5.53 ppm (<sup>3</sup>J<sub>H-H</sub> = 1.6 Hz) due to coupling with its neighbouring methine proton (H<sub>b</sub>). Methine proton (H<sub>b</sub>), which coupled to both of H<sub>a</sub> and its adjacent methyl group, showed as apparent quartet at 4.23 ppm with <sup>3</sup>J<sub>H-H</sub> coupling constants of 5.3 and 7.2 Hz. The other methine proton (H<sub>c</sub>) coupled with its adjacent methyl protons and appeared as a quartet at 4.28 ppm with <sup>3</sup>J<sub>H-H</sub> = 7.2 Hz. The H<sub>b</sub> and H<sub>c</sub> signals are partially overlapping. However, the signals became more separated as the temperature was increased (223-253 K). The ratio of relative integration of H<sub>a</sub>:(H<sub>b</sub> and H<sub>c</sub>) as 1:2 further supported the assignments of these three protons on the non-opened ring LA. Methylene and methyl protons of free BEt<sub>3</sub> signals could be seen as quartet at 0.45 ppm (<sup>3</sup>J<sub>H-H</sub> = 7.7 Hz) and triplet at 0.75 ppm (<sup>3</sup>J<sub>H-H</sub> = 7.7 Hz), respectively. Signals corresponding to Me(H<sub>b</sub>) and Me(H<sub>c</sub>) assigned to one set of doublet at 1.36 ppm (<sup>3</sup>J<sub>H-H</sub> = 6.5 Hz). The HSQC spectrum revealed two cross peaks exhibiting correlation between two different carbon shifts at 18.7 (CH<sub>b</sub>Me) and 15.0 (CH<sub>c</sub>Me) ppm with one doublet of methyl protons at 1.36 ppm. Additionally, the COSY spectrum displayed the through-bond correlation between methine protons, H<sub>b</sub> and H<sub>c</sub> (δ = 4.28, 4.23 ppm) with the CHMe protons of LA-H (δ = 1.36 ppm).



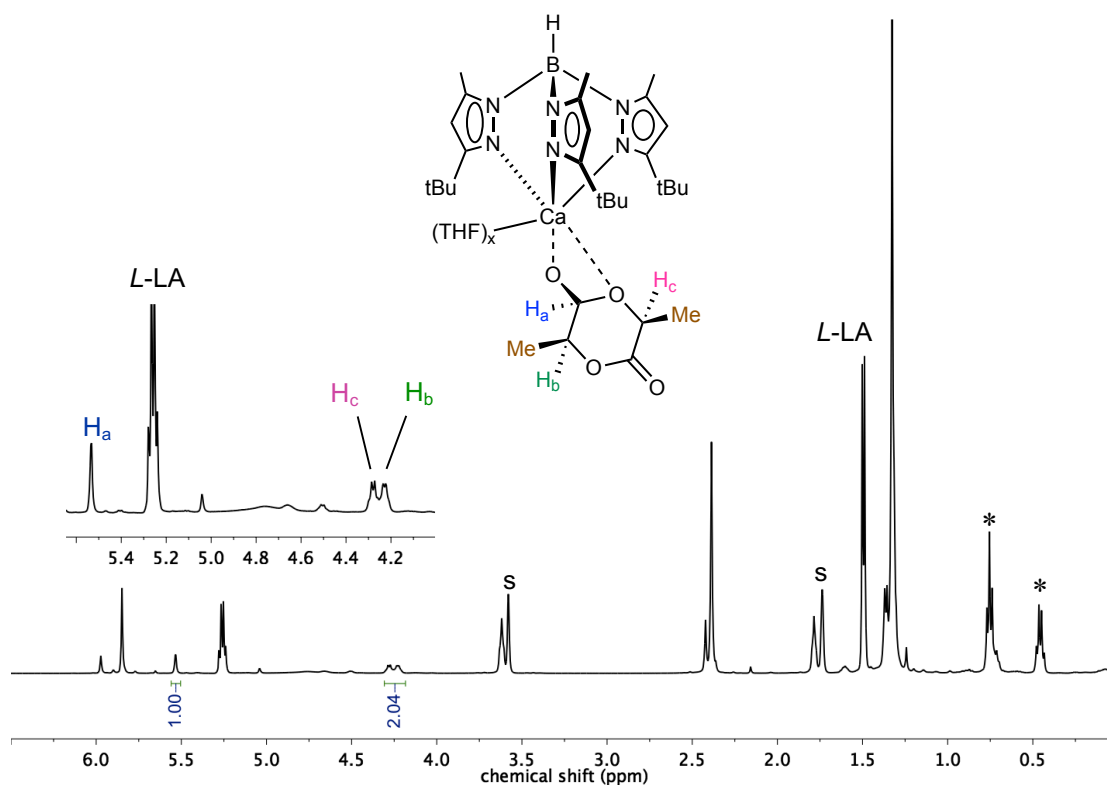


**Figure 2.23**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 223 K) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$  generated *in situ* from reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) and 5 equiv. of *L*-LA. “s” denotes residual protio-solvent. “\*” denotes free  $\text{BEt}_3$ . “*L*-LA” denotes unreacted *L*-LA.

ROESY NMR experiment was used to allow a full assignment based on through-space correlations. The ROESY spectrum shown in Figure 2.24 presents the expected correlation between  $\text{H}_a$  to *tert*-butyl groups on  $\text{Tp}^{\text{tBu,Me}}$  ligand, and  $\text{H}_a$  to  $\text{H}_b$  and  $\text{H}_c$ . The correlation of  $\text{H}_b$  and  $\text{H}_c$  to *tert*-butyl groups on the ligand was also visible. The  $^{11}\text{B}$  NMR spectrum recorded at 223 K revealed two broad singlets at 25.5 and -9.7 ppm corresponding to  $\text{BEt}_3$  and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively.

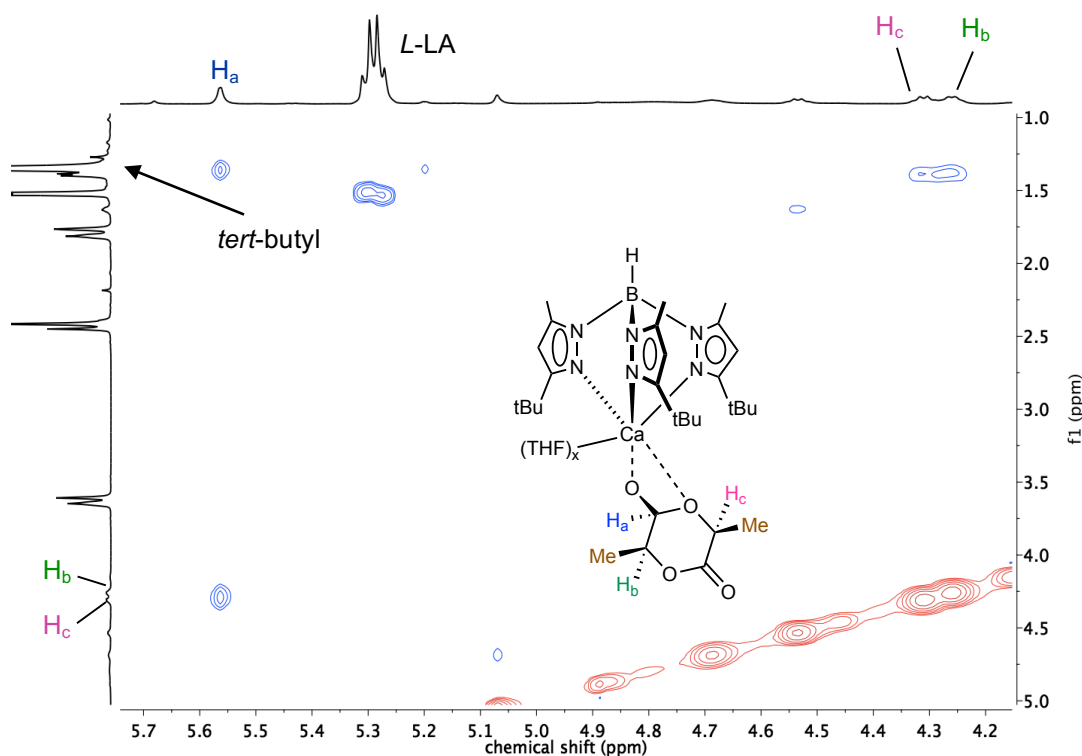


**Figure 2.24** ROESY NMR spectrum (THF- $d_8$ , 499.9 MHz, 223 K) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$  generated *in situ* from reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) and 5 equiv. of *L*-LA. “*L*-LA” denotes unreacted *L*-LA.

The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra were monitored at variable temperature from 223 K to 298 K. The  $^{11}\text{B}$  NMR spectrum recorded at 253 K showed a minor doublet at -2.1 ppm and a broad singlet at -8.4 ppm, suggesting the formation of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**). The  $^1\text{H}$  NMR spectrum recorded at 253 K (Figure 2.25) shows other set of signals consistent with three protons on a LA-H unit, tentatively indicating the presence of  $\text{Ca}(\text{L-LA-H})_2(\text{THF})_x$ . A doublet at 5.17 ppm ( $^3J_{\text{H-H}} = 3.3$  Hz) corresponds to  $\text{H}_d$  of  $\text{Ca}(\text{L-LA-H})_2(\text{THF})_x$ . A quartet at 4.50 ppm ( $^3J_{\text{H-H}} = 6.8$  Hz) and a quartet of doublets at 4.11 ppm ( $^3J_{\text{H-H}} = 6.5, 3.5$  Hz) are assigned to  $\text{H}_f$  and  $\text{H}_e$  of  $\text{Ca}(\text{L-LA-H})_2(\text{THF})_x$ , respectively. The relative integration ratio of 1.1:1.1:1.0 ( $\text{H}_d:\text{H}_f:\text{H}_e$ ) supports the identification of  $\text{Ca}(\text{L-LA-H})_2(\text{THF})_x$  species.

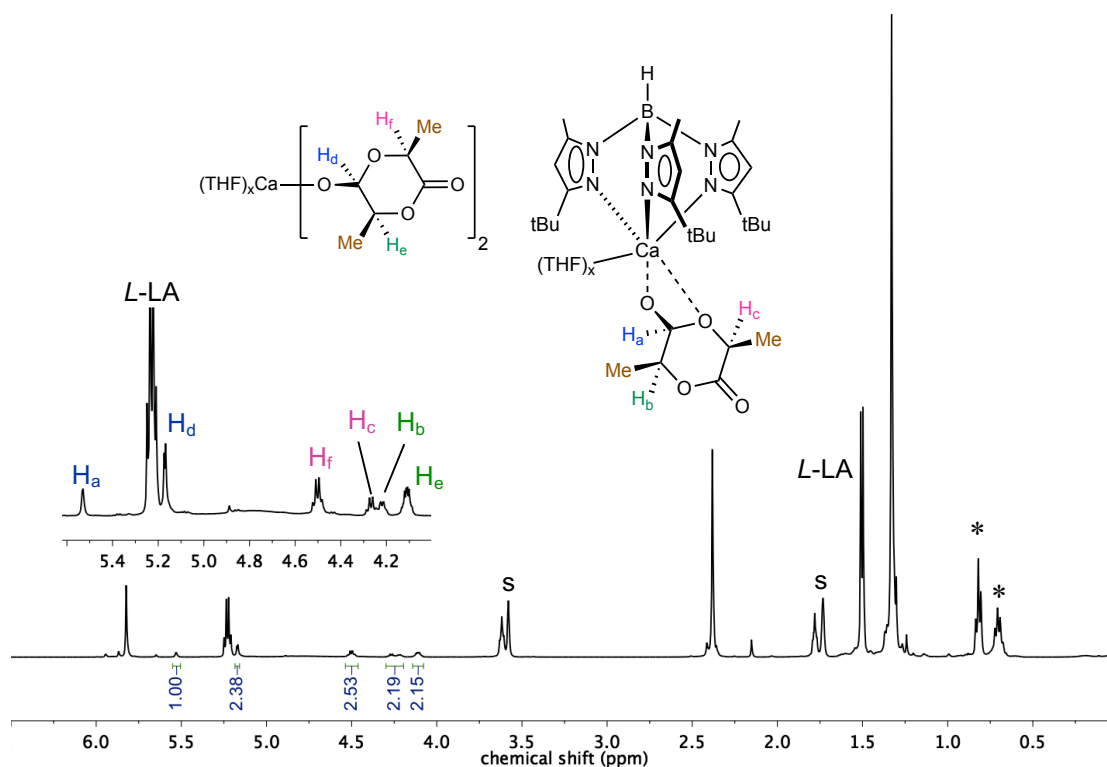


**Figure 2.25**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 253 K) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$  and  $\text{Ca}(\text{L-LA-H})_2(\text{THF})_x$  generated *in situ* from reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**) and 5 equiv. of *L*-LA. “s” denotes residual protio-solvent. “\*” denotes free  $\text{BEt}_3$ . “*L*-LA” denotes unreacted *L*-LA.

The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of the reaction of **1** with 5 equiv. of *L*-LA in  $\text{THF-}d_8$  was continuously recorded at 273 and 298 K. From the  $^1\text{H}$  NMR spectra, the characteristic signals of the first hydride transfer species were significantly diminished as the oligomeric LA formed. However, the non-opened ring LA as the end group of oligomeric LA coordinated to calcium could not be identified from the  $^1\text{H}$  NMR spectra at 273 or 298 K. The  $^{11}\text{B}$  NMR spectrum recorded at 298 K showed signals at 74.1 and -6.4 ppm corresponding to  $\text{BEt}_3$  and an unknown species containing a  $\text{Tp}^{\text{tBu,Me}}$  ligand, respectively.

#### 2.4.4 Identification of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{S-lactate})$ (**9**) from reaction of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$ (**5**) with *S*-methyl lactate

According to the proposed mechanism for the ROP of LA with alkaline earth organohydroborate complexes shown in Scheme 2.1, the propagating species containing an oligomeric chain terminated with LA-H initiating group on calcium was expected to be obtained from the reaction of **1** and 5 equiv. of *L*-LA. However, the

generation of the propagating species was not observed by  $^1\text{H}$  NMR. In an attempt to mimic the propagating species, an NMR tube scale reaction of **5** with *S*-methyl lactate was undertaken in  $\text{THF-}d_8$  at 223 K (Equation 2.2). The  $^1\text{H}$  NMR spectrum recorded at 223 K after 10 min (Figure 2.26) shows a quartet ( $\delta = 4.78$  ppm,  $^3J = 5.2$  Hz) and signal at 1.32 ppm corresponding to  $\text{CaOCH}$  and  $\text{CaOCH}(\text{Me})$  of **9**, respectively, imitating the formation of the first ring-opened LA unit from initiation step. The through-space correlations between *tert*-butyl on  $\text{Tp}^{\text{tBu,Me}}$  ligand to  $\text{OCH}$  and  $\text{OCH}(\text{Me})$  on the *S*-lactate unit were observed from the ROESY spectrum recorded at 223 K. The observation confirms the presence of lactate unit attached on calcium.

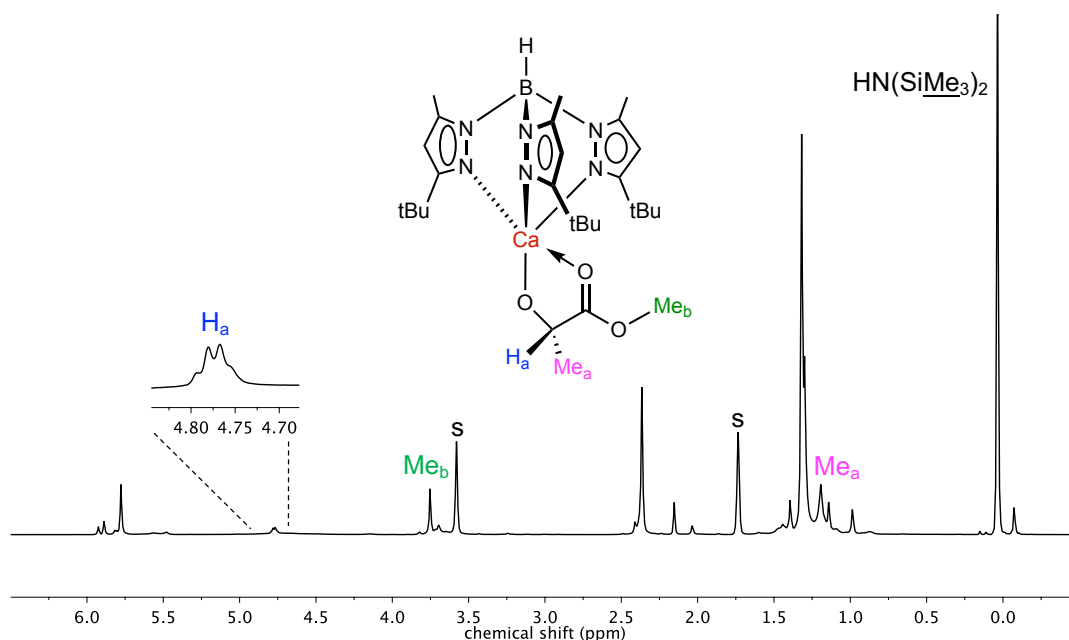
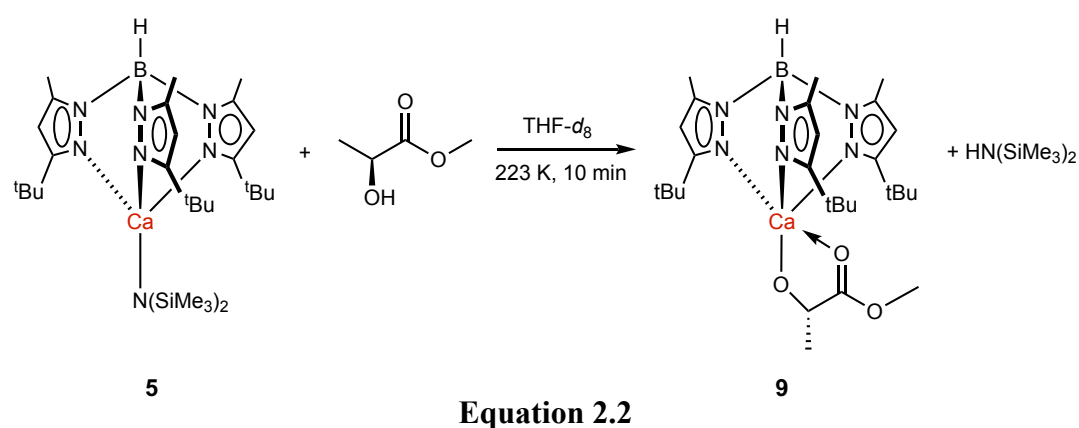
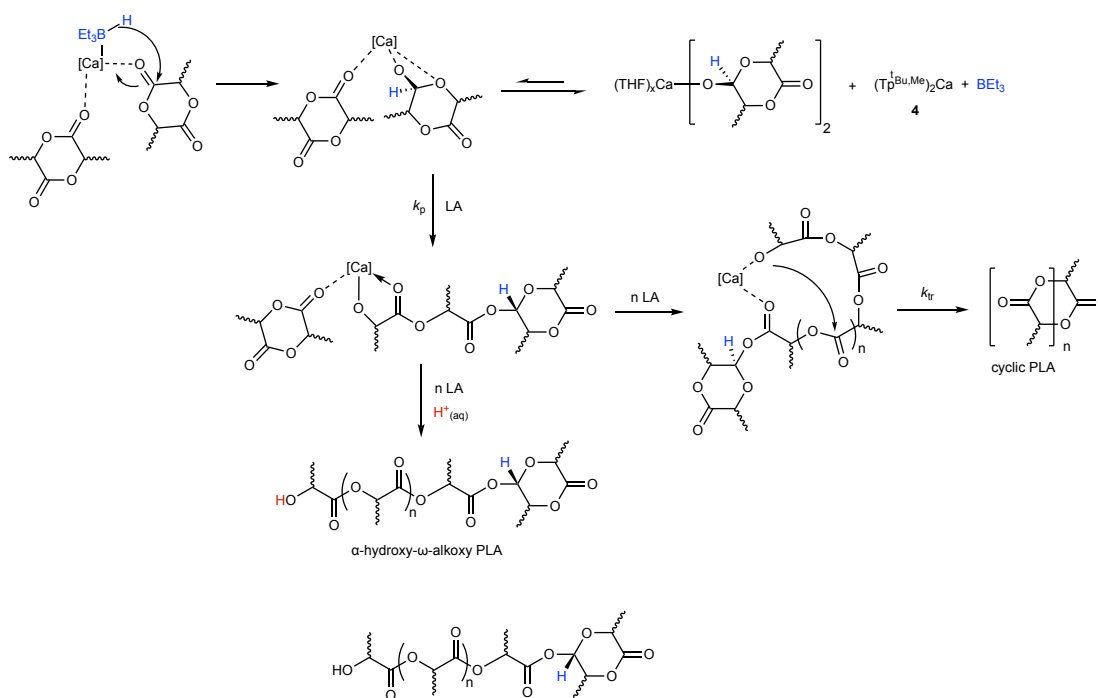


**Figure 2.26**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 223 K) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{S-lactate})(\text{THF})_x$  (**9**) generated *in situ* from reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) with *S*-methyl lactate. “s” denotes residual protio-solvent.

### 2.4.5 Proposed mechanism for the ROP of LA using $(\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{HBEt}_3)(\text{THF}))$ (1)

The mechanism for the ROP of LA using  $(\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{HBEt}_3)(\text{THF}))$  (1) is proposed based on the NMR spectroscopic data and polymerisation studies (Scheme 2.2). Hydride transfer from 1 to LA monomer generates the non-open LA ring alkoxide species,  $(\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{LA-H})(\text{THF})_x$  and free  $\text{BEt}_3$ , clearly identified in the  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra ( $\text{THF-}d_8$ ) recorded at 223 K.  $(\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{LA-H})(\text{THF})_x$  participates in the Schlenk equilibrium to produce  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (4) and  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$  observed by  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra.  $(\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{LA-H})(\text{THF})_x$  can act as the ROP initiator, with free  $\text{BEt}_3$  being innocent. A growing polymer chain terminated with non-opened LA ring group on calcium is formed during propagation, resulting in PLA terminated with a non-opened LA-H ring and  $-\text{OH}$  groups. In the later stages of polymerisation, intramolecular transesterification occurs extensively leading to the formation of cyclic PLA, as confirmed by MALDI-ToF mass spectrometry.



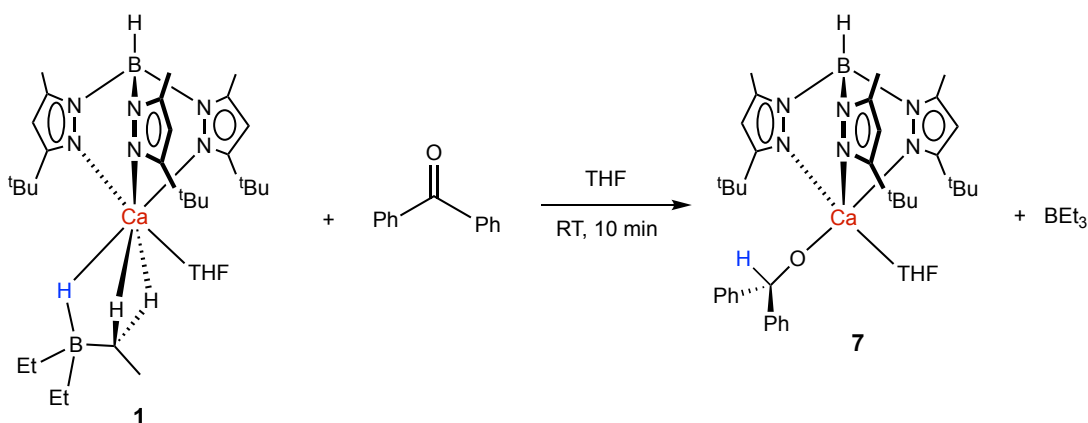
**Scheme 2.2** Proposed mechanism for the ROP of LA initiated by  $(\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{HBEt}_3)(\text{THF}))$  (1).  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{THF})_x$ .

## 2.5 Models for $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$

### 2.5.1 Synthesis and characterisation of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$ (**7**)

To confirm the role of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  as a ROP initiator, analogous calcium alkoxide complexes serving as models of the initiating species in the ROP catalysed by **1** were synthesised *via* reaction of **1** with ketones and aldehyde. Bulky ketones and aldehydes were selected to react with **1** in order to prevent the heteroleptic calcium complexes redistributing *via* the Schlenk equilibrium.

$(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) was instantaneously formed by an NMR tube scale reaction of **1** with 1 equiv. of benzophenone in  $\text{C}_6\text{D}_6$  or  $\text{THF-}d_8$ . The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra in  $\text{C}_6\text{D}_6$  or  $\text{THF-}d_8$  recorded after 10 min showed the signals corresponding to **7** and free  $\text{BEt}_3$ . It is worth noting that  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) was not observed in the  $^1\text{H}$  or  $^{11}\text{B}$  NMR spectra. The scale-up synthesis of **7** was achieved *via* reaction of **1** with benzophenone in a 1:1 molar ratio in THF (Equation 2.3). Diffraction-quality crystals of **7** were grown from a concentrated solution of **7** in THF:pentane (1:5, v/v) at  $-30\text{ }^\circ\text{C}$ . The molecular structure and selected distances and angles are shown in Figure 2.27 and Table 2.5.



Equation 2.3

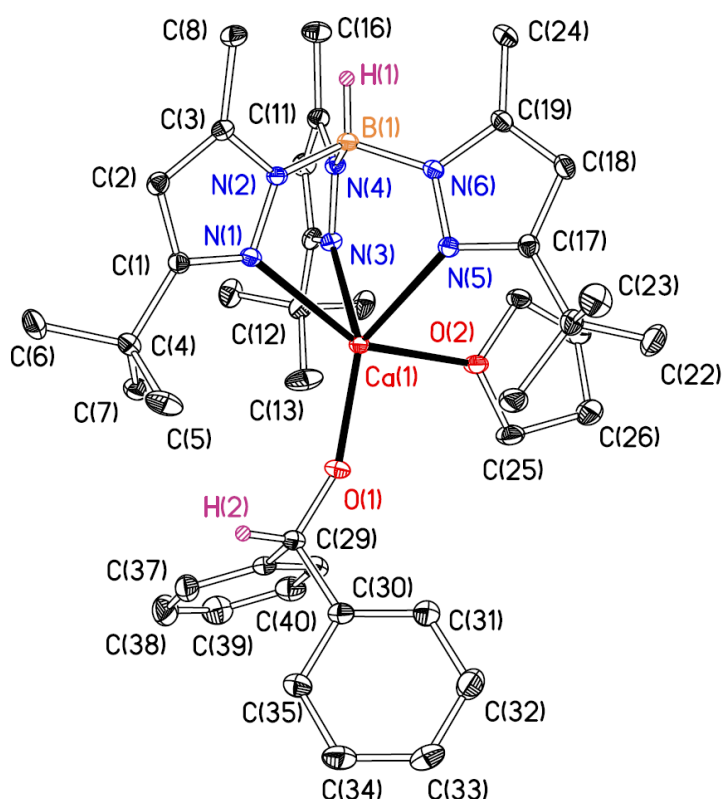


**Figure 2.27** Displacement ellipsoid plot of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**). H atoms are omitted. Ellipsoids are drawn at the 20% probability level.

**Table 2.5** Selected bond lengths (Å) and angles (°) for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**).

|                  |           |                 |           |
|------------------|-----------|-----------------|-----------|
| Ca(1)-O(1)       | 2.1102(7) | Ca(1)-N(1)      | 2.4821(8) |
| Ca(1)-N(3)       | 2.4790(8) | Ca(1)-N(5)      | 2.4813(8) |
| Ca(1)-O(2)       | 2.4134(7) |                 |           |
| O(1)-Ca(1)-N(1)  | 110.93(3) | O(1)-Ca(1)-N(3) | 141.54(3) |
| O(1)-Ca(1)-N(5)  | 128.17(3) | N(1)-Ca(1)-N(3) | 74.39(3)  |
| N(1)-Ca(1)-N(5)  | 80.43(3)  | N(3)-Ca(1)-N(5) | 90.16(3)  |
| N(1)-Ca(1)-O(2)  | 153.05(3) | N(3)-Ca(1)-O(2) | 84.12(3)  |
| N(5)-Ca(1)-O(2)  | 83.62(3)  | O(1)-Ca(1)-O(2) | 96.01(3)  |
| C(29)-O(1)-Ca(1) | 158.15(7) |                 |           |

Complex **7** is five-coordinated where calcium is bonded to the three nitrogen atoms on pyrazolyl rings, O atom on the aryloxy ligand and O atom from THF molecule, to give a distorted trigonal bipyramidal geometry. The crystal structure of **7** shows calcium sharing the plane with O(1), N(3) and N(5) in the equatorial site. The angles N(3)-Ca(1)-N(5), O(1)-Ca(1)-N(3) and O(1)-Ca(1)-N(5) equal to 90.16(3), 141.54(3)

and  $128.17(3)^\circ$ , respectively. The O(2) from THF molecule and N(1) bind to calcium in the axial positions with a distinctly non-linear angle O(2)-Ca(1)-N(1) of  $153.05(3)^\circ$ . The average Ca-N bond distances are  $2.4808(8)$  Å. The Ca(1)-O(1) distance of  $2.1102(7)$  Å is comparable to the Ca-O<sub>aryl</sub> bond length of  $2.106(1)$  Å of (Tp<sup>tBu</sup>)Ca(O-2,6-C<sub>6</sub>H<sub>3</sub><sup>i</sup>Pr<sub>2</sub>) (**2.15**).<sup>26</sup>

### 2.5.2 ROP of *rac*- and *meso*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**)

The polymerisation of *rac*-LA was conducted in THF at RT with a [*rac*-LA]<sub>0</sub>:**7**<sub>0</sub> ratio of 800:1 (Table 2.6, entry 1). Complex **7** exhibits high ROP activity, reaching 94% conversion within 3 min. Similar to the ROP with *rac*-LA using **1**, an induction period was not observed using **7**. The plot of  $1/[rac\text{-}LA]_0$  vs. time is linear (Figure 2.28), indicating a second-order dependence on [*rac*-LA] ( $k_{app} = 0.176(9) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.989$ ). Thus, the rate of polymerisation can be written as  $-d[rac\text{-}LA]/dt = k_{app}[rac\text{-}LA]^2$ , where  $k_{app} = k_p[\mathbf{7}]^x$  and  $k_p$  is the propagation rate constant. Further polymerisations were conducted with various concentrations of **7** in THF at RT in order to establish  $k_p$  and the kinetic order in **7**. Second-order dependence on [*rac*-LA] was observed (Figure 2.28), and values of  $k_{app}$  are reported in Table 2.6. The gradient of  $1.12(10)$  ( $R^2 = 0.984$ ) obtained from the plot between  $-\ln(k_{app})$  vs.  $-\ln[\mathbf{7}]_0$  (Figure 2.29, right) is indicative of a first-order dependence on **7**. The  $k_p$  value of  $332(24) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.990$ ) is calculated from the fitted line between  $k_{app}$  vs.  $[\mathbf{7}]_0$  (Figure 2.29, left). Therefore, the overall rate law is  $-d[rac\text{-}LA]/dt = k_p[rac\text{-}LA]^2[\mathbf{7}]$ , where  $k_p = 332(24) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.990$ ).



**Table 2.6** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**).<sup>a</sup>

| Entry | [ <i>rac</i> -LA] <sub>0</sub> : [ <b>7</b> ] <sub>0</sub> | Conv. <sup>b</sup><br>(%) | Time<br>(s) | <i>M</i> <sub>n</sub> (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>k</i> <sub>app</sub> <sup>f</sup><br>(M <sup>-1</sup> s <sup>-1</sup> ) | <i>R</i> <sup>2f</sup> | <i>P</i> <sub>r</sub> <sup>g</sup> |
|-------|------------------------------------------------------------|---------------------------|-------------|--------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------|----------------------------------------------------------------------------|------------------------|------------------------------------|
| 1     | 800                                                        | 94                        | 180         | 77,580                                                             | 108,547                                                              | 1.57                  | 0.176(9)                                                                   | 0.989                  | 0.82                               |
| 2     | 500                                                        | 93                        | 120         | 68,580                                                             | 67,191                                                               | 1.27                  | 0.249(14)                                                                  | 0.991                  | 0.78                               |
| 3     | 300                                                        | 94                        | 60          | 40,940                                                             | 40,820                                                               | 1.20                  | 0.533(14)                                                                  | 0.999                  | 0.82                               |
| 4     | 200                                                        | 94                        | 40          | 36,280                                                             | 27,275                                                               | 1.28                  | 0.775(30)                                                                  | 0.999                  | 0.83                               |
| 5     | 100                                                        | 96                        | 30          | 10,960                                                             | 14,018                                                               | 1.59                  | <sup>h</sup>                                                               | <sup>h</sup>           | 0.81                               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub> = 0.5 M, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated *M*<sub>n</sub> (g mol<sup>-1</sup>) for –OH and –OCHPh<sub>2</sub> end groups, *M*<sub>n</sub> (entry 1-5) = conv. (%) × [*rac*-LA]<sub>0</sub>: [**7**]<sub>0</sub> × 144.1 + 184.1. <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> Apparent second order rate constant for consumption of monomer with standard error and *R*<sup>2</sup> determined by linear regression analysis. <sup>g</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>h</sup> Not measured.

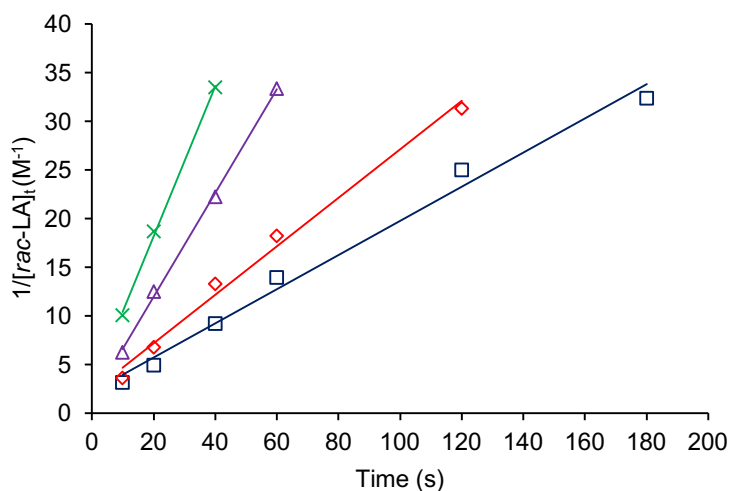


**Figure 2.28** ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**). Plots of  $1/[rac-LA]_0$  vs. time. Conditions: 6 mL THF, RT,  $[rac-LA]_0 = 0.5$  M. Squares:  $[rac-LA]_0:[7]_0 = 800:1$  ( $k_{app} = 0.176(0) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.989$ ). Diamonds:  $[rac-LA]_0:[7]_0 = 500:1$  ( $k_{app} = 0.249(14) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.991$ ). Triangles:  $[rac-LA]_0:[7]_0 = 300:1$  ( $k_{app} = 0.533(14) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.999$ ). Crosses:  $[rac-LA]_0:[7]_0 = 200:1$  ( $k_{app} = 0.775(30) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.999$ ).

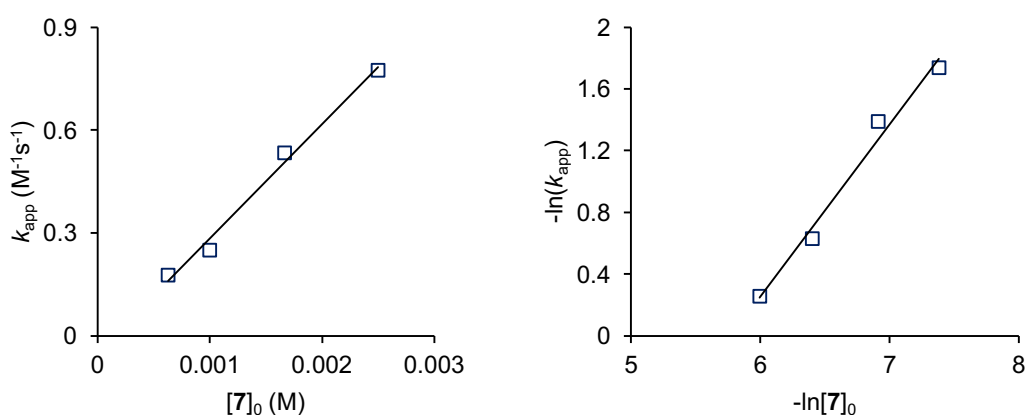


**Figure 2.29** Left, plot of  $k_{app}$  vs.  $[7]_0$ , for ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**),  $k_p = 332(24) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.990$ ). Right, plot of  $-\ln(k_{app})$  vs.  $-\ln[7]_0$  shows an order in  $[7]$  equal to  $1.12(10)$  ( $R^2 = 0.984$ ).

Similar to the ROP with **1**, the greater propagation rate than initiation rate was more pronounced when  $[rac-LA]_0:[7]_0 = 500, 300$  or  $200$ . Therefore, close agreement between measured and calculated  $M_n$  based on one growing polymer chain per metal centre was observed from the ROP with  $[rac-LA]_0:[7]_0 = 500, 300$  and  $200$  (Figure 2.30). For  $[rac-LA]_0:[7]_0 = 800$ , poor agreement between measured and calculated  $M_n$  based on one polymer chain per metal centre was visible due to intramolecular

transesterification reaction occurred extensively at high conversions (Figure 2.30). Narrow to moderate  $\bar{D}$  values (1.05-1.57) were obtained. Heterotactically-enriched PLAs ( $P_r = 0.78$ -0.83) were achieved. It is worth noting that a degree of heteroselectivity observed from ROP of *rac*-LA using **1** or **7** is comparable.

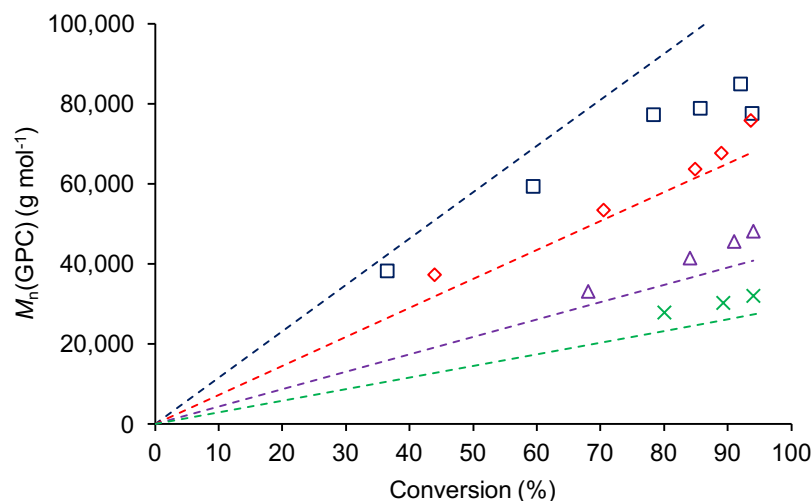


**Figure 2.30** Plots of  $M_n$ (GPC) vs. conversion (%) for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**). Conditions: 6 mL THF, RT,  $[\text{rac-LA}]_0 = 0.5$  M. The dashed lines represent  $M_n(\text{calcd})$  for one PLA chain per metal centre. Squares:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 800:1$ ,  $\bar{D} = 1.05$ -1.57. Diamonds:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 500:1$ ,  $\bar{D} = 1.06$ -1.27. Triangles:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 300:1$ ,  $\bar{D} = 1.09$ -1.20. Crosses:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 200:1$ ,  $\bar{D} = 1.12$ -1.28.

End-group analysis by MALDI-ToF mass spectrometry (Figure 2.31) demonstrates an occurrence of intramolecular transesterification as a major distribution of cyclic PLA observed. The peak envelopes are separated by  $\Delta m/z = 72.0$  Da indicating transesterification reactions. PLA chains terminated with  $-\text{OCHPh}_2$  and  $-\text{OH}$  groups are presented as a minor contribution. For example, a peak envelope centred at 975.4 Da is assigned to cyclic PLA containing 13 units of half LA with  $\text{K}^+$ . Another peak envelope centred at 1087.6 Da is attributed to PLA terminated with  $-\text{OCHPh}_2$  comprising 12 units of half LA with  $\text{K}^+$   $[72.0(12) + 184.1 + 39.1]$ . The  $^1\text{H}$  NMR spectrum of isolated PLA (Figure 2.32) shows a singlet for the  $-\text{OCHPh}_2$  end group at 6.88 ppm, and the signals of  $-\text{OCHPh}_2$  at 7.29-7.34 ppm.

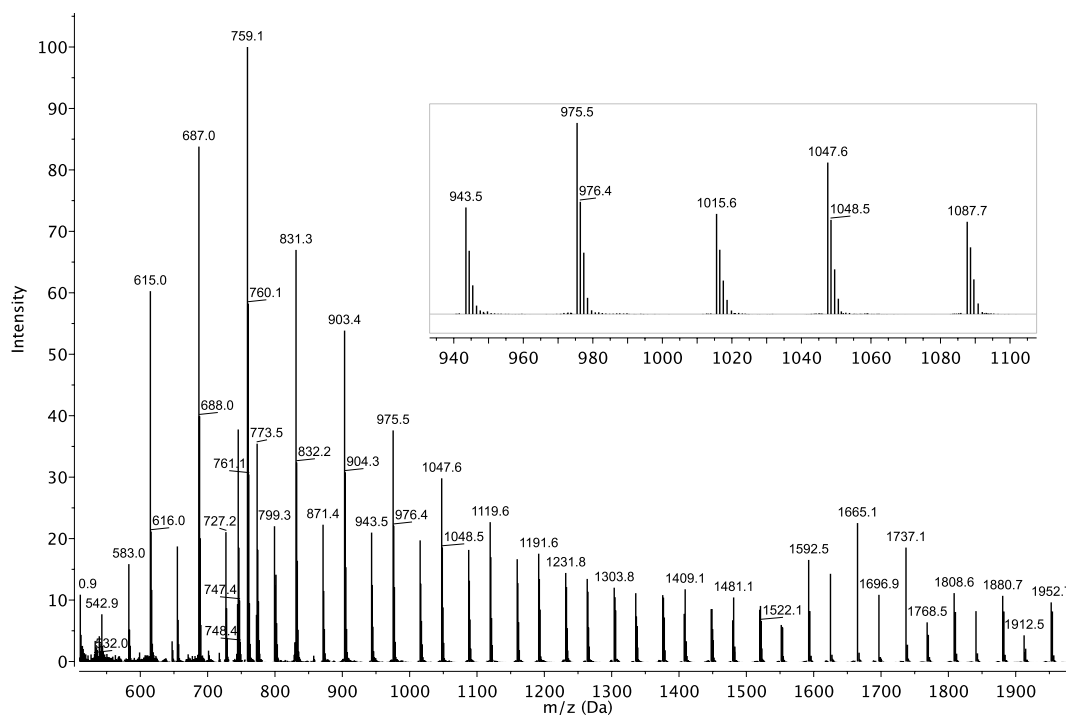


**Figure 2.31** MALDI-ToF MS of PLA synthesised from  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**).  $M_n(\text{GPC}) = 3,140 \text{ g mol}^{-1}$ ,  $D = 1.28$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ , 1.0 mL THF at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes.

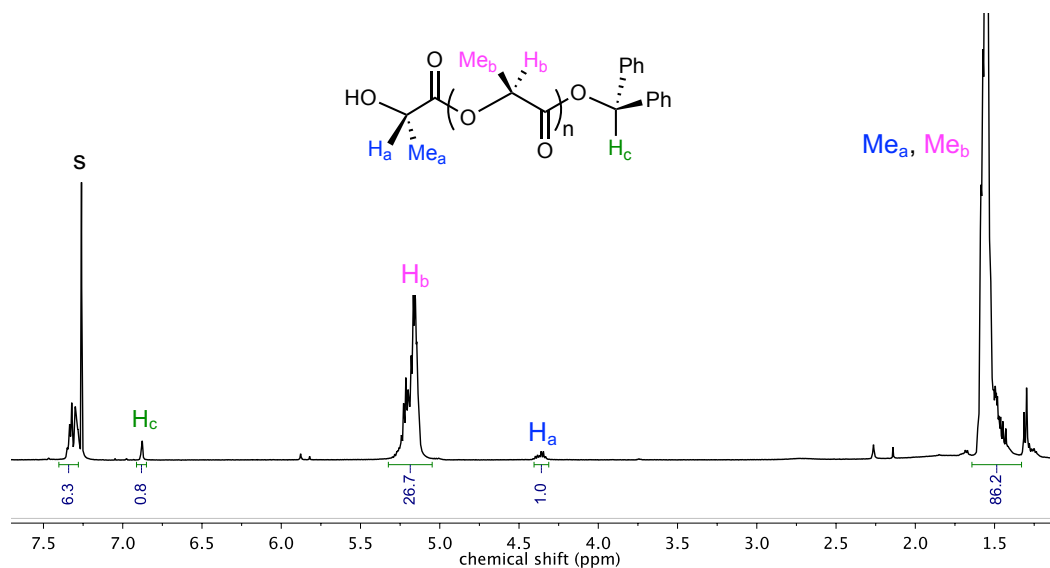


**Figure 2.32**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PLA synthesised from using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**).  $M_n(\text{NMR})$  for  $-\text{OH}$  and  $-\text{OCHPh}_2$  terminated PLA =  $4,031 \text{ g mol}^{-1}$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ , 1.0 mL THF at RT. “s” denotes residual protio-solvent.

An NMR tube scale reaction of **7** with 1 equiv. of *L*-LA was performed in THF-*d*<sub>8</sub> at 223 K in order to observe the propagating species. However, the <sup>1</sup>H NMR spectrum showed only signals of **7** and *L*-LA, indicating the initiation step was absent at 223 K. The temperature was then increased to 263 K. The <sup>1</sup>H NMR spectrum recorded at 263 K (Figure 2.33) shows a quartet at 4.82 ppm (<sup>3</sup>*J* = 6.8 Hz) corresponding to the methine proton (*H*<sub>a</sub>) of the LA unit chelated with calcium. This *H*<sub>a</sub> coupled with its adjacent methyl protons (*Me*<sub>a</sub>) results in a doublet signal at 1.38 ppm (<sup>3</sup>*J* = 6.0 Hz). Multiple signals in the region of 5.0-5.5 ppm correspond to non-chelated methine protons in conjunction with signals of unreacted **7** suggest that more than one LA unit incorporated with the growing chain on calcium due to the faster propagation than initiation rate. A singlet at 6.90 ppm was assigned to *H*<sub>c</sub> of the OCHPh<sub>2</sub> end group.

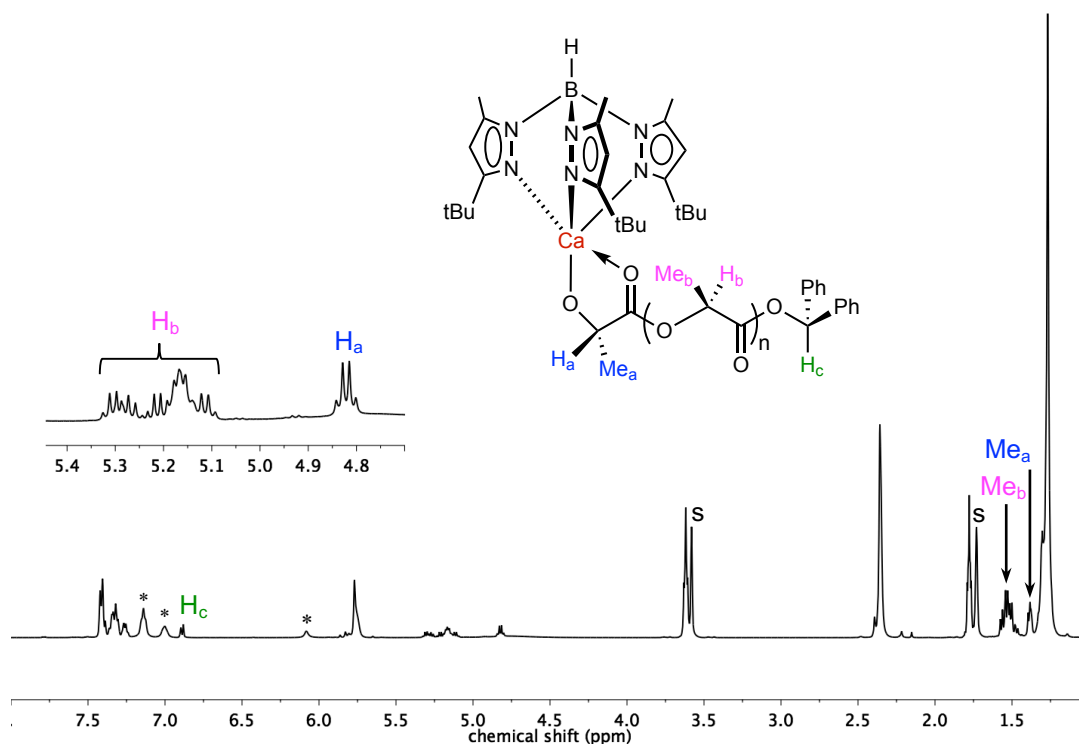


**Figure 2.33** <sup>1</sup>H NMR spectrum (THF- *d*<sub>8</sub>, 499.9 MHz, 263 K) of reaction of (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**) with 1 equiv. of *L*-LA. “s” denotes residual protio-solvent. “\*” denotes unreacted **7**.

The ROESY spectrum confirms the assignment for the propagating species by providing through-space correlation of *tert*-butyl groups on the Tp<sup>tBu,Me</sup> ligand with the methine protons (*H*<sub>a</sub> and *H*<sub>b</sub>) on the ring-opened LA unit and the methine proton (*H*<sub>c</sub>) on the end group. The <sup>11</sup>B NMR spectrum showed a broad singlet at -8.1 ppm corresponding to the apical B-H of the Tp<sup>tBu,Me</sup> ligand. It is worth noting that the signals

corresponding to  $H_a$  and  $Me_a$  appeared in a similar region to those obtained from reaction of **5** and *S*-methyl lactate as described in section 2.4.4.

In order to study the effect of  $BEt_3$  on the polymerisation rate and polymer tacticity, ROP of *rac*-LA using **7** with addition of 1 equiv. of  $BEt_3$  (Table 2.7, entry 2) or *in situ* generated catalyst **1** with 1 equiv. of benzophenone (Table 2.7, entry 3) were performed under analogous conditions to compare with the ROP of *rac*-LA using **7** (Table 2.7, entry 1).

**Table 2.7** Selected data for the ROP of *rac*-LA using  $(Tp^{tBu,Me})Ca(HBEt_3)(THF)$  (**1**) and  $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$  (**7**) with additives.<sup>a</sup>

| Entry | Initiator | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>7</b>  | -        | 94                        | 180         | 77,580                                                | 108,547                                                 | 1.57                   | 0.82               |
| 2     | <b>7</b>  | $BEt_3$  | 94                        | 180         | 75,590                                                | 108,547                                                 | 1.41                   | 0.78               |
| 3     | <b>1</b>  | PhCOPh   | 94                        | 180         | 79,220                                                | 108,547                                                 | 1.42                   | 0.82               |

<sup>a</sup> Conditions:  $[rac\text{-LA}]_0:[\text{initiator}]_0:[\text{additive}]_0 = 800:1$  as stated,  $[rac\text{-LA}]_0 = 0.5$  M,  $[\text{initiator}]_0 = 625$   $\mu$ M, 6.0 mL THF at RT. <sup>b</sup> Measured by  $^1H$  NMR ( $CDCl_3$ ) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4$   $\mu$ L g<sup>-1</sup> and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for  $-OH$  and  $-OCHPh_2$  end groups = conv. (%)  $\times 800 \times 144.1 + 184.1$ . <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by  $^1H\{^1H\}$  NMR ( $CDCl_3$ ) analyses.

In each case, the monomer consumption was up to 94% after 3 min. As shown in Figure 2.34 (left), the second order  $k_{app}$  values measured by using **7** with  $BEt_3$  or **1** with benzophenone are identical within error compared to that from **7**. Plots of  $M_n(\text{GPC})$  vs. conversion (%) exhibit the dominant of transesterification reactions in the final ROP stages resulting in poor agreement between experiment and calculated  $M_n$  values (Figure 2.34, right). Heterotactically-enriched PLAs with  $P_r = 0.78\text{--}0.82$  were attained (Table 2.7). The MALDI-ToF mass spectrometry of PLA synthesised *via* **7** and  $BEt_3$  showed two types of polymer, cyclic PLA and PLA terminated with  $-OH$  and  $-OCHPh_2$  groups. Due to the identical  $k_{app}$  values, comparable  $M_n(\text{GPC})$  and similar degree of hetero-selectivity of PLA obtained from the ROP of *rac*-LA using **7** with and without  $BEt_3$ , the innocent role of  $BEt_3$  on the ROP activity and stereoselectivity was determined.

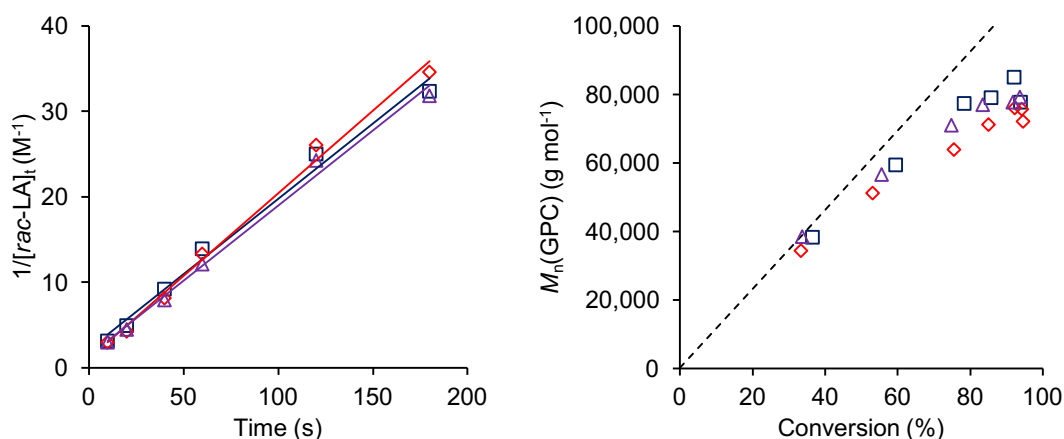


**Figure 2.34 Left**, Plots of  $1/[rac-LA]_0$  vs. time. Squares:  $[rac-LA]_0:[7]_0 = 800:1$  ( $k_{app} = 0.176(9)\ M^{-1}s^{-1}$ ,  $R^2 = 0.989$ ). Diamonds:  $[rac-LA]_0:[7]_0:[BET_3] = 800:1:1$  ( $k_{app} = 0.193(8)\ M^{-1}s^{-1}$ ,  $R^2 = 0.993$ ). Triangles:  $[rac-LA]_0:[1]_0:[PhCOPh] = 800:1:1$  ( $k_{app} = 0.176(8)\ M^{-1}s^{-1}$ ,  $R^2 = 0.993$ ). **Right**, Plots of  $M_n(GPC)$  ( $g\ mol^{-1}$ ) vs. conversion (%). Squares:  $[rac-LA]_0:[7]_0 = 800:1$ ,  $\bar{D} = 1.05-1.57$ . Diamonds:  $[rac-LA]_0:[7]_0:[BET_3] = 800:1:1$ ,  $\bar{D} = 1.10-1.41$ . Triangles:  $[rac-LA]_0:[1]_0:[PhCOPh] = 800:1:1$ ,  $\bar{D} = 1.08-1.42$ . The dashed line represents  $M_n(calcd)$  for one PLA chain per metal centre.

The ROP of *meso*-LA promoted by **7** was very active, reaching 94% conversion after 1 min. The first order dependence on  $[meso-LA]$  was observed ( $k_{app} = 0.0401(4)\ s^{-1}$ ,  $R^2 = 0.999$ ) (Figure 2.35, left). The shift of kinetic order dependence on monomer concentration exhibited, from the second order on  $[rac-LA]$  to the first order on  $[meso-LA]$ . This observation is consistent with that for the ROP of *meso*-LA with **1**. Poor agreement between measured and calculated  $M_n$  values was observed due to transesterification reactions at high conversions (Figure 2.35, right). Syndiotactically-enriched PLA with  $P_r = 0.87$  was produced.

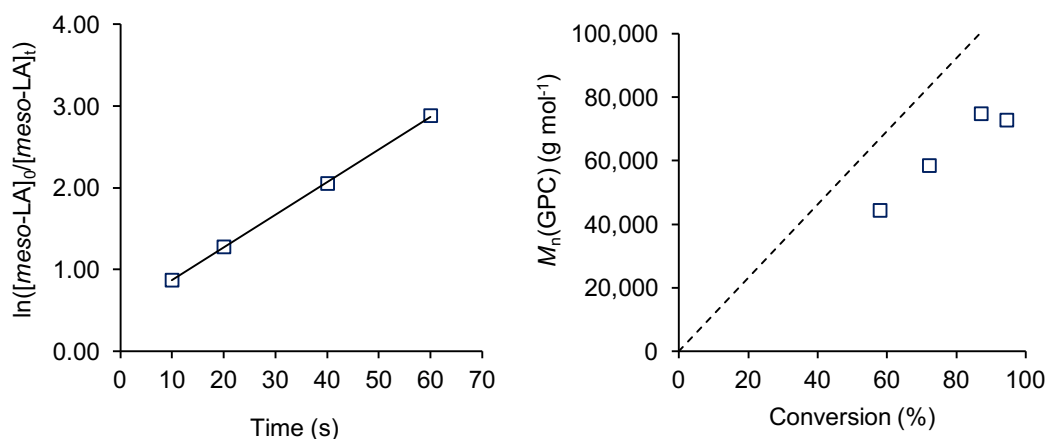
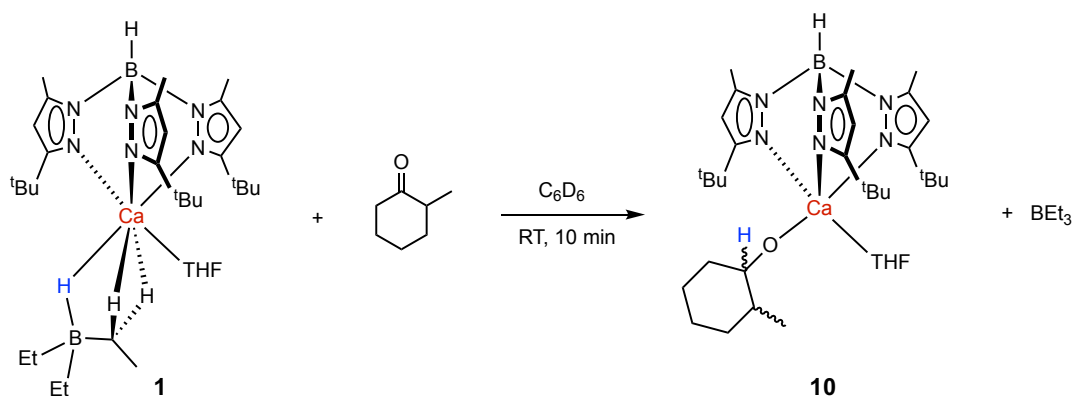


**Figure 2.35** Left, plot of  $\ln([meso-LA]_0/[meso-LA]_t)$  vs. time ( $k_{app} = 0.0401(4) \text{ s}^{-1}$ ,  $R^2 = 0.999$ ). Right, plot of  $M_n(\text{GPC})$  vs. conversion (%). The dashed line represents  $M_n(\text{calcd})$  for one PLA chain per metal centre.  $\bar{D} = 1.07\text{--}1.21$ . Condition: 6 mL THF, RT,  $[meso-LA]_0:[7]_0 = 800:1$ ,  $[meso-LA]_0 = 0.5 \text{ M}$ .

### 2.5.3 Synthesis and characterisation of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$ (**10**)

Following the promising ROP studies using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**),  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) was introduced as another model of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$ . An NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**) with 1 equiv. of 2-methylcyclohexanone was performed in  $\text{C}_6\text{D}_6$ , giving the immediate formation of **10** with  $\text{BEt}_3$  (Equation 2.4).



**Equation 2.4**

Homoleptic  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) was not observed from  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra. Due to the two possible conformations of 2-methylcyclohexanone, hydride reduction could occur at either the axial or equatorial sides of the carbonyl carbon, yielding *cis*- and *trans*- isomeric complexes, giving possible four chair conformations. The  $^1\text{H}$  NMR spectrum of **10** synthesised from reaction of **1** and 2-methylcyclohexanone was shown



in Figure 2.36. A doublet of doublet of doublets at 3.67 ppm with  $^3J_{\text{H-H}} = 11.1, 7.5, 4.0$  ppm is assigned to the methine proton (OCH) of the *trans* isomer. While a multiplet at 4.43 ppm corresponds to the analogous proton of the *cis* isomer. The integral ratio of these two peaks is 1:9 indicating the formation of the *trans* isomer as a major product.

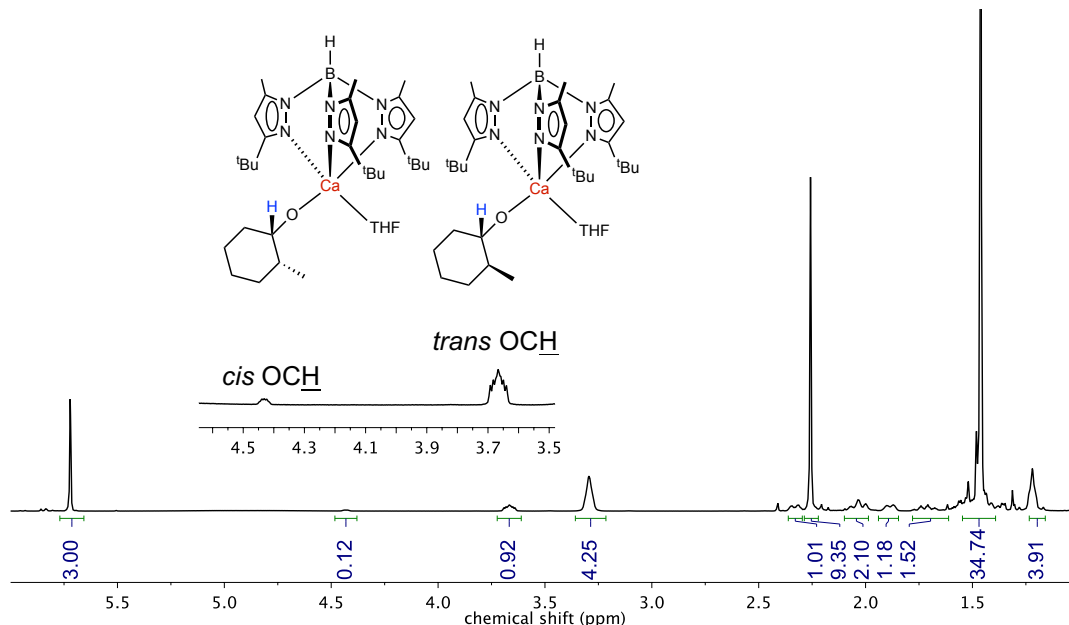
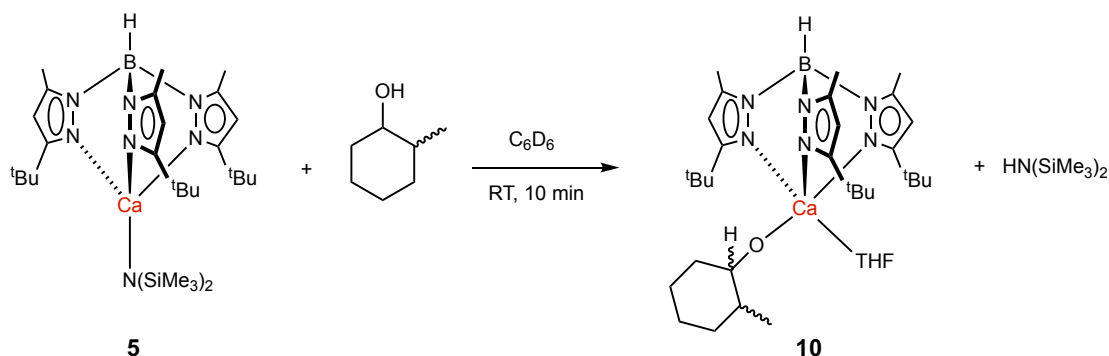


**Figure 2.36**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) synthesised from reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) and 2-methylcyclohexanone.

Complex **10** was alternatively synthesised *via* reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) with a mixture of *cis* and *trans* 2-methylcyclohexanol in a 1:1 molar ratio in  $\text{C}_6\text{D}_6$  (Equation 2.5).



**Equation 2.5**

The  $^1\text{H}$  NMR spectrum of **10** prepared *via* reaction of **5** and 2-methylcyclohexanol (Figure 2.37) displayed two sets of signals corresponding to the methine proton (OCH) of the *cis*- and *trans*- isomers, with the integration ratio of 1:1. Based on the vicinal

coupling constant ( $^3J_{\text{H-H}}$ ), a triplet of doublets shown at 3.56 ppm with  $^3J_{\text{H-H}} = 9.4, 4.1$  Hz is assigned to methine proton (OCH) of the *trans*-isomer, while a doublet of triplets appeared at 4.34 ppm with  $^3J_{\text{H-H}} = 5.7, 2.7$  Hz corresponds to methine proton (OCH) of the *cis*-isomer (Figure 2.37).

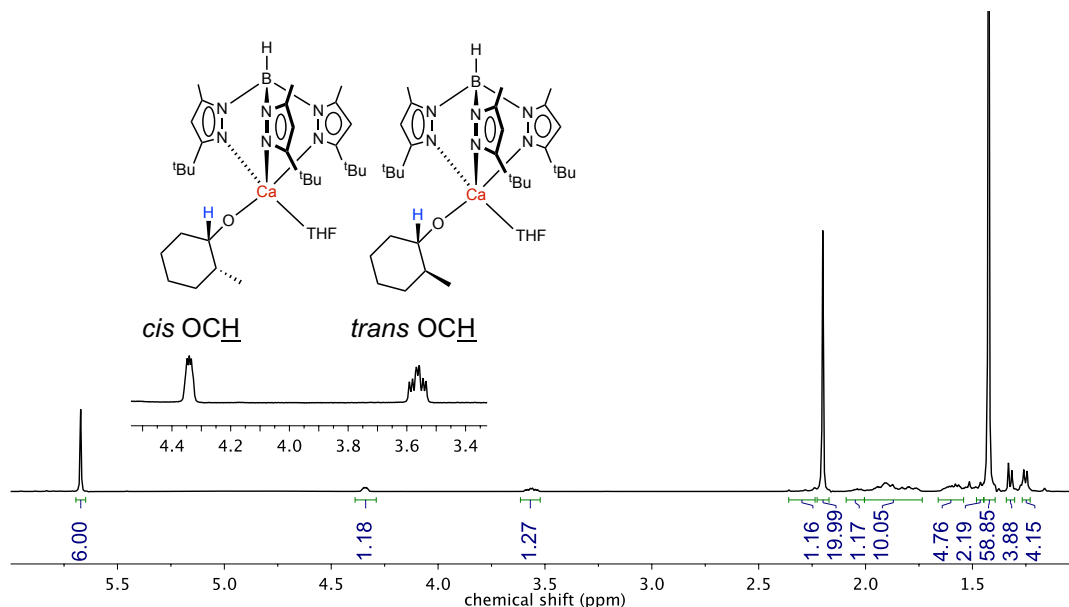


**Figure 2.37**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) generated *in situ* from reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) and 2-methylcyclohexanol.

Diffraction-quality crystals of **10** were grown from a concentrated solution of **10** in benzene at 4 °C. The molecular structure and selected distances and angles are shown in Figure 2.38 and Table 2.8.

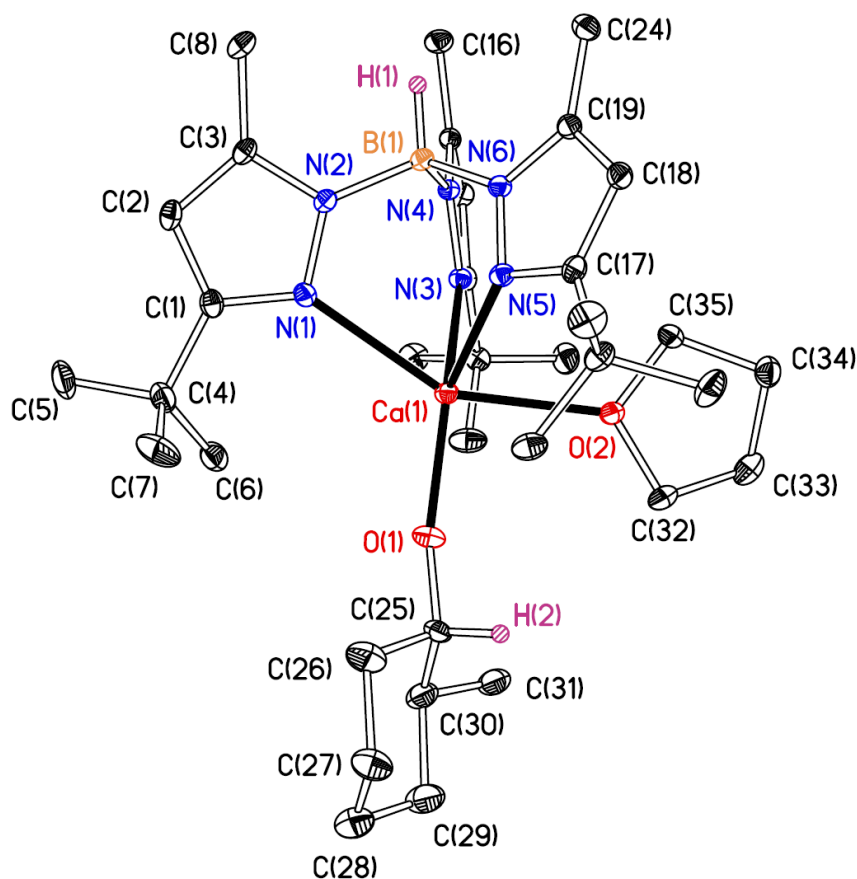


**Figure 2.38** Displacement ellipsoid plot of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**). H atoms are omitted. Ellipsoids are drawn at the 20% probability level.

**Table 2.8** Selected bond lengths (Å) and angles (°) for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**).

|                 |            |                 |            |
|-----------------|------------|-----------------|------------|
| Ca(1)-O(1)      | 2.0821(16) | Ca(1)-O(2)      | 2.4247(16) |
| Ca(1)-N(1)      | 2.4750(19) | Ca(1)-N(3)      | 2.4898(17) |
| Ca(1)-N(5)      | 2.4590(18) |                 |            |
| O(1)-Ca(1)-N(1) | 116.59(7)  | O(1)-Ca(1)-N(3) | 141.61(7)  |
| O(1)-Ca(1)-N(5) | 126.69(7)  | O(1)-Ca(1)-O(2) | 91.12(6)   |
| N(1)-Ca(1)-N(3) | 74.42(6)   | N(1)-Ca(1)-N(5) | 79.46(6)   |
| N(3)-Ca(1)-N(5) | 90.63(6)   | N(1)-Ca(1)-O(2) | 152.17(6)  |

Complex **10** has a five-coordinated calcium that is bonded to three N donors on the pyrazolyl rings, O donor from 2-methylcyclohexanoxide ring and O atom from THF molecule. The geometry of **10** is described as distorted trigonal bipyramidal. Ca(1) lies at the centre of the plane and surrounded by N(3), N(5) and O(1). The bond angles for each atom in the equatorial positions, N(3)-Ca(1)-N(5), O(1)-Ca(1)-N(3) and O(1)-

Ca(1)-N(5) are 90.63(6), 141.61(7) and 126.69(7)°, respectively. The apical positions are occupied by O(2) of the THF molecule and N(1) from the pyrazolyl ligand, giving the non-linear bond angle of 152.17(6)° caused by the distortion. The average Ca-N bond distances are 2.4746(18) Å. The Ca(1)-O(1) distance of 2.0821(16) Å is shorter than the Ca(1)-O(1) bond of 2.1102(7) Å from (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**).

#### 2.5.4 ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF) (**10**)

The polymerisation of *rac*-LA using **10** was performed in THF at RT with [*rac*-LA]<sub>0</sub>:**10**<sub>0</sub> = 800:1. Complex **10** proved to be highly active in the ROP of *rac*-LA, reaching 91% monomer conversion after 3 min (Table 2.9, entry 1).

**Table 2.9** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**), (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**) and (Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF) (**10**) with additives.<sup>a</sup>

| Entry | Initiator | Additive | Conv.<br>(%) <sup>b</sup> | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>10</b> | -        | 91                        | 180         | 97,950                                                | 105,019                                                 | 1.55                   | 0.84               |
| 2     | <b>1</b>  | CyMeO    | 94                        | 180         | 93,750                                                | 108,477                                                 | 1.40                   | 0.80               |
| 3     | <b>5</b>  | CyMeOH   | 93                        | 180         | 94,270                                                | 107,325                                                 | 1.39                   | 0.83               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:[initiator]<sub>0</sub>:[additive]<sub>0</sub> = 800:1:as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for -OH and -OCyMe end groups,  $M_n$  (entry 1-3) = conv. (%) × 800 × 144.1 + 114.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

ROP of *rac*-LA with **10** featured a second order dependence on monomer concentration with  $k_{app} = 0.159(8) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.989$ ), evidenced by linear plot between  $1/[\textit{rac}\text{-LA}]_t$  vs. time (Figure 2.39, left). The  $M_n$ (GPC) values were higher than those calculated for one chain per metal centre due to the greater propagation rate than initiation rate at low conversion, followed by a poor agreement between measured and calculated  $M_n$  values due to transesterification reactions occurring at later polymerisation stages (Figure 2.39, right). The resultant PLA showed a high degree of heterotactic enrichment with  $P_r = 0.84$ .

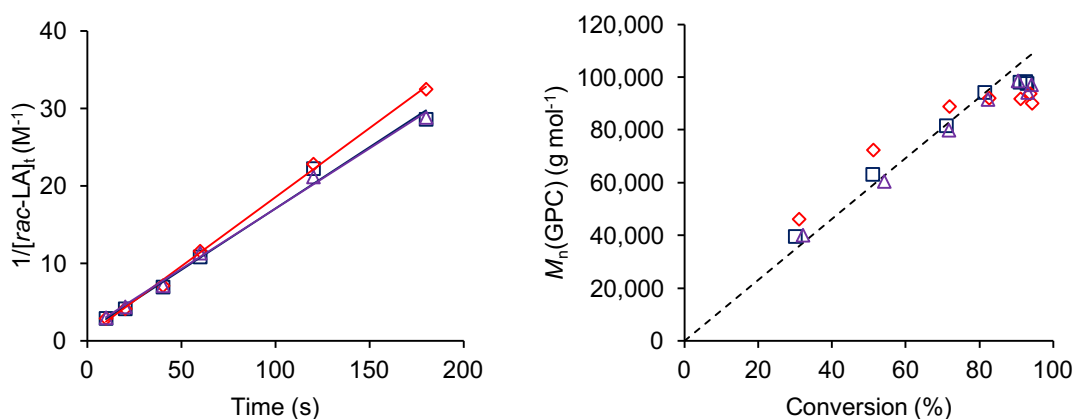


**Figure 2.39** Left, Plots of  $1/[rac-LA]_0$  vs. time. Squares:  $[rac-LA]_0:[\mathbf{10}]_0 = 800:1$  ( $k_{app} = 0.159(8) M^{-1}s^{-1}$ ,  $R^2 = 0.989$ ). Diamonds:  $[rac-LA]_0:[\mathbf{1}]_0:[CyMeO]_0 = 800:1:1$  ( $k_{app} = 0.178(4) M^{-1}s^{-1}$ ,  $R^2 = 0.998$ ). Triangles:  $[rac-LA]_0:[\mathbf{5}]_0:[CyMeOH]_0 = 800:1:1$  ( $k_{app} = 0.156(5) M^{-1}s^{-1}$ ,  $R^2 = 0.996$ ). Right, Plots of  $M_n$ (GPC) vs. conversion. Squares:  $[rac-LA]_0:[\mathbf{10}]_0 = 800:1$ ,  $\bar{D} = 1.05-1.55$ . Diamonds:  $[rac-LA]_0:[\mathbf{1}]_0:[CyMeO] = 800:1:1$ ,  $\bar{D} = 1.05-1.40$ . Triangles:  $[rac-LA]_0:[\mathbf{5}]_0:[CyMeOH] = 800:1:1$ ,  $\bar{D} = 1.05-1.39$ . The dashed line represents  $M_n$ (calcd) for one PLA chain per metal centre.

The *in situ* generated **10** used as ROP catalyst was prepared *via* two different routes, reaction of **1** and 2-methylcyclohexanone and reaction of **5** and 2-methylcyclohexanol (Table 2.9, entry 2 and 3). The  $k_{app}$  value obtained from the ROP using *in situ* generated *cis* and *trans*-**10** (Figure 2.39, left, triangles) is identical within error compared to those obtained by using *trans*-**10** (Figure 2.39, left, squares and diamonds), indicating that the geometry of **10** does not affect polymerisation rate. Heterotactically-enriched PLAs with  $P_r = 0.80-0.84$  were given (Table 2.9).

MALDI-ToF mass spectrum (Figure 2.40) shows a major distribution of cyclic PLA with a repeating unit of  $\Delta(m/z) = 72.0$  Da between each peak envelope as a consequence of transesterification reactions. A minor distribution of peak envelopes was assigned to PLA end capped with  $-OH$  and  $-OCyMe$  termini. For example, the peak envelope centred at 1911.9 Da corresponds to cyclic PLA with 26 units of half LA with  $K^+$ . Another peak envelope centred at 2025.9 Da is assigned to 26 LA units of half LA terminated with a  $-OCyMe$  and  $-OH$  end groups with  $K^+$  [ $72.0(26) + 114.1 + 39.1$ ].

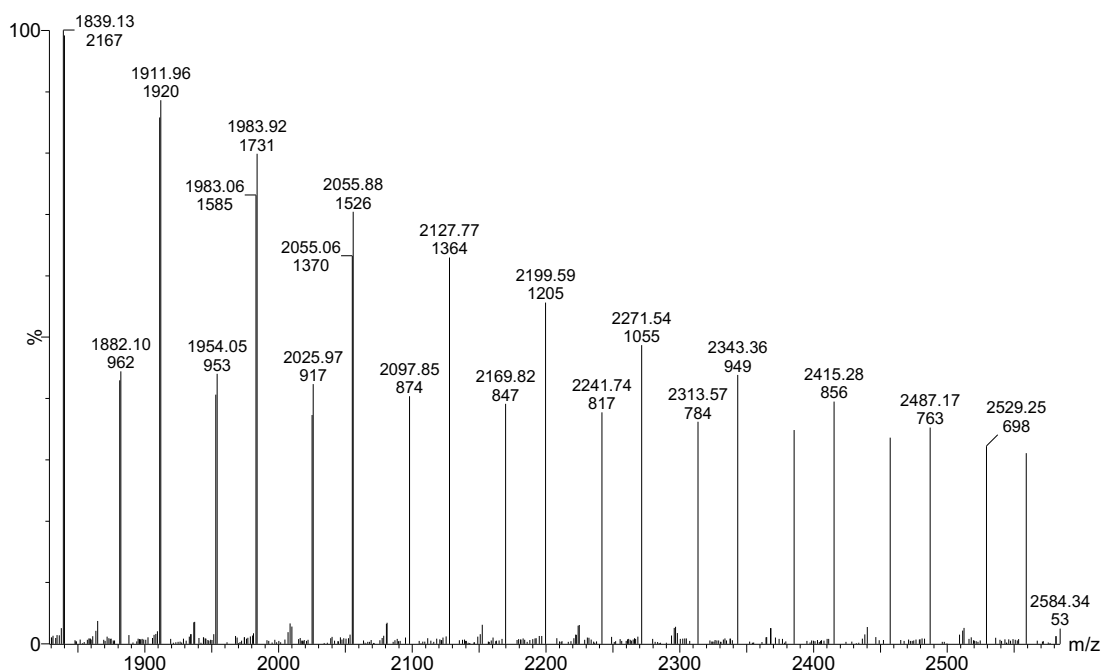
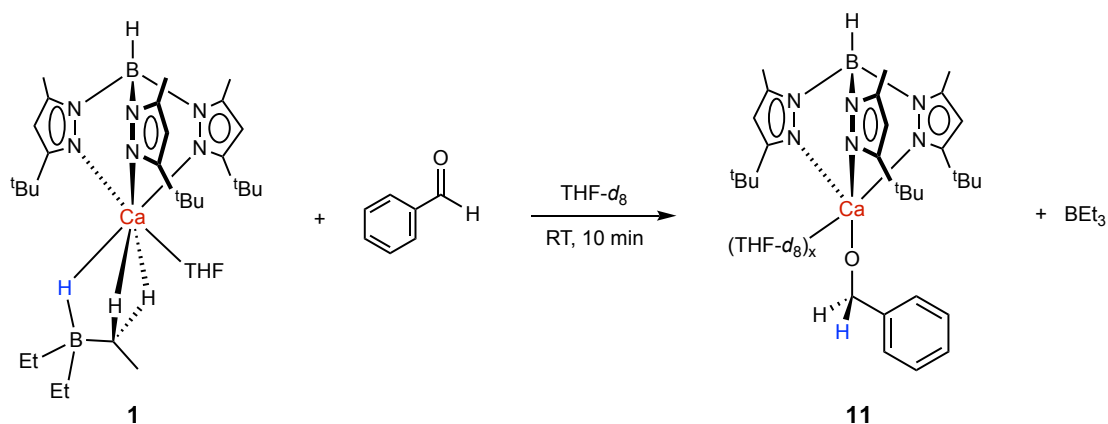


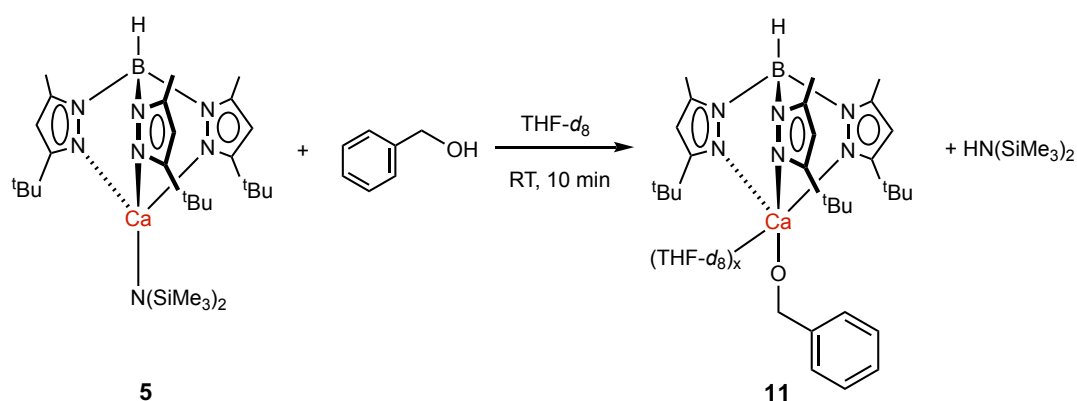
**Figure 2.40** MALDI-ToF MS of PLA synthesised from  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**).  $M_n(\text{GPC}) = 3,430 \text{ g mol}^{-1}$ ,  $D = 1.50$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{10}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes.

### 2.5.5 ROP of *rac*-LA using *in situ* generated $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$ (**11**)

An NMR tube scale reaction of **1** with 1 equiv. of benzaldehyde was performed in  $\text{THF-}d_8$  at RT (Equation 2.6). The  $^1\text{H}$  NMR spectrum recorded after 10 min showed signals corresponding to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and free  $\text{BEt}_3$ . A characteristic singlet corresponding to the methylene protons ( $\text{OCH}_2\text{Ph}$ ) was found at 5.07 ppm. The  $^{11}\text{B}$  NMR spectrum revealed respective broad singlets of  $\text{BEt}_3$  and apical B-H at 73.3 and -8.6 ppm, respectively. An attempt to isolate the **11** was made. A solution of *in situ* generated **11** in  $\text{THF-}d_8$  was evaporated to dryness under reduced pressure and redissolved in  $\text{C}_6\text{D}_6$ . The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra ( $\text{C}_6\text{D}_6$ ) showed the presence of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) and unidentified species. Complex **11** therefore could not be isolated. Another route to synthesise **11** was performed *via* reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) with 1 equiv. of benzylalcohol in  $\text{THF-}d_8$  at RT (Equation 2.7).



Equation 2.6



Equation 2.7

Complex **11** was highly active in the ROP of *rac*-LA in THF at RT, reaching over 90% conversion after 3 min (Table 2.10). As shown in Figure 2.41 (left), the ROP of *rac*-LA using **11** gave second order dependence on  $[\textit{rac}\text{-LA}]$ . Plots of  $M_n(\text{GPC})$  vs. conversion (%) (Figure 2.41, right) show well-control molecular weights with moderate  $D$  values ranging from 1.03 to 1.43 as conversion increased. The back-biting become significant at high monomer conversions confirmed by poor agreement between measured and calculated  $M_n$  values. Heterotactically-enriched PLAs with  $P_r = 0.82$  were obtained.

**Table 2.10** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**) and (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**) with additives.<sup>a</sup>

| Entry | Initiator | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>1</b>  | PhCHO    | 91                        | 180         | 83,090                                                | 105,012                                                 | 1.39                   | 0.82               |
| 2     | <b>5</b>  | BnOH     | 93                        | 180         | 82,000                                                | 107,319                                                 | 1.41                   | 0.82               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:[initiator]<sub>0</sub>:[additive]<sub>0</sub> = 800:1:1, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OBn end groups,  $M_n = \text{conv. (\%)} \times 800 \times 144.1 + 108.1$ . <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

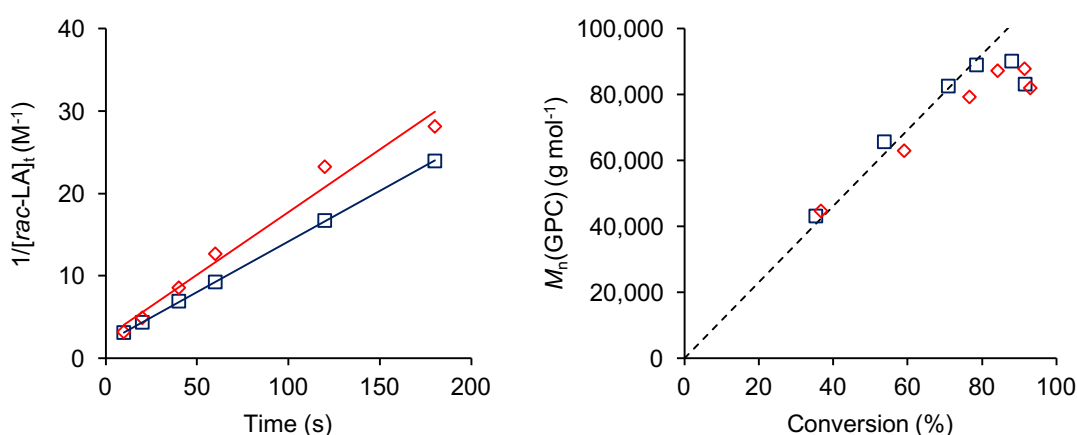


**Figure 2.41 Left**, Plots of  $1/[rac-LA]_0$  vs. time. Squares: [*rac*-LA]<sub>0</sub>:[**1**]<sub>0</sub>: [PhCHO]<sub>0</sub> = 800:1:1 ( $k_{app} = 0.123(4) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.999$ ). Diamonds: [*rac*-LA]<sub>0</sub>:[**5**]<sub>0</sub>: [BnOH]<sub>0</sub> = 800:1:1 ( $k_{app} = 0.152(11) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.978$ ). **Right**, Plots of  $M_n(\text{GPC})$  vs. conversion (%). Squares: [*rac*-LA]<sub>0</sub>:[**1**]<sub>0</sub>: [PhCHO]<sub>0</sub> = 800:1:1,  $\bar{D} = 1.03\text{--}1.41$ . Diamonds: [*rac*-LA]<sub>0</sub>:[**5**]<sub>0</sub>: [BnOH]<sub>0</sub> = 800:1:1,  $\bar{D} = 1.04\text{--}1.43$ . The dashed line represents  $M_n(\text{calcd})$  for one PLA chain per metal centre.

MALDI-ToF mass spectrum (Figure 2.42) shows signals for cyclic PLA as a major contribution with a repeating unit of  $\Delta(m/z) = 72.0$  Da between peak envelopes confirming the occurrence of transesterification reactions. Peak envelopes corresponding to PLA terminated with –OH and –OBn end groups were also observed as a minor contribution. For example, the peak envelope centred at 1,046.9 Da corresponds to cyclic PLA with 14 units of half LA with K<sup>+</sup>. Another peak envelope centred at 1,155.1 Da is assigned to 14 units of half LA terminated with –OBn and –OH groups and K<sup>+</sup> [ $72.0(14) + 108.1 + 39.1$ ].



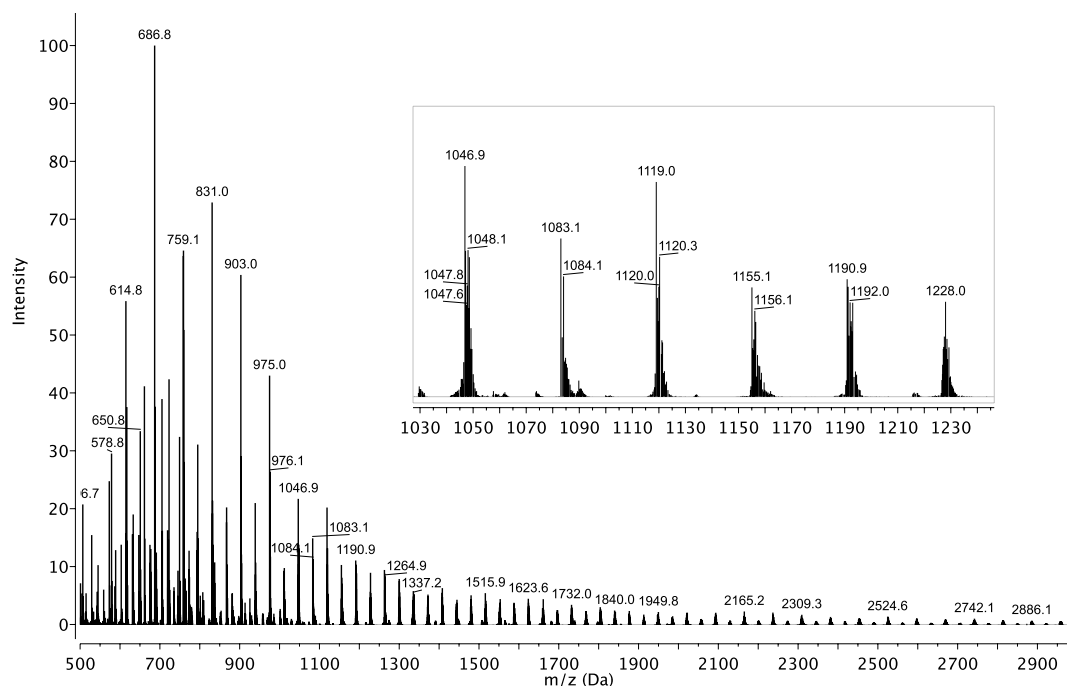
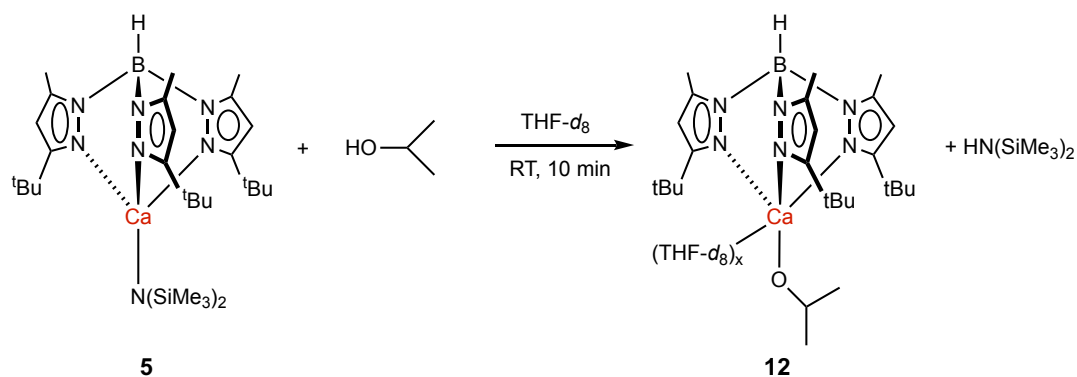


**Figure 2.42** MALDI-ToF MS of PLA synthesised from  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) with 1 equiv. of PhCHO.  $M_n(\text{GPC}) = 3,130 \text{ g mol}^{-1}$ ,  $D = 1.37$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{1}]_0:[\text{PhCHO}]_0 = 20:1:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ , 1.0 mL THF at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes.

### 2.5.6 ROP of *rac*-LA using *in situ* generated $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{O}^i\text{Pr})(\text{THF})_x$ (**12**)

Due to an unsuccessful synthesis of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{S-lactate})$  (**9**) at RT as a model of a propagating species (section 2.4.4),  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{O}^i\text{Pr})(\text{THF})_x$  (**12**) was introduced to mimic **9**. Similar to Chisholm's  $(\text{Tp}^{\text{tBu}})\text{Ca}(\text{O-2,6-C}_6\text{H}_3^i\text{Pr}_2)(\text{THF})$  prepared from  $(\text{Tp}^{\text{tBu}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**2.14**) with 2,6- $\text{C}_6\text{H}_3^i\text{Pr}_2\text{OH}$  in THF,<sup>26</sup> an NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) with 1 equiv. of  $^i\text{PrOH}$  in THF- $d_8$  gave **12** and  $\text{HN}(\text{SiMe}_3)_2$  (Equation 2.8). Attempted isolation of **12** was unsuccessful. The  $^1\text{H}$  NMR spectrum of **12** in THF- $d_8$  shows a heptet at 4.15 ppm with  $^3J = 5.9 \text{ Hz}$  corresponding to the methine proton ( $\text{CHMe}_2$ ). The doublet corresponding to the methyl protons ( $\text{CHMe}_2$ ) was also observed at 1.04 ppm ( $^3J = 5.9 \text{ Hz}$ ). The  $^{11}\text{B}$  NMR spectrum revealed a broad singlet of the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  ligand of **12** at -8.2 ppm.



The ROP of *rac*-LA using **12** showed second order dependence on  $[rac\text{-LA}]$  with  $k_{\text{app}} = 0.144(6) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.994$ ) (Figure 2.43, left). Good agreement between measured and calculated  $M_n$  values was observed from the plot of  $M_n(\text{GPC})$  vs conversion (%) (Figure 2.43, right). The effect of transesterification reactions on molecular weights was visible at later stage of polymerisation, resulting in  $M_n(\text{GPC})$  values lower than those calculated. Heterotactically-enriched PLA was obtained with  $P_r = 0.83$ . MALDI-ToF mass spectrum showed peak envelopes corresponding to cyclic PLA with a repeating unit of 72.0 Da between peak envelopes as a result of transesterification reactions. Other peak envelopes correspond to PLA terminated with  $-\text{OH}$  and  $-\text{O}^i\text{Pr}$  groups.

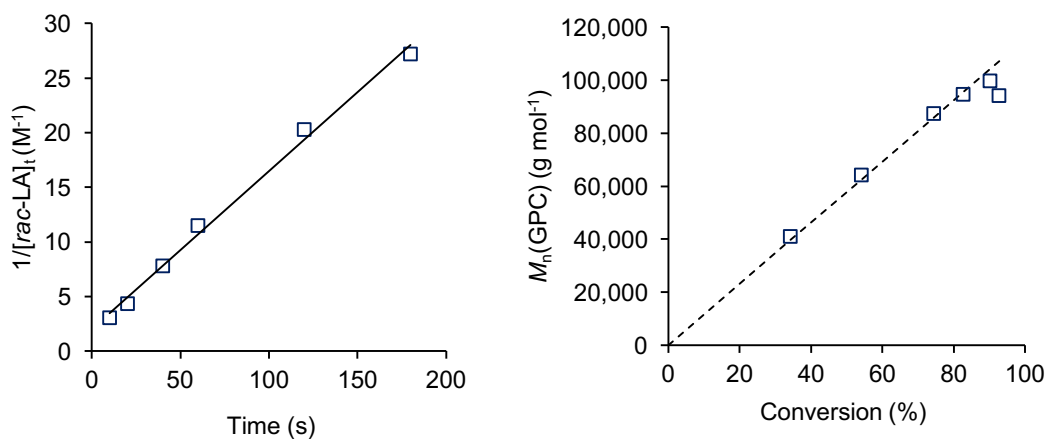


**Figure 2.43** Left, plot of  $1/[rac\text{-LA}]_0$  vs. time ( $k_{\text{app}} = 0.144(6) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.994$ ). Right, plot of  $M_n(\text{GPC})$  vs. conversion (%). The dashed line represents  $M_n(\text{calcd})$  for one PLA chain per metal centre. Condition: 6 mL THF, RT,  $[rac\text{-LA}]_0:[\mathbf{5}]_0:[^i\text{PrOH}]_0 = 800:1:1$ ,  $[rac\text{-LA}]_0 = 0.5 \text{ M}$ .  $D = 1.04\text{-}1.32$ .

### 2.5.7 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$ (**5**)

The poorly controlled ROP initiated by amide complexes over the rate and molecular weight is precedent in the literature.<sup>13, 25, 26, 78-80</sup> Chisholm *et al.* reported the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**2.14**) or  $(\text{Tp}^{\text{tBu}})\text{Ca}(\text{O}-2,6\text{-C}_6\text{H}_3^{\text{iPr}})_2$  (**2.15**).<sup>25, 26</sup> The PLAs obtained from **2.14** or **2.15** showed broad  $\bar{D}$  values (1.74 and 1.68, respectively). The measured  $M_n$  values were also much higher than those calculated indicating the slower initiation rate of the ROP with **2.14** or **2.15** than propagation and transesterification rates.

The polymerisation behaviour of **5** was investigated in the absence of any additives in order to compare the polymerisation activity with those of **5** with 1 equiv. of 2-methylcyclohexanol, BnOH or <sup>i</sup>PrOH. The ROP of 800 equiv. of *rac*-LA using complex **5** as an initiator was carried out in THF at RT. Complex **5** was found to be highly active, reaching to 92% conversion in 3 min. The induction period was observed at initial stages. After 40 s, the polymerisation demonstrated the second order dependence on  $[\textit{rac}\text{-LA}]$  with  $k_{\text{app}} = 0.144(8) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.994$ ) (Figure 2.44, left).

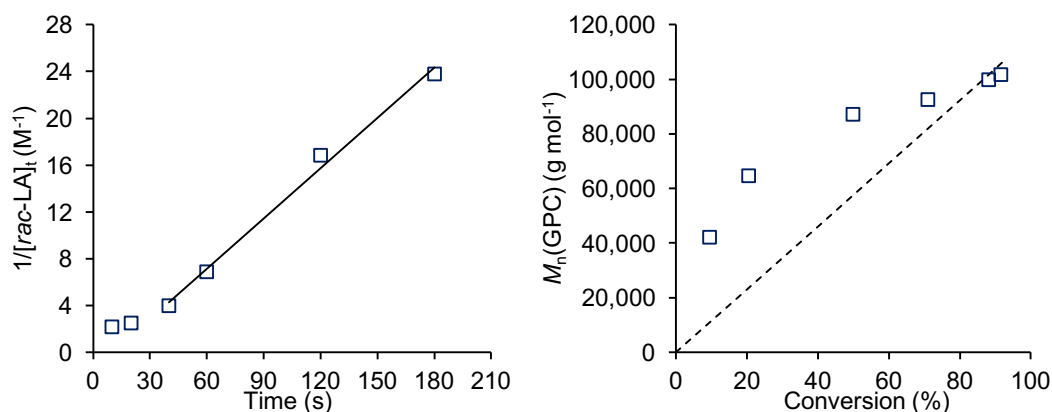


**Figure 2.44** Left, plot of  $1/[\textit{rac}\text{-LA}]_0$  vs. time ( $k_{\text{app}} = 0.144(8) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.994$ ). Right, plot of  $M_n(\text{GPC})$  vs. conversion.  $\bar{D} = 1.08\text{-}1.46$ . The dashed line represents  $M_n(\text{calcd})$  for one PLA chain per metal centre. Condition: 6 mL THF, RT,  $[\textit{rac}\text{-LA}]_0:[\textbf{5}]_0 = 800:1$ ,  $[\textit{rac}\text{-LA}]_0 = 0.5 \text{ M}$ .

Compared to good agreement between  $M_n(\text{GPC})$  and  $M_n(\text{calcd})$  of PLAs formed by  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})_x$  (**10**),  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{O}^{\text{iPr}})(\text{THF})_x$  (**12**) (generated *in situ* from **5** with the corresponding alcohols) during initial stages of polymerisation, the  $M_n(\text{GPC})$  values were found to be much higher than those calculated for one chain per metal centre (Figure 2.44, right),

with moderate  $\bar{D}$  values (1.08-1.46). Poor agreement between  $M_n(\text{GPC})$  and  $M_n(\text{calcd})$  observed from the ROP using **5** compared with those using alkoxide initiators was attributed to the slower initiation rate by the amide initiator than the alkoxide initiator due to the lower nucleophilicity of silylamide group.<sup>78</sup> In the MALDI-ToF mass spectrum, peak envelopes corresponding to PLA terminated with  $-\text{N}(\text{SiMe}_3)_2$  and  $-\text{OH}$  groups were absent, which is typical for the ROP with silylamide initiators.<sup>78</sup> However, cyclic PLA dominates together with the repeating unit of 72.0 Da between peak envelopes, indicating transesterification reactions. The resultant PLA has a similar degree of heterotactic enchainment ( $P_r = 0.82$ ) compared to PLA produced from organohydroborate (**1**) or alkoxide complexes (**7**, **10**, **11** and **12**).

## 2.6 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBEt}_3)(\text{THF})_2$ (**2**)

Over the last two decades, the synthesis of heavy alkaline earth metal complexes and their activity for the ROP of cyclic esters such as  $\epsilon$ -CL and LA have been extensively studied.<sup>16, 20-35</sup> Most of this work is focused on calcium catalysts while the application of strontium complexes as ROP initiators remains very rare. For examples,  $\text{Sr}(\text{O}^i\text{Pr})_2$ ,<sup>81</sup>  $\{\text{O}_4\text{NO}^{\text{Aryl}}\}\text{Sr}\{\text{N}(\text{SiMe}_2\text{H})_2\}_2(\text{THF})_x$  (**2.22**),<sup>32</sup> cationic  $[(\text{L})_n\text{Sr}][\text{H}_2\text{N}\{\text{B}(\text{C}_6\text{F}_5)_3\}_2]$ ,<sup>33</sup> strontium 2,4-di-*tert*-butylphenolates with  $\text{BnOH}$  or  $\text{BnNH}_2$  as co-initiators,<sup>50</sup> and strontium complexes supported by tetrahydroborate ligands<sup>82, 83</sup> were reported as catalysts for the ROP of  $\epsilon$ -CL or LA. Recently, Panda *et al.* reported heavy alkaline earth metal (Ca, Sr and Ba) complexes supported by 1,2-phenylene(bis-diphenylphosphinothioic/selenoic amine) for the ROP of *rac*-LA and  $\epsilon$ -CL in toluene at RT.<sup>84</sup> Isotactically-enriched PLAs with  $P_m = 0.78$ -0.87 were obtained from calcium complexes. Whereas moderate iso-selectivity PLAs ( $P_m = 0.68$ -0.75) and atactic PLAs were produced from strontium and barium complexes, respectively. Kinetic studies indicated the relative order of polymerisation rate with increase in the size of the metal ion:  $\text{Ba} > \text{Sr} > \text{Ca}$ . In general, larger strontium complexes have been reported to be more active than calcium congeners in the ROP of cyclic esters due to the ionic radii for coordination number = 6 ( $\text{Ca}^{2+} = 1.00$ ,  $\text{Sr}^{2+} = 1.18 \text{ \AA}$ )<sup>85 33, 68, 83, 84, 86-91</sup>.

$(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBEt}_3)(\text{THF})_2$  (**2**) was found to be an extremely fast but poorly controlled initiator for the ROP of *rac*-LA, approaching 92% conversion after 1 min. Accurate kinetic studies could not be achieved. Therefore, the ROP of 800 equiv. of *rac*-LA with **2** was carried out in THF at RT and the polymerisation solution was quenched after 1

min with degassed, wet THF. Notably, strontium complex (**2**) is more active for the ROP of *rac*-LA than calcium complex, (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**) under the same ROP conditions. The measured  $M_n$  value was lower than that calculated due to very extensive inter- and intramolecular transesterification reactions (Table 2.11).

**Table 2.11** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Sr(HBEt<sub>3</sub>)(THF)<sub>2</sub> (**2**).<sup>a</sup>

| Entry | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$ (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$ (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|---------------------------|-------------|----------------------------------------------------|------------------------------------------------------|------------------------|--------------------|
| 1     | 80                        | 10          | 60,560                                             | 92,226                                               | 1.44                   | <sup>g</sup>       |
| 2     | 92                        | 60          | 67,080                                             | 106,060                                              | 1.55                   | 0.72               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:**2**<sub>0</sub> = 800:1, [*rac*-LA]<sub>0</sub> = 0.5 M, **2**<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –LA-H end groups,  $M_n$  = conv. (%) × 800 × 144.1 + 2. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>g</sup> Not measured.

Complex **2** exhibits the stereoselectivity over the ROP of *rac*-LA, yielding lower heterotactic-degree ( $P_r$  = 0.72) than **1** ( $P_r$  = 0.82). The stereoselective polymerisation of *rac*-LA with analogous complexes containing Tp<sup>tBu,Me</sup> ligand is postulated to operate *via* the chain-end control.<sup>25, 26, 35</sup> Complex **2** possesses a larger coordination sphere compared to **1** resulted in higher rate of polymerisation. This also enhances the intramolecular transesterification of the polymer chains leading to the formation of cyclic PLA together with a decrease in  $M_n$  and broader  $\bar{D}$ . The high level of transesterifications of the growing polymer chain leads to scrambling of stereochemistry and reduction in stereocontrol of the polymerisation.

MALDI-ToF mass spectrum (Figure 2.45) shows the presence of cyclic PLA as a major redistribution and the separation of  $\Delta(m/z)$  = 72.0 Da between each peak envelope due to transesterification reactions. A minor distribution of peak envelopes is assigned to PLA end capped with non-opened ring LA (–LA-H) and –OH groups. For example, the peak envelope centred at  $m/z$  = 903.9 Da corresponds to cyclic PLA with 12 units of half LA with K<sup>+</sup>. Another peak envelope centred at  $m/z$  = 905.9 Da is assigned to PLA with 10 units of half LA terminated with non-opened ring LA (–LA-H) and –OH groups [72.0(10) + 146.1 + 39.1]. Similar to what observed from <sup>1</sup>H NMR spectra of crude or isolated PLA samples formed by **1**, evidence for the –LA-H end group was not found by <sup>1</sup>H NMR of those formed by **2**.

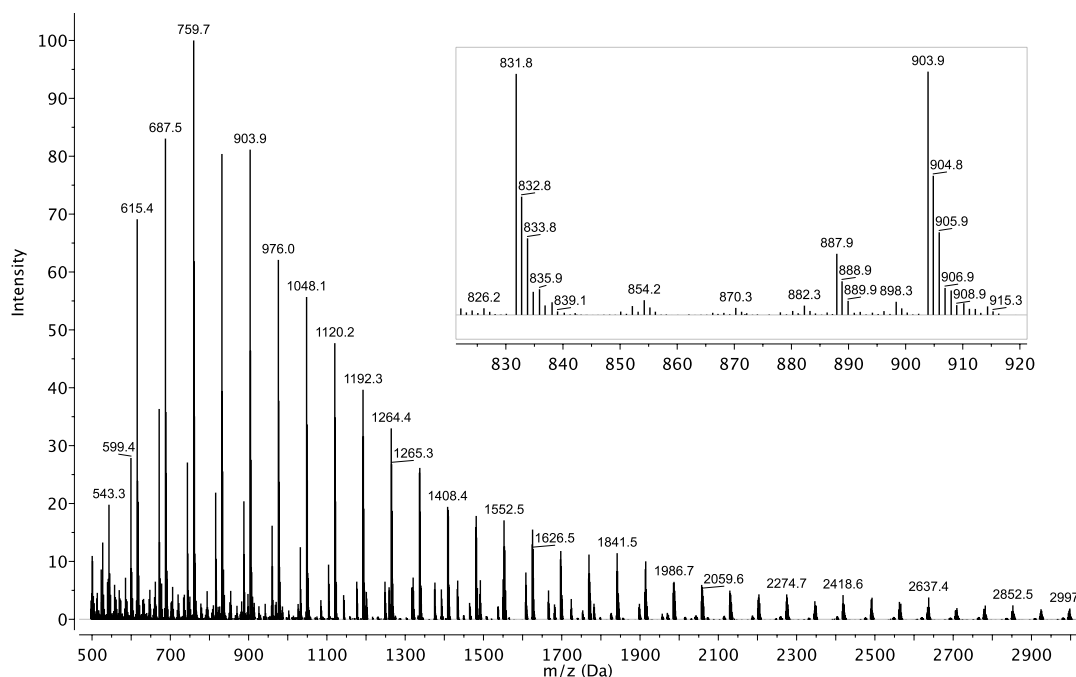


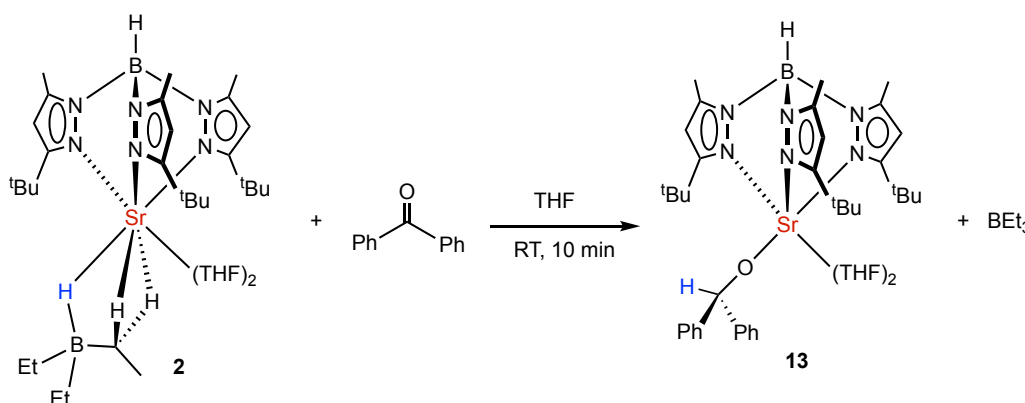
**Figure 2.45** MALDI-ToF MS of PLA synthesised from  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBEt}_3)(\text{THF})_2$  (**2**).  $M_n(\text{GPC}) = 2,770 \text{ g mol}^{-1}$ ,  $D = 1.21$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{2}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes.

To study the polymerisation behaviour of **2** for the ROP of *rac*-LA,  $^1\text{H}$  and  $^{11}\text{B}$  NMR analyses of the NMR tube-scale reactions between **2** and 1 equiv. of *rac*-LA in  $\text{THF-}d_8$  were undertaken. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min indicated the formation of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**), free  $\text{BEt}_3$  and an unknown  $\text{Tp}^{\text{tBu,Me}}$  species which does not correspond to the first hydride transfer product,  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{LA-H})(\text{THF})_x$ . The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of **2** and 5 equiv. of *rac*-LA in  $\text{THF-}d_8$  of also showed signals of an unknown  $(\text{Tp}^{\text{tBu,Me}})$  species and free  $\text{BEt}_3$ . The formation of **3** suggests a redistribution of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{LA-H})(\text{THF})_x$  by the Schlenk equilibrium during polymerisation. A series of NMR tube-scale reactions of **2** with various ketones and aldehyde were performed to try to mimic the hydride transfer step from **2** to *rac*-LA.

An NMR tube scale reaction of complex **2** with 1 equiv. of benzophenone in  $\text{C}_6\text{D}_6$  or  $\text{THF-}d_8$  produced  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_x$  (**13**) after 15 min, while an NMR tube-scale reaction of **2** with 1 equiv. of 2-methylcyclohexanone in  $\text{THF-}d_8$  formed  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCyMe})(\text{THF})_x$  along with a minor amount of **3**. The presence of **3** and unknown species containing a  $\text{Tp}^{\text{tBu,Me}}$  ligand were observed from reactions of **2** with 1 equiv. of benzaldehyde in  $\text{THF-}d_8$ .

## 2.7 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$ (**13**)

$(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) was synthesised by reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBET}_3)(\text{THF})_2$  (**2**) and 1 equiv. of benzophenone in THF for 15 min (Equation 2.9). Complex **2** was obtained as a white solid in 67% isolated yield by precipitation in THF/pentane (1:5, v/v). The  $^{11}\text{B}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) of **13** showed a characteristic signal of the apical B-H of  $(\text{Tp}^{\text{tBu,Me}})$  ligand appeared as a broad singlet at -7.4 ppm. The  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ ) showed a singlet at 6.49 ppm corresponding to methine proton ( $\text{OCHPh}_2$ ) of **13**.



Equation 2.9

Complex **13** was found to be more reactive than  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) for ROP of *rac*-LA under the analogous conditions, achieving 95 % conversion after 10 s. Similar to the ROP with **2**, a loss in stereocontrol was observed. The PLA formed with **13** showed modest heterotactic enchainment with  $P_r = 0.68$  while that formed by **7** had  $P_r = 0.82$ . The existence of transesterification reactions was confirmed by a very poor agreement between  $M_n(\text{GPC})$  value ( $69,550 \text{ g mol}^{-1}$ ) and that calculated ( $109,700 \text{ g mol}^{-1}$ ) for one chain per metal centre, with a moderate  $D$  value (1.56). MALDI-ToF mass spectrum (Figure 2.46) displays a major distribution of cyclic PLA and a minor distribution of PLA terminated with  $-\text{OH}$  and  $-\text{OCHPh}_2$  groups. For example, peak envelope centred at 759.2 Da corresponds to cyclic PLA comprising 10 units of half LA and  $\text{K}^+$ . Another peak envelope centred at 943.5 Da is indicative of PLA with 10 units of half LA end capped with  $-\text{OH}$  and  $-\text{OCHPh}_2$  groups and  $\text{K}^+$  [ $72.0(10) + 184.1 + 39.1$ ].

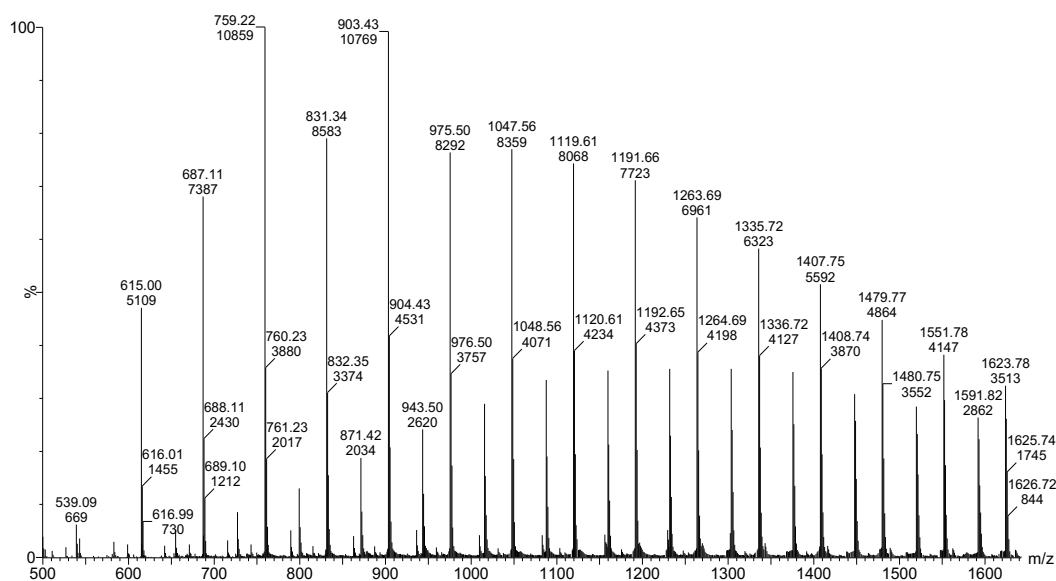


**Figure 2.46** MALDI-ToF MS of PLA synthesised from  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**).  $M_n(\text{GPC}) = 2,730 \text{ g mol}^{-1}$ ,  $D = 1.35$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{13}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes.

## 2.8 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$ (**3**)

The formation of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**) was observed in the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBET}_3)(\text{THF})_2$  (**2**) with 1 equiv. of *rac*-LA in  $\text{THF-}d_8$ . Complex **3** was synthesised *via* a salt elimination reaction between 2 equiv. of  $\text{K}(\text{Tp}^{\text{tBu,Me}})$  and  $\text{SrI}_2$ .<sup>47</sup> The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of reaction of **3** with 10 equiv. of *rac*-LA carried out in  $\text{THF-}d_8$  showed signals corresponding to an unknown species containing  $\text{Tp}^{\text{tBu,Me}}$  ligand and oligomeric PLA. The *rac*-LA ROP activity of **3** was examined. Complex **3** was found to be more active than **2** as 93 % conversion was reached after 20 s (Table 2.12). Poor agreement between measured and calculated  $M_n$  values together with a broad  $D$  value (1.62) was observed due to transesterification reactions. It is noteworthy that  $M_n(\text{GPC})$  value of PLA catalysed by **3** is higher than those catalysed by **2** or  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) under analogous conditions. It is hypothesised that a lower proportion of **3** involving in the initiation step than either **2** or **13**, along with a faster propagation rate than initiation rate resulted in longer polymer chains growing on the metal centre. The isolated PLA was slightly heterotactically-enriched ( $P_r = 0.67$ ) in comparison to that obtained by **2** ( $P_r = 0.72$ ) or **13** ( $P_r = 0.68$ ). MALDI-ToF mass spectrum (Figure 2.47) displays a single set of peak envelopes corresponding to cyclic



PLA and a separation of  $\Delta(m/z) = 72.0$  Da between peak envelopes due to transesterification reactions.

**Table 2.12** Selected data for the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**).<sup>a</sup>

| Entry | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n(\text{GPC})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | $P_r^f$      |
|-------|---------------------------|-------------|-----------------------------------------------|-------------------------------------------------|-------------|--------------|
| 1     | 85                        | 10          | 89,020                                        | 97,988                                          | 1.52        | <sup>g</sup> |
| 2     | 93                        | 20          | 92,750                                        | 107,210                                         | 1.62        | 0.67         |

<sup>a</sup> Conditions:  $[\text{rac-LA}]_0:[\mathbf{3}]_0 = 800:1$ ,  $[\text{rac-LA}]_0 = 0.5$  M,  $[\mathbf{3}]_0 = 625$   $\mu\text{M}$ , 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4$   $\mu\text{L g}^{-1}$  and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for cyclic PLA,  $M_n = \text{conv. (\%)} \times 800 \times 144.1$ . <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>g</sup> Not measured.

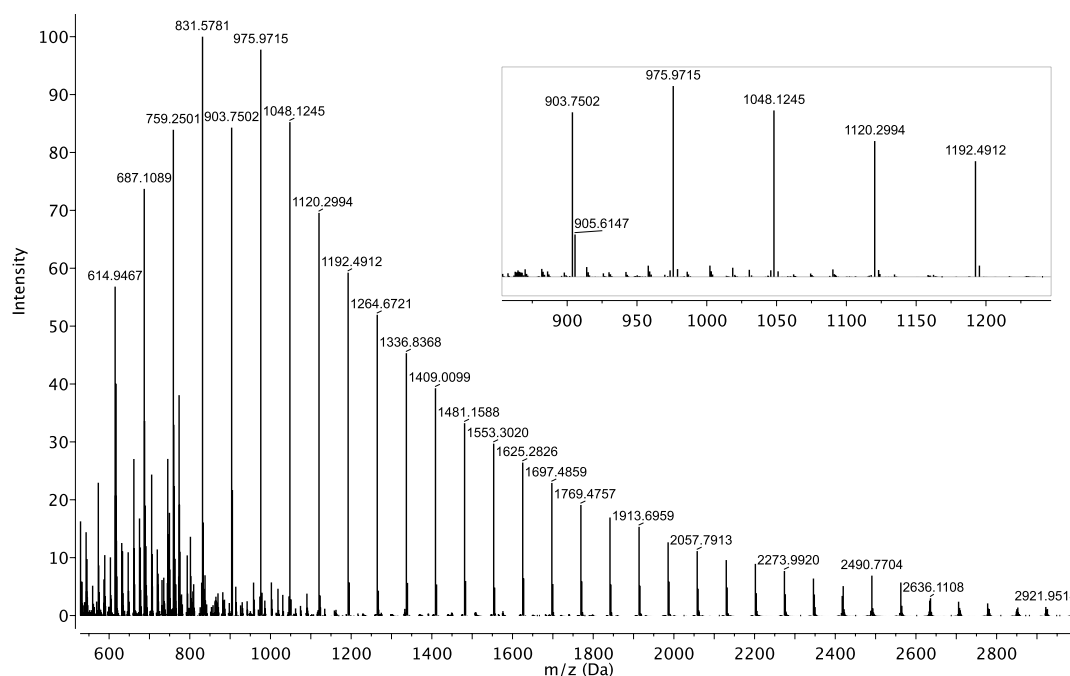


**Figure 2.47** MALDI-ToF MS of PLA synthesised from  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**).  $M_n(\text{GPC}) = 2,770$  g mol<sup>-1</sup>,  $\bar{D} = 1.74$ . Conditions:  $[\text{rac-LA}]_0:[\mathbf{3}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5$  M, 1.0 mL THF at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0$  Da between peak envelopes.

The absence of PLA terminated with non-opened ring LA (–LA–H) and –OH groups suggests that the ROP with **3** was not initiated by the reduced LA alkoxide species (LA–H). To probe whether **3** could undergo hydride transfer reaction with unsaturated species, NMR tube scale reactions of **3** with 1 equiv. of benzophenone, 2-methylcyclohexanone or benzaldehyde were performed in THF-*d*<sub>8</sub>. As anticipated, no reaction was observed by the <sup>1</sup>H or <sup>11</sup>B NMR spectroscopy at RT after 24 h.

## 2.9 ROP of *meso*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBEt}_3)(\text{THF})_2$ (**2**), $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$ (**13**) or $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$ (**3**)

Complexes **2**, **13** and **3** were tested for their activity towards the ROP of *meso*-LA. The faster ROP rate and reduction of stereoselectivity of PLA was gained from Sr complexes vs. Ca complexes. In the case of **2**, **13** and **3** with  $[\text{meso-LA}]_0:[\text{initiator}]_0 = 800:1$ , over 95% conversion was achieved within 20 s (Table 2.13).

**Table 2.13** Selected data for the ROP of *meso*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBEt}_3)(\text{THF})_2$  (**2**),  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) and  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**).<sup>a</sup>

| Entry | Initiator | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n(\text{GPC})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | $P_r^f$ |
|-------|-----------|---------------------------|-------------|-----------------------------------------------|-------------------------------------------------|-------------|---------|
| 1     | <b>2</b>  | 97                        | 20          | 38,140                                        | 111,824                                         | 1.43        | 0.82    |
| 2     | <b>13</b> | 96                        | 10          | 55,460                                        | 110,853                                         | 1.55        | 0.82    |
| 3     | <b>3</b>  | 95                        | 20          | 84,310                                        | 109,516                                         | 1.37        | 0.83    |

<sup>a</sup> Conditions:  $[\text{meso-LA}]_0:[\text{initiator}]_0 = 800:1$ ,  $[\text{meso-LA}]_0 = 0.5$  M,  $[\text{initiator}]_0 = 625$   $\mu\text{M}$ , 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4$   $\mu\text{L g}^{-1}$  and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>),  $M_n$  (entry 1) for -LA-H and -OH end groups = conv. (%)  $\times 800 \times 144.1 + 2$ ,  $M_n$  (entry 2) for -OCHPh<sub>2</sub> and -OH end groups = conv. (%)  $\times 800 \times 144.1 + 184.1$ ,  $M_n$  (entry 3) for cyclic PLA,  $M_n = \text{conv.}(\%) \times 800 \times 144.1$ . <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

Poor agreement between measured and calculated  $M_n$  values was observed as a consequence of extensive intratransesterification reaction. Given the fact the ROP of *rac*-LA using **2**, **13** or **3** provided moderately heterotactic PLAs ( $P_r = 0.64$ - $0.72$ ), therefore, it was not surprising that highly syndiotactic PLAs were formed by the ROP of *meso*-LA operated by chain-end control. The isolated PLA obtained in each case revealed a decrease in syndioselectivity giving  $P_r = 0.82$ - $0.83$  (Table 2.13) in comparison to that obtained using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) ( $P_r = 0.87$ ). The  $M_n(\text{GPC})$  value of resulting PLA obtained from **3** was higher than those obtained by using **2** or **13** attributed to a lower proportion of initiating form of **3** than **2** or **13**, leading to longer polymer chains growing on the metal centre.

## 2.10 Summary and conclusions for Chapter Two

This Chapter described the catalytic activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBEt}_3)(\text{THF})_2$  (**2**) for the ROP of LA. The analogous heavy alkaline earth metal alkoxide complexes (**7**, **10**, **11**, **12** and **13**) and their ROP activities were

presented. Complex **1** was very active in the ROP of *rac*-LA, polymerising 100 up to 800 equiv. of *rac*-LA in THF at RT within 3 min. Poor agreement between measured and calculated  $M_n$  values was observed. Higher than expected  $M_n$  values in the initial ROP stages are a consequence of slow initiation with respect to propagation rate. Lower than calculated  $M_n$  values in the later ROP stages are attributed to inter- and intramolecular transesterification reactions. The kinetic studies showed second order and first order dependency on  $[rac\text{-LA}]$  and  $[1]$ , respectively with the measurement of  $k_p = 258(14) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.994$ ). Moderate  $D$  values of PLAs were obtained (1.39-1.88). The resulting PLA is reasonably heterotactic with  $P_r$  values = 0.78-0.82. MALDI-ToF mass spectrometry showed the presence of cyclic PLA and PLA end capped with non-opened ring LA ( $-\text{LA-H}$ ) and  $-\text{OH}$  groups. The ROP of *meso*-LA using **1** was also very active, reaching 96% conversion of 800 equiv. of *meso*-LA after 2 min. Syndiotactically-enriched PLA was formed with  $P_r = 0.87$ . First order dependence on  $[meso\text{-LA}]$  was determined. The ROP of *L*- and *D*-LA with **1** was less active than *rac*- or *meso*-LA. Only *ca.* 80 % conversion was obtained after 30 min under analogous conditions. The presence of  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) was observed from NMR tube scale reaction of **1** with 1 equiv. of *rac*-LA in THF- $d_8$ .  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**) was synthesised in an unsuccessful attempt to react with  $\text{PhSiH}_3$  to give **4**. However, a small quantity of **4** was obtained by ligand redistribution in the Schlenk equilibrium of **5** in benzene at 4 °C. The identification of non-opened ring LA species,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  was achieved *via* NMR tube scale reaction of **1** and 5 equiv. of *L*-LA in THF- $d_8$  at 223 K and characterised by NMR spectroscopy.  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(S\text{-lactate})$  (**9**) prepared *via* NMR tube scale reaction of **5** with *S*-methyl lactate in THF- $d_8$  at 223 K was presented as a model of the first ring-opened LA species on the metal centre.

A series of calcium alkoxide complexes serving as models of initiating species in the ROP of LA and their catalytic activities in the ROP of LA were described.  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) were synthesised by reaction of **1** with 1 equiv. of benzophenone or 2-methylcyclohexanone, respectively. While  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{O}^i\text{Pr})(\text{THF})_x$  (**12**) were generated *in situ* from reaction of **1** with benzaldehyde or reaction of **5** with  $\text{BnOH}$  or  $^i\text{PrOH}$  in THF, respectively. The analogous alkoxide complexes (**7**, **10**, **11** and **12**) were capable of polymerising up to 800 equiv. of *rac*-LA within 3 min in THF

at RT. The monomer consumption followed second-order dependency with  $k_{app} = 0.176(9)\text{--}0.123(4) \text{ M}^{-1}\text{s}^{-1}$ . The overall rate law in the ROP of *rac*-LA with **7** was presented as  $-d[rac\text{-LA}]/dt = k_p[rac\text{-LA}]^2[\mathbf{7}]$ ;  $k_p = 332(24) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.990$ ). Heterotactically-enriched PLAs were obtained with  $P_r = 0.78\text{--}0.83$ . The ROP of *meso*-LA with **7** (94% conversion, 1 min) produced syndiotactically-enriched PLA with  $P_r = 0.87$ . MALDI-ToF MS of PLAs formed by calcium alkoxide catalysts (**7**, **10**, **11** and **12**) showed a major distribution of cyclic PLA with a separation between each peak envelope by  $\Delta(m/z) = 72.0 \text{ Da}$  due to transesterification reactions. A minor distribution of PLA terminated by  $-\text{OH}$  and  $-\text{OR}$  groups was also observed. Comparable kinetic results ( $k_{app}$  and  $k_p$ ) and stereoselectivity ( $P_r$ ) are indicative of similar polymerisation behaviour in the ROP of *rac*-LA employing **1** or a series of alkoxide complexes (**7**, **10**, **11** and **12**).

$(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{HBET}_3)(\text{THF})_2$  (**2**),  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) and  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**) were found to be more active than the analogous calcium-based complexes (**1**, **7**, **10**, **11** and **12**). The polymerisation of 800 equiv. of *rac*-LA or *meso*-LA was completed within 1 min as expected based on the increased radius of  $\text{Sr}^{2+}$ . Very poor control of the ROP was observed;  $M_n(\text{GPC}) \ll M_n(\text{calcd})$ ,  $D = 1.37\text{--}1.62$ . Partially heterotactic PLAs ( $P_r = 0.72\text{--}0.68$ ) or highly syndiotactic PLAs ( $P_r = 0.82$ ) were produced from the ROP of *rac*-LA or *meso*-LA, respectively. The polymerisation rate of strontium complexes is faster than these of calcium complexes, whereas the stereoselectivity is the opposite with strontium complexes showing poor stereocontrol compared to calcium complexes. This can be attributed to larger size of  $\text{Sr}^{2+}$  vs.  $\text{Ca}^{2+}$ .

The proposed mechanism for the ROP of LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**) was examined. The non-opened ring LA species,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$ , formed by a hydride transfer reaction of **1** with LA is labile, undergoing Schlenk-type redistribution to form  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) and  $\text{Ca}(\text{LA-H})_2(\text{THF})_x$ .  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  can act as ROP initiator leading to the formation of PLA terminated with  $-\text{OH}$  group at one end and the non-opened LA ring ( $-\text{LA-H}$ ) at the other. Extensive transesterification reactions also occurred giving cyclic PLA.

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## **Chapter Three**

**Calcium cyclic organohydroborate complex for  
the ROP of LA and its mechanistic investigation**

## Chapter Three

### 3.1 Overview

This Chapter will describe detailed investigations into the ROP of LA using the cyclic organohydroborate calcium complex,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**). Detailed polymerisation studies for ROP of *rac*- and *meso*-LA using **14** will be presented in conjunction with an in-depth mechanistic evaluation of the ROP of LA by NMR spectroscopy. The synthesis and characterisation of analogous alkoxide complexes serving as models for intermediate species, together with their catalytic activities will be discussed. The role of borinic esters  $\text{R}_2\text{B}(\text{OR}')$  ( $\text{R}, \text{R}' = \text{alkyl}$ ) as chain transfer agents in the ROP of *rac*-LA will also be presented.

### 3.2 Introduction

#### 3.2.1 Alkaline earth cyclic organohydroborate $([\text{H}_2\text{BC}_8\text{H}_{14}]^-)$ complexes

Various metal cyclic organohydroborate  $([\text{H}_2\text{BC}_8\text{H}_{14}]^-)$  complexes containing Group 4 metals (Ti, Zr, Hf),<sup>1-8</sup> Y,<sup>9</sup> Eu,<sup>10, 11</sup> Yb,<sup>10, 11</sup> Tm,<sup>12</sup> Ru,<sup>13</sup> Re<sup>14</sup> and K<sup>15</sup> have been prepared and characterised. However, alkaline earth cyclic organohydroborate complexes of  $[\text{H}_2\text{BC}_8\text{H}_{14}]^-$  are relatively less developed. Hill *et al.* reported the synthesis of  $(\text{DippNacNac})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**3.1**) *via*  $\sigma$ -bond metathesis reaction of  $(\text{DippNacNac})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}(\text{THF})$  with  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  (9-BBN).<sup>16</sup> The solid state structure of **3.1** analysed by NMR, IR and X-Ray diffraction displays two conformers, pseudo-*trans* (**3.1a**) and pseudo-*cis* (**3.1b**), as shown in Figure 3.1.

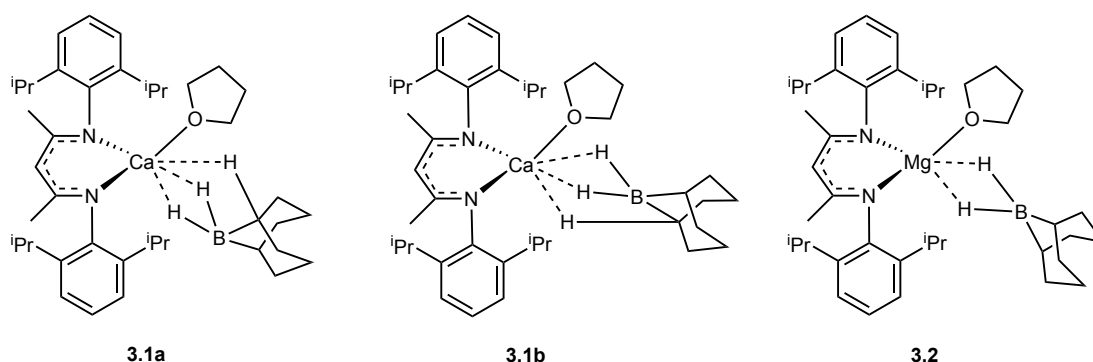


**Figure 3.1** Alkaline earth cyclic organohydroborate complexes (**3.1a**, **3.1b** and **3.2**).<sup>16,</sup>  
17

Each conformation was described as an octahedral geometry containing Ca centre coordinated to two nitrogens from  $\text{DippNacNac}$  ligand, oxygen from THF, two hydrides

from  $\text{H}_2\text{BC}_8\text{H}_{14}$  moiety and methine hydrogen of  $\text{BC}_8\text{H}_{14}$  unit *via* agostic interaction. The different route to synthesise **3.1** reported by Harder and Spielmann was *via* reaction of dinuclear complex,  $[(^{\text{Dipp}}\text{NacNac})\text{Ca}(\mu\text{-H})(\text{THF})]_2$  with  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$ .<sup>18</sup> Catalytic activity of **3.1** was examined in the hydroboration of 1,1-diphenylethylene and catecholborane in  $\text{C}_6\text{H}_6$  at RT with 5 mol% of **3.1**. However, the activity was poor, reaching 43% conversion after 192 h. Recently, Hill *et al.* reported dehydrocoupling of boranes (pinacolborane and  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$ ) and a range of amines and anilines in the presence of  $(^{\text{Dipp}}\text{NacNac})\text{Mg}(\text{}^n\text{Bu})$  as a precatalyst.<sup>17</sup>  $(^{\text{Dipp}}\text{NacNac})\text{Mg}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**3.2**, Figure 3.1) was isolated from a stoichiometric reaction of  $(^{\text{Dipp}}\text{NacNac})\text{Mg}(\text{}^n\text{Bu})$ , 2,6-diisopropylphenyl aniline and  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  in toluene.<sup>17</sup>

### 3.2.2 Alkaline earth cyclic organohydroborate $[\text{H}_2\text{BC}_8\text{H}_{14}]^-$ complex for the ROP of *rac*-LA

$(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) was developed by the Mountford group and a preliminary study of its catalytic activity in the ROP of *rac*-LA has been reported.<sup>19</sup> Complex **14** was synthesised *via* the salt elimination reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{I})(\text{THF})$  and  $\text{Na}[\text{H}_2\text{BC}_8\text{H}_{14}]$  in THF at RT. The solid state structure of **14** shows the  $\text{H}_2\text{BC}_8\text{H}_{14}$  ligand coordinated to Ca *via*  $\kappa^2$ -binding mode through two bridging hydrides (Figure 3.2). Unlike **3.1a** and **3.1b**,<sup>16</sup> no agostic interaction was observed between Ca and the methine hydrogen of  $\text{BC}_8\text{H}_{14}$  due to the  $\kappa^3$ -coordination of  $\text{Tp}^{\text{tBu,Me}}$ .

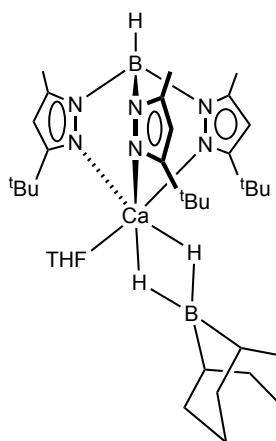
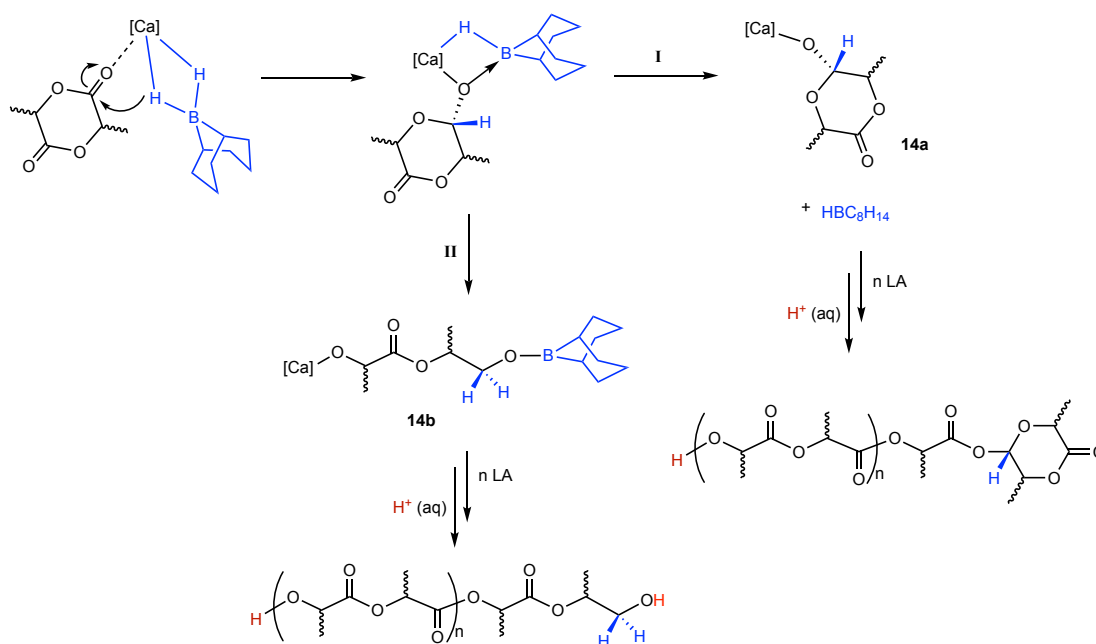


**Figure 3.2**  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) as ROP of *rac*-LA catalyst.<sup>19</sup>

Complex **14** showed high activity in the ROP of *rac*-LA in THF with  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 100$ , reaching 97% conversion within 1 min.<sup>19</sup> Good agreement between measured  $M_n$  (14,560  $\text{g mol}^{-1}$ ) and calculated  $M_n$  for one chain per metal centre (13,990  $\text{g mol}^{-1}$ )

was observed, with a moderate  $D$  value (1.47). Heterotactically-enriched PLA with  $P_r = 0.83$  was obtained. Polymer end-group analysis by MALDI-ToF mass spectrometry revealed three types of PLA synthesised by ROP of LA using **14**; cyclic PLA, PLA terminated with non-opened LA ring ( $-LA-H$ ) and a hydroxy group ( $-OH$ ) chain ends, and  $\alpha,\omega$ -dihydroxytelechelic PLA. These were indicative of two initiation pathways shown in Scheme 3.1. The first pathway was proposed to involve a non-opened LA ring species (**14a**) as a result of first hydride transfer reaction of **14** and LA. ROP of LA initiated by **14a** produced PLA end capped with non-opened LA ring alkoxide end group ( $-LA-H$ ). The second pathway was proposed to involve a ring-opened species,  $(Tp^{tBu,Me})Ca\{OCHMeC(O)OCHMeCH_2O(BC_8H_{14})\}$  (**14b**) generated by two successive hydride transfer of **14** with the carbonyl carbon of LA. Polymerisation of LA initiated *via* **14b** gave  $\alpha,\omega$ -dihydroxytelechelic PLA. An NMR tube scale reaction of **14** and 5 equiv. of *rac*-LA was carried out in THF- $d_8$  at RT. The presence of **14a** and **14b** was not observed from  $^1H$  NMR spectrum. The  $^{11}B$  NMR spectrum showed a broad signal at 57.5 ppm suggesting the possible formation of **14b**.



**Scheme 3.1** Proposed mechanism for the ROP of LA initiated by  $(Tp^{tBu,Me})Ca\{(\mu-H)_2BC_8H_{14}\}(THF)$  (**14**).  $[Ca] = (Tp^{tBu,Me})Ca(THF)_x$ .<sup>19</sup>

### 3.3 ROP of *rac*-LA using $(Tp^{tBu,Me})Ca\{(\mu-H)_2BC_8H_{14}\}(THF)$ (**14**)

The aim of this Chapter is to investigate catalytic activity and mechanism of  $(Tp^{tBu,Me})Ca\{(\mu-H)_2BC_8H_{14}\}(THF)$  (**14**) for the ROP of *rac*-LA. Polymerisations of

*rac*-LA with **14** were carried out in THF at RT in a glove-box under an N<sub>2</sub> atmosphere. The conversion of *rac*-LA was followed by collecting aliquots at regular intervals and quenched with degassed, wet THF. The polymer samples were analysed by NMR spectroscopy, MALDI-ToF mass spectrometry and Gel Permeation Chromatography (GPC).

Similar to the ROP activity of (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**) reported in Chapter Two, **14** was extremely active in the ROP of 100 equiv. of *rac*-LA, reaching 95% conversion after 30 s (Table 3.1, entry 5). In order to measure the kinetic order of the ROP using **14**, the high monomer loading of [*rac*-LA]<sub>0</sub>:**14**<sub>0</sub> = 800 was performed, reaching 90% conversion after 3 min (Table 3.1, entry 1). As shown in Figure 3.3, a second order dependence on [*rac*-LA] was determined from the linear plot of 1/[*rac*-LA]<sub>t</sub> vs. time ( $k_{app} = 0.083(5) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.985$ ). No induction period was observed.

In order to determine kinetic order dependence on concentration of **14** and propagation rate constant ( $k_p$ ), ROP of *rac*-LA using various concentrations of **14** was carried out under analogous conditions. The initial *rac*-LA concentration was held constant at 0.5 M while catalyst concentration was varied, providing a ratio of [*rac*-LA]<sub>0</sub>:**14**<sub>0</sub> = 800, 500, 300 and 200. The ROP results are summarised in Table 3.1. Second order plots are shown in Figure 3.3, giving a rate law of  $-d[\textit{rac-LA}]/dt = k_{app}[\textit{rac-LA}]^2$  where  $k_{app} = k_p[\textbf{14}]^x$  ( $k_p$  = propagation rate constant).

**Table 3.1** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**).<sup>a</sup>

| Entry | [ <i>rac</i> -LA] <sub>0</sub> : <b>14</b> <sub>0</sub> | Conv. <sup>b</sup><br>(%) | Time<br>(s) | <i>M</i> <sub>n</sub> (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>k</i> <sub>app</sub> <sup>f</sup><br>(M <sup>-1</sup> s <sup>-1</sup> ) | <i>R</i> <sup>2f</sup> | <i>P</i> <sub>r</sub> <sup>g</sup> |
|-------|---------------------------------------------------------|---------------------------|-------------|--------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------|----------------------------------------------------------------------------|------------------------|------------------------------------|
| 1     | 800                                                     | 89                        | 180         | 71,930                                                             | 102,601                                                              | 1.51                  | 0.083(5)                                                                   | 0.985                  | 0.83                               |
| 2     | 500                                                     | 87                        | 120         | 27,440                                                             | 62,686                                                               | 1.97                  | 0.107(14)                                                                  | 0.952                  | 0.83                               |
| 3     | 300                                                     | 90                        | 90          | 19,700                                                             | 38,909                                                               | 1.96                  | 0.206(7)                                                                   | 0.996                  | 0.83                               |
| 4     | 200                                                     | 90                        | 60          | 17,240                                                             | 25,940                                                               | 1.74                  | 0.326(35)                                                                  | 0.977                  | 0.83                               |
| 5     | 100                                                     | 95                        | 30          | 11,340                                                             | 13,692                                                               | 1.76                  | <sup>h</sup>                                                               | <sup>h</sup>           | 0.82                               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub> = 0.5 M, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated *M*<sub>n</sub> (g mol<sup>-1</sup>) for –OH and –LA-H end groups, *M*<sub>n</sub>(calcd) (entry 1-5) = conv. (%) × [*rac*-LA]<sub>0</sub>:**14**<sub>0</sub> × 144.1 + 2. <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> Apparent second order rate constant for consumption of monomer with standard error and *R*<sup>2</sup> determined by linear regression analysis. <sup>g</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>h</sup> Not measured

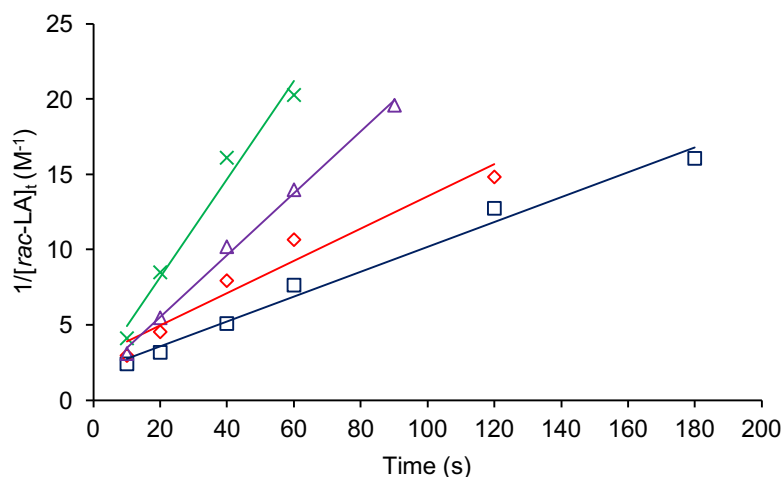


**Figure 3.3** Plots of  $1/[rac-LA]_t$  vs. time. Conditions: 6 mL THF, RT,  $[rac-LA]_0 = 0.5$  M. Squares:  $[rac-LA]_0:[mathbf{14}]_0 = 800:1$  ( $k_{app} = 0.083(5) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.985$ ). Diamonds:  $[rac-LA]_0:[mathbf{14}]_0 = 500:1$  ( $k_{app} = 0.107(14) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.952$ ). Triangles:  $[rac-LA]_0:[mathbf{14}]_0 = 300:1$  ( $k_{app} = 0.206(7) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.996$ ). Crosses:  $[rac-LA]_0:[mathbf{14}]_0 = 200:1$  ( $k_{app} = 0.326(35) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.977$ ).

The gradient of 1.02(11) ( $R^2 = 0.976$ ) from the plot of  $-\ln(k_{app})$  vs.  $-\ln[\mathbf{14}]_0$  is indicative of a first order dependence on concentration of **14** (Figure 3.4, right). The propagation rate constant ( $k_p$ ) of 133(10)  $\text{M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.989$ ) was calculated from the gradient of the plot between  $k_{app}$  vs.  $[\mathbf{14}]_0$  (Figure 3.4, left). The overall rate law was determined as  $-d[rac-LA]/dt = k_p[rac-LA]^2[\mathbf{14}]$ ,  $k_p = 133(10) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.989$ ).

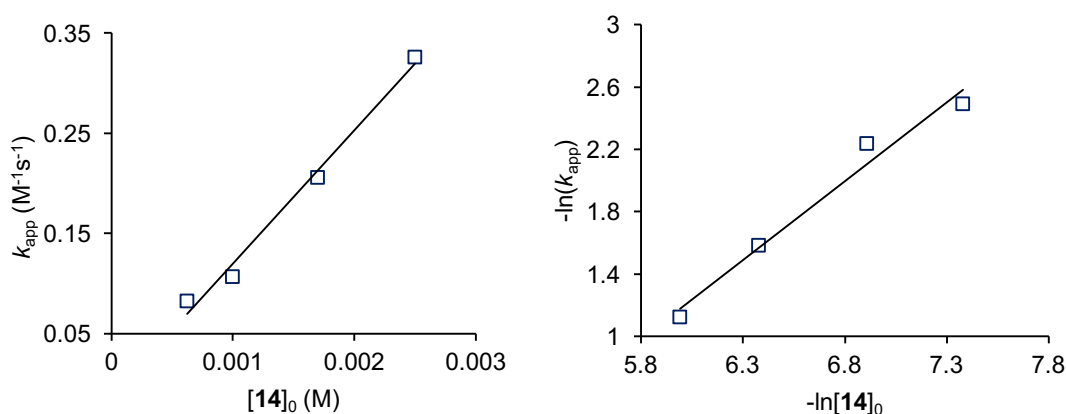


**Figure 3.4** Left, plot of  $k_{app}$  vs.  $[\mathbf{14}]_0$  shows  $k_p = 133(10) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.989$ ). Right, plot of  $-\ln(k_{app})$  vs.  $-\ln[\mathbf{14}]_0$  shows an order in **14** equal to 1.02(11) ( $R^2 = 0.976$ ).



As shown in Figure 3.5,  $M_n(\text{GPC})$  were slightly higher than those calculated at low monomer conversion (<40%) due to greater propagation than initiation rate. At high monomer conversion (>60%),  $M_n(\text{GPC})$  values deviated from those calculated for one growing chain per metal centre due to intramolecular transesterification reaction.  $\bar{D}$  values were narrow at low conversion and then become broader at high conversion ( $\bar{D} = 1.07\text{--}1.51$ ). Heterotactically-enriched PLAs were obtained with  $P_r = 0.82\text{--}0.83$  (Table 3.1).

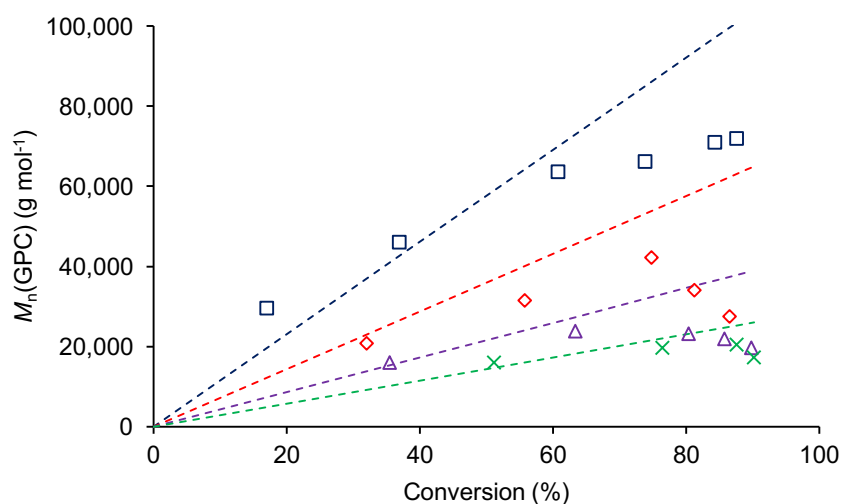


**Figure 3.5** Plots of  $M_n(\text{GPC})$  vs. conversion (%) for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}}\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\})(\text{THF})$  (**14**). Conditions: 6 mL THF, RT,  $[\text{rac-LA}]_0 = 0.5$  M. The dashed lines represent  $M_n(\text{calcd})$  for one PLA chain per metal centre. Squares:  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 800:1$ ,  $\bar{D} = 1.07\text{--}1.51$ . Diamonds:  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 500:1$ ,  $\bar{D} = 1.18\text{--}1.97$ . Triangles:  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 300:1$ ,  $\bar{D} = 1.26\text{--}1.96$ . Crosses:  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 200:1$ ,  $\bar{D} = 1.27\text{--}1.74$ .

The end groups of PLA formed by **14** were analysed by MALDI-ToF mass spectrometry. The resultant PLA was prepared from the ROP with  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 20$ . The polymerisation solution was quenched immediately after the addition of the catalyst solution into the *rac*-LA solution to suppress the transesterification reactions. MALDI-ToF mass spectrum (Figure 3.6) shows that the intra- and intermolecular transesterifications took place extensively giving cyclic PLA together with peak envelopes separated by  $\Delta m/z = 72.0$  Da. For example, the peak envelope centred at 1479.7 Da corresponds to cyclic PLA containing 20 units of half LA with  $\text{K}^+$ . Other two sets of peak envelopes correspond to PLA end capped with  $-\text{OH}$  and  $-\text{LA-H}$

termini, in conjunction with  $\alpha,\omega$ -dihydroxytelechelic PLA. For instance, the peak envelope centred at 1481.7 Da corresponds to PLA containing 18 units of half LA terminated by  $-\text{OH}$  and  $-\text{LA-H}$  chain ends with  $\text{K}^+$  [ $72.0(18) + 146.1 + 39.1$ ]. Another peak envelope centred at 1483.7 Da is assigned to PLA with 18 units of half LA end capped by  $-\text{OH}$  at both ends [ $72.0(18) + 148.1 + 39.1$ ]. A series of theoretical isotopic distributions of these three polymer adducts ( $m/z(\text{calcd}) = 1479.3, 1481.4$  and  $1483.4$  Da) was simulated and compared with the measured ones (Figure A2). Good agreement between the theoretical and measured isotopic distributions of three types of polymer adducts was observed, confirming the formation of PLA end capped with  $-\text{LA-H}$  unit,  $\alpha,\omega$ -dihydroxytelechelic PLA, and cyclic PLA.

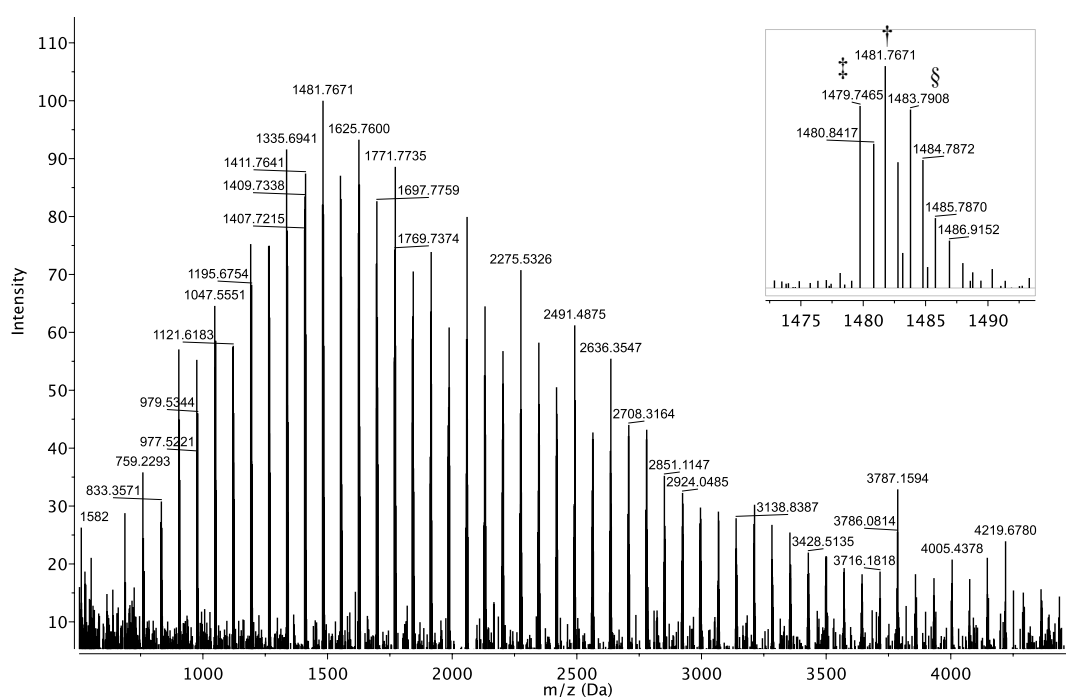


**Figure 3.6** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**).  $M_n(\text{GPC}) = 4,300 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.46$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{14}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0$  Da between peak envelopes. “‡” denotes cyclic PLA. “†” denotes PLA with non-opened LA ring ( $-\text{LA-H}$ ) and  $-\text{OH}$  end groups. “§” denotes  $\alpha,\omega$ -dihydroxytelechelic PLA.

In contrast to MALDI-ToF analysis, the  $^1\text{H}$  NMR spectra of crude or isolated PLA samples (Figure 3.7, b and c) show PLA with an absence of terminal groups either a non-opened LA ring ( $-\text{LA-H}$ ) or  $-\text{OH}$  groups (no signals at 2.67 and 3.82 ppm corresponding to  $-\text{CH}_2\text{OH}$  end group<sup>20</sup>). Similar to that observed from

(Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**), the <sup>1</sup>H NMR spectrum of the filtrate from polymer precipitation (Figure 3.7, a) shows two doublets at 5.46 and 5.36 ppm corresponding to OCH<sub>2</sub> proton on the non-opened LA chain end (–LA–H) of PLA.<sup>21</sup> These results supported the formation of low molecular weight PLA end capped with –OH and –LA–H as a very minor product with cyclic PLA as a major product.

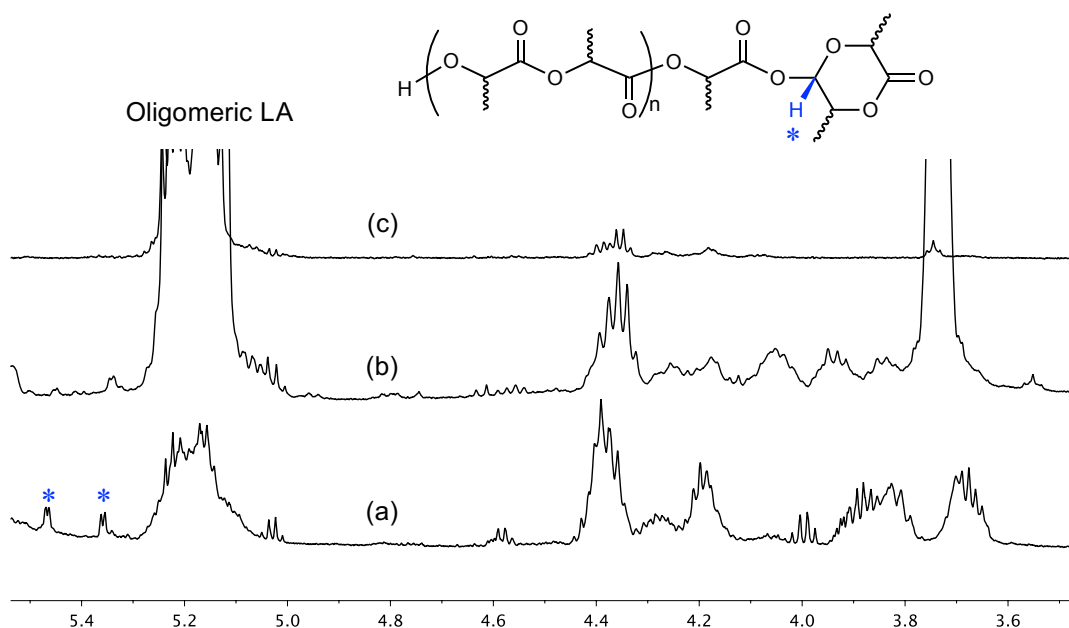


**Figure 3.7** <sup>1</sup>H NMR spectra (CDCl<sub>3</sub>, 499.9 MHz, 298 K) of the filtrate from polymer precipitation (a), crude PLA sample (b), and isolated PLA sample (c) obtained from the large scale ROP of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>} (THF) (**14**) with 20 equiv. of *rac*-LA in THF at RT. “\*” denotes OCH<sub>2</sub> proton of the non-opened LA ring chain end (–LA–H).

### 3.4 ROP of *meso*-LA using (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>} (THF) (**14**)

Complex **14** showed higher activity in the ROP of *meso*-LA than *rac*-LA, reaching 93% conversion after 1 min under analogous conditions. The plot of ln([*meso*-LA]<sub>0</sub>/[*meso*-LA]<sub>t</sub>) vs. time is linear (Figure 3.8, left), indicating polymerisation proceeding with first order dependence on [*meso*-LA] ( $k_{app} = 0.044(2) \text{ s}^{-1}$ ,  $R^2 = 0.997$ ). Poor agreement between measured and theoretical  $M_n$  values was observed over the entire conversion range due to a predominance of transesterification reactions (Figure 3.8, right), giving PLAs with moderate  $\bar{D}$  values (1.05-1.28). Syndiotactically-enriched PLA was produced with  $P_r = 0.87$ .

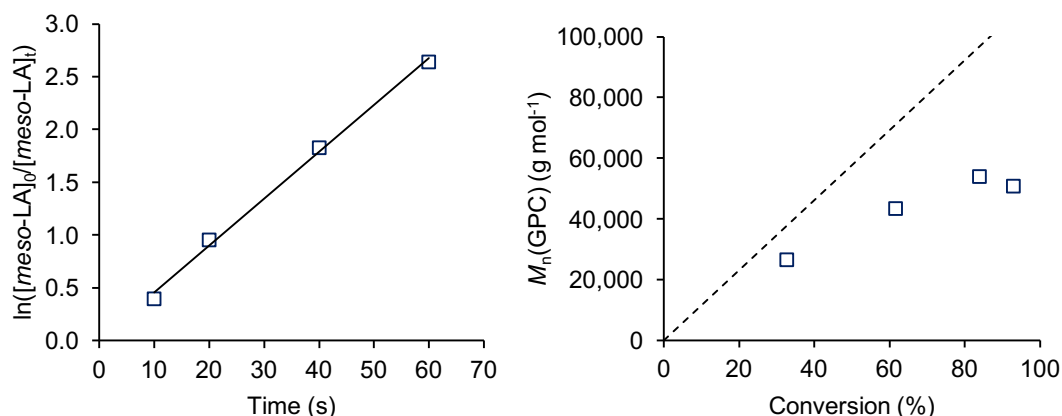


**Figure 3.8** Left, plot of  $\ln([meso-LA]_0/[meso-LA]_t)$  vs. time. ( $k_{app} = 0.044(2) \text{ s}^{-1}$ ,  $R^2 = 0.997$ ). Right, plot of  $M_n(\text{GPC})$  vs. conversion (%). The dashed line represents  $M_n(\text{calcd})$  for one PLA chain per metal centre.  $D = 1.05\text{--}1.28$ . Conditions: 6 mL THF, RT,  $[meso-LA]_0:[14]_0 = 800:1$ ,  $[meso-LA]_0 = 0.5 \text{ M}$ .

### 3.5 Mechanistic investigations of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**) for ROP of LA

According to the initial proposed mechanism for the ROP of LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) presented in Scheme 3.1, the polymerisation could proceed *via* two pathways. The first route is the ROP initiated by the non-opened ring LA,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  (**14a**) generated from first hydride transfer step. The second route occurs *via* two successive hydride transfer from **14** to LA producing an opened-LA ring species,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{OCHMeC(O)OCHMeCH}_2\text{O}(\text{BC}_8\text{H}_{14})\}$  (**14b**) as an initiator. The existence of first hydride transfer species was fully investigated and described in Chapter Two. Further evidence for the identification of the second hydride transfer product is reported in the following section.

#### 3.5.1 NMR tube scale studies of the ROP of LA with $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**)

An attempt to observe **14a** and **14b** was unsuccessful from an NMR tube scale reaction of **14** with 10 equiv. of *rac*-LA in THF-*d*<sub>8</sub> at RT. An unknown  $\text{Tp}^{\text{tBu,Me}}$  species was observed from <sup>1</sup>H and <sup>11</sup>B NMR spectra which are reminiscent of those obtained by using **1** (section 2.4.1). The signal at 57.1 ppm in the <sup>11</sup>B NMR fall in the range of 52.0–58.1 ppm corresponding to a borinic ester species  $\text{R}_2\text{B}(\text{OR}')$  (R, R' = alkyl).<sup>22</sup> To investigate the polymerisation behaviour of **14** for the ROP of LA, <sup>1</sup>H and <sup>11</sup>B NMR

analyses of the NMR tube scale reaction of **14** with 5 equiv. of *L*-LA was prepared in THF-*d*<sub>8</sub> at 195 K. The <sup>1</sup>H NMR spectrum recorded after 10 min at 223 K (Figure 3.9) shows signals corresponding to (Tp<sup>tBu,Me</sup>)Ca(*L*-LA-H)(THF)<sub>x</sub> (**14.1**) which are analogous to those observed by using **1** reported in Chapter Two (section 2.4.3).

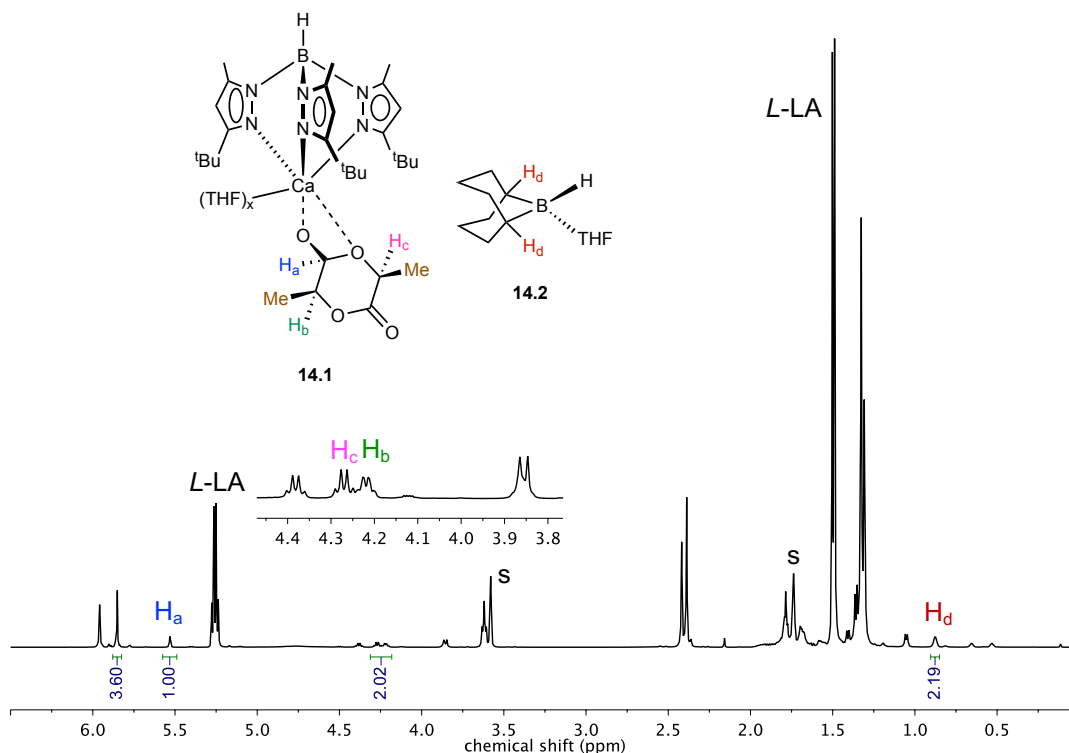


**Figure 3.9** <sup>1</sup>H NMR spectrum (THF-*d*<sub>8</sub>, 499.9 MHz, 223 K) of (Tp<sup>tBu,Me</sup>)Ca(*L*-LA-H)(THF)<sub>x</sub> (**14.1**) and (HBC<sub>8</sub>H<sub>14</sub>)(THF) (**14.2**) generated *in situ* by reaction of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>} (14) and 5 equiv. of *L*-LA. “s” denotes residual protio-solvent. “*L*-LA” denotes unreacted *L*-LA.

Methine proton H<sub>a</sub> appeared at 5.53 ppm. Methine proton H<sub>b</sub> coupled to its neighbouring methyl protons and methine proton H<sub>a</sub> to give an apparent quartet at 4.21 ppm. Methine proton H<sub>c</sub> coupled with its adjacent methyl protons to give a quartet at 4.28 ppm. A doublet at 1.36 ppm is assigned to methyl protons, Me(H<sub>b</sub>) and Me(H<sub>c</sub>). A distinctive singlet at 0.88 ppm is assigned to two methine protons H<sub>d</sub> of (HBC<sub>8</sub>H<sub>14</sub>)(THF) (**14.2**). The relative integration ratio of H<sub>a</sub>:H<sub>c</sub> and H<sub>b</sub>:H<sub>d</sub> = 1:2:2 supports the structural assignment for **14.1** and **14.2**. The <sup>11</sup>B NMR spectrum shows two signals at 12.6 and -8.3 ppm corresponding to **14.2**<sup>23</sup> and the apical B-H of Tp<sup>tBu,Me</sup> ligand, respectively.

The signals assigned to an opened-LA ring species formed by double hydride transfer ( $\text{Tp}^{\text{tBu,Me}}\text{Ca}\{\text{OCHMeC(O)OCHMeCH}_2\text{O(BC}_8\text{H}_{14})\}$  (**14.3**) were also observed in the  $^1\text{H}$  NMR spectrum shown in Figure 3.9. The assignment of **14.3** is separately described in Figure 3.10 which shows the same  $^1\text{H}$  NMR spectrum as in Figure 3.9.

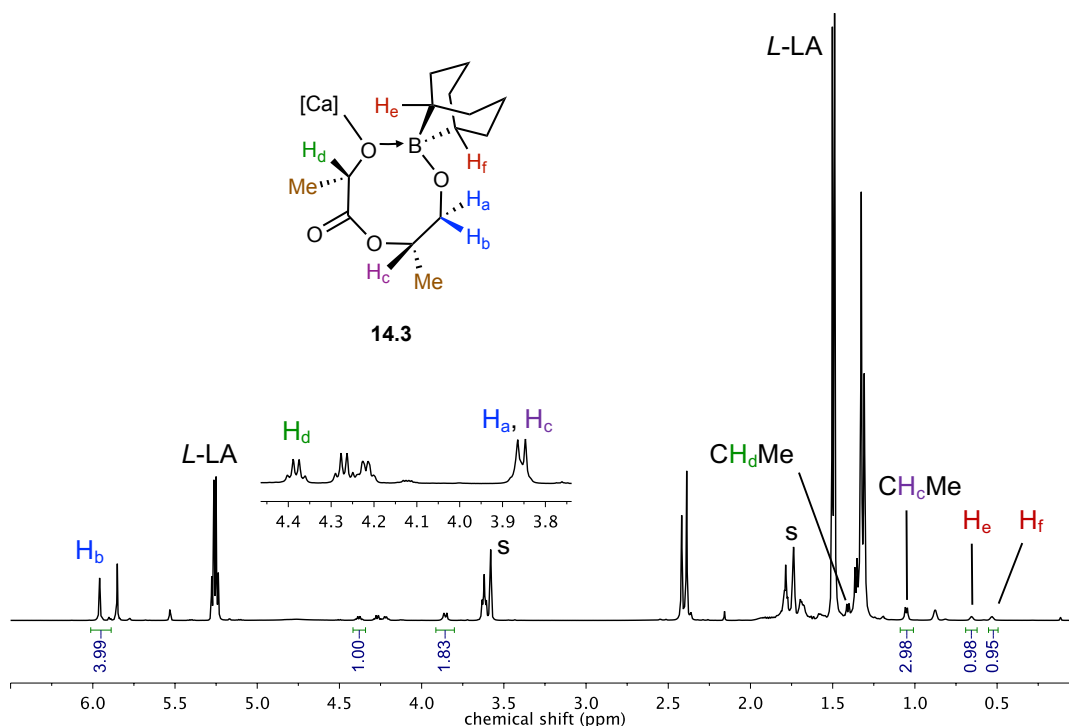


**Figure 3.10**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 223 K) of ( $\text{Tp}^{\text{tBu,Me}}\text{Ca}\{\text{OCHMeC(O)OCHMeCH}_2\text{O(BC}_8\text{H}_{14})\}$  (**14.3**) generated *in situ* via reaction of ( $\text{Tp}^{\text{tBu,Me}}\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}$  (THF) (**14**) and 5 equiv. of L-LA. “s” denotes residual protio-solvent. “L-LA” denotes unreacted L-LA.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}}\text{Ca}(\text{THF})_x$ .

The methylene protons ( $\text{H}_a$  and  $\text{H}_b$ ) of **14.3** are inequivalent resulting in two signals at 5.96 and 3.85 ppm. A singlet at 5.96 ppm corresponding to the methylene proton  $\text{H}_b$  overlapped with three methine protons on the  $\text{Tp}^{\text{tBu,Me}}$  ligand of **14.3**. Methylene proton  $\text{H}_a$  overlapped with methine proton  $\text{H}_c$  appeared as a multiplet at 3.85 ppm. Methine proton  $\text{H}_d$  appeared as a quartet at 4.39 ppm ( $^3J_{\text{H-H}} = 7.1$  Hz). The methyl protons of  $\text{CH}_d\text{Me}$  displayed as a doublet at 1.41 ppm ( $^3J_{\text{H-H}} = 6.8$  Hz). The other methyl protons  $\text{CH}_c\text{Me}$  were observed as a doublet at 1.04 ppm ( $^3J_{\text{H-H}} = 6.2$  Hz). The  $^1\text{H}$  NMR spectrum recorded at 223 K after 3 h shows that the intensity of **14.3** was increased whereas that of **14.1** was diminished. These suggested that **14.1** and **14.2** undergo bridging to form ( $\text{Tp}^{\text{tBu,Me}}\text{Ca}(\mu\text{-H})(\mu\text{-OR})(\text{BC}_8\text{H}_{14})$  (OR = L-LA-H moiety) (**14\_int1**). The hydride of

HBC<sub>8</sub>H<sub>14</sub> moiety was rapidly transferred to *L*-LA-H unit giving **14.3** (Scheme 3.2). The solution structure of **14.3** was assigned to be an eight-membered ring containing ring-opened *L*-LA terminated with BC<sub>8</sub>H<sub>14</sub> (Figure 3.10). Two singlets at 0.66 and 0.53 ppm were assigned to two inequivalent methine protons on BC<sub>8</sub>H<sub>14</sub> moiety, H<sub>e</sub> and H<sub>f</sub>, respectively. The assignment for these methine, methylene and methyl protons is supported by COSY and HSQC NMR spectra as shown in Figures A13 and A14.

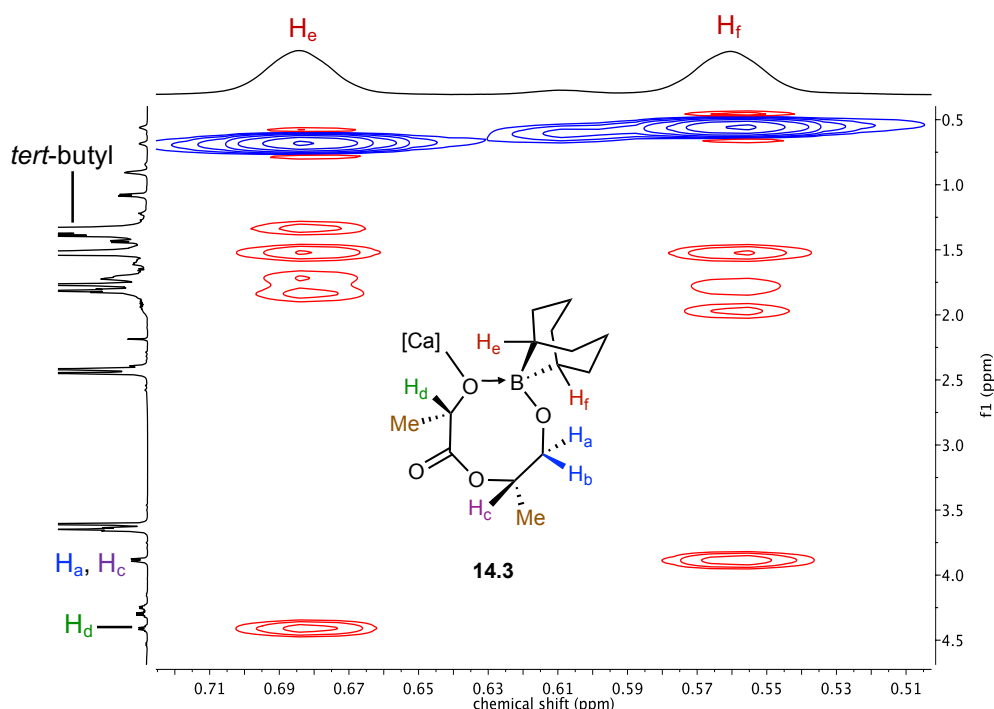
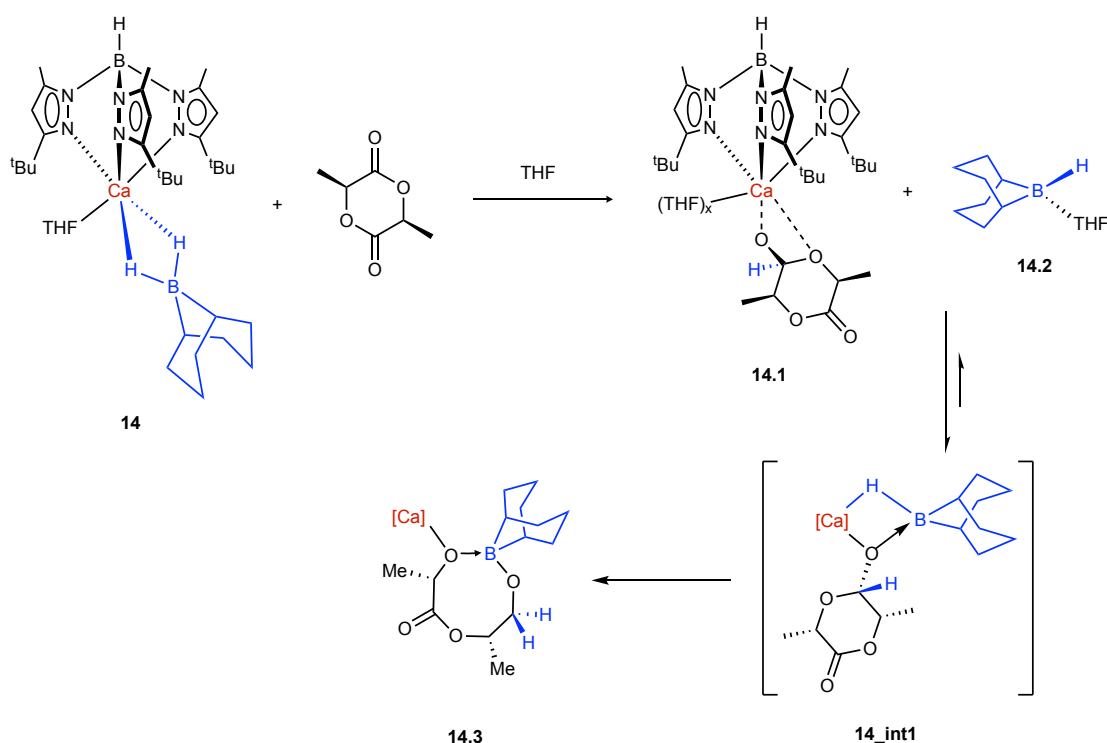


**Figure 3.11** ROESY spectrum (THF-*d*<sub>8</sub>, 499.9 MHz, 223 K) of (Tp<sup>tBu,Me</sup>)Ca{OCHMeC(O)OCHMeCH<sub>2</sub>O(BC<sub>8</sub>H<sub>14</sub>)} (**14.3**) generated *in situ* via reaction of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**) and 5 equiv. of *L*-LA. [M] = (Tp<sup>tBu,Me</sup>)Ca(THF)<sub>x</sub>.

The ROESY spectrum recorded at 223 K (Figure 3.11) showed through-space correlation between methine proton H<sub>d</sub> on the first half of LA unit on Ca and H<sub>e</sub> on BC<sub>8</sub>H<sub>14</sub> moiety. Other correlation between H<sub>e</sub> and *tert*-butyl groups on the Tp<sup>tBu,Me</sup> ligand of **14.3** was also observed. These correlations are indicative of a close proximity between BC<sub>8</sub>H<sub>14</sub> moiety and the Tp<sup>tBu,Me</sup> ligand on Ca. Overall, the structure of **14.3** contains Ca centre coordinated to an opened-LA ring terminated with BC<sub>8</sub>H<sub>14</sub> moiety, together with a B-O interaction between O donor of CaOCHMe and B of BC<sub>8</sub>H<sub>14</sub> giving the eight-membered ring. The <sup>11</sup>B NMR spectrum recorded at 223 K after 3 h supports the cyclic structure of **14.3** by showing a signal at 3.8 ppm assigned to (OR)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub> of

**14.3** which fits in the region (*ca.*  $\delta = 2\text{--}6$  ppm) for tetra-coordinated borate containing species.<sup>22</sup> Other signals appeared at 12.6 and  $-8.3$  ppm corresponding to **14.2** and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  ligand, respectively.

Scheme 3.2 shows the proposed mechanism for the reaction of **14** with 1 equiv. of *L*-LA in THF based on NMR spectroscopic data. The first hydride of **14** migrates to LA giving **14.1** and **14.2**. The formation of **14\_int1** from **14.1** and **14.2** is followed by reduction of non-opened LA ring by hydride from  $\text{HBC}_8\text{H}_{14}$  moiety, generating **14.3**.



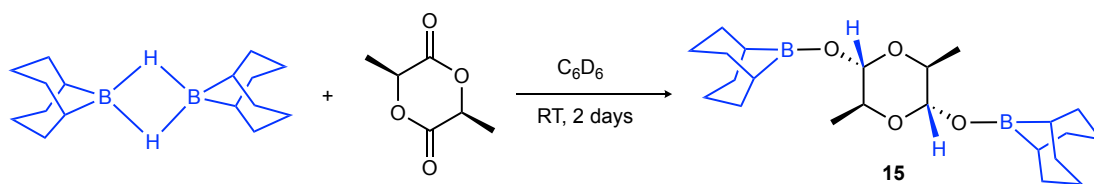
**Scheme 3.2** Proposed mechanism for the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with *L*-LA in THF.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

### 3.5.2 Identification of the first and second hydride transfer products of *L*-LA with $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$

As  $(\text{HBC}_8\text{H}_{14})(\text{THF})$  (**14.2**) was observed from  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 5 equiv. of *L*-LA in  $\text{THF-}d_8$  at 223 K (*vide supra*), a role of **14.2** in the ROP of LA was investigated. Control experiments were performed in order to gain an understanding of how **14.2** reacts with *L*-LA and whether this is competitive with the ROP of LA. An NMR tube scale reaction of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  with 1 equiv. of *L*-LA was performed in  $\text{THF-}d_8$  at RT providing similar



results compared to those performed in  $C_6D_6$ . The latter was employed as the preferred NMR solvent due to better signal separation (Equation 3.1).



**Equation 3.1**

The  $^1H$  NMR spectrum recorded after 2 days (Figure 3.12) shows signals corresponding to the first hydride transfer product (3,6-dimethyl-1,4-dioxane-2,5-diyl)bis(oxy)bis(9-borabicyclo[3.3.1]nonane (**15**). Three doublets and a multiplet in the region of 5.0–6.0 ppm are assigned to methine protons of  $OCHCHMe$  of the alkoxy LA ring. Additionally, a group of multiplets between 4.20–4.50 ppm and a quartet of doublet at 4.04 ppm ( $^3J_{H-H} = 6.3, 3.4$  Hz) are assigned to methine protons of  $OCHCHMe$ . The  $^{11}B$  NMR spectrum gives a broad singlet at 58.7 ppm falling in a range of signal corresponding to  $R_2B(OR')$  ( $R, R' = \text{alkyl}$ ), which is consistent with the structural assignment of **15**.<sup>24, 25</sup> The absence of unreacted  $(\mu-H)_2(BC_8H_{14})_2$  also supports the hypothesis that two ester groups of *L*-LA are reduced by  $(\mu-H)_2(BC_8H_{14})_2$  to form **15**. The formation of **15** is further supported by the ESI-HRMS  $m/z$  found at 406.3307 Da ( $m/z(\text{calcd})$  for  $(M+NH_4)^+ = 406.3302$  Da). The complicated  $^1H$  NMR spectrum is due to various conformations and stereocentres of **15**. The roofing effect is observed at 3.91 and 3.73 ppm corresponding to methylene protons of the second hydride transfer product (**16**) (*vide infra*).

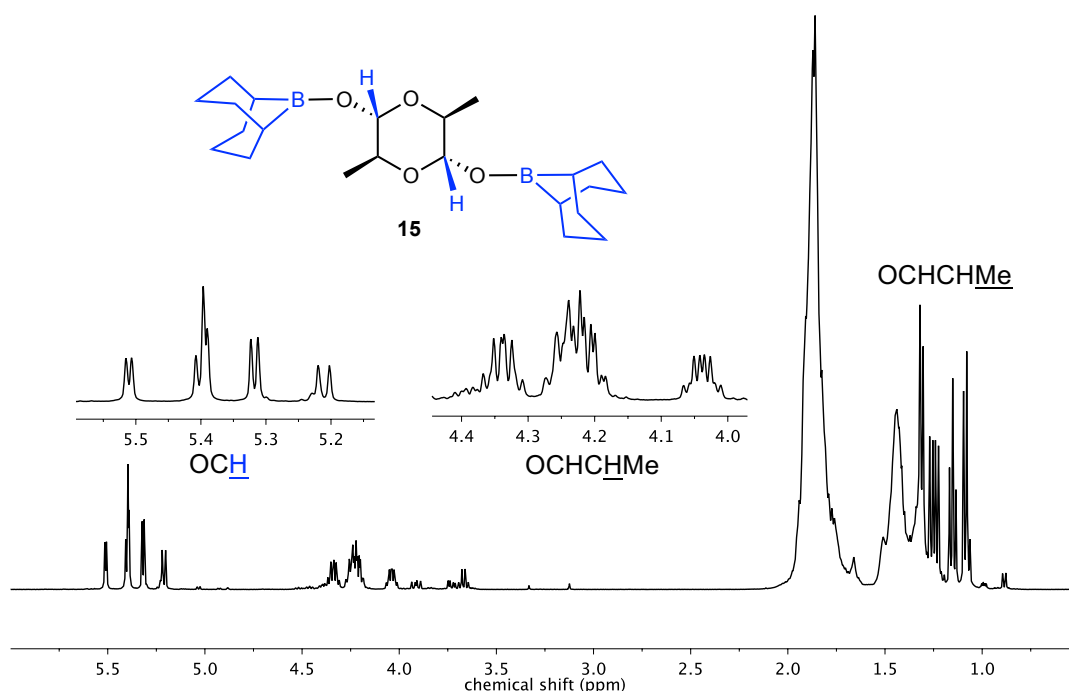
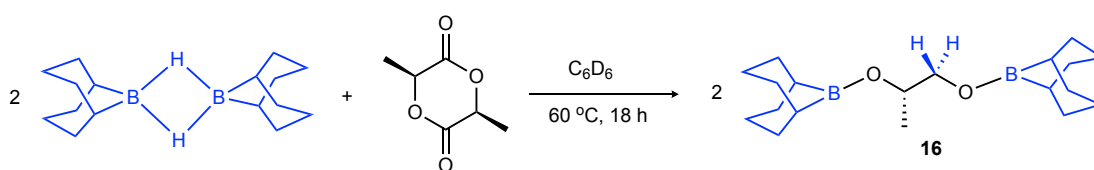


**Figure 3.12**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of the first hydride transfer product (**15**) generated *in situ* by reaction of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  with 1 equiv. of *L*-LA.

An NMR tube scale reaction of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  with *L*-LA in a 2:1 molar ratio was performed in  $\text{C}_6\text{D}_6$  at 60 °C for 18 h (Equation 3.2). Two hydrides from  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  migrated to each ester group on *L*-LA, followed by an acyl bond cleavage to generate the second hydride transfer product (propane-1,2-diyl)bis(oxy)bis(9-borabicyclo[3.3.1]nonane (**16**).



**Equation 3.2**

The  $^1\text{H}$  NMR spectrum of **16** (Figure 3.13) shows a multiplet at 4.39 ppm. Two methylene protons  $\text{OCHMeCH}_2$  are considered as diastereotopic protons due to the presence of a chiral centre in the molecule. Two doublet of doublets at 3.91 ppm ( $^3J_{\text{H-H}} = 10.7, 7.4$  Hz) and 3.73 ppm ( $^3J_{\text{H-H}} = 10.7, 3.9$  Hz) are assigned to inequivalent methylene protons. The  $^{11}\text{B}$  NMR spectrum shows a broad singlet for the two inequivalent borons at 56.8 ppm corresponding to  $\text{R}_2\text{BOR}'$  of **16**. The formation of **16**

is also supported by the ESI-HRMS  $m/z = 314.2799$  Da ( $m/z(\text{calcd})$  for  $[\text{M}]^+ = 314.2812$  Da).

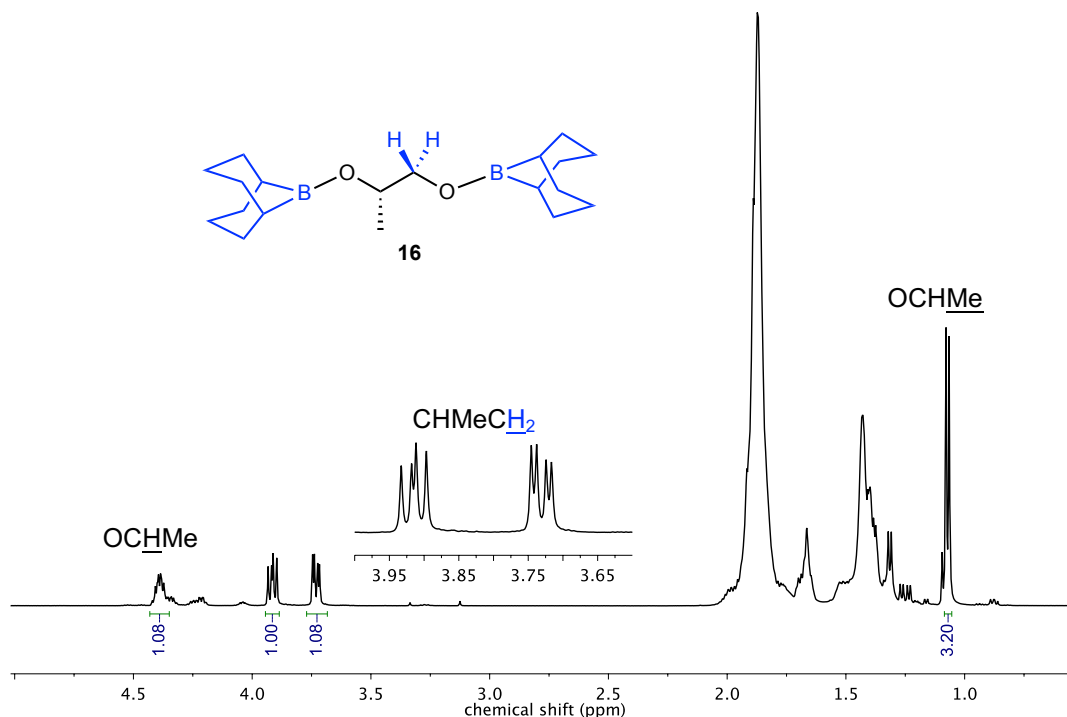


**Figure 3.13**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of the second hydride transfer product (**16**) generated *in situ* by reaction of 2 equiv. of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  with 1 equiv. of *L*-LA.

Another example of ring-opening of LA *via* ester cleavage and hydroboration was reported by Sadow *et al.*<sup>26</sup> With the presence of  $\text{To}^{\text{M}}\text{MgMe}$  ( $\text{To}^{\text{M}} = \text{tris}(4,4\text{-dimethyl-2-oxazolinyl})\text{phenylborate}$ ) as a catalyst, a reaction of *rac*-LA with pinacolborane (HBpin) in a 1:4 molar ratio produced a dialkoxyboronic acid pinacol ester (pinBOCHMeCH<sub>2</sub>OBpin), the analogue of **16** at RT. The same 1,2-diboronate ester was reported to be obtained *via* depolymerisation of PLA with HBpin catalysed by  $\text{To}^{\text{M}}\text{MgMe}$ .

Similar C-O cleavage reaction was also observed by Hill *et al.* during hydroboration of  $\text{CO}_2$  with 3 equiv. of HBpin catalysed by  $(^{\text{Dipp}}\text{NacNac})\text{M}\{\text{HB}(\text{C}_6\text{F}_5)_3\}(\text{THF})_x$  ( $\text{M} = \text{Mg}$ ,  $x = 0$  and  $\text{M} = \text{Ca}$ ,  $x = 1$ ).<sup>27</sup> The reaction was performed in THF at 60 °C for 4-6 days to produce diboroxane,  $(\text{pinB})_2\text{O}$  and MeOBpin. The *in-situ* monitoring of the NMR scale reaction showed the presence of minor quantities of pinBOCHO and pinBOCH<sub>2</sub>OBpin, suggesting the catalytic cycle proceeded *via* C=O/M-H insertion and B-H/M-O  $\sigma$ -bond metathesis events.

Examples of hydroboration of CO<sub>2</sub> with HBC<sub>8</sub>H<sub>14</sub> have been reported using various catalytic systems such as phosphine-borane,<sup>28-30</sup> organocatalysts<sup>31-33</sup> or (pincer)Ni hydride.<sup>34</sup> The formation of O(BC<sub>8</sub>H<sub>14</sub>)<sub>2</sub>, and MeO(BC<sub>8</sub>H<sub>14</sub>) were obtained as final products. It is noteworthy that these catalytic hydroboration reactions of LA or CO<sub>2</sub> involve an excess of organoboranes. Whereas the ROP of *rac*-LA with **14** involves a large excess of *rac*-LA.

Despite of the successful hydroboration of *L*-LA using (μ-H)<sub>2</sub>(BC<sub>8</sub>H<sub>14</sub>)<sub>2</sub>, the rate of hydroboration is relatively slow compared to the polymerisation rate of *rac*-LA using **14**. This indicated that the direct hydride transfer from (HBC<sub>8</sub>H<sub>14</sub>)(THF) (**14.2**) to LA giving **15** or **16** does not occur during polymerisation. The next consideration is whether (Tp<sup>tBu,Me</sup>)Ca(*L*-LA-H)(THF)<sub>x</sub> (**14.1**) and **14.2** undergo Ca-O/B-H σ-bond metathesis through **14\_int1** to form (BC<sub>8</sub>H<sub>14</sub>)(*L*-LA-H) (**14.4**) and (Tp<sup>tBu,Me</sup>)Ca(H) (**14\_int2**).

Examples of catalytic reactions where σ-bond metathesis plays a crucial role are presented. In 2006, Harder and Brettar reported the synthesis of [(<sup>Dipp</sup>NacNac)Ca(μ-H)(THF)]<sub>2</sub> *via* σ-bond metathesis of PhSiH<sub>3</sub> with (<sup>Dipp</sup>NacNac)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>}(THF).<sup>35</sup> Extensive studies of hydroboration of ketones and aldehydes catalysed by metal hydrides *i.e.* Mg,<sup>36</sup> Ge,<sup>37</sup> Sn,<sup>37</sup> Ti,<sup>38</sup> Zn,<sup>39</sup> Mn<sup>40</sup> or organocatalysts<sup>41</sup> have been reported with the presence of σ-bond metathesis in the catalytic cycle. The hydroboration of other unsaturated compounds such as imines,<sup>42</sup> nitriles,<sup>43</sup> isonitriles,<sup>44</sup> carbodiimides,<sup>45</sup> or pyridines<sup>46</sup> catalysed by (<sup>Dipp</sup>NacNac)Mg(<sup>n</sup>Bu) were also shown to undergo *via* σ-bond metathesis event.

An NMR tube scale reaction of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**) with 1 equiv. of benzophenone was performed in THF-*d*<sub>8</sub> at RT to imitate a reaction of **14** and 1 equiv. of LA. It is worth noting that benzophenone can only accept one hydride, whereas LA can accept two hydrides because of acyl-oxygen bond cleavage. The <sup>1</sup>H NMR spectrum recorded after 10 min (Figure 3.14, a) shows signals at 5.84 ppm and 5.76 ppm corresponding to methine protons on the Tp<sup>tBu,Me</sup> ligand of **14** and (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**), respectively. The methine proton of (BC<sub>8</sub>H<sub>14</sub>)(OCHPh<sub>2</sub>) (**17**) is observed as a singlet at 6.36 ppm. Unreacted benzophenone is also observed from the <sup>1</sup>H NMR spectrum. The <sup>11</sup>B NMR spectrum monitored after 10 min (Figure 3.15, a) shows a singlet at 27.9 ppm and a doublet at 13.6 ppm corresponding to (μ-H)<sub>2</sub>(BC<sub>8</sub>H<sub>14</sub>)<sub>2</sub> and B-H of **14.2**, respectively. A broad singlet at

57.8 ppm corresponds to **17**. Other signals at -8.3 and -10.9 ppm correspond to the apical B-H of the  $\text{Tp}^{\text{tBu,Me}}$  ligand of **7** and **14**, and  $\text{Ca}(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})$  of **14**, respectively. The  $^1\text{H}$  NMR spectrum recorded after 18 h (Figure 3.14, b) shows the signals corresponding to **14**, **7** and **17**, in a 1:1:1 ratio. The  $^{11}\text{B}$  NMR spectrum recorded after 18 h (Figure 3.15, b) shows three signals corresponding to **17** ( $\delta = 57.8$  ppm), **7** and **14** ( $\delta = -8.3, -10.9$  ppm) with the absence of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  ( $\delta = 27.9$  ppm) and **14.2** ( $\delta = 13.6$  ppm). This result suggests that **14** reacts in a 1:2 stoichiometry with benzophenone. The reaction of **14** and 2 equiv. of benzophenone was also performed in  $\text{THF-}d_8$ , giving consumption of **14** and production of **7** and **17** (*vide supra*).

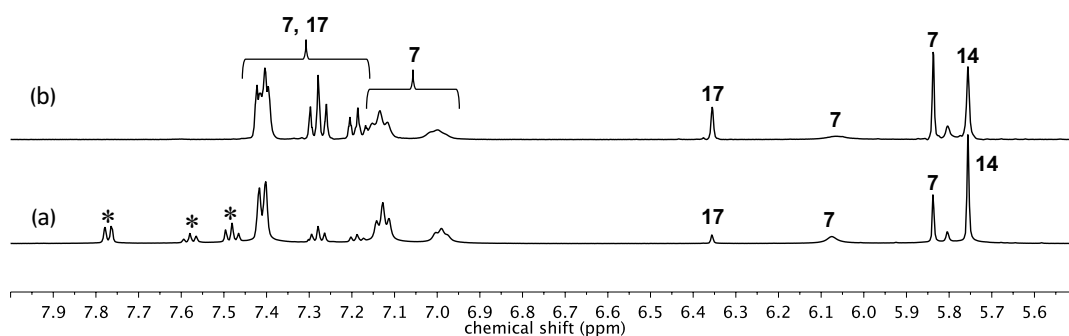


**Figure 3.14**  $^1\text{H}$  NMR spectra ( $\text{THF-}d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 1 equiv. of benzophenone after 10 min (a) and after 18 h (b). “\*” denotes unreacted benzophenone.

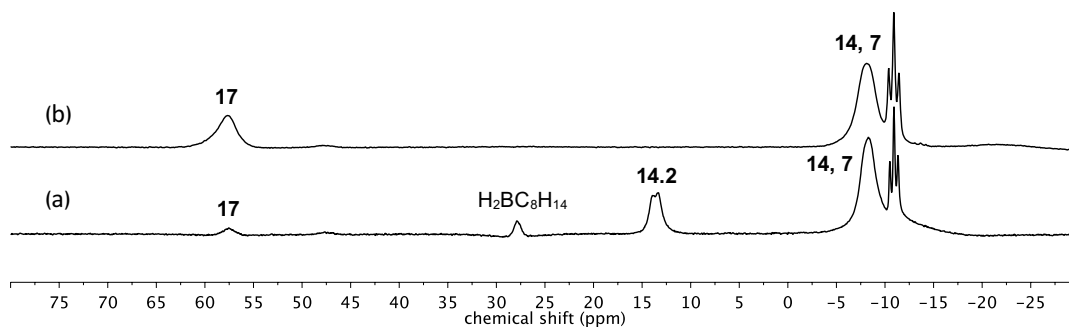
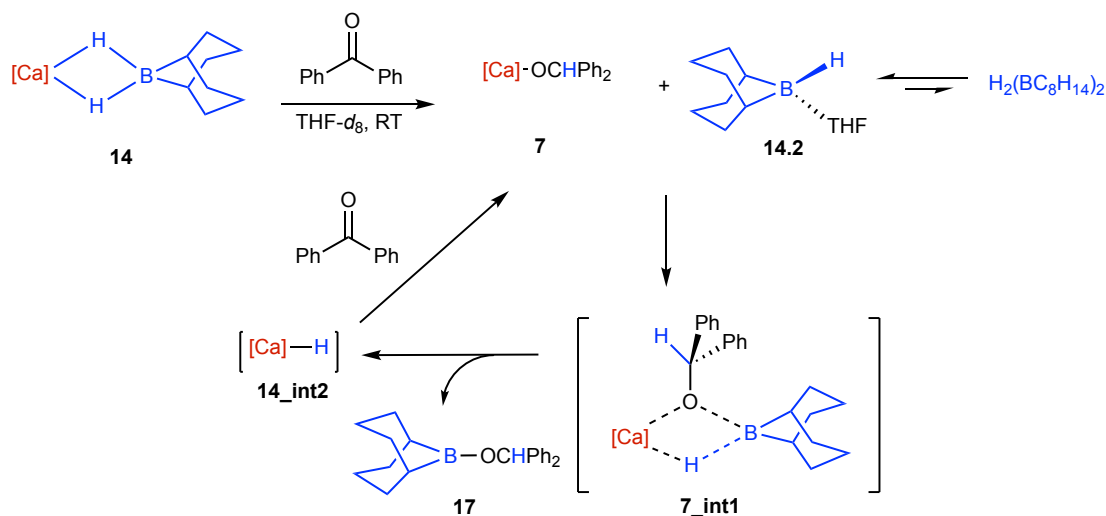


**Figure 3.15**  $^{11}\text{B}$  NMR spectra ( $\text{THF-}d_8$ , 160.4 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 1 equiv. of benzophenone after 10 min (a) and after 18 h (b).

The reaction pathway displayed in Scheme 3.3 is proposed based on the NMR spectroscopic data. Complex **14** reacts with 1 equiv. of benzophenone to give **7** and **14.2**. These two species undergo the B-H/Ca-O  $\sigma$ -bond metathesis through four-

membered ring (**7\_int1**) to release **17** and transient calcium hydride species (**14\_int2**). Hydride from **14\_int2** migrates to 1 equiv. of benzophenone, forming **7**.



**Scheme 3.3** Proposed mechanism for the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with benzophenone in THF-*d*<sub>8</sub>.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

In order to gain evidence for the proposed mechanism (Scheme 3.3), an NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and 0.5 equiv. of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  was carried out in THF-*d*<sub>8</sub> at RT. The <sup>11</sup>B NMR spectrum recorded after 18 h shows signals at 57.6, -8.2 and -10.9 ppm, assigned to **17**, the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  of **7** and **14**, and  $\text{Ca}(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  of **14**, respectively. The <sup>1</sup>H NMR spectrum recorded after 18 h (Figure 3.16, b) shows signals of **14**, **17** and unreacted **7**, in a 1:1:1 ratio. These indicated that **7** reacts in a 1:1 stoichiometry with  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  (Equation 3.3), and **14\_int2** can coordinate to **14.2**, giving **14** in an absence of excess benzophenone. An NMR tube scale reaction of **7** and 1 equiv. of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  was performed in THF-*d*<sub>8</sub> at RT. The <sup>1</sup>H (Figure 3.16, a) and <sup>11</sup>B NMR spectra recorded after 18 h show signals attributing to **14** and **17**. These results strongly confirmed the  $\sigma$ -bond metathesis of **7** and **14.2**, generating **17** and **14\_int2** as shown in Scheme 3.3.

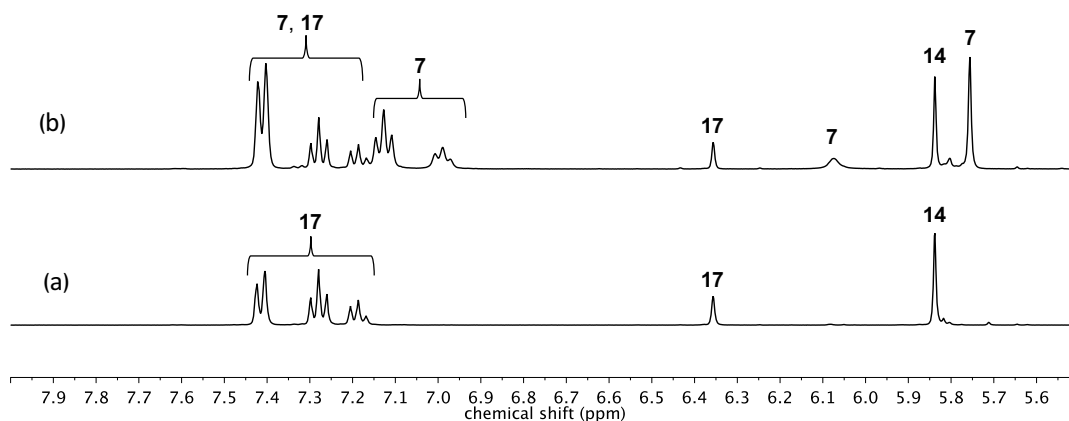
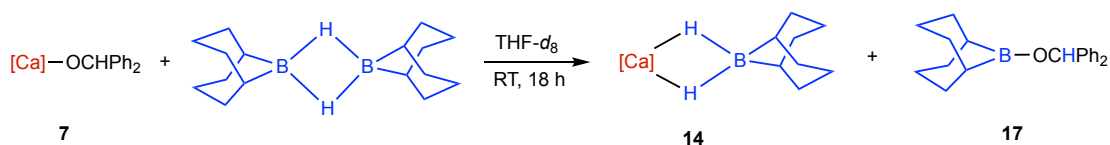
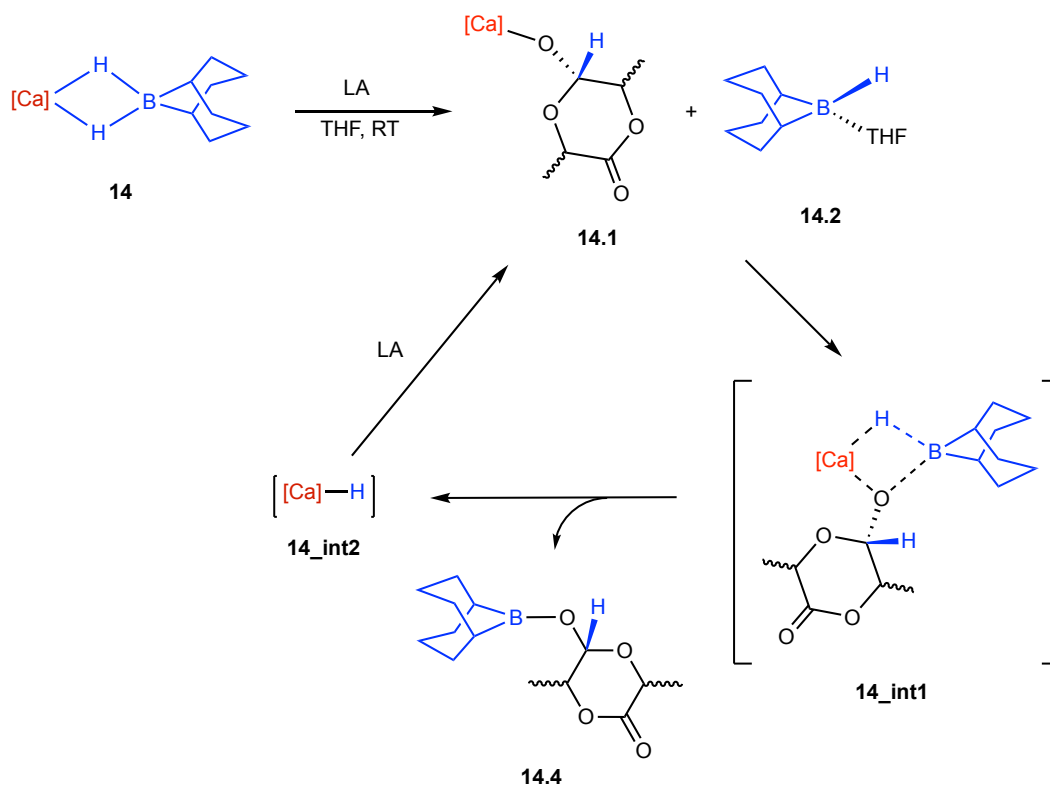


**Figure 3.16**  $^1\text{H}$  NMR spectra ( $\text{THF-}d_8$ , 400.2 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with 1 equiv. (a) or 0.5 equiv. (b) of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  recorded after 18 h.



**Equation 3.3**  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

The presence of **17** is indicative of B-H/Ca-O  $\sigma$ -bond metathesis of **14.1** and **14.2** through **14\_int1**, producing  $(\text{BC}_8\text{H}_{14})(\text{LA-H})$  (**14.4**) and **14\_int2**, as shown in Scheme 3.4. Hydride migration from **14\_int2** to LA subsequently occurs, giving **14.1** acting as an initiator. Therefore, the  $^{11}\text{B}$  NMR signal at 57.1 ppm, obtained from an NMR tube scale reaction of **14** and 10 equiv. of *rac*-LA in  $\text{THF-}d_8$  at RT after 10 min, can be attributed to the B-O of **14.4**.

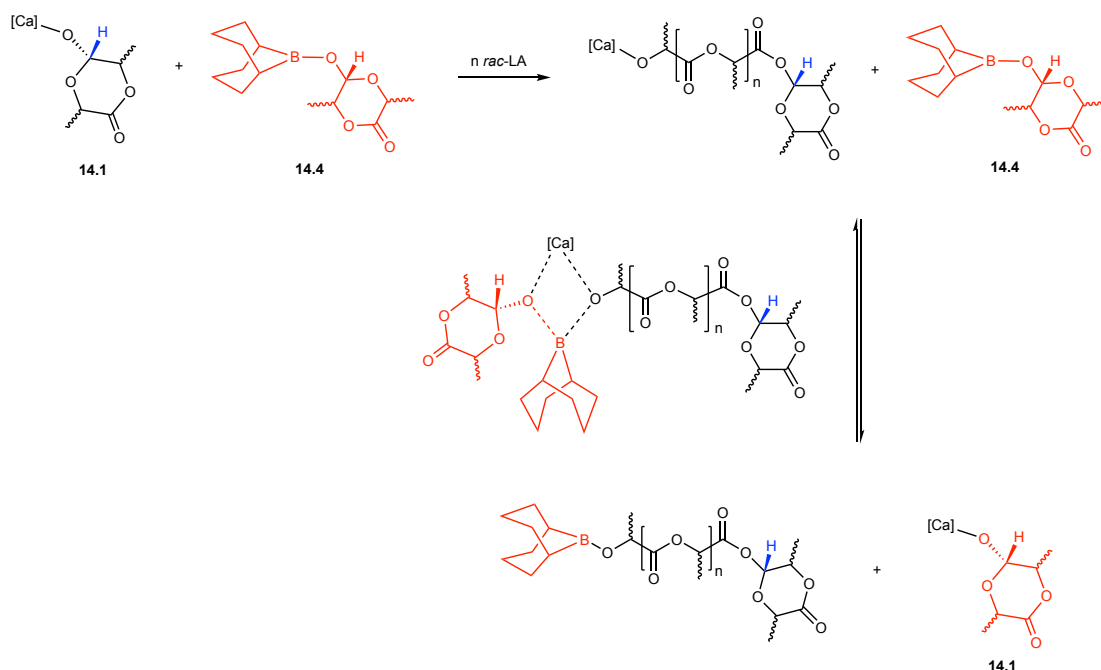


**Scheme 3.4** Proposed mechanism for the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with LA in THF.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

### 3.6 Immortal ROP of *rac*-LA using calcium alkoxide complexes and borinic esters as chain transfer agents

According to Scheme 3.4, the formation of **14.4** was anticipated in the ROP of LA initiated by **14**. This raised the question whether **14.4** could act as the chain transfer agent and exchange with the polymeric chain on Ca. Hypothesising a potential chain transfer ability of **14.4** in the immortal ROP of *rac*-LA, it was expected that measured  $M_n$  values would be consistent with those calculated for two polymer chains growing per metal centre. This would attribute to an exchange between **14.4** and growing polymeric chain on Ca *via* Ca-O/B-O metathesis to give polymeric chain terminated with  $\text{BC}_8\text{H}_{14}$  group at one end and the non-open ring LA (-LA-H) at the other end (Scheme 3.5).





**Scheme 3.5** Proposed pathway for immortal ROP of *rac*-LA with  $(\text{BC}_8\text{H}_{14})(\text{LA-H})$  (**14.4**) as chain transfer agent.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

The use of borate esters including  $\text{B}(\text{OBn})_3$  and  $\text{B}(\text{OMe})_3$  as effective chain transfer agents in the ROP of *rac*-LA or  $\varepsilon$ -CL using magnesium alkoxide complexes have been reported (more details will be discussed in Chapter Four).<sup>19</sup> Polymers obtained from ROP with the presence of borate esters showed good agreement between measured  $M_n$  values and those calculated based on four polymer chains per metal centre. Dong *et al.* also reported polymerisation of ethylene and styrene using  $\text{BET}_3$  as chain transfer agent.<sup>47</sup> The successful chain transfer reactions using  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$ , dimesitylborane and bis(2,4,6-triisopropylphenyl)borane have been reported in metallocene-mediated olefin polymerisations leading to borane terminated polyolefins.<sup>48-52</sup> The chain transfer reaction in metallocene-mediated olefin polymerisation was proposed to occur *via* an exchange between the growing polymer chains coordinating to the metal centre and the borane reagents ( $\text{B-X/M-C}$  metathesis where  $\text{X} = \text{C}$  or  $\text{H}$ ). The molecular weights of polyolefins are inversely proportional to the ratio of  $[\text{borane}]_0:[\text{olefin}]_0$ .

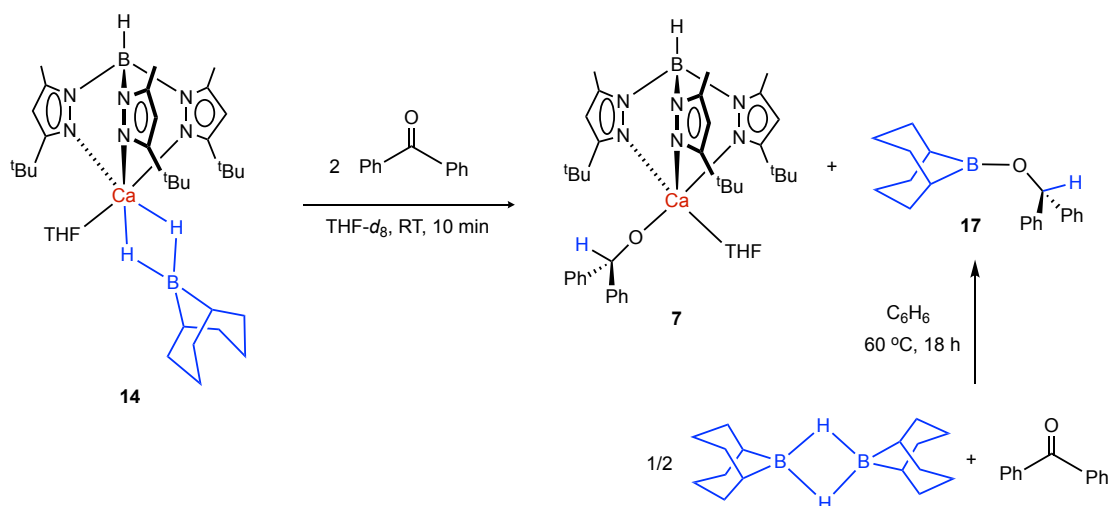
### 3.6.1 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**) with additives

Reactions of **14** with benzophenone, 2-methylcyclohexanone or benzaldehyde in a molar ratio of 1:2 were performed to give analogous alkoxide complexes and borinic

esters serving as models of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  (**14.1**) and  $(\text{BC}_8\text{H}_{14})(\text{LA-H})$  (**14.4**).

### 3.6.1.1 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**) with benzophenone

Complex **14** was reacted with 2 equiv. of benzophenone in  $\text{THF-}d_8$  for 10 min to give  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**) (Scheme 3.6). The  $^1\text{H}$  NMR spectrum (Figure 3.17) shows two singlets at 6.36 and 6.07 ppm corresponding to methine protons ( $\text{OCHPh}_2$ ) of *in-situ* generated **7** and **17**, respectively. The  $^{11}\text{B}$  NMR spectrum displays two signals at 57.8 and -8.8 ppm assigned to the B-O of **17** and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  of **7**, respectively.  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**) was independently synthesised *via* reaction of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  and benzophenone in a molar ratio of 1:2 in  $\text{C}_6\text{H}_6$  at 60 °C for 18 h (Scheme 3.6). Analogous reaction of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  and  $\text{HOCH(Ph)Tol}$  in a 1:2 molar ratio to form  $(\text{BC}_8\text{H}_{14})(\text{OCH(Ph)Tol})$  has been reported.<sup>53</sup>



**Scheme 3.6** Reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of benzophenone and reaction of 0.5 equiv. of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  with benzophenone.

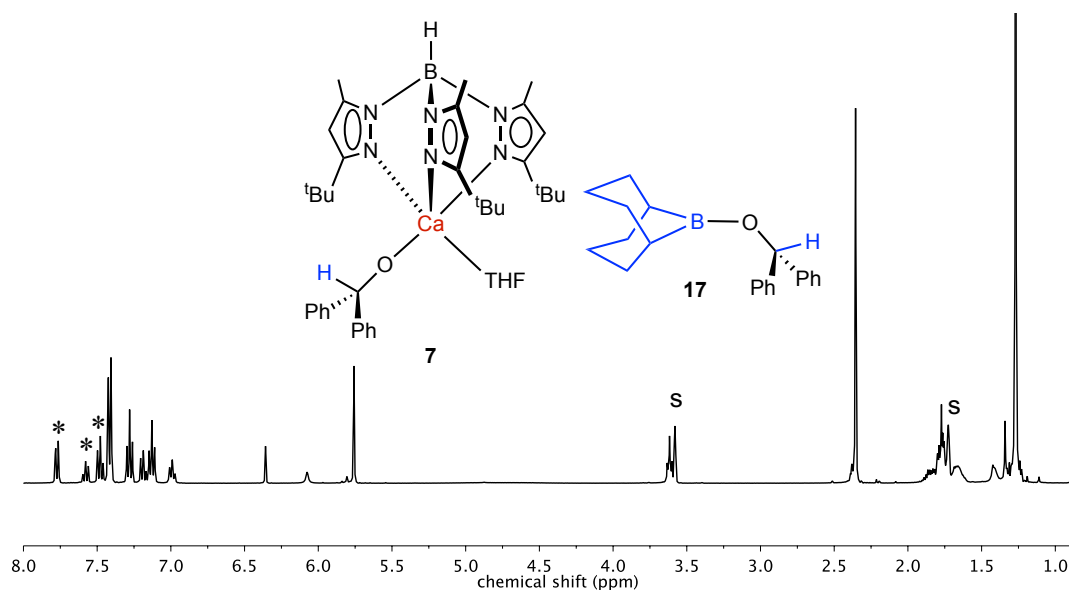


**Figure 3.17**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of benzophenone after 10 min giving  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**). “s” denotes residual protio-solvent. “\*” denotes unreacted benzophenone.

An NMR tube scale reaction of 10 equiv. of *rac*-LA with *in situ* generated **7** and **17** was performed in  $\text{THF-}d_8$  at RT. The  $^{11}\text{B}$  NMR spectrum recorded after 10 min shows signals at 57.6 and -6.4 ppm corresponding to **17** and the apical B-H of the  $\text{Tp}^{\text{tBu,Me}}$  ligand of an unknown species, respectively. The results were similar to these observed from the reaction of **14** and 10 equiv. of *rac*-LA.

A reaction of **14** with 2 equiv. of benzophenone was performed in THF at RT to produce **7** and **17** after 10 min. After an addition of 800 equiv. of *rac*-LA, 93% of monomer conversion was reached within 3 min. Second order dependence on  $[\text{rac-LA}]$  was observed with  $k_{\text{app}} = 0.138(11) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.977$ ). The effect of **17** on the ROP rate and stereoselectivity was investigated by the comparative analysis between the ROP of *rac*-LA using *in situ* generated **7** and **17** and that using **7** (Table 3.2). The presence of **17** has a negligible impact on the polymerisation rate as  $k_{\text{app}}$  values obtained from the ROP of *rac*-LA with and without **17** are identical within error (Figure 3.18, left). In each case, good agreement between  $M_n(\text{GPC})$  values and those calculated for one PLA chain per metal centre was observed at low conversion (<40%, Figure 3.18, right), indicating the poor efficiency of **17** as chain transfer agent. A mismatch between measured and calculated  $M_n$  and the moderate  $D$  values (1.10-1.34) were observed at

high conversion (>50%) due to intramolecular transesterification reaction (Figure 3.18, right). The effect of **17** on stereocontrol was insignificant as heterotactically-enriched PLA with  $P_r = 0.84$  compared to 0.82 obtained from ROP with only **7**. (Table 3.2).

**Table 3.2** Selected data for the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with additive.<sup>a</sup>

| Entry | Initiator | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>14</b> | 2 PhCOPh | 93                        | 180         | 75,510                                                | 107,395                                                 | 1.34                   | 0.84               |
| 2     | <b>7</b>  | -        | 94                        | 180         | 75,580                                                | 108,547                                                 | 1.37                   | 0.82               |

<sup>a</sup> Conditions:  $[\text{rac-LA}]_0:[\text{initiator}]_0:[\text{additive}]_0 = 800:1$  as stated,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $[\text{initiator}]_0 = 625 \mu\text{M}$ , 6.0 mL THF at RT. <sup>b</sup> Measured by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4 \mu\text{L g}^{-1}$  and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for  $-\text{OH}$  and  $-\text{OCHPh}_2$  end groups,  $M_n(\text{entry } 1, 2) = \text{conv. } (\%) \times 800 \times 144.1 + 184.1$ . <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by  $^1\text{H}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) analyses.

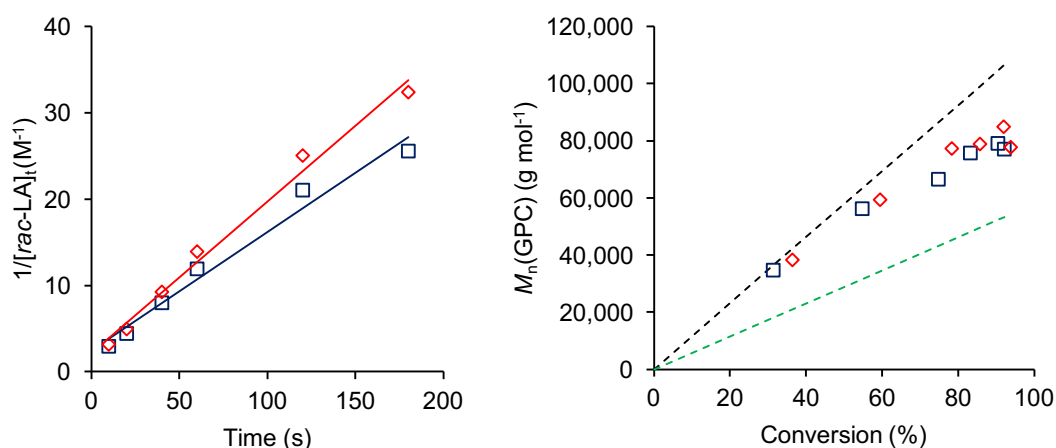


**Figure 3.18** Left, plots of  $1/[\text{rac-LA}]_t$  vs. time. Squares:  $[\text{rac-LA}]_0:[\text{14}]_0:[\text{PhCOPh}]_0 = 800:1:2$  ( $k_{\text{app}} = 0.138(11) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.977$ ), Diamonds:  $[\text{rac-LA}]_0:[\text{7}]_0 = 800:1$  ( $k_{\text{app}} = 0.176(9) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.989$ ). Right, plots of  $M_n(\text{GPC})$  vs. conversion (%). Squares:  $[\text{rac-LA}]_0:[\text{14}]_0:[\text{PhCOPh}]_0 = 800:1:2$ ,  $\bar{D} = 1.05\text{--}1.34$ . Diamonds:  $[\text{rac-LA}]_0:[\text{7}]_0 = 800:1$ ,  $\bar{D} = 1.05\text{--}1.57$ . The black and green dashed lines represent  $M_n(\text{calcd})$  for one and two PLA chains per metal centre, respectively.

MALDI-ToF mass spectrum (Figure 3.19) shows peak envelopes corresponding to cyclic PLA and a separation between peak envelopes by  $\Delta m/z = 72.0 \text{ Da}$  due to inter- and intramolecular transesterification reactions. For example, the peak envelope centred at 903.5 Da is assigned to cyclic PLA containing 12 units of half LA with  $\text{K}^+$ . Another set of peak envelopes corresponds to PLA terminated with  $-\text{OCHPh}_2$  and  $-\text{OH}$

end groups. The peak envelope centred at 1015.7 Da corresponds to PLA containing 11 units of half LA end capped by  $-\text{OCHPh}_2$  and  $-\text{OH}$  groups with  $\text{K}^+$  [ $72.0(11) + 184.1 + 39.1$ ].

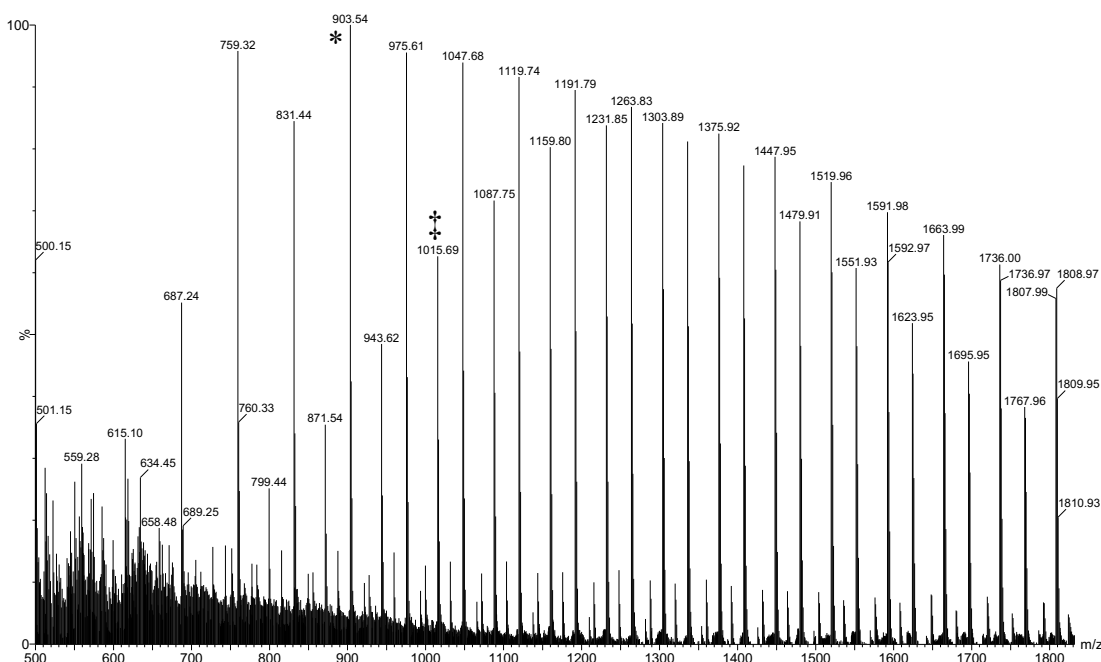
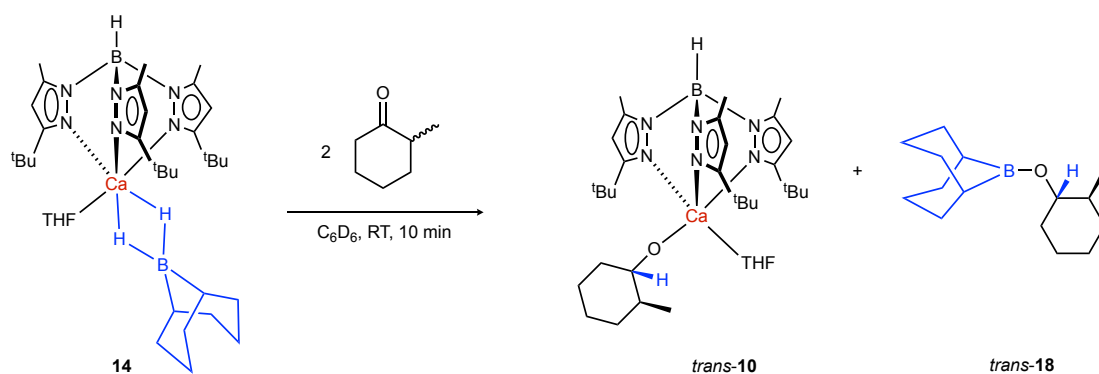


**Figure 3.19** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of benzophenone.  $M_n(\text{GPC}) = 1,670 \text{ g mol}^{-1}$ ,  $\mathcal{D} = 1.67$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{14}]:[\text{PhCOPh}]_0 = 20:1:2$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-\text{OCHPh}_2$  and  $-\text{OH}$  end groups.

### 3.6.1.2 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**) with 2-methylcyclohexanone

An NMR tube scale reaction of **14** with 2 equiv. of 2-methylcyclohexanone in  $\text{THF-}d_8$  or  $\text{C}_6\text{D}_6$  at RT formed  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) with  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  (**18**). The latter was employed as the preferred NMR solvent due to better signal separation (Equation 3.4) The reaction is stereoselective with the formation of *trans*-**10** (90%) and *trans*-**18** (90%).



Equation 3.4

The  $^1\text{H}$  NMR spectrum recorded after 10 min (Figure 3.20) shows a triplet of doublets at 3.51 ppm ( $^3J = 9.5, 4.4$  Hz) and a multiplet at 4.21 ppm corresponding to the methine proton  $\text{OCHCHMe}$  of the *trans*- and *cis*-isomers of **10**, respectively. The integral ratio of two sets of signals (*trans* and *cis* isomers) is 9:1. The same phenomenon was observed for the signals assigned to the *trans*- and *cis*-**18** (Figure 3.20). The  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed two signals at 55.8 and -8.1 ppm corresponding to the B-O of **18** and the apical B-H of the  $\text{Tp}^{\text{tBu,Me}}$  ligand of **10**, respectively.

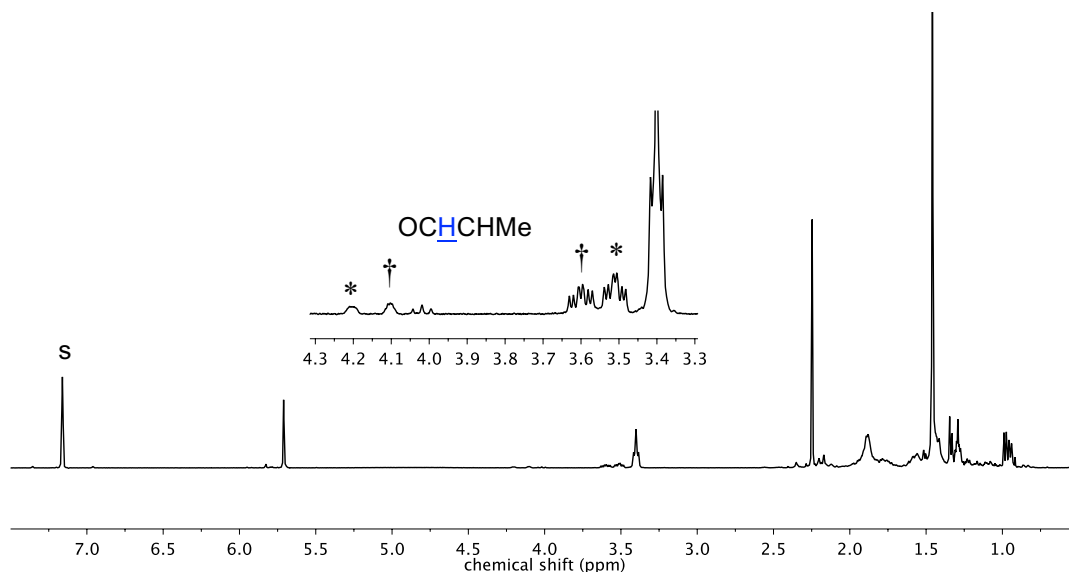
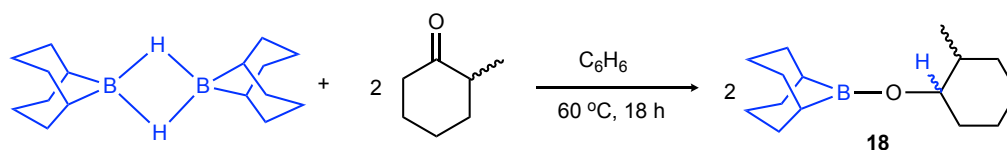


**Figure 3.20**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of 2-methylcyclohexanone after 10 min giving  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) with  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  (**18**). “s” denotes residual protio-solvent. “\*” denotes the *cis*- and *trans*-**10**. “†” denotes the *cis*- and *trans*-**18**.

Compound **18** was independently synthesised *via* reaction of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  and 2 equiv. of 2-methylcyclohexanone in  $\text{C}_6\text{H}_6$  at 60 °C for 18 h (Equation 3.5). No stereoselectivity was observed with the formation of the *cis*- and *trans*-**18** in a 1:1 ratio.



**Equation 3.5**

The  $^1\text{H}$  NMR spectrum (Figure 3.21) shows a triplet of doublets at 3.60 ppm ( $^3J = 10.3$ , 4.6 Hz) and a multiplet at 4.10 ppm corresponding to the methine proton ( $\text{OCHCHMe}$ ) of the *trans*- and *cis*-**18**, respectively. The integral ratio of two sets of signals (the *trans* and *cis* isomers) is 1:1. The  $^{11}\text{B}$  NMR spectrum showed a singlet at 55.8 ppm corresponding to the B-O of **18**.

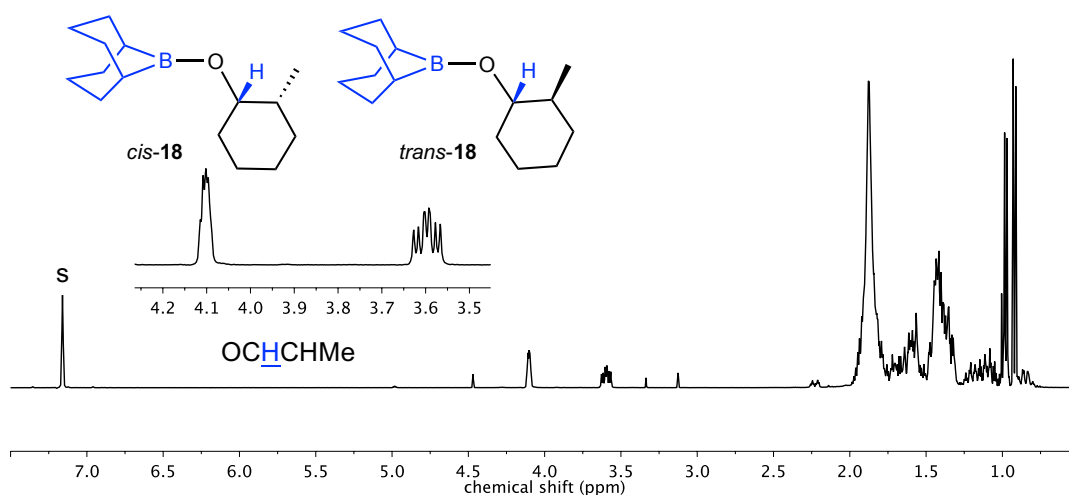
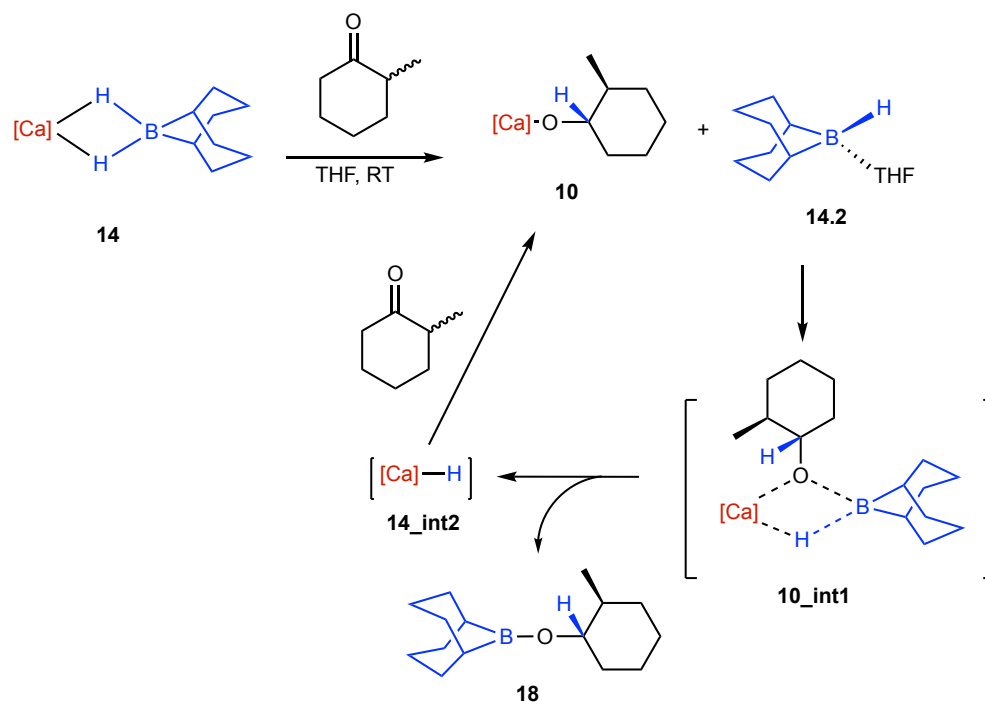


**Figure 3.21**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  (**18**). “s” denotes residual protio-solvent.

The stereoselective formation of **18** obtained *via* reaction of **14** and 2 equiv. of 2-methylcyclohexanone indicated that the direct hydride transfer to 2-methylcyclohexanone by  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  is disfavoured. In contrast, the hydride migrates from **14** to 2-methylcyclohexanone generating **10** and **14.2**, followed by a Ca-O/B-H metathesis through **10\_int1**, giving **14\_int2** and **18**. The hydride transfer takes place from **14\_int2** to 2-methylcyclohexanone providing **10**. This pathway is

significantly faster than the direct migration of the hydride from  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  and allowed the stereocontrol in the formation of **10** and **18** (Scheme 3.7).



**Scheme 3.7** Proposed mechanism for the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of 2-methylcyclohexanone in THF.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})$ .

A reaction of **14** and 2-methylcyclohexanone in a 1:2 molar ratio was carried out in THF at RT to give **10** and **18** after 10 min, followed by an addition of 800 equiv. of *rac*-LA. The ROP of *rac*-LA using *in situ* generated **10** and **18** was highly active, reaching 91% conversion after 3 min. A second order dependence on  $[\text{rac-LA}]$  was observed with  $k_{\text{app}} = 0.117(2) \text{ M}^{-1}\text{S}^{-1}$  ( $R^2 = 0.998$ , Figure 3.22, left). Poor agreement between  $M_n(\text{GPC})$  and those calculated for one PLA chain per metal centre was observed at high conversion (>60%) due to intramolecular transesterification reaction (Figure 3.22, right). Moderate  $\bar{D}$  values were obtained (1.05-1.50). Heterotactically-enriched PLA was formed with  $P_r = 0.84$  (Table 3.3). The ROP of *rac*-LA using only **10** showed the results which are comparable to these obtained from the ROP using **10** and **18**, indicating an inefficiency of **18** as chain transfer agent.



**Table 3.3** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>} (THF) (**14**) or (Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF) (**10**) with additive.<sup>a</sup>

| Entry | Initiator | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r^f$ |
|-------|-----------|----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|---------|
| 1     | <b>14</b> | 2 CyMeO  | 91                        | 180         | 77,070                                                | 105,019                                                 | 1.41                   | 0.84    |
| 2     | <b>10</b> | -        | 91                        | 180         | 97,950                                                | 105,019                                                 | 1.45                   | 0.81    |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:[initiator]<sub>0</sub>:[additive]<sub>0</sub> = 800:1:as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OCyMe end groups,  $M_n$  (entry 1, 2) = conv. (%) × 800 × 144.1 + 114.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

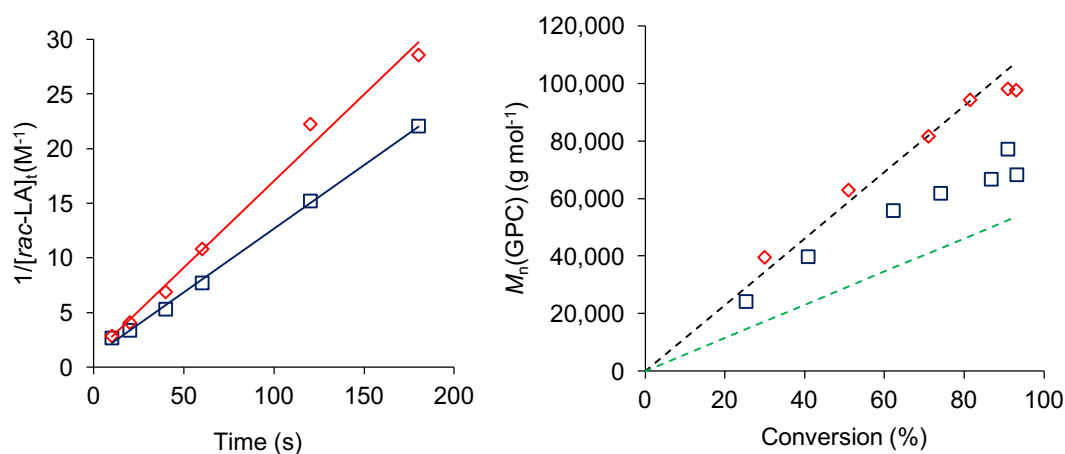


**Figure 3.22** Left, plots of  $1/[rac-LA]_t$  vs. time. Squares: [*rac*-LA]<sub>0</sub>:**14**<sub>0</sub>: [CyMeO]<sub>0</sub> = 800:1:2 ( $k_{app} = 0.117(2) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.998$ ). Diamonds: [*rac*-LA]<sub>0</sub>:**10**<sub>0</sub> = 800:1. ( $k_{app} = 0.157(7) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.990$ ). Right, plots of  $M_n$ (GPC) vs. conversion (%). Squares: [*rac*-LA]<sub>0</sub>:**14**<sub>0</sub>: [CyMeO]<sub>0</sub> = 800:1:2,  $\bar{D} = 1.05$ -1.50. Diamonds: [*rac*-LA]<sub>0</sub>:**10**<sub>0</sub> = 800:1.  $\bar{D} = 1.04$ -1.55. The black and green dashed lines represent  $M_n$ (calcd) for one and two PLA chains per metal centre, respectively.

MALDI-ToF mass spectrum (Figure 3.23) of PLA synthesised by *in situ* generated **10** and **18** shows a major distribution of peak envelopes corresponding to cyclic PLA indicating back-biting. A minor distribution of peak envelopes is attributed to PLA with –OCyMe and –OH end groups. The repeating unit between each peak envelope by  $\Delta m/z = 72.0$  Da was due to transesterification reactions. For example, the peak envelope centred at 1479.7 Da is assigned to cyclic PLA containing 20 units of half LA with K<sup>+</sup>. Another peak envelope centred at 1521.8 Da corresponds to PLA containing 19 units of half LA terminated by –OCyMe and –OH groups with K<sup>+</sup> [ $72.0(19) + 114.1 + 39.1$ ].

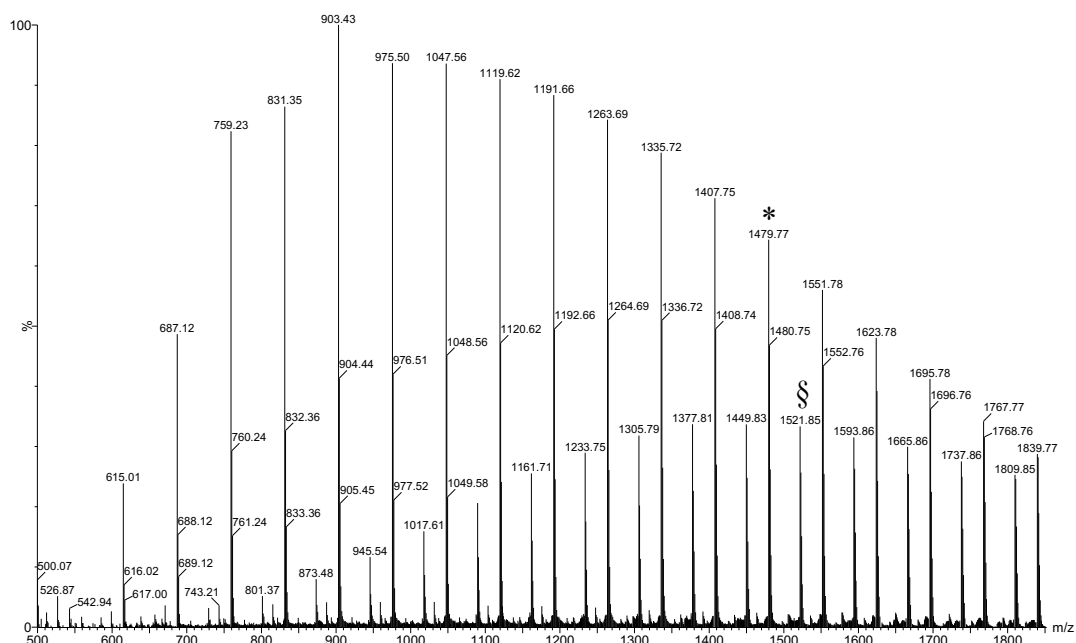


**Figure 3.23** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of 2-methylcyclohexanone.  $M_n(\text{GPC}) = 1,910 \text{ g mol}^{-1}$ ,  $D = 1.70$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{14}]_0:[\text{CyMeO}]_0 = 20:1:2$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “\*” denotes cyclic PLA. “§” denotes PLA with  $-\text{OCyMe}$  and  $-\text{OH}$  end groups.

### 3.6.1.3 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**) with benzaldehyde

An NMR tube scale reaction of **14** with 2 equiv. of benzaldehyde in  $\text{THF-}d_8$  at RT formed  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**) (Equation 3.6). The  $^{11}\text{B}$  NMR spectrum monitored after 10 min showed two signals at 57.2 and -8.1 ppm corresponding to the B-O of **19** and the apical B-H of the  $\text{Tp}^{\text{tBu,Me}}$  ligand of **11**, respectively. The methylene protons ( $\text{OCH}_2\text{Ph}$ ) of **19** and **11** appeared as two singlets at 5.08 and 5.04 ppm, respectively (Figure 3.24).

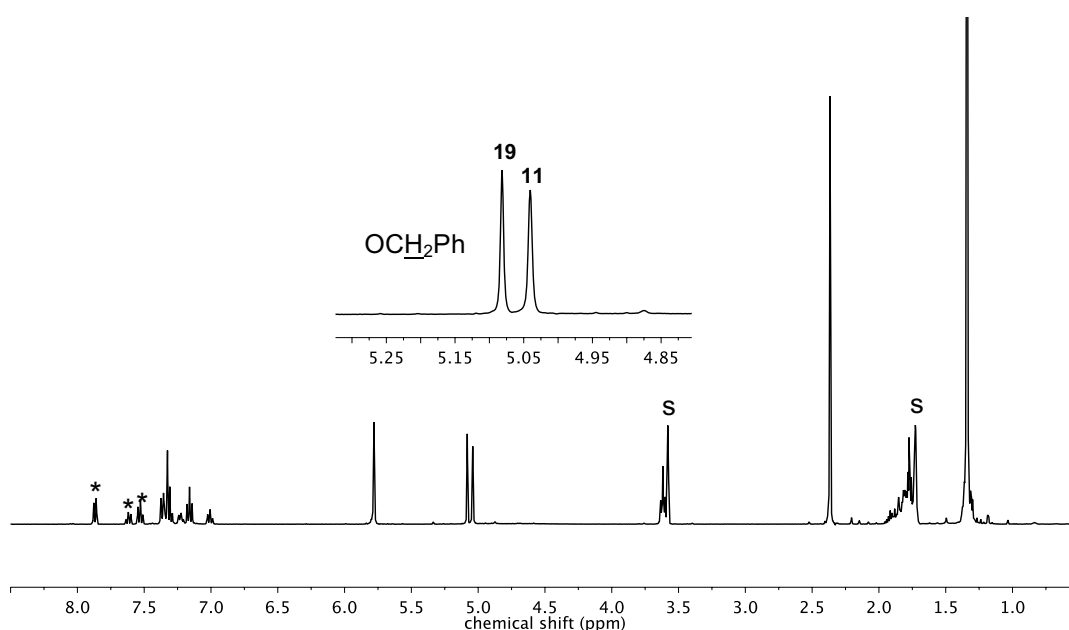
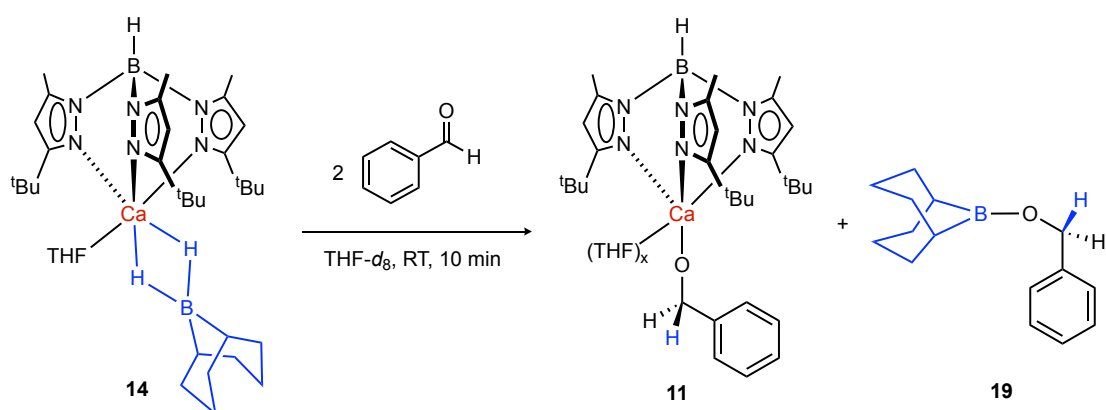


**Figure 3.24**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) with 2 equiv. of benzaldehyde after 10 min giving  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})$  (**11**) with  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**). “s” denotes residual protio-solvent. “\*” denotes unreacted benzaldehyde.

A reaction of **14** and benzaldehyde in a 1:2 molar ratio was performed in THF at RT to give **11** and **19** after 10 min, followed by an addition of 800 equiv. of *rac*-LA. A difference in polymerisation rate was observed between the ROP of *rac*-LA using **11** and that using *in-situ* generated **11** and **19** (Figure 3.25, left). At  $[\text{rac-LA}]_0:[\textbf{11}]_0:[\textbf{19}]_0 = 800:1:1$ , two polymerisation stages were observed, 73% conversion was reached after 5 min, then 89% after 4 h. Each stage does not follow either a first or second order

dependence on *rac*-LA concentration (Table 3.4, Entry 1, 2). In contrast, the ROP of *rac*-LA using only **11** was very active, reaching 91% conversion after 3 min (Table 3.4, Entry 3). A second order dependency on [*rac*-LA] was observed with  $k_{\text{app}} = 0.123(4) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.999$ ).

**Table 3.4** Selected data for the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) with additive.<sup>a</sup>

| Entry | Initiator | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(min) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | $P_r^f$ |
|-------|-----------|----------|---------------------------|---------------|-------------------------------------------------------|---------------------------------------------------------|-------------|---------|
| 1     | <b>14</b> | 2 PhCHO  | 73                        | 5             | 49,750                                                | 42,050                                                  | 1.45        | 0.81    |
| 2     | <b>14</b> | 2 PhCHO  | 89                        | 240           | 34,950                                                | 51,460                                                  | 1.46        | 0.77    |
| 3     | <b>11</b> | -        | 91                        | 3             | 83,090                                                | 105,030                                                 | 1.39        | 0.82    |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>: [initiator]<sub>0</sub>: [additive]<sub>0</sub> = 800:1:as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4 \text{ μL g}^{-1}$  and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OBn end groups,  $M_n$  (entry 1, 2) = (conv. (%) × 800 × 144.1)/2 + 108.1,  $M_n$  (entry 3) = conv. (%) × 800 × 144.1 + 108.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

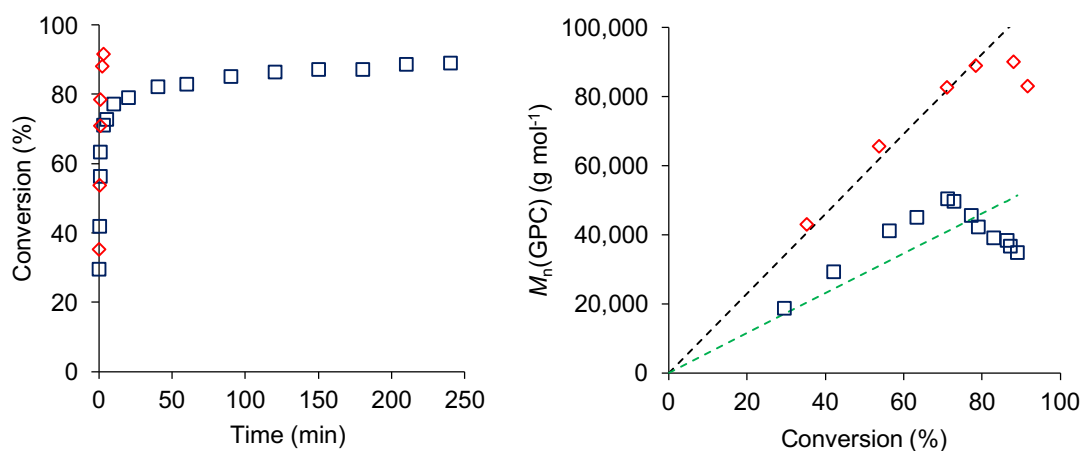
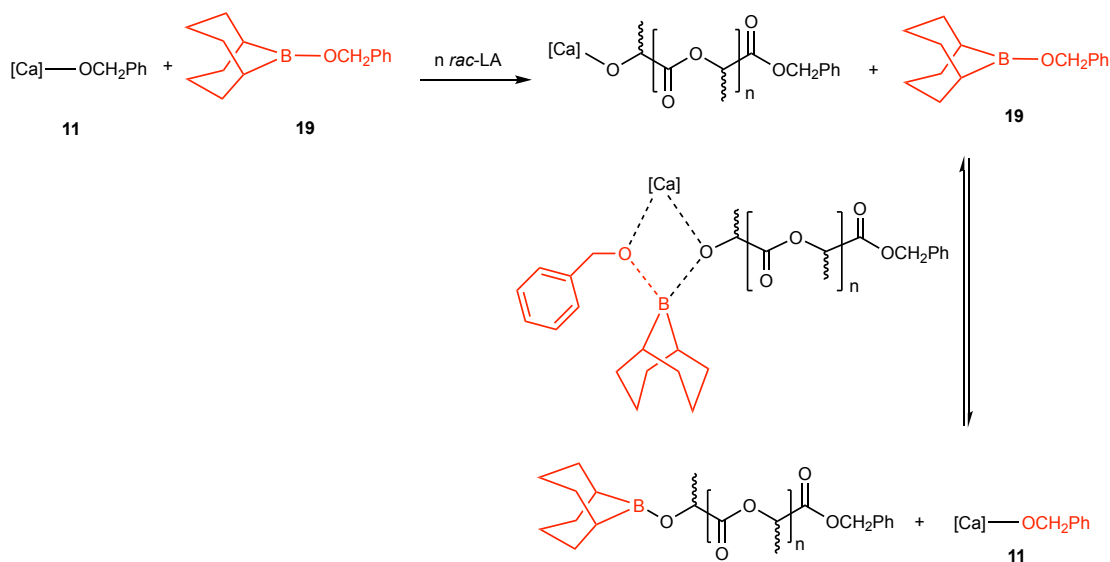


**Figure 3.25** Left, plots of conversion (%) vs. time. Squares: [*rac*-LA]<sub>0</sub>: [**14**]<sub>0</sub>: [PhCHO]<sub>0</sub> = 800:1:2. Diamonds: [*rac*-LA]<sub>0</sub>: [**11**]<sub>0</sub> = 800:1. Right, plots of  $M_n(\text{GPC})$  vs. conversion (%). Squares: [*rac*-LA]<sub>0</sub>: [**14**]<sub>0</sub>: [PhCHO]<sub>0</sub> = 800:1:2,  $\bar{D} = 1.05$ -1.46. Diamonds: [*rac*-LA]<sub>0</sub>: [**11**]<sub>0</sub> = 800:1,  $\bar{D} = 1.05$ -1.43. The black and green dashed lines represent  $M_n(\text{calcd})$  for one and two PLA chains per metal centre, respectively.

The impact of  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**) on  $M_n(\text{GPC})$  is apparent in Figure 3.25 (right). Good agreement between  $M_n(\text{GPC})$  and those calculated for two growing chains per metal centre was observed up to ca. 73% conversion due to the greater chain transfer rate than

propagation rate. Afterwards,  $M_n(\text{GPC})$  values started to decline in the range of *ca.* 77-89% conversion, attributed to intramolecular transesterification reaction. In the absence of **19**, close agreement between  $M_n(\text{GPC})$  and those calculated for one chain per metal centre was observed (Figure 3.25, right).

Heterotactically-enriched PLA with  $P_r = 0.81$  was obtained after 5 min polymerisation suggesting the negligible impact of **19** on stereocontrol during this stage (Table 3.4, entry 1). The diminished stereoselectivity ( $P_r = 0.77$ ) was observed from the resulting PLA synthesised after 4 h due to transesterification reactions and chain transfer reaction (Table 3.4, entry 2). The polymerisation rate and  $M_n(\text{GPC})$  data confirmed the role of **19** as the chain transfer agent. The exchange between **19** with growing polymer chain on metal centre occurred leading to the formation of **11** as active species and PLA terminated with  $\text{BC}_8\text{H}_{14}$  and  $-\text{OCHPh}_2$  groups as dormant species (Scheme 3.8).



**Scheme 3.8** Proposed mechanism for the ROP of LA using *in situ* generated  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) with  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**).  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

MALDI-ToF mass spectrum (Figure 3.26) shows a major distribution of peak envelopes corresponding to PLA terminated with  $-\text{OBn}$  and  $-\text{OH}$  end groups. The separation between peak envelopes by  $\Delta m/z = 72.0$  Da reflects the transesterification reactions. A minor distribution of peak envelopes corresponds to cyclic PLA formed by back-biting. This suggests that the chain transfer reaction could inhibit the back biting of the growing polymer chain compared to the ROP with  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**) or  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  (**18**). For example, the peak envelope centred at 1479.7 Da is assigned to cyclic PLA containing 20 units of half LA with  $\text{K}^+$ . Another peak

envelope centred at 1587.8 Da corresponds to PLA containing 20 units of half LA terminated by –OBn and –OH end groups with  $K^+$   $[72.0(20) + 108.1 + 39.1]$ .

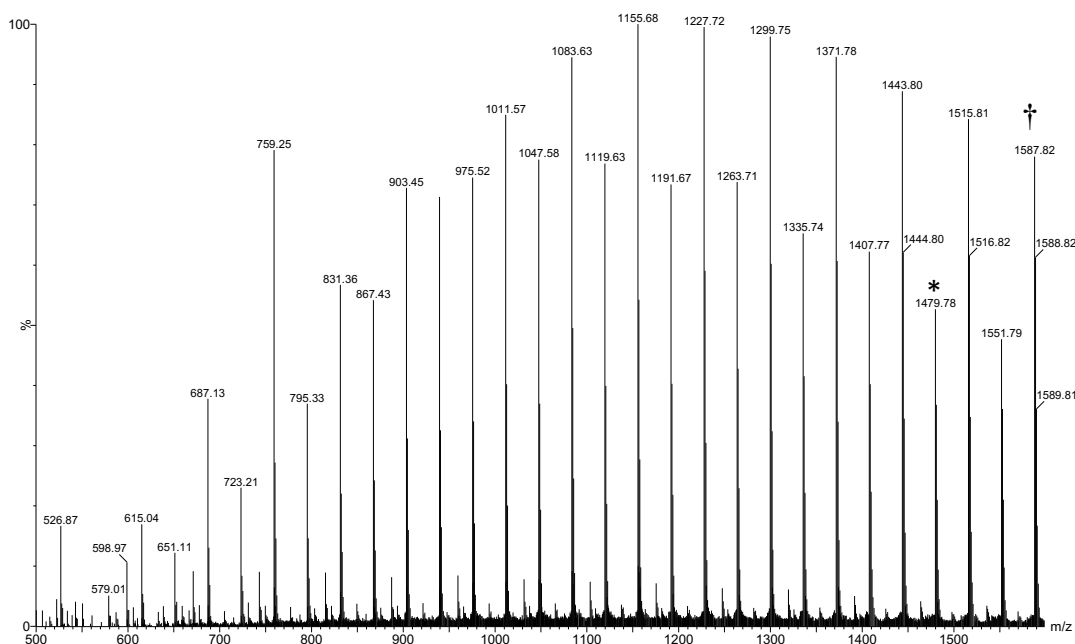


**Figure 3.26** MALDI-ToF MS of PLA synthesised using  $(Tp^{tBu,Me})Ca\{(\mu-H)_2BC_8H_{14}\}(THF)$  (**14**) with 2 equiv. of benzaldehyde.  $M_n(GPC) = 1,890 \text{ g mol}^{-1}$ ,  $D = 1.62$ . Conditions:  $[rac-LA]_0:[\mathbf{14}]_0:[PhCHO]_0 = 20:1:2$ ,  $[rac-LA]_0 = 0.5 \text{ M}$ , 1.0 mL THF at RT.  $K^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “†” denotes PLA with –OBn and –OH end groups. “\*” denotes cyclic PLA.

### 3.6.2 ROP of *rac*-LA using $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$ (**7**) with various borinic esters (**17**, **18** and **19**)

Previous studies have shown poor chain transfer ability of borinic esters with sterically demanding substituents including  $(BC_8H_{14})(OCHPh_2)$  (**17**) and  $(BC_8H_{14})(OCyMe)$  (**18**). To further support the inefficiency of **17** and **18** as chain transfer agents, ROP of *rac*-LA using **7** with 1 equiv. of **17** and **18** was performed. An NMR tube scale reaction of **7** with 1 equiv. of **17** or **18** was performed in  $THF-d_8$ , which were found to remain as discrete species after 18 h.

The ROP initiated by **7** with externally added **17** or **18** were found to be highly active, reaching 92% conversion (800 equiv. of *rac*-LA) within 3 min in THF at RT (Table 3.5). A second order dependence on  $[rac-LA]$  was observed in the polymerisations involving **17** and **18**, with  $k_{app} = 0.130(5) \text{ M}^{-1}\text{S}^{-1}$  ( $R^2 = 0.994$ ) and  $0.121(4) \text{ M}^{-1}\text{S}^{-1}$  ( $R^2 = 0.995$ ), respectively (Figure 3.27, left).

**Table 3.5** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**) with (BC<sub>8</sub>H<sub>14</sub>)(OCHPh<sub>2</sub>) (**17**) or (BC<sub>8</sub>H<sub>14</sub>)(OCyMe) (**18**).<sup>a</sup>

| Entry | Additive  | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>17</b> | 92                        | 180         | 75,690                                                | 106,242                                                 | 1.49                   | 0.83               |
| 2     | <b>18</b> | 92                        | 180         | 75,510                                                | 106,242                                                 | 1.47                   | 0.82               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:[**7**]<sub>0</sub>:[additive]<sub>0</sub> = 800:1:1, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OCHPh<sub>2</sub> end groups,  $M_n$  (entry 1, 2) = conv. (%) × 800 × 144.1 + 184.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

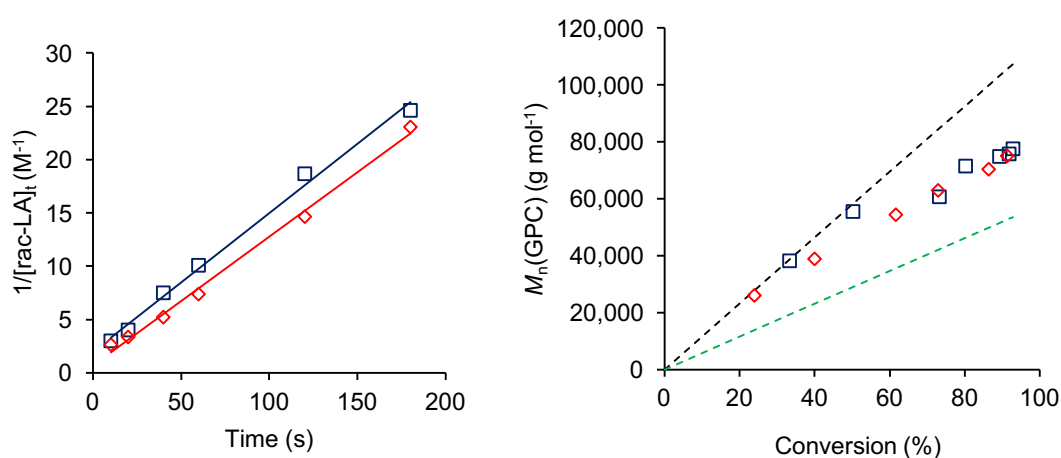


**Figure 3.27** Left, plots of  $1/[rac-LA]_t$  vs. time. Squares: [*rac*-LA]<sub>0</sub>:[**7**]<sub>0</sub>:[**17**]<sub>0</sub> = 800:1:1 ( $k_{app} = 0.130(5) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.994$ ). Diamonds: [*rac*-LA]<sub>0</sub>:[**7**]<sub>0</sub>:[**18**]<sub>0</sub> = 800:1:1 ( $k_{app} = 0.121(4) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.995$ ). Right, plots of  $M_n$ (GPC) vs. conversion (%). Squares: [*rac*-LA]<sub>0</sub>:[**7**]<sub>0</sub>:[**17**]<sub>0</sub> = 800:1:1,  $\bar{D} = 1.14$ -1.49. Diamonds: [*rac*-LA]<sub>0</sub>:[**7**]<sub>0</sub>:[**18**]<sub>0</sub> = 800:1:1,  $\bar{D} = 1.13$ -1.47. The black and green dashed lines represent  $M_n$ (calcd) for one and two PLA chains per metal centre, respectively.

Good agreement between  $M_n$ (GPC) and those calculated for one chain per metal centre was observed in each polymerisation up to ca. 50% (Figure 3.27, right). At the later polymerisation stages, poor agreement between  $M_n$ (GPC) and  $M_n$ (calcd) was observed due to intramolecular transesterification reaction.

MALDI-ToF mass spectrum of PLA synthesised using **7** and **18** (Figure 3.28) shows the presence of the expected –OCHPh<sub>2</sub> end group. For example, the peak envelope centred at 1663.9 Da corresponds to PLA containing 20 units of half LA end capped with –OCHPh<sub>2</sub> and –OH groups with K<sup>+</sup> [72.0(20) + 184.1 + 39.1]. No –OCyMe end

group was observed indicating the inability of **18** to exchange with growing polymer chain on Ca. Cyclic PLA was also observed due to back-biting, for instance, the peak envelope centred at 1479.8 Da corresponds to cyclic PLA containing 20 units of half LA with  $K^+$ .

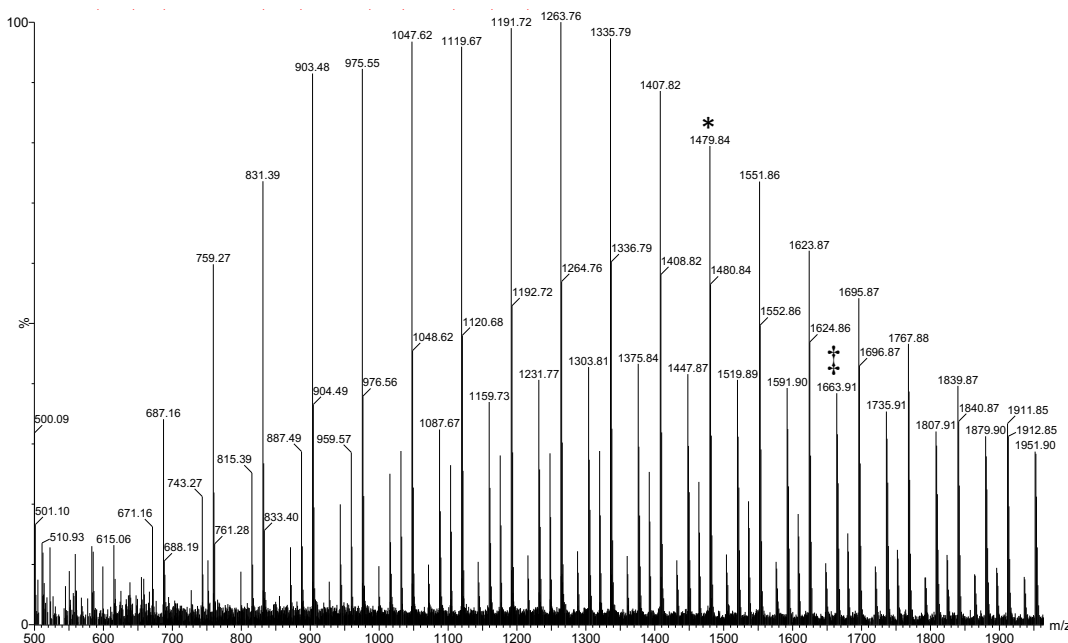
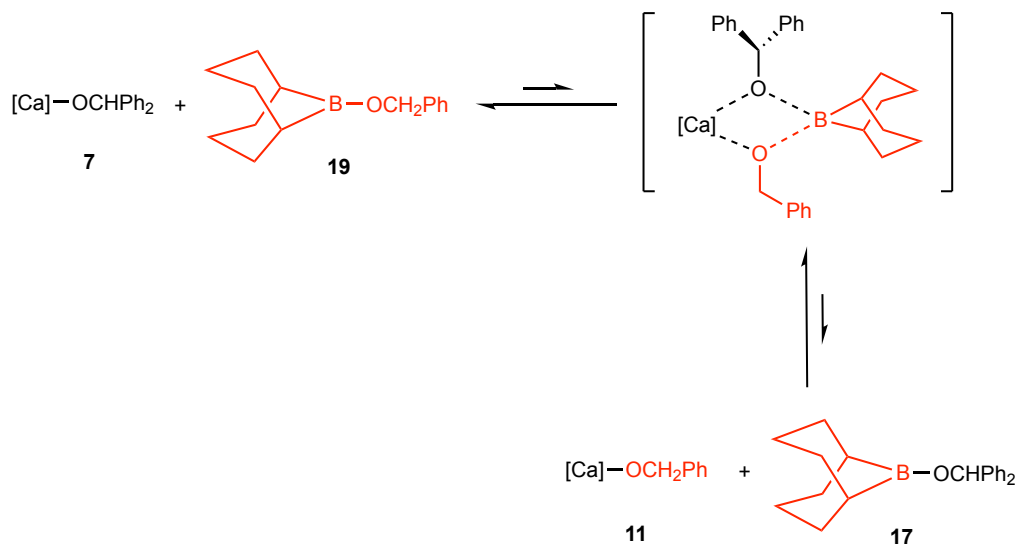


**Figure 3.28** MALDI-ToF MS of PLA synthesised using  $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$  (**7**) with 1 equiv. of  $(BC_8H_{14})(OCyMe)$  (**18**).  $M_n(GPC) = 1,780 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.60$ . Conditions:  $[rac-LA]_0:[\mathbf{7}]_0:[\mathbf{18}]_0 = 20:1:1$ ,  $[rac-LA]_0 = 0.5 \text{ M}$ , 1.0 mL THF at RT.  $K^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-OCHPh_2$  and  $-OH$  end groups.

An NMR tube scale reaction of  $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$  (**7**) and  $(BC_8H_{14})(OBn)$  (**19**) was carried out in THF- $d_8$  at RT. In contrast to **17** and **18**, **19** was able to partially exchange with **7** to form  $(BC_8H_{14})(OCHPh_2)$  (**17**) and  $(Tp^{tBu,Me})Ca(OBn)(THF)_x$  (**11**) (Scheme 3.9). The  $^1H$  NMR spectrum recorded after 10 min (Figure 3.29) shows two singlets at 6.36 and 4.96 ppm corresponding to the methine proton ( $OCHPh_2$ ) of **17** and the methylene protons ( $OCH_2Ph$ ) of **11**, respectively. Complex **7** and **19** did not completely convert to **11** and **17**, evidenced by two singlets at 6.05 and 5.08 ppm corresponding to the methine proton ( $OCHPh_2$ ) of **7** and the methylene protons ( $OCH_2Ph$ ) of **19**, respectively (Figure 3.29). The  $^1H$  NMR spectrum was unchanged after 18 h. The equilibrium constant ( $K_{eq} = [11][17]/[7][19]$ ) determined from the relative integration ratio from the  $^1H$  NMR spectrum (Figure 3.29) equals to 0.17. The



$^{11}\text{B}$  NMR spectrum recorded after 10 min showed two signals at 57.2 and -8.2 ppm corresponding to the B-O of **17** or **19** and the B-H of  $\text{Tp}^{\text{tBu,Me}}$  of **7** or **11**, respectively.



**Scheme 3.9** Reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**).

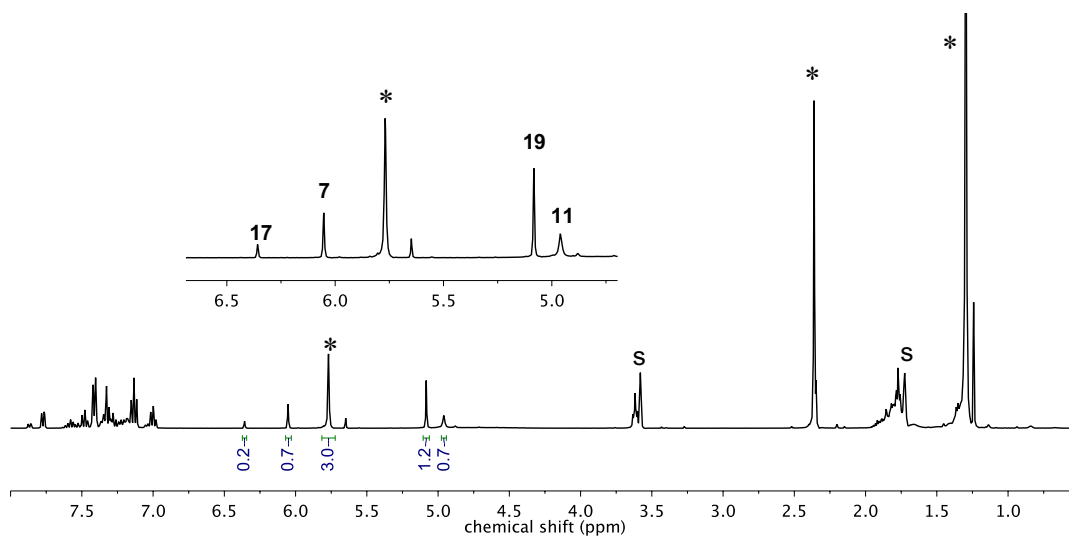


**Figure 3.29**  $^1\text{H}$  NMR spectrum ( $\text{THF-}d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with 1 equiv. of  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**) after 10 min. “s” denotes residual protio-solvent. “\*” denotes  $\text{Tp}^{\text{tBu,Me}}$  ligand of **7** and **11**.

A reaction of **7** and **19** was performed in THF at RT for 10 min followed by an addition of 800 equiv. of *rac*-LA into the catalyst solution. Unlike **17** or **18**, the presence of **19** had a significant impact on the polymerisation rate as 85% conversion was achieved after 5 h (Table 3.6). Similar to the ROP using **14** with 2 equiv. of benzaldehyde (Table 3.4), 73% conversion was reached after 5 min, then 85% conversion after 5 h (Table

3.6). The polymerisation followed neither a first nor second order dependence on [*rac*-LA]. Heterotactically-enriched PLA with  $P_r = 0.78$  was produced.

**Table 3.6** Selected data for the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**).<sup>a</sup>

| Entry | Conv. <sup>b</sup><br>(%) | Time<br>(min) | $M_n(\text{GPC})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | $P_r^f$      |
|-------|---------------------------|---------------|-----------------------------------------------|-------------------------------------------------|-------------|--------------|
| 1     | 22                        | 0.3           | 23,510                                        | 12,789                                          | 1.13        | <sup>g</sup> |
| 2     | 73                        | 5             | 40,120                                        | 42,185                                          | 1.58        | <sup>g</sup> |
| 3     | 85                        | 300           | 41,480                                        | 49,102                                          | 1.41        | 0.78         |

<sup>a</sup> Condition: [*rac*-LA]<sub>0</sub>:**7**:**19** = 800:1:1, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OBn end groups,  $M_n$  (entry 1-3) = (conv. (%) × 800 × 144.1)/2 + 108.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>g</sup> Not measured.

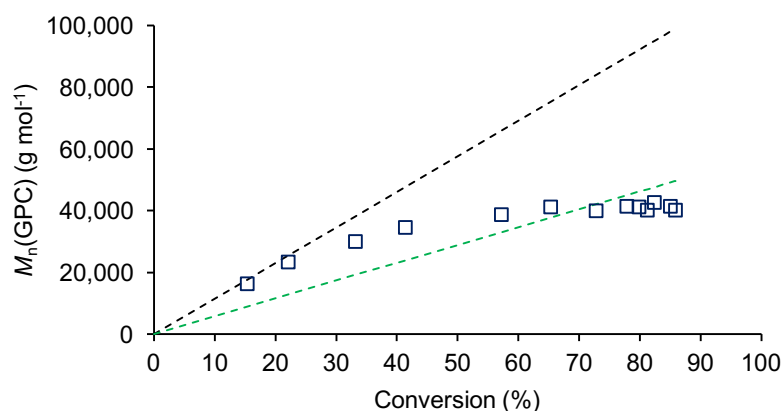


**Figure 3.30** Plot of  $M_n(\text{GPC})$  vs. conversion (%) for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with 1 equiv. of  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**). The black and green dashed lines represent  $M_n(\text{calcd})$  for one and two PLA chains per metal centre, respectively. Conditions: 6 mL THF, RT, [*rac*-LA]<sub>0</sub> = 0.5 M.  $\bar{D} = 1.11$ -1.41.

$M_n(\text{GPC})$  values were in close agreement with those calculated for one chain per metal centre at low monomer conversion (*ca.* 22%, 20 s) indicating greater propagation rate than chain transfer rate (Figure 3.30). At higher conversion (*ca.* >30%, 40 s until 5 min),  $M_n(\text{GPC})$  values deviated from those calculated for one chain per metal centre towards those calculated for two chains per metal centre (Figure 3.30) suggesting the chain transfer reaction is competitive with propagation. From 73% to 85% conversion, the  $M_n(\text{GPC})$  values were lower than calculated values for two chains per metal centre due to extensive transesterification reactions and chain transfer reaction.

MALDI-ToF mass spectrum (Figure 3.31) of the resulting PLA shows the presence of two types of end groups ( $-\text{OCHPh}_2$  and  $-\text{OBn}$ ). For example, the peak envelope centred at 1875.8 Da is attributed to PLA containing 24 units of half LA terminated with  $-\text{OH}$  and  $-\text{OBn}$  groups with  $\text{K}^+$  [ $72.0(24) + 108.1 + 39.1$ ]. Another peak envelope centred at 1952.7 Da corresponds to PLA containing 24 units of half LA end capped with  $-\text{OH}$  and  $-\text{OCHPh}_2$  groups with  $\text{K}^+$  [ $72.0(24) + 184.1 + 39.1$ ]. The presence of cyclic PLA containing 24 units of half LA is also visible at the peak envelope centred at 1767.7 Da.

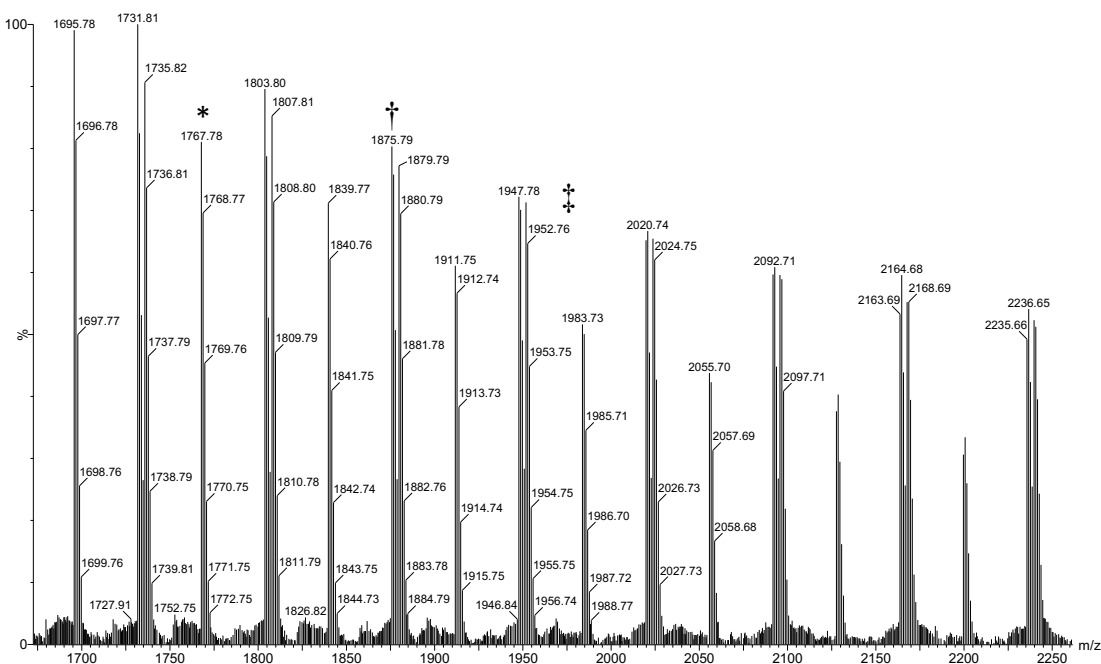


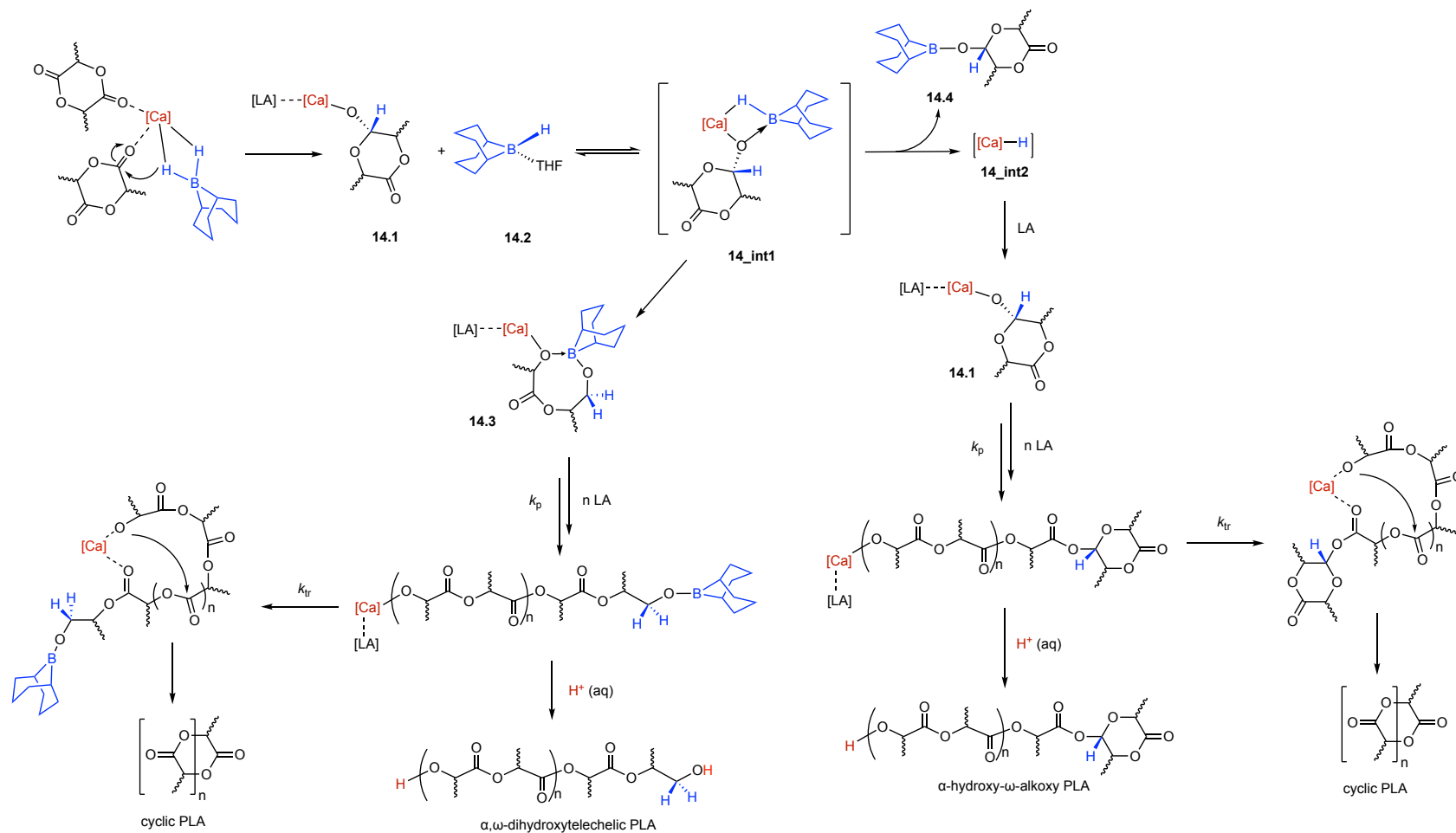
**Figure 3.31** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with 1 equiv. of  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**).  $M_n(\text{GPC}) = 1,910 \text{ g mol}^{-1}$ ,  $D = 1.58$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{7}]_0:[\textbf{19}]_0 = 20:1:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-\text{OBn}$  and  $-\text{OH}$  end groups. “‡” denotes PLA with  $-\text{OCHPh}_2$  and  $-\text{OH}$  end groups.

**17-19** were introduced as models of  $(\text{BC}_8\text{H}_{14})(\text{LA-H})$  (**14.4**) and their role as chain transfer agents was studied. By comparing the ROP results which involve the use of **17**, **18** or **19** to those which do not, it is apparent that the borinic ester species with sterically hindered substituents such as **17** or **18** exhibit poor chain transfer ability. While **19** could exchange with polymer chain on the metal centre to give  $M_n(\text{GPC})$  consistent with those calculated for two chains per metal centre. PLA obtained by the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) shows good agreement between

$M_n$ (GPC) and  $M_n$ (calcd) based on one polymer chain per metal centre. It is therefore proposed that **14.4** does not exchange with growing polymer chain on the metal centre.

### 3.7 Proposed mechanism for the ROP of LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$ (**14**)

The mechanism for the ROP of LA using **14** is proposed based on NMR spectroscopic data and polymerisation studies (Scheme 3.10). The first hydride migrates from the  $\text{H}_2\text{BC}_8\text{H}_{14}$  ligand of **14** to the carbonyl carbon of LA leading to the formation of an alkoxide species  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  (**14.1**) with  $(\text{HBC}_8\text{H}_{14})(\text{THF})$  (**14.2**). Afterwards, a reaction between **14.1** and **14.2** could proceed *via* two pathways. The first pathway is *via* second hydride transfer step between  $\text{HBC}_8\text{H}_{14}$  and non-opened LA ring of **14\_int1** giving  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{OCHMeC}(\text{O})\text{OCHMeCH}_2\text{O}(\text{BC}_8\text{H}_{14})\}$  (**14.3**). Initiator **14.3** could form  $\alpha,\omega$ -dihydroxytelechelic PLA. An alternative pathway is a  $\sigma$ -bond metathesis *via* **14\_int1** to give  $(\text{BC}_8\text{H}_{14})(\text{LA-H})$  (**14.4**) and transient calcium hydride species (**14\_int2**). **14\_int2** subsequently reacts with LA to form **14.1**. While **14.4** does not act as chain transfer agent during polymerisation. PLA terminated with non-opened LA ring ( $-\text{LA-H}$ ) and  $-\text{OH}$  end groups was formed by the ROP initiated by **14.1**. Cyclic PLA is obtained due to the intramolecular transesterification reaction occurred at the later polymerisation stages. To investigate the rate-determining step of the ROP of LA using **14**, DFT calculations have to be performed to obtain a detailed mechanistic analysis of this reaction (especially with respect to transition state energies).



**Scheme 3.10** Proposed mechanism for the ROP of LA by  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) in THF.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .  $[\text{LA}] =$  coordinated LA.

### 3.8 Summary and conclusions for Chapter Three

This Chapter described the catalytic activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) in the ROP of LA. Complex **14** was highly active in the ROP of *rac*-LA, polymerising 800 equiv. of *rac*-LA in THF at RT within 3 min. The kinetic studies showed a second order and first order dependence on concentrations of *rac*-LA and **14**, respectively. The propagation rate constant  $k_p = 133(10) \text{ M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.989$ ) was calculated. Poor agreement between  $M_n(\text{GPC})$  and  $M_n(\text{calcd})$  for one chain per metal centre was observed at high conversion due to inter- and intramolecular transesterification reactions. Moderate  $D$  values were obtained in the range of 1.08-1.97. Heterotactically-enriched PLAs were formed with  $P_r = 0.83$  analysed by  $^1\text{H}\{^1\text{H}\}$  NMR spectroscopy. MALDI-ToF mass spectrometry showed three types of PLA including cyclic PLA, PLA terminated with non-opened ring LA ( $-\text{LA-H}$ ) and  $-\text{OH}$  groups, and  $\alpha,\omega$ -dihydroxytelechelic PLA. The ROP of *meso*-LA initiated by **14** was very active, reaching 93% conversion (800 equiv. of *meso*-LA) after 1 min. Syndiotactically-enriched PLA was produced with  $P_r = 0.87$ .

The identification of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  (**14.1**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{OCHMeC(O)OCHMeCH}_2\text{O}(\text{BC}_8\text{H}_{14})\}$  (**14.3**) formed by the first and second hydride transfer reactions between **14** and 5 equiv. of *L*-LA in  $\text{THF-}d_8$  at 223 K was analysed by NMR spectroscopy. Compounds **15** and **16** were prepared from the reactions of *L*-LA with 1 or 2 equiv. of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$ , respectively.

A series of borinic esters (**17-19**) serving as models of  $(\text{BC}_8\text{H}_{14})(\text{LA-H})$  (**14.4**) was used as potential chain transfer agents in the ROP of *rac*-LA. Poor ability of  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**) and  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  **18** as chain transfer agents was determined due to their negligible effect on polymerisation rate and polymer tacticity obtained from the ROP with and without **17** or **18**. Close agreement between  $M_n(\text{GPC})$  and  $M_n(\text{calcd})$  for one chain per metal centre was also observed, indicating the poor nature of **14.4** as chain transfer agent. In contrast,  $(\text{BC}_8\text{H}_{14})(\text{OCH}_2\text{Ph})$  **19** can act as a chain transfer agent in the ROP of *rac*-LA using *in situ* generated  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and **19**. The slow ROP rate compared to the ROP without **19**, and good agreement between  $M_n(\text{GPC})$  and  $M_n(\text{calcd})$  based on two chains per metal centre were observed.

Two pathways for the mechanism of the ROP of *rac*-LA using **14** are proposed. The first route involves the initiation by **14.1** to form PLA with non-opened LA ring (–LA–H) and –OH end groups. The second pathway involves two-successive hydride transfer to form **14.3** acting as the ROP initiator, resulting in  $\alpha,\omega$ -dihydroxytelechelic PLA. (BC<sub>8</sub>H<sub>14</sub>)(LA–H) (**14.4**) formed by a Ca–O/B–H  $\sigma$ -bond metathesis of **14\_int1**, is determined not to exchange with growing polymeric chain on the metal centre as chain transfer agent.

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# **Chapter Four**

**Alkaline earth tetrahydroborate complexes for  
the ROP of LA and their mechanistic  
investigations**

## Chapter Four

### 4.1 Overview

This Chapter will describe detailed investigations into activity and mechanism of a series of heavy alkaline earth tetrahydroborate complexes,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**) in the ROP of LA. The use of borate esters  $\text{B}(\text{OR})_3$  ( $\text{R} = \text{alkyl}$ ) as chain transfer agents in the ROP of *rac*-LA will also be discussed.

### 4.2 Introduction

#### 4.2.1 Tetrahydroborate initiators for the ROP of cyclic esters

##### 4.2.1.1 Lanthanide tetrahydroborate initiators for the ROP of cyclic esters

In the last decades, lanthanide metal complexes with tetrahydroborate ligands have been widely studied as effective initiators in the polymerisation of MMA and cyclic esters such as *rac*-LA,  $\epsilon$ -CL, *rac*-BBL,  $\delta$ -VL or TMC.<sup>1-22</sup> Pioneering work by Guillaume *et al.* presented the series  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$  where  $\text{Ln} = \text{La}$  (**4.1**),  $\text{Nd}$  (**4.2**) and  $\text{Sm}$  (**4.3**) as effective initiators for the ROP of  $\epsilon$ -CL.<sup>1, 3</sup> The formation of  $\alpha,\omega$ -dihydroxytelechelic PCL with a narrow  $\bar{D}$  value ( $<1.3$ ) was described. Good agreement between observed and calculated  $M_n$  based on three growing polymer chains per metal centre was observed at low monomer conversion followed by a deviation from the expected trend at high monomer conversion due to transesterification reactions. A series of monocationic bis(tetrahydroborate) complexes  $[\text{Ln}(\text{BH}_4)_2(\text{THF})_5][\text{BPh}_4]$  where  $\text{Ln} = \text{La}$  (**4.4**),  $\text{Nd}$  (**4.5**) or  $\text{Sm}$  (**4.6**) developed by Okuda *et al.* efficiently initiated the ROP of  $\epsilon$ -CL.<sup>9</sup> Higher activities and similar  $\bar{D}$  values were observed compared to those obtained by using the neutral complexes (**4.1**, **4.2** or **4.3**). The first heteroleptic tetrahydroborate lanthanide complex,  $\text{Cp}^*_2\text{Sm}(\text{BH}_4)(\text{THF})$  (**4.7**, Figure 4.1) was shown to be active in the ROP of  $\epsilon$ -CL.<sup>2</sup> A mismatch between experimental and calculated  $M_n$  was observed at high ratio of  $[\epsilon\text{-CL}]_0:[\textbf{4.7}]_0$  (*ca.* 400-1,000). The propagating species in the ROP using **4.7** was proposed to be  $\text{Cp}^*_2\text{Sm}\{\text{O}(\text{CH}_2)_6\text{O}(\text{BH}_2)\}$ , producing  $\alpha,\omega$ -dihydroxytelechelic PCL after hydrolysis.

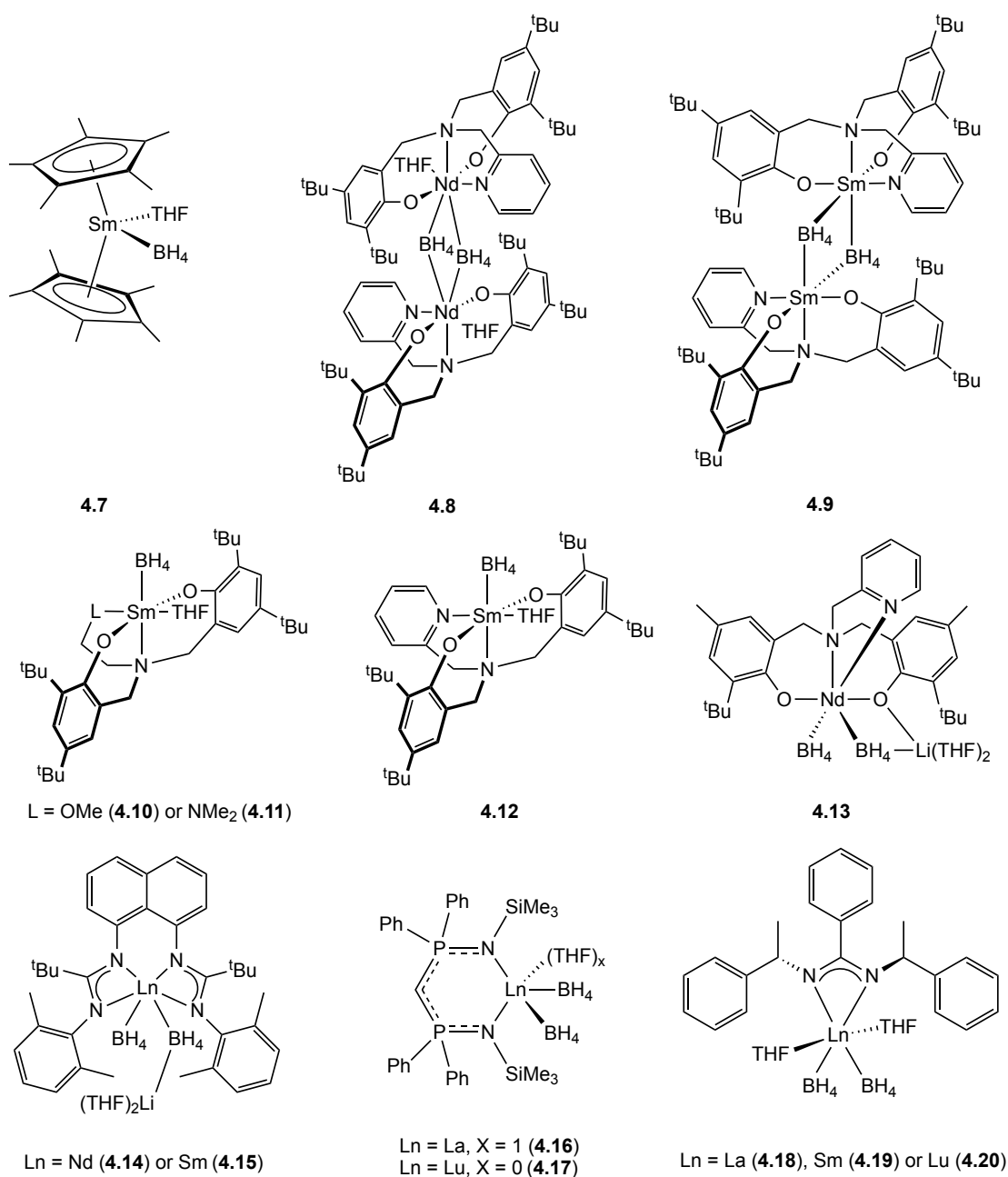


**Figure 4.1** Lanthanide tetrahydroborate complexes for the ROP of cyclic esters (4.7-4.20).<sup>2, 4, 12-15, 19, 23</sup>

Mountford *et al.* reported a series of lanthanide tetrahydroborate complexes supported by a diamino-bis(phenoxide) ligand (ONNO), [(OONN)M( $\mu$ -BH<sub>4</sub>)(THF)<sub>x</sub>]<sub>2</sub> (M = Nd, x = 1 (4.8) or M = Sm, x = 0 (4.9) shown in Figure 4.1) for the ROP of  $\epsilon$ -CL, and *L*- and *rac*-LA.<sup>4</sup> Both complexes were active in the ROP of  $\epsilon$ -CL in toluene at RT, producing PCL with well-controlled  $M_n$  but moderate  $D$  values (1.6-1.8). Complex 4.9 was found to be more active than 4.8 in the ROP of *rac*-LA, giving moderately heterotactic PLA with  $P_r = 0.72$ . However, observed molecular weights were generally

lower than those calculated for one chain growing per metal centre due to transesterification reactions. A series of bis(phenolate)amine-supported samarium tetrahydroborate complexes,  $\text{Sm}(\text{O}_2\text{N}^{\text{L}})(\text{BH}_4)(\text{THF})$  ( $\text{L} = \text{OMe}$  (**4.10**),  $\text{NMe}_2$  (**4.11**) or  $\text{py}$  (**4.12**) shown in Figure 4.1) was also reported as ROP of  $\varepsilon$ -CL or *rac*-LA catalysts.<sup>12</sup> Complexes **4.10-4.12** were active in the ROP of  $\varepsilon$ -CL giving  $\alpha,\omega$ -dihydroxytelechelic PCL. Complex **4.11** was observed to be more active in the ROP of *rac*-LA than **4.10** or **4.12** and showed good agreement between experimental and calculated  $M_n$  together with a moderate  $D$  value (1.41). Complexes **4.10-4.12** gave heterotactically-enriched PLAs with  $P_r = 0.82$ – $0.84$ . MALDI-ToF MS analysis of PLA synthesised by **4.11** appeared to suggest both  $-\text{CHMeCHO}$  and  $-\text{CHMeCH}_2\text{OH}$  end groups, whereas  $\alpha,\omega$ -dihydroxytelechelic PLA was observed from PLA formed by **4.10** or **4.12**.

Trifonov *et al.* reported the activity of heterobimetallic tetrahydroborate neodymium complexes supported by a diamino-bis(phenoxide) ligand (OONN),  $(\text{OONN})\text{Nd}(\text{BH}_4)(\mu\text{-BH}_4)\text{Li}(\text{THF})_2$  (**4.13**, Figure 4.1) in the ROP of *rac*-LA under mild conditions, giving atactic PLA.<sup>14</sup> The experimental  $M_n$  values of PLA were observed to be half of those calculated for one growing polymer chain per metal centre, suggesting both tetrahydroborate groups were active during initiation step for the ROP of *rac*-LA. A similar phenomenon was also observed from the ROP of *rac*-LA initiated by lanthanide (Nd (**4.14**) and Sm (**4.15**), Figure 4.1) tetrahydroborate complexes supported by *ansa*-bis(amidinate) ligand.<sup>15</sup> The experimental  $M_n$  values were consistent with those calculated for two growing polymer chains per metal centre during low monomer conversion followed by a deviation from the expected trend at higher monomer conversion due to transesterification reactions. Moderately heterotactic PLAs ( $P_r = 0.53$ – $0.62$ ) with moderate  $D$  values (1.4–1.7) were obtained.

Roesky *et al.* reported the synthesis and ROP activity of bis(phosphinimino)methanide tetrahydroborate lanthanide complexes  $\{\text{CH}(\text{PPh}_2\text{NSiMe}_3)_2\}\text{M}(\text{BH}_4)_2(\text{THF})$  ( $\text{M} = \text{La}$  (**4.16**) and  $\text{Lu}$  (**4.17**), Figure 4.1).<sup>13</sup> Both complexes were active in the ROP of  $\varepsilon$ -CL, giving PCL with well-controlled  $M_n$  and moderate  $D$  values (1.10–1.50). In 2013, Roesky *et al.* synthesised enantiopure lanthanide tetrahydroborate complexes supported by *N,N'*-bis((*S*)-1-phenylethyl)-benzamidinate ((*S*)-PEBA),  $\text{M}\{(\text{S})\text{-PEBA}\}(\text{BH}_4)_2(\text{THF})_2$  ( $\text{M} = \text{La}$  (**4.18**),  $\text{Sm}$  (**4.19**) and  $\text{Lu}$  (**4.20**), Figure 4.1).<sup>19</sup> All complexes were active in the ROP of *rac*-LA under mild conditions, providing atactic  $\alpha,\omega$ -dihydroxytelechelic PLA. Close agreement between calculated  $M_n$  values and

those calculated for two growing polymer chains per metal centre was observed, suggesting that two tetrahydroborate groups were involved during the initiation step and subsequent propagation.

#### 4.2.1.2 Alkaline earth tetrahydroborate initiators for the ROP of cyclic esters

The first cationic calcium tetrahydroborate complexes  $[\text{Ca}(\text{BH}_4)(\text{THF})_5][\text{BPh}_4]$  (**2.24**) and  $[(\text{Tpm})\text{Ca}(\text{BH}_4)(\text{THF})_2][\text{BPh}_4]$  (**2.25**,  $\text{Tpm} = \text{HB}(\text{Me}_2\text{pz})_3$ ) were briefly communicated by Mountford and Cushion.<sup>24</sup> Their activity in the ROP of *rac*-LA was reported in Chapter Two. The ROP of *rac*-LA with  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) was also introduced in this work, giving heterotactically-enriched PLA with  $P_r = 0.88\text{--}0.90$  ( $-20\text{ }^\circ\text{C}$ ) or *ca.* 0.80 (RT). The kinetic and mechanistic investigations of complex **8** in the ROP of *rac*-LA will be discussed later in this Chapter.

Mountford *et al.* subsequently reported a series of  $\beta$ -diketiminate-supported alkaline earth tetrahydroborate complexes as shown in Figure 4.2,  $(^{\text{Dipp}}\text{NacNac})\text{M}(\text{BH}_4)(\text{THF})_x$  ( $\text{M} = \text{Mg}$  (**4.21**),  $x = 1$  and  $\text{M} = \text{Ca}$  (**4.22**),  $x = 2$ ) and  $\{\text{CH}(\text{PPh}_2\text{NDipp})_2\}\text{Mg}(\text{BH}_4)(\text{THF})_2$  (**4.23**).<sup>25</sup> Complex **4.21** was found to be more active in the ROP of *rac*-LA than **4.22** or **4.23**. High degree of heteroselectivity was also observed for PLA formed by **4.21** ( $P_r = 0.74\text{--}0.86$ ) whereas no stereocontrol was obtained using **4.22** or **4.23** ( $P_r = 0.50$ ). **4.21** showed good agreement between experimental and calculated  $M_n$  for one growing polymer chain per metal centre. At higher conversions, the  $M_n$  started to tail off due to transesterification reactions, leading to chain-shortening effects. For the ROP of *rac*-LA initiated by **4.22** or **4.23**, much poorer agreement between experimental and calculated  $M_n$  values was observed together with moderate  $\bar{D}$  values (1.15–1.79). MALDI-ToF MS analysis of PLAs formed using **4.21**, **4.22** or **4.23** appeared to show two types of end group;  $-\text{CH}_2\text{OH}$  and  $-\text{CHMeCHO}$  based on  $m/z$  values although NMR data were unclear. While the predominance of cyclic PLA and the minor distribution of PLA terminated by  $-\text{CH}_2\text{OH}$  and  $-\text{CHMeCHO}$  were observed from PLA formed using **4.22**.

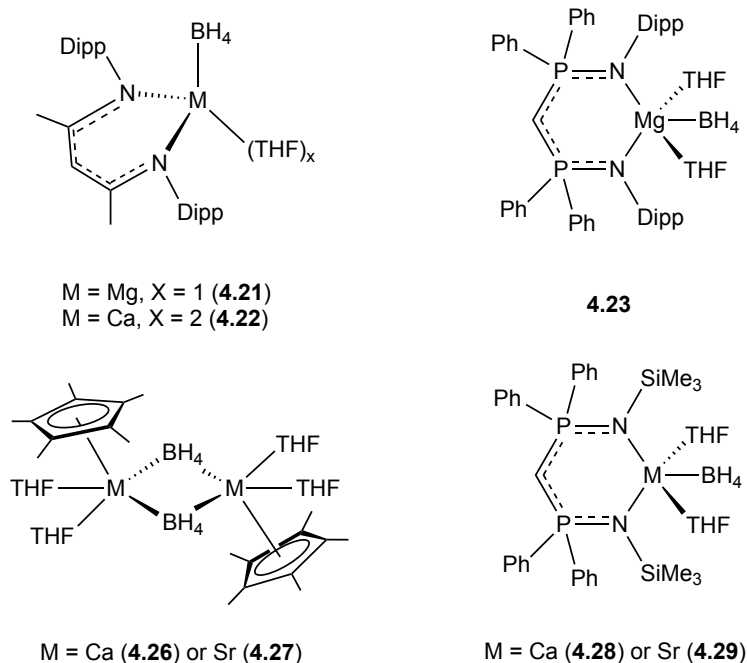
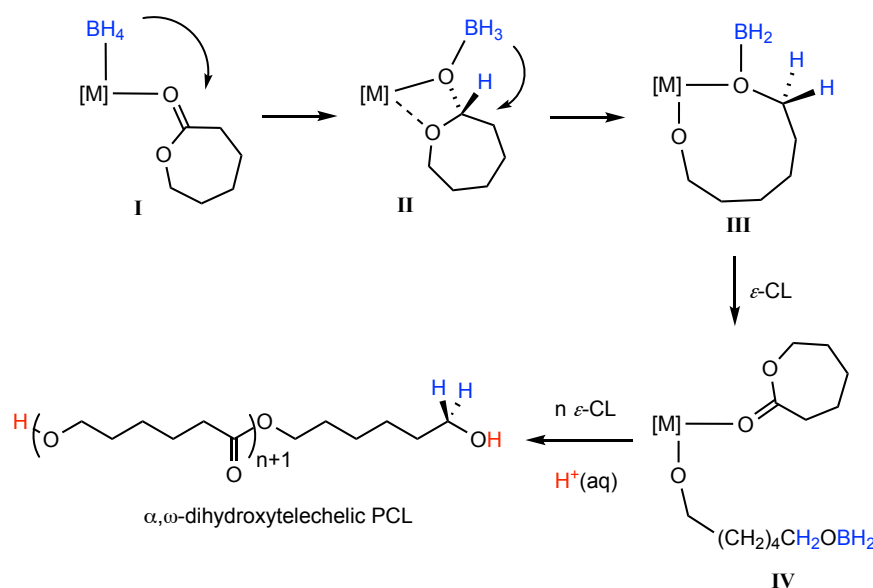


**Figure 4.2** Alkaline earth metal tetrahydroborate complexes for the ROP of cyclic esters (**4.21-4.23** and **4.26-4.29**).<sup>23, 25-27</sup>

Roesky, Guillaume and Maron reported a series of  $M(BH_4)_2(THF)_2$  ( $M = Ca$  (**4.24**), Sr (**4.25**)),  $[Cp^*M(BH_4)(THF)_2]_2$  ( $M = Ca$  (**4.26**), Sr (**4.27**)) and  $\{CH(PPh_2NSiMe_3)_2\}M(BH_4)(THF)_2$  ( $M = Ca$  (**4.28**), Sr (**4.29**)) complexes (Figure 4.2).<sup>26, 27</sup> All complexes were active in the ROP of  $\epsilon$ -CL and showed well-controlled  $M_n$  and moderate  $D$  values (1.30-1.85). Overall, the calcium complexes **4.24** and **4.26** were generally more active in the ROP of  $\epsilon$ -CL and  $L$ -LA than the strontium analogues **4.25** and **4.27**. For example, **4.26** polymerised 500 equiv. of  $\epsilon$ -CL to full conversion after 20 min while **4.27** required 4 h to reach 75% under analogous conditions. Complex **4.29** was more active than **4.28** in the ROP of  $\epsilon$ -CL and  $L$ -LA. For example, **4.29** polymerised 100 equiv. of  $L$ -LA after 12.5 h while 80% conversion was reached after 15 h for **4.28**.

#### 4.2.2 Proposed mechanism for ROP of cyclic esters by tetrahydroborate initiator

The first mechanistic investigation of the ROP of  $\epsilon$ -CL with  $(L)Ln-BH_4$  complex was reported by Mountford, Guillaume and Maron *et al.*<sup>28</sup> The mechanism for the ROP of  $\epsilon$ -CL was proposed based on the experimental and computational studies as shown in Scheme 4.1.



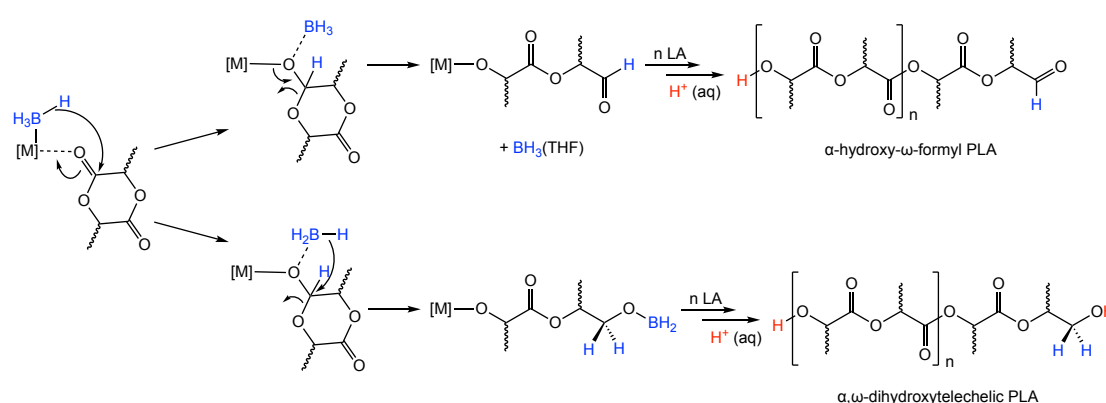
**Scheme 4.1** The proposed mechanism for the ROP of  $\varepsilon\text{-CL}$  using tetrahydroborate initiator reported by Mountford, Guillaume and Maron *et al.*<sup>28</sup>

The mechanism begins with the coordination of  $\varepsilon\text{-CL}$  to the metal centre through the carbonyl group forming **I**. The hydride transfers to the carbonyl carbon of  $\varepsilon\text{-CL}$  followed by the transfer of  $\text{BH}_3$  to the anionic oxygen leading to the formation of **II**. The oxygen-acyl bond cleavage subsequently occurs *via* a second hydride transfer to the same carbon affording **III**. The incoming monomer undergoes ring-opening through a coordination-insertion route, generating a polymeric chain terminated with  $\text{OBH}_2$  coordinated to the metal centre. Hydrolysis of the  $\text{Ln-O}$  bond and the  $\text{OBH}_2$  moiety generate  $\alpha,\omega$ -dihydroxytelechelic PCL.<sup>1, 2, 5</sup> However, the ROP of cyclic esters does not necessarily produce  $\alpha,\omega$ -dihydroxy polymer. For example, Guillaume *et al.* reported poly(TMC) formed by  $\text{Sm}(\text{BH}_4)_3(\text{THF})_3$  containing  $-\text{CHO}$  and  $-\text{CH}_2\text{OH}$  end groups.<sup>7</sup> Carpentier and Trifonov *et al.* also reported the PLA terminated with  $-\text{CH}_2\text{OH}$  and ambiguous end group which was tentatively assigned to  $-\text{CHO}$  by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.<sup>8, 10</sup>

Mountford *et al.* proposed two types of end groups analysed by MALDI-ToF MS of PLA formed by  $\text{Sm}(\text{O}_2\text{N}^{\text{NMe}_2})(\text{BH}_4)(\text{THF})$  (**4.11**),  $-\text{CHMeCHO}$  and  $-\text{CHMeCH}_2\text{OH}$ .<sup>12</sup> The DFT investigation was carried out using  $\text{Eu}(\text{O}_2\text{N}^{\text{NMe}_2})(\text{BH}_4)$  as a model with *L*-LA in order to study the origin of the two different chain ends and the initiation step in the tetrahydroborate-catalysed ROP of *rac*-LA. Two possible initiation steps were reported as shown in Scheme 4.2. The first reaction pathway involves the ring-opening



of LA with a second hydride transfer step leading to a growing polymer chain on metal terminated with  $-\text{CHMeCH}_2\text{OBH}_2$  which was reminiscent of the previous calculation for the ROP of  $\epsilon\text{-CL}$ .<sup>13</sup> The second pathway involves the ring-opening of LA without the second hydride transfer leading to the  $\text{BH}_3$  capped chelating aldehyde group,  $-\text{CHMeCHO}\cdot\text{BH}_3$ , on metal followed by the dissociation of  $\text{BH}_3$ . The second hydride transfer from  $\text{BH}_3$  to the  $-\text{CHMeCHO}$  carbonyl carbon could occur as it was found to be more thermodynamically favourable. Nonetheless, the experimental assignment of the aldehyde ( $-\text{CHMeCHO}$ ) terminated PLA from MALDI-ToF MS supported the two-stage mechanism for the ROP using tetrahydroborate initiator.



**Scheme 4.2** The proposed mechanism for the ROP of LA using tetrahydroborate initiator reported by Mountford *et al.*<sup>12</sup>

For the last seven years, the Mountford group has developed tetrahydroborate initiators supported by various ligands for the ROP of cyclic esters (Figure 4.3).<sup>23, 29, 30</sup> A series of alkaline earth metal tetrahydroborate complexes supported by a 3-methyl, 5-*tert*-butyl tris(pyrazolyl)hydroborate ( $\text{Tp}^{\text{tBu,Me}}$ ) ligand has been reported.<sup>29</sup> ( $\text{Tp}^{\text{tBu,Me}}$ ) $\text{M}(\text{BH}_4)(\text{THF})_x$  ( $\text{M} = \text{Mg}$ ,  $x = 0$  (**20**),  $\text{M} = \text{Ca}$ ,  $x = 1$  (**8**),  $\text{M} = \text{Sr}$ ,  $x = 2$  (**21**)) were prepared *via* reactions of  $\text{K}(\text{Tp}^{\text{tBu,Me}})$  and  $\text{M}(\text{BH}_4)_2(\text{THF})_x$  ( $\text{M} = \text{Mg}$ ,  $x = 0$  and  $\text{M} = \text{Ca}$  and  $\text{Sr}$ ,  $x = 2$ ). Complex **20** was less active in the ROP of  $\epsilon\text{-CL}$  in toluene at RT than **8** or **21**. At  $[\epsilon\text{-CL}]_0:[\text{initiator}]_0 = 200$ , over 80% conversion was reached within 1 min or 7 min for the ROP with **8** or **21**, respectively. While **20** took 80 min to reach 95% conversion. The polymerisation was slower when THF was used as a solvent due to the competition between monomer and THF molecules coordinating to the metal centre. For example, **20** took 2 h to reach 84% conversion under analogous conditions in THF. At  $[\text{rac-LA}]_0:[\text{20}]_0 = 100$ , **20** was inactive at RT in THF after 12 h. At 70 °C, the polymerisation reached 86% conversion after 4.5 h with an induction period for 2

h, giving atactic PLA. The observed  $M_n$  values were considerably lower than those calculated for one growing chain per metal centre. Complexes **8** and **21** were more active in the ROP of *rac*-LA than **20**, over 95% conversion was reached within 5 min in THF at RT. PLAs with greater  $M_n$ (GPC) than expected and moderate  $D$  values (1.3-1.5) were observed. Heterotactic-rich PLAs were obtained with  $P_r = 0.80$  and 0.67 from **8** and **21**, respectively. The mechanistic considerations for the ROP of *rac*-LA using **8** or **21** were poorly understood compared to the analogous magnesium complex (**20**) due to their rapid polymerisation activity and side reactions such as transesterification reactions (*vide infra*).

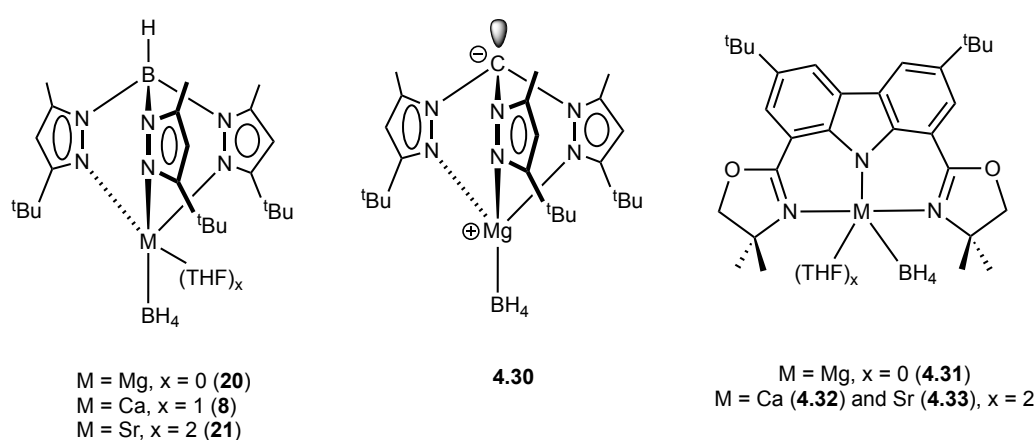
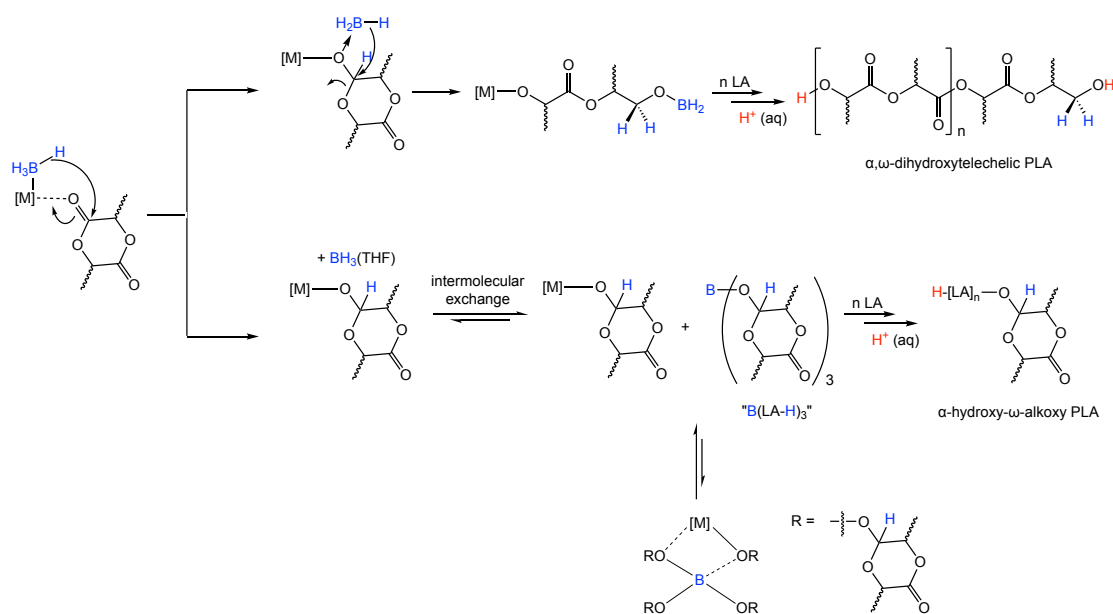


**Figure 4.3** Alkaline earth tetrahydroborate initiators reported by Mountford *et al.*<sup>23, 29, 30</sup>

The magnesium tetrahydroborate complex supported by tris(pyrazolyl)methanide ( $\text{Tpm}^{*\text{d}}$ ) ligand,  $(\text{Tpm}^{*\text{d}})\text{Mg}(\text{BH}_4)(\text{THF})$  (**4.30**), was active for the ROP of *rac*-LA, reaching 90% conversion within 6 h in THF at RT.<sup>23</sup> The  $M_n$ (GPC) values were half of those calculated for one chain per metal centre. Moderately heterotactic PLA was obtained with  $P_r = 0.62$ . Alkaline earth tetrahydroborate complexes supported by the carbazole-bis(oxazoline) ligand  $\text{CzOx}^{\text{Me}_2}$ ,  $\text{M}(\text{CzOx}^{\text{Me}_2})(\text{BH}_4)(\text{THF})_x$  ( $M = \text{Mg}, x = 0$  (**4.31**),  $M = \text{Ca}$  (**4.32**) and  $\text{Sr}$  (**4.33**),  $x = 2$ ), have also been reported.<sup>30</sup> All complexes are active in the ROP of *rac*-LA in THF at RT, with the activity order  $\text{Sr} > \text{Mg} > \text{Ca}$ . At  $[\text{rac-LA}]_0 : [\text{initiator}]_0 = 100$ , over 88% conversion was reached within 2, 120 or 180 min from **4.33**, **4.31** or **4.32**, respectively. Close agreement between  $M_n$ (GPC) and  $M_n$ (calcd) and narrow  $D$  value (1.14) were observed from the ROP with **4.31**. While a mismatch between  $M_n$ (GPC) and  $M_n$ (calcd) and moderate  $D$  values (1.50-1.70) were

observed from **4.32** and **4.33**. **4.31** gave highly heterotactic PLAs with  $P_r = 0.82$ - $0.84$ , whereas **4.32** and **4.33** gave moderately heterotactic PLAs ( $P_r = 0.60$ - $0.67$ ).

In-depth spectroscopic studies with the tetrahydroborate magnesium complexes provided an alternative mechanism for the ROP of LA (Scheme 4.3). The first hydride transfer product containing non-opened LA ring coordinated to the metal centre,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{LA-H})$  was observed from the reaction between **20** and 5 equiv. of *rac*-LA in THF- $d_8$  at RT, and fully characterised by NMR spectroscopy.<sup>29</sup> The polymerisation of LA could be initiated by  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{LA-H})$  via a coordination-insertion pathway. The MALDI-ToF MS analysis of PLA formed by **20** showed two types of polymers;  $\alpha,\omega$ -dihydroxytelechelic PLA, and PLA end capped with non-opened ring LA ( $-\text{LA-H}$ ) and  $-\text{OH}$ , together with a separation between peak envelopes of  $\Delta(m/z) = 144.0$  Da. No cyclic PLA was observed indicating the absence of transesterification reactions. It is worth noting that the non-opened LA ring end capped PLA provided the identical isotopic distribution pattern in MALDI-ToF MS as the previously postulated aldehyde end capped PLA. However, the NMR spectroscopic data disproved the formation of  $-\text{CHMeCHO}$  growing polymer chain.

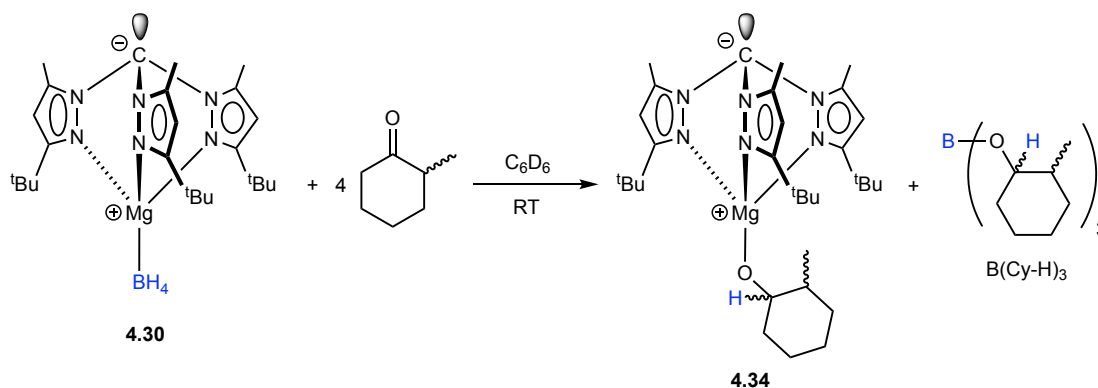


**Scheme 4.3** The proposed mechanism for the ROP of LA initiated by a magnesium tetrahydroborate complex.<sup>23, 29, 30</sup>  $[M] = (\text{Tp}^{\text{tBu,Me}})\text{Mg}$ ,  $(\text{CzOx}^{\text{Me}_2})\text{Mg}$  or  $(\text{Tpm}^{\text{*d}})\text{Mg}$ .

As shown in scheme 4.3, two consecutive hydride migrations occurred followed by ring-opening led to the dihydroxy PLA formed after hydrolysis. For the other route, the hydride migrated from  $\text{BH}_4$  moiety to the carbonyl carbon of LA monomer. Instead of

the subsequent ring-opening to form the aldehyde end capped adduct, the alkoxide species featuring non-opened LA ring,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{LA-H})$  was formed together with the free  $\text{BH}_3(\text{THF})$ . Then,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{LA-H})$  and  $\text{BH}_3(\text{THF})$  underwent an exchange to form a borate ester species,  $\text{B}(\text{LA-H})_3$ . However, the identity of  $\text{B}(\text{LA-H})_3$  is ambiguous as non-opened LA ring or ring-opened LA could be presented in the structure. The first hydride transfer product,  $\text{Tpm}^{\text{*d}}\text{Mg}(\text{LA-H})$  was also observed from the reaction of **4.30** with 5 equiv. of *L*-LA in THF- $d_8$  at RT. The role of  $\text{B}(\text{LA-H})_3$  as chain transfer agent in the ROP of *rac*-LA was investigated.

A reaction of **4.30** and 4 equiv. of 2-methylcyclohexanone produced  $(\text{Tpm}^{\text{*d}})\text{Mg}(\text{OCyMe})$  (**4.34**) and  $\text{B}(\text{OCyMe})_3$  serving as models of  $(\text{Tpm}^{\text{*d}})\text{Mg}(\text{LA-H})$  and  $\text{B}(\text{LA-H})_3$ , respectively (Equation 4.1).<sup>23</sup> The poor chain transfer ability of  $\text{B}(\text{OCyMe})_3$  was shown as  $M_n(\text{GPC})$  values were higher than those calculated for one chain per metal centre. However,  $M_n(\text{GPC})$  values of PLA formed by **4.30** were much lower than those calculated for one chain per metal. Therefore, it was hypothesised that  $\text{B}(\text{LA-H})_3$  was not only the bulky borate ester with a similar size as  $\text{B}(\text{OCyMe})_3$  but also that with a smaller alkyl group. The smaller borate ester could exchange with alkoxy species or growing polymeric chain on the metal centre as a chain transfer agent.



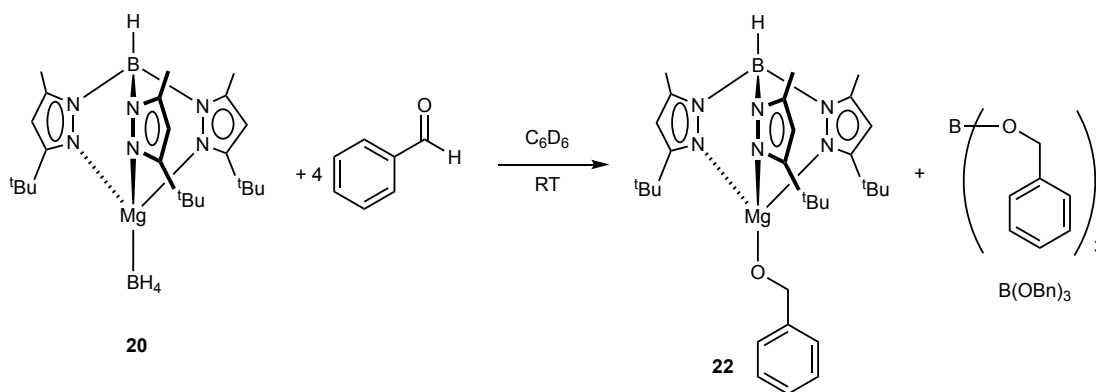
Equation 4.1

#### 4.2.3 Immortal ROP of *rac*-LA using a magnesium alkoxide initiator with borate ester species as chain transfer agents

Shen *et al.* reported the one-pot reaction of  $\text{M}(\text{BH}_4)_3(\text{THF})_3$  ( $\text{M} = \text{Nd}$  or  $\text{Y}$ ) with 12 equiv. of various aldehydes and ketones followed by addition of  $\epsilon$ -CL and then stirred at certain times at 60 °C.<sup>31</sup> Mechanistic studies showed that  $\text{M}(\text{BH}_4)_3(\text{THF})_3$  reacted with  $\text{RCOR}'$  forming  $\text{M}(\text{OCHRR})_3$  and released 3 equiv. of  $\text{BH}_3(\text{THF})$  which could

reduce the leftover  $\text{RCOR}'$  giving 3 equiv. of  $\text{B}(\text{OCHRR}')_3$ . The ROP catalytic activity of *in situ* generated  $\text{M}(\text{OCHRR}')_3$  was examined, giving PCL end capped with alkoxide end groups. The lack of reactivity of  $\text{B}(\text{OCHRR}')_3$  as a ROP initiator was reported, although the chain transfer ability was not investigated.

The role of borate esters  $\text{B}(\text{OR})_3$  ( $\text{R}$  = alkyl) as chain transfer agents in the immortal ROP of *rac*-LA has been previously reported by the Mountford group.<sup>23, 29, 30</sup> The pioneering work came from the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) with 4 equiv. of benzaldehyde in  $\text{C}_6\text{D}_6$ , giving  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) and trialkyl borate ester  $\text{B}(\text{OBn})_3$  (Equation 4.2).<sup>29</sup> The ROP of *rac*-LA using *in situ* generated **22** and  $\text{B}(\text{OBn})_3$  was conducted in THF at RT, reaching 97% conversion after 12 h. While the ROP using only **22** reached 86% conversion after 17 h. PLA formed by the immortal ROP showed a good agreement between  $M_n(\text{GPC})$  values and those calculated for four growing chains per metal centre indicating chain transfer ability of  $\text{B}(\text{OBn})_3$ , and relatively narrow  $D$  values (1.11-1.19). In contrast, PLA formed by **22** showed close agreement between  $M_n(\text{GPC})$  values and those calculated for one growing chain per metal centre and narrow  $D$  values (1.06-1.13). However,  $\text{B}(\text{OBn})_3$  has no influence over polymer tacticity as moderately heterotactic PLAs ( $P_r = 0.61$ -0.65) were produced from both polymerisations.



**Equation 4.2**

The high activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**) in the ROP of *rac*-LA was reported in previous studies.<sup>24, 29</sup> However, the mechanisms involving **8** or **21** were not thoroughly investigated due to their rapid rate of polymerisation and prevalence of transesterification reactions. The following sections describe detailed studies to improve the understanding of the mechanisms involving these complexes.

### 4.3 ROP of *rac*- and *meso*-LA using (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**)

Polymerisation of *rac*-LA with  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 100$  was performed in THF at RT, 88% conversion was reached after 30 s (Table 4.1, entry 5). The polymerisation was too rapid to follow the monomer conversion over time for kinetic analysis. Therefore, the ROP of *rac*-LA with  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 800:1$  was conducted, reaching 87% conversion after 3 min (Table 4.1, entry 1). The linear plot of  $1/[rac\text{-LA}]_t$  vs. time (Figure 4.4) indicates second order dependence on *rac*-LA concentration with  $k_{app} = 0.073(8) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.960$ ). In order to determine the kinetic order dependence on **[8]** and therefore the propagation rate constant ( $k_p$ ), the polymerisations of *rac*-LA using various ratios of  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 800, 500, 300$  and 200 with a constant *rac*-LA concentration of 0.5 M were carried out. Second order plots are shown in Figure 4.4, providing a rate law of  $-d[rac\text{-LA}]/dt = k_{app}[rac\text{-LA}]^2$  where  $k_{app} = k_p[\mathbf{8}]^x$ . The ROP results are summarised in Table 4.1.

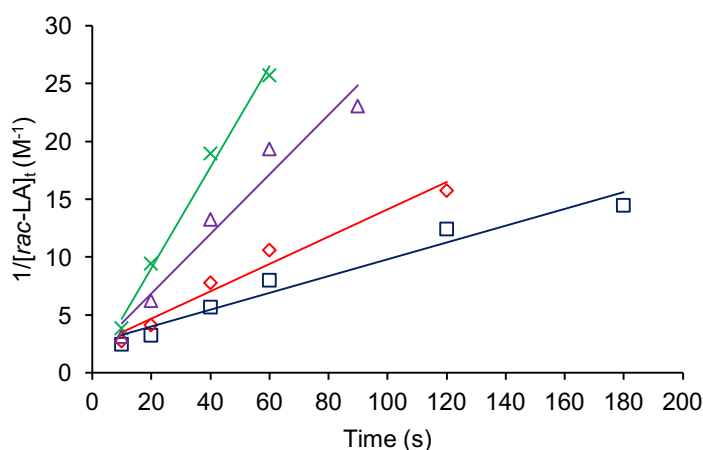


**Figure 4.4** ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**). Plots of  $1/[rac\text{-LA}]_t$  vs. time. Conditions: 6 mL THF, RT,  $[rac\text{-LA}]_0 = 0.5 \text{ M}$ . Squares:  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 800:1$  ( $k_{app} = 0.073(8) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.960$ ). Diamonds:  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 500:1$  ( $k_{app} = 0.118(12) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.970$ ). Triangles:  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 300:1$  ( $k_{app} = 0.257(30) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.960$ ). Crosses:  $[rac\text{-LA}]_0:[\mathbf{8}]_0 = 200:1$  ( $k_{app} = 0.437(31) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.990$ ).

**Table 4.1** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**).<sup>a</sup>

| Entry | [ <i>rac</i> -LA] <sub>0</sub> : <b>[8]</b> <sub>0</sub> | Conv. <sup>b</sup><br>(%) | Time<br>(s) | <i>M</i> <sub>n</sub> (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>k</i> <sub>app</sub> <sup>f</sup><br>(M <sup>-1</sup> s <sup>-1</sup> ) | <i>R</i> <sup>2f</sup> | <i>P</i> <sub>r</sub> <sup>g</sup> |
|-------|----------------------------------------------------------|---------------------------|-------------|--------------------------------------------------------------------|----------------------------------------------------------------------|-----------------------|----------------------------------------------------------------------------|------------------------|------------------------------------|
| 1     | 800                                                      | 87                        | 180         | 62,320                                                             | 100,296                                                              | 1.49                  | 0.073(8)                                                                   | 0.960                  | 0.77                               |
| 2     | 500                                                      | 87                        | 120         | 39,150                                                             | 62,686                                                               | 1.40                  | 0.118(12)                                                                  | 0.970                  | 0.76                               |
| 3     | 300                                                      | 91                        | 90          | 21,110                                                             | 39,341                                                               | 1.67                  | 0.257(30)                                                                  | 0.960                  | 0.74                               |
| 4     | 200                                                      | 92                        | 60          | 14,490                                                             | 26,516                                                               | 1.80                  | 0.437(31)                                                                  | 0.990                  | 0.75                               |
| 5     | 100                                                      | 88                        | 30          | 8,860                                                              | 12,683                                                               | 1.62                  | <sup>h</sup>                                                               | <sup>h</sup>           | 0.77                               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub> = 0.5 M, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated *M*<sub>n</sub> (g mol<sup>-1</sup>) for –OH and –LA-H end groups, *M*<sub>n</sub> (entry 1-5) = conv. (%) × [*rac*-LA]<sub>0</sub>:**[8]**<sub>0</sub> × 144.1 + 2. <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> Apparent second order rate constant for consumption of monomer with standard error and *R*<sup>2</sup> determined by linear regression analysis. <sup>g</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses. <sup>h</sup> Not measured.

The gradient of 1.31(7) ( $R^2 = 0.995$ ) calculated from the plot of  $-\ln(k_{\text{app}})$  vs.  $-\ln[\mathbf{8}]$  (Figure 4.5, right) is indicative of the first order dependence on  $[\mathbf{8}]$ . The propagation rate constant ( $k_p$ ) of 198(13)  $\text{M}^2\text{s}^{-1}$  ( $R^2 = 0.992$ ) is calculated from the gradient of the plot between  $k_{\text{app}}$  vs.  $[\mathbf{8}]$  (Figure 4.5, left). The overall rate law is determined as  $-\text{d}[\text{rac-LA}]/\text{dt} = k_p[\text{rac-LA}]^2[\mathbf{8}]$ ,  $k_p = 198(13) \text{ M}^2\text{s}^{-1}$  ( $R^2 = 0.992$ ).

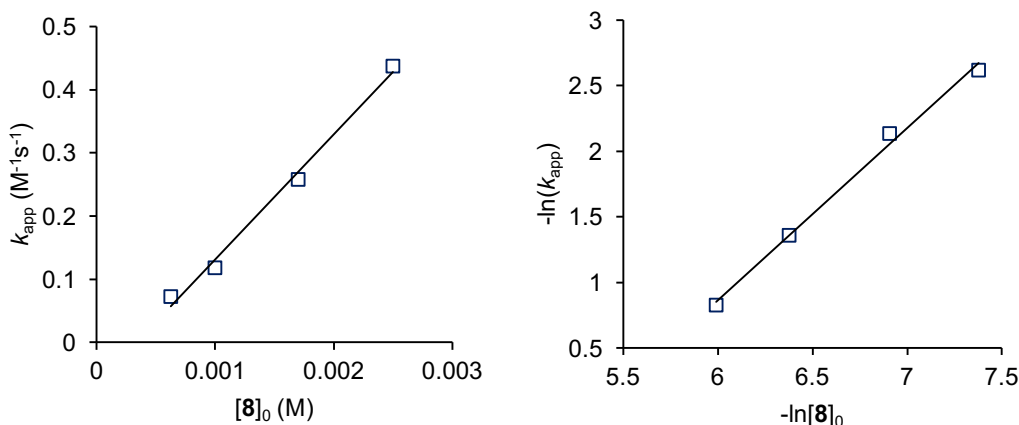


**Figure 4.5 Left**, plot of  $k_{\text{app}}$  vs.  $[\mathbf{8}]_0$ , for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) shows  $k_p = 198(13) \text{ M}^2\text{s}^{-1}$  ( $R^2 = 0.992$ ). **Right**, plot of  $-\ln(k_{\text{app}})$  vs.  $-\ln[\mathbf{8}]_0$  shows an order in  $[\mathbf{8}]$  equal to 1.31(7) ( $R^2 = 0.995$ ).

Regarding the ROP of *rac*-LA using **8**,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**), second and first order dependence on monomer and catalyst concentrations were observed. Values of  $k_p$  calculated from the ROP with **8** and **14** ( $198(13)$  and  $133(10) \text{ M}^2\text{s}^{-1}$ , respectively) are identical within error, but lower than that calculated by using **1** ( $258(14) \text{ M}^2\text{s}^{-1}$ ). This is presumably due to the presence of  $\text{BH}_3(\text{THF})$  or  $(\text{HBC}_8\text{H}_{14})(\text{THF})$  in the polymerisation by **8** or **14**, which undergo intermolecular exchange with  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$ , and cause a slight decrease in propagation rate.

Plots of  $M_n(\text{GPC})$  vs. conversion (%) (Figure 4.6) show that  $M_n(\text{GPC})$  values were considerably lower than those calculated for one growing polymer chain per metal centre from *ca.* 40% conversion onward. This could be attributed to intramolecular transesterification in accordance with the presence of cyclic PLA displayed in MALDI-ToF mass spectrum (Figure 4.8) (*vide infra*). Moderate  $\bar{D}$  values were obtained ( $\bar{D} = 1.30\text{--}1.80$ ). Moderately heterotactic PLAs were produced with  $P_r = 0.74\text{--}0.77$ . The deviation of  $M_n$  from the expected trend from the ROP of *rac*-LA using



tetrahydroborate lanthanide or alkaline earth metal complexes has been well reported.<sup>3, 14, 15, 25, 27, 32</sup>

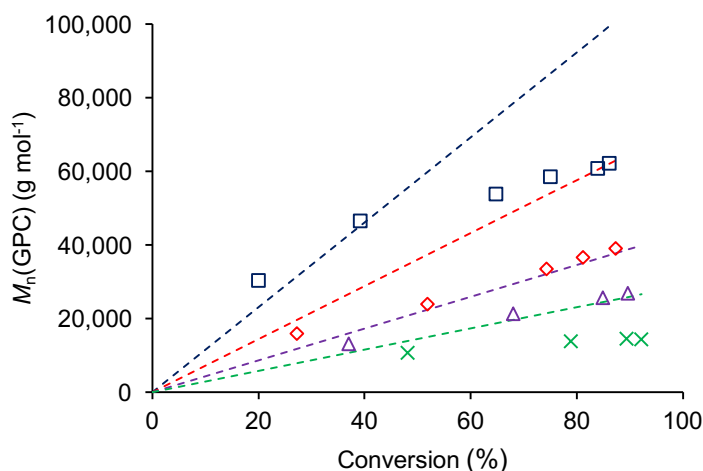


**Figure 4.6** Plots of  $M_n$ (GPC) vs. conversion (%) for ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**). Conditions: 6 mL THF, RT,  $[\text{rac-LA}]_0 = 0.5$  M. The dashed lines represent  $M_n$ (calcd) for one PLA chain per metal centre. Squares:  $[\text{rac-LA}]_0:[\textbf{8}]_0 = 800:1$ ,  $\bar{D} = 1.10\text{--}1.50$ . Diamonds:  $[\text{rac-LA}]_0:[\textbf{8}]_0 = 500:1$ ,  $\bar{D} = 1.32\text{--}1.40$ . Triangles:  $[\text{rac-LA}]_0:[\textbf{8}]_0 = 300:1$ ,  $\bar{D} = 1.35\text{--}1.67$ . Crosses:  $[\text{rac-LA}]_0:[\textbf{8}]_0 = 200:1$ ,  $\bar{D} = 1.50\text{--}1.80$ .

Complex **8** was more active in the ROP of *meso*-LA than that of *rac*-LA, reaching 96% conversion (800 equiv. of *meso*-LA) after 1 min under analogous conditions. First order dependence on  $[\text{meso-LA}]$  was observed with  $k_{\text{app}} = 0.048(2) \text{ s}^{-1}$  ( $R^2 = 0.996$ , Figure 4.7, left). Similar to the ROP of *rac*-LA, the  $M_n$ (GPC) values were almost half of those calculated for one PLA chain per metal centre from 50% conversion onwards, giving PLA with moderate  $\bar{D}$  values (1.13–1.56) (Figure 4.7, right). Syndiotactically-enriched PLA was produced with  $P_r = 0.85$ .

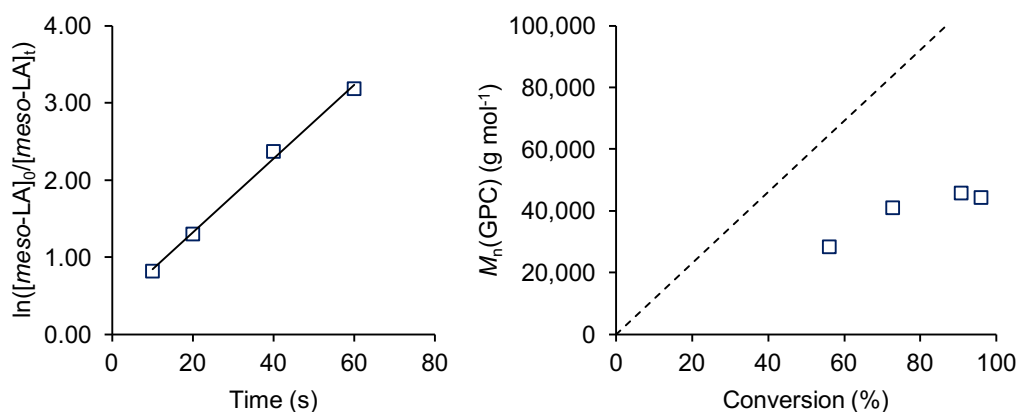


**Figure 4.7 Left**, plot of  $\ln([meso-LA]_0/[meso-LA]_t)$  vs. time shows  $k_{app} = 0.048(2) \text{ s}^{-1}$  ( $R^2 = 0.996$ ). **Right**, plot of  $M_n$ (GPC) vs. conversion (%).  $\bar{D} = 1.13\text{-}1.56$ . The dashed line represents  $M_n$ (calcd) for one PLA chain per metal centre.

MALDI-ToF mass spectrum of low molecular weight PLA catalysed by **8** (Figure 4.8) shows the presence of three types of PLA including cyclic PLA, PLA terminated with non-opened LA ring (–LA-H) and –OH end groups, and  $\alpha,\omega$ -dihydroxytelechelic PLA. The separation between peak envelopes by  $\Delta(m/z) = 72.0$  Da confirmed an occurrence of transesterification reactions. For example, the peak envelope centred at 1479.7 Da is assigned to cyclic PLA containing 20 units of half LA with  $K^+$ . Another peak envelope centred at 1481.7 Da corresponds to PLA containing 18 units of half LA with –LA-H and –OH chain ends with  $K^+$  [ $72.0(18) + 146.1 + 39.1$ ]. Whereas the  $\alpha,\omega$ -dihydroxytelechelic PLA containing 18 units of half LA with  $K^+$  was observed as the peak envelope centred at 1483.7 Da [ $72.0(18) + 148.1 + 39.1$ ].

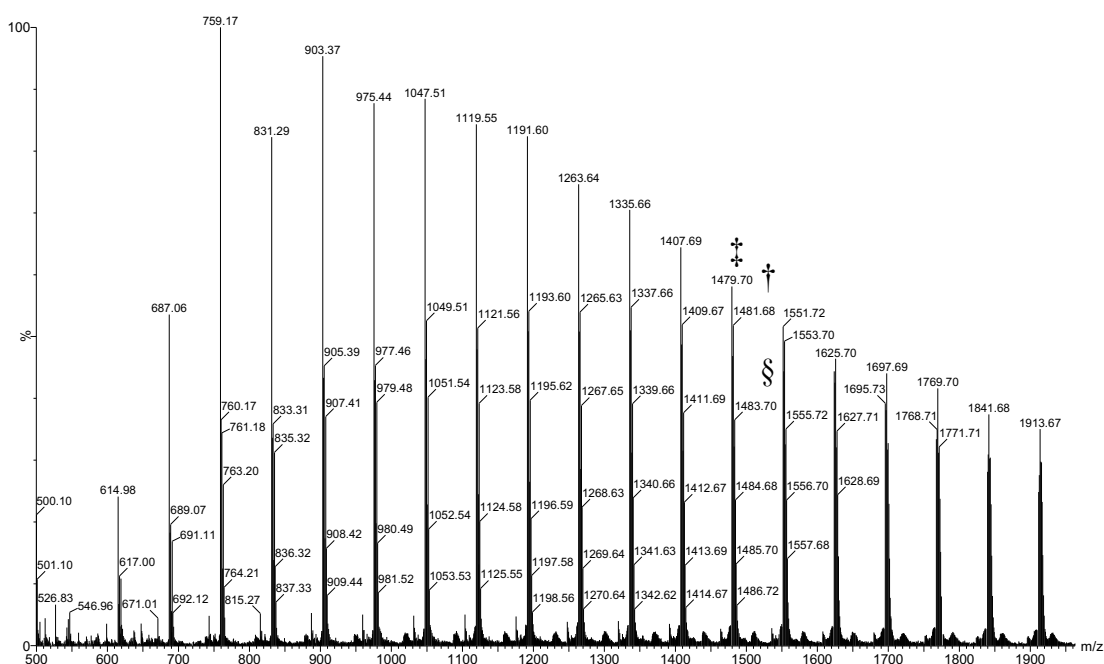


**Figure 4.8** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**).  $M_n(\text{GPC}) = 2,230 \text{ g mol}^{-1}$ ,  $D = 1.70$ . Conditions:  $[\text{rac-LA}]_0 : [\textbf{8}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “‡” denotes cyclic PLA. “†” denotes PLA with  $-\text{LA-H}$  and  $-\text{OH}$  end groups. “§” denotes  $\alpha,\omega$ -dihydroxytelechelic PLA.

#### 4.4 Mechanistic investigations of $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$ (**8**) for the ROP of LA

According to the proposed mechanism for the ROP of LA initiated by magnesium tetrahydroborate initiators (Scheme 4.3), the first hydride transfer species  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  was proposed to act as an initiator for the ROP of LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**). An NMR tube scale reaction of **8** with 5 equiv. of *L*-LA was performed in  $\text{THF-}d_8$  at 195 K. The  $^1\text{H}$  NMR spectrum recorded after 10 min at 223 K (Figure 4.9, a) shows the signals corresponding to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$  (**8.1**) and  $\text{Ca}(\text{L-LA-H})_2(\text{THF})_x$  (**8.2**) (ratio = 6:4 by integration), which are analogous to those observed by using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**) reported in Chapter Two (section 2.4.3). The assignment of **8.1** and **8.2** was confirmed by deuterium labelling experiment using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) and 5 equiv. of *L*-LA in  $\text{THF-}d_8$  at 223 K. The  $^1\text{H}$  NMR spectrum recorded after 10 min (Figure 4.9, b) shows the absence of two doublets at 5.53 and 5.17 ppm indicating replacement of  $\text{H}_a$  of **8.1** and  $\text{H}_d$  of **8.2** with deuterium, respectively.

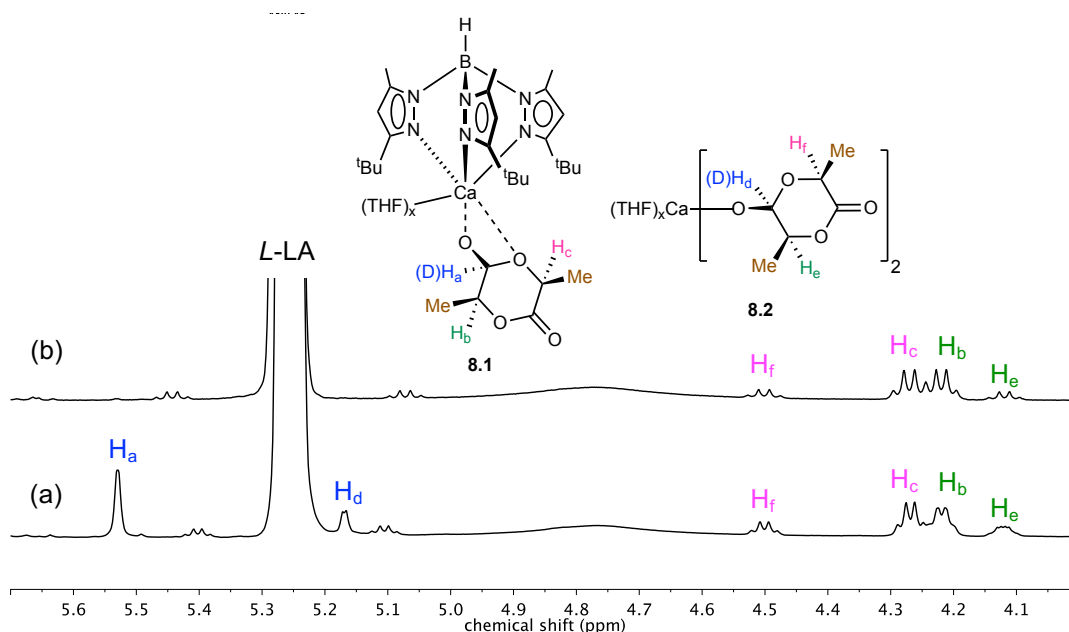


**Figure 4.9**  $^1\text{H}$  NMR spectra ( $\text{THF-}d_8$ , 499.9 MHz, 223 K) of (a) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 5 equiv. of *L*-LA after 10 min and (b) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) with 5 equiv. of *L*-LA after 10 min. “*L*-LA” denotes unreacted *L*-LA.

The  $^2\text{H}$  NMR spectrum in protio-THF recorded at 223 K (Figure 4.10) shows signals at 5.48, 2.41 and 0.26 ppm corresponding to  $\text{CaOCD}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{L-LA-D})(\text{THF})_x$ , free  $\text{BD}_3(\text{THF})$ , and coordinated  $\text{BD}_4$  of **8-d<sub>4</sub>**, respectively.

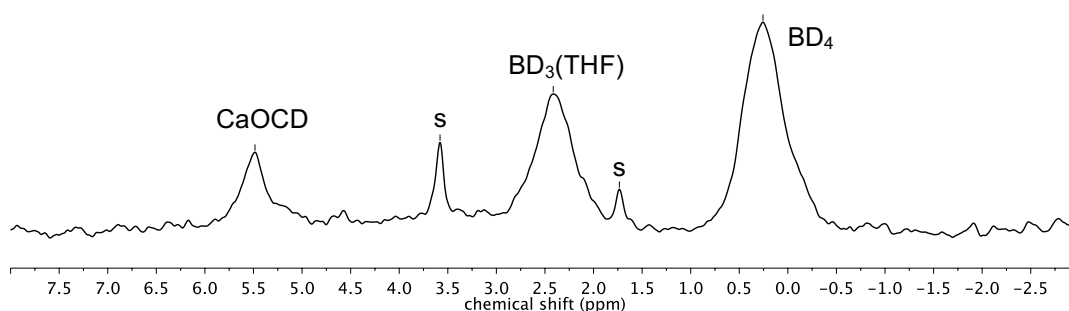


**Figure 4.10**  $^2\text{H}$  NMR spectrum (THF, 76.7 MHz, 223 K) of the reaction between  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) with 5 equiv. of *L*-LA after 10 min. “s” denotes residual  $\text{THF-}d_8$ .

The  $^{11}\text{B}$  NMR spectrum of **8** with 5 equiv. of *L*-LA monitored at 223 K after 10 min (Figure 4.11) shows signals at -1.3, -8.1 and -33.2 ppm corresponding to  $\text{BH}_3(\text{THF})$ , the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  ligand and coordinated  $\text{BH}_4$  of **8**, respectively.

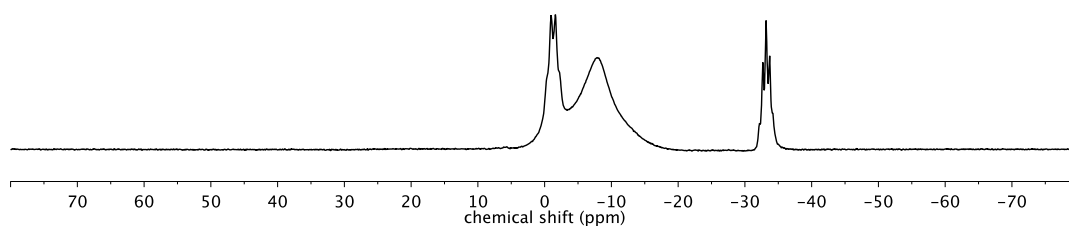


**Figure 4.11**  $^{11}\text{B}$  NMR spectrum ( $\text{THF-}d_8$ , 160.4 MHz, 223 K) of the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 5 equiv. of *L*-LA recorded after 10 min.

According to the proposed ROP mechanism using the tetrahydroborate initiator shown in Scheme 4.3,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{OCHMeOCOCHMeCH}_2\text{O}(\text{BH}_2)\}$  (**8.3**) was expected as a result of second hydride transfer step. In order to probe the existence of **8.3**, the  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra of the reaction between **8** and 5 equiv. of *L*-LA were monitored at 223 K after 4 h. Signals assigned to  $(\text{Tp}^{\text{tBu,Me}})_2\text{Ca}$  (**4**) and **8.2** were visible in the  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra. However, the anticipated signal at 56.5 ppm corresponding to the  $-\text{OBH}_2$  of **8.3** was not observed in the  $^{11}\text{B}$  NMR spectrum. The  $^{11}\text{B}$  NMR resonance of  $-\text{OBH}_2$  was evaluated at 56.5 ppm by DFT calculations and will be described in more detail in Chapter Five.

MALDI-ToF mass spectrum of PLA catalysed by **8-*d*<sub>4</sub>** (Figure 4.12) shows cyclic PLA and PLA terminated with expected end groups including  $-\text{LA-D}$  and  $-\text{CHMeCD}_2\text{OH}$ . For example, the peak envelope centred at 1335.4 Da corresponds to cyclic PLA containing 18 units of half LA with  $\text{K}^+$ . Another peak envelope centred at 1338.5 Da is assigned to  $-\text{LA-D}$  and  $-\text{OH}$  terminated PLA containing 16 units of half LA with  $\text{K}^+$   $[72.0(16) + 147.1 + 39.1]$ . Whereas the other peak envelope centred at 1341.5 Da is assigned to PLA with  $-\text{CHMeCD}_2\text{OH}$  and  $-\text{OH}$  end groups with  $\text{K}^+$   $[72.0(16) + 150.1 + 39.1]$ .

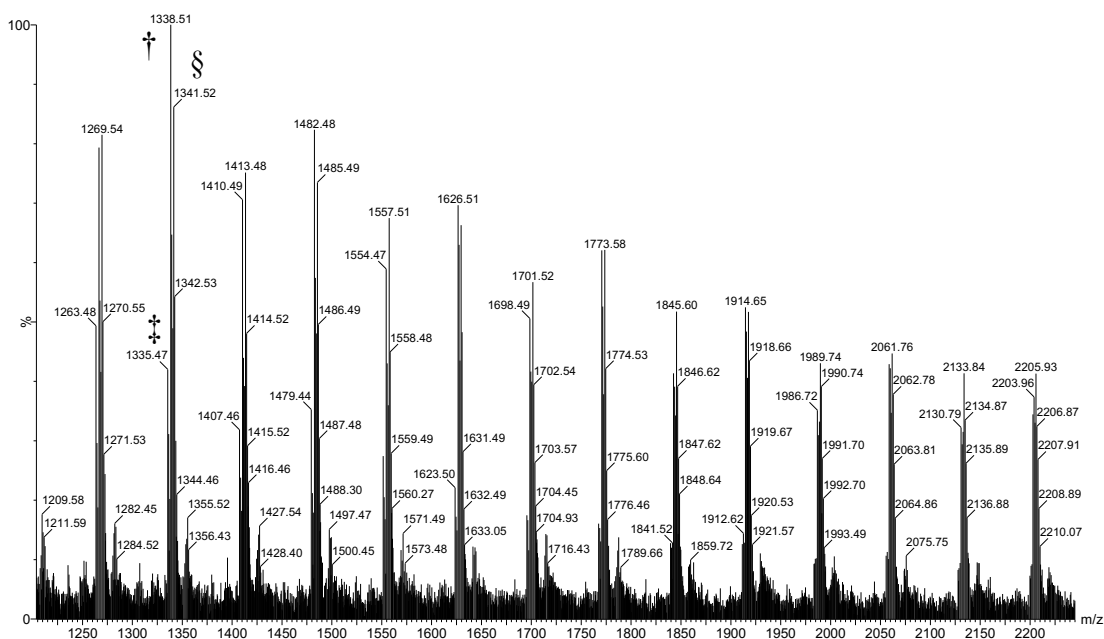


**Figure 4.12** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**).  $M_n(\text{GPC}) = 2,840 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.74$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{8-d}_4]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “‡” denotes cyclic PLA. “†” denotes PLA with  $-\text{LA-D}$  and  $-\text{OH}$  end groups. “§” denotes PLA with  $-\text{CHMeCD}_2\text{OH}$  and  $-\text{OH}$  end groups.

The non-opened LA ring ( $-\text{LA-H}$ ) and  $-\text{OH}$  chain ends were observed from  $^1\text{H}$  NMR spectrum of PLA formed by **8** (Figure 4.13, a). The methine proton (OCH) of non-opened LA ring end group appeared as two doublets at 5.46 and 5.36 ppm. The assignment of the non-opened LA ring ( $-\text{LA-H}$ ) end group was supported by the absence of the two doublets in the  $^1\text{H}$  NMR spectrum of PLA prepared by **8-d<sub>4</sub>** (Figure 4.13, b). In addition, the  $^2\text{H}$  NMR spectrum (Figure 4.14) shows a broad signal between 5.0-6.0 ppm corresponding with OCD of the  $-\text{LA-D}$  terminus. The other broad signal in the region of 3.5-4.5 ppm in the  $^2\text{H}$  NMR spectrum (Figure 4.14) is assigned to  $\text{CHMeCD}_2\text{OH}$ . The presence of  $-\text{LA-H}$  and  $-\text{CHMeCH}_2\text{OH}$  end groups have been reported in the ROP of *rac*-LA studies using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**),<sup>29</sup>  $(\text{Tpm}^*\text{d})\text{Mg}(\text{BH}_4)$  (**4.30**)<sup>23</sup> and  $\text{Mg}(\text{CzOx}^{\text{Me}_2})(\text{BH}_4)$  (**4.31**).<sup>30</sup>

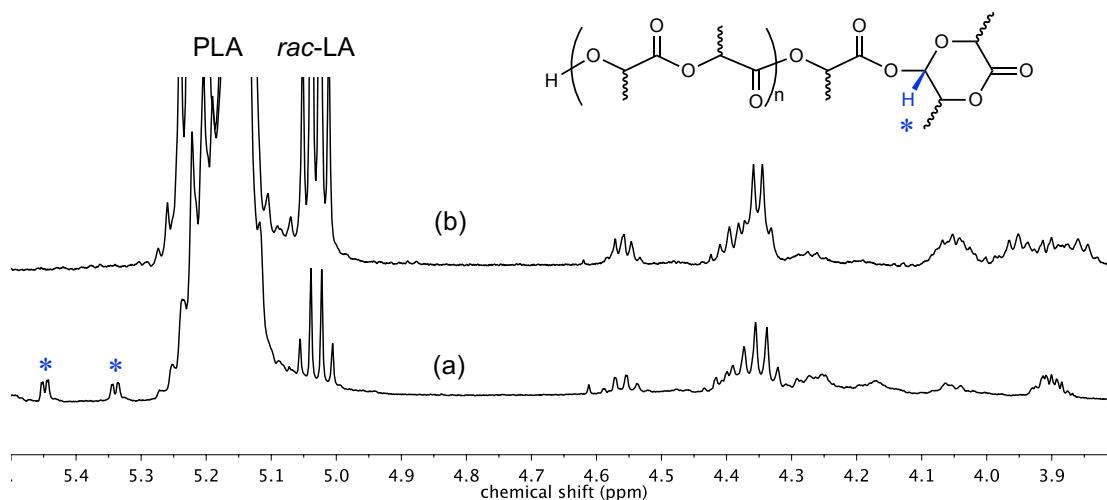


**Figure 4.13**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of crude PLA obtained from the polymerisation of (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) or (b)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) with 20 equiv. of *rac*-LA. “\*” denotes OCH of non-opened LA ring end group ( $-\text{LA}-\text{H}$ ).

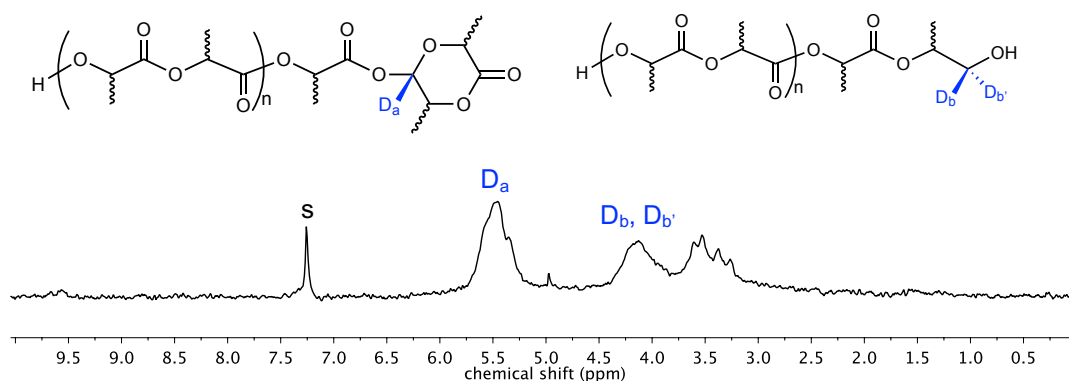


**Figure 4.14**  $^2\text{H}$  NMR spectrum ( $\text{CHCl}_3$ , 76.7 MHz, 298 K) of crude PLA obtained from the polymerisation of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) and 20 equiv. of *rac*-LA. “s” denotes residual  $\text{CDCl}_3$ .

Based on the NMR spectroscopic data and polymerisation studies, the proposed mechanism for the ROP of LA using **8** is analogous to that using magnesium tetrahydroborate complexes as shown in Scheme 4.3. The first hydride transfer product (**8.1**) acts as initiator, giving PLA terminated by  $-\text{LA}-\text{H}$  and  $-\text{OH}$  groups. The formation of  $\alpha,\omega$ -dihydroxytelechelic PLA observed from NMR and MALDI-ToF MS is a result of the second hydride transfer step. The borate ester containing non-opened LA ring,  $\text{B}(\text{LA}-\text{H})_3$ , does not exchange with polymeric chain on metal centre through immortal polymerisation as  $M_n(\text{GPC})$  values are not in close agreement with those

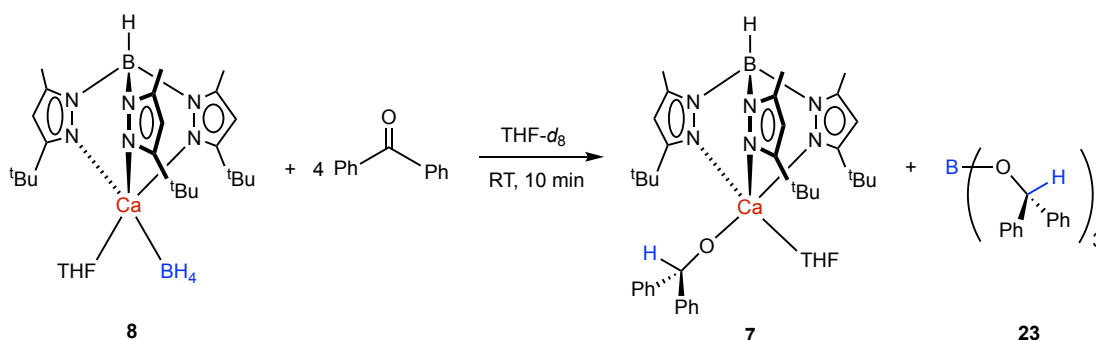
calculated for four chains per metal centre. Transesterification reactions occur extensively at the later stages of polymerisation resulting in shorter polymer chains and cyclic PLA.

#### 4.5 ROP of *rac*-LA using *in situ* generated $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OR})(\text{THF})_x$ and borate esters $\text{B}(\text{OR})_3$

$(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) was reacted with 4 equiv. of benzophenone, 2-methylcyclohexanone or benzaldehyde in order to generate corresponding alkoxide complexes (**7**, **10** and **11**) with their borate ester congeners,  $\text{B}(\text{OR})_3$ . The role of borate esters as chain transfer agents in the ROP of *rac*-LA was investigated. The chain transfer between the polymeric chain on the metal centre and  $\text{B}(\text{OR})_3$  is proposed to proceed *via* Ca-O/B-O metathesis.

##### 4.5.1 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$ (**8**) with benzophenone

An NMR tube scale reaction of **8** and 4 equiv. of benzophenone was carried out in  $\text{THF-}d_8$  at RT to give  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and  $\text{B}(\text{OCHPh}_2)_3$  (**23**) (Equation 4.3). The  $^{11}\text{B}$  NMR spectrum monitored after 10 min showed signals at 18.5 and -8.2 ppm corresponding to **23** and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  ligand of **7**, respectively.



**Equation 4.3**

Complex **8** was reacted with 4 equiv. of benzophenone in THF at RT to produce **7** and **23** after 10 min, followed by an addition of 800 equiv. of *rac*-LA. The ROP was very active, reaching 94% conversion after 3 min (Table 4.2, entry 1). Second order dependence on  $[\textit{rac}\text{-LA}]$  ( $k_{\text{app}} = 0.197(6) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.996$ ) was measured (Figure 4.15, left). Good agreement between experimental and calculated  $M_n$  values based on one growing chain per metal centre was observed, attributed to the size of **23** which was too large to exchange with the polymeric chain growing on the metal centre (Figure 4.15, right). Heterotactically-enriched PLA with  $P_r = 0.82$  was produced. The ROP of



*rac*-LA using only **7** (Table 4.2, entry 2) gave comparable results indicating the negligible effect of **23** on the rate,  $M_n$  and polymer tacticity. MALDI-ToF mass spectrum (Figure 4.16) shows the presence of cyclic PLA and PLA with  $-\text{OCHPh}_2$  and  $-\text{OH}$  end groups.

**Table 4.2** Selected data for the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with additive.<sup>a</sup>

| Entry | Initiator | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | $P_r^f$ |
|-------|-----------|----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|-------------|---------|
| 1     | <b>8</b>  | 4 PhCOPh | 94                        | 180         | 70,780                                                | 108,547                                                 | 1.37        | 0.84    |
| 2     | <b>7</b>  | -        | 94                        | 180         | 75,580                                                | 108,547                                                 | 1.57        | 0.82    |

<sup>a</sup> Conditions:  $[\text{rac-LA}]_0:[\text{initiator}]_0:[\text{additive}]_0 = 800:1$  as stated,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $[\text{initiator}]_0 = 625 \mu\text{M}$ , 6.0 mL THF at RT. <sup>b</sup> Measured by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4 \mu\text{L g}^{-1}$  and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for  $-\text{OH}$  and  $-\text{OCHPh}_2$  end groups,  $M_n(\text{entry } 1, 2) = \text{conv. } (\%) \times 800 \times 144.1 + 184.1$ . <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by  $^1\text{H}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) analyses.

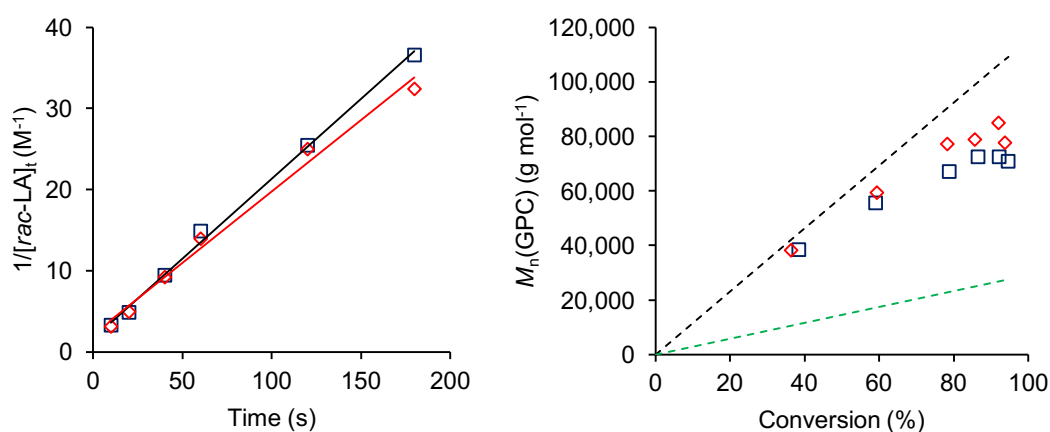


**Figure 4.15** Left, plots of  $1/[\text{rac-LA}]_t$  vs. time. Squares:  $[\text{rac-LA}]_0:[\textbf{8}]_0:[\text{PhCOPh}]_0 = 800:1:4$  ( $k_{\text{app}} = 0.197(6) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.996$ ). Diamonds:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 800:1$  ( $k_{\text{app}} = 0.176(9) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.989$ ). Right, plots of  $M_n(\text{GPC})$  vs. conversion (%). Squares:  $[\text{rac-LA}]_0:[\textbf{8}]_0:[\text{PhCOPh}]_0 = 800:1:4$ ,  $\bar{D} = 1.07\text{--}1.37$ . Diamonds:  $[\text{rac-LA}]_0:[\textbf{7}]_0 = 800:1$ ,  $\bar{D} = 1.05\text{--}1.57$ . The black and green dashed lines represent  $M_n(\text{calcd})$  for one and four PLA chains per metal centre, respectively.

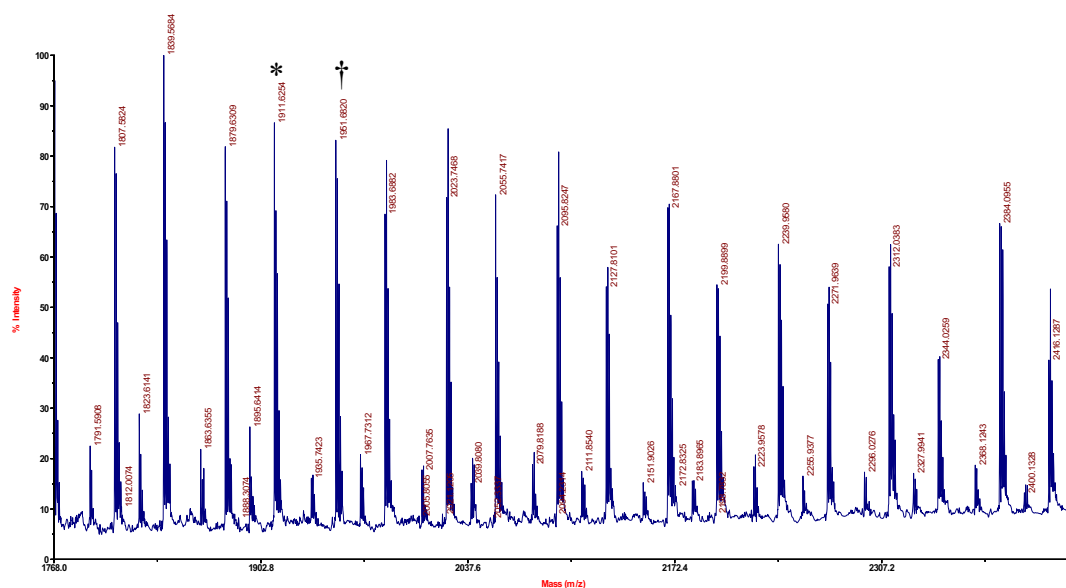


**Table 4.3** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**) or (Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF) (**10**) with additives.<sup>a</sup>

| Entry | initiator | Additive  | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|-----------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>8</b>  | 4 CyMeO   | 90                        | 180         | 60,680                                                | 103,866                                                 | 1.60                   | 0.83               |
| 2     | <b>10</b> | <b>24</b> | 91                        | 180         | 67,170                                                | 105,019                                                 | 1.58                   | 0.83               |
| 3     | <b>10</b> | -         | 91                        | 180         | 97,950                                                | 105,019                                                 | 1.55                   | 0.84               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>: [initiator]<sub>0</sub>: [additive]<sub>0</sub> = 800:1: as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for -OH and -OCyMe end groups,  $M_n$  (entry 1-3) = conv. (%) × 800 × 144.1 + 114.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

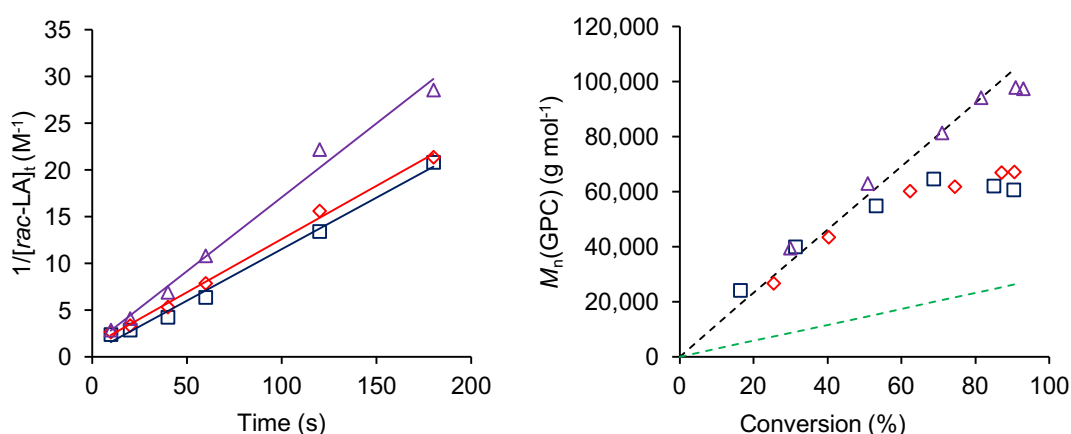


**Figure 4.17** Left, plots of  $1/[rac\text{-}LA]_t$  vs. time. Squares: [*rac*-LA]<sub>0</sub>: [**8**]<sub>0</sub>: [CyMeO]<sub>0</sub> = 800:1:4 ( $k_{app} = 0.110(5) \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.993$ ). Diamonds: [*rac*-LA]<sub>0</sub>: [**10**]<sub>0</sub>: [**24**]<sub>0</sub> = 800:1:1 ( $k_{app} = 0.114(3) \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.996$ ). Triangles: [*rac*-LA]<sub>0</sub>: [**10**]<sub>0</sub> = 800:1 ( $k_{app} = 0.157(7) \text{ M}^{-1} \text{ s}^{-1}$ ,  $R^2 = 0.990$ ). Right, plots of  $M_n(\text{GPC})$  vs. conversion (%). Squares: [*rac*-LA]<sub>0</sub>: [**8**]<sub>0</sub>: [CyMeO]<sub>0</sub> = 800:1:4,  $\bar{D} = 1.05\text{-}1.60$ . Diamonds: [*rac*-LA]<sub>0</sub>: [**10**]<sub>0</sub>: [**24**]<sub>0</sub> = 800:1:1,  $\bar{D} = 1.05\text{-}1.58$ . Triangles: [*rac*-LA]<sub>0</sub>: [**10**]<sub>0</sub> = 800:1,  $\bar{D} = 1.05\text{-}1.55$ . The black and green dashed lines represent  $M_n(\text{calcd})$  for one and four PLA chains per metal centre, respectively.

The ROP of 800 equiv. of *rac*-LA using *in situ* generated **10** and **24** was very active, reaching 92% monomer conversion after 3 min (Table 4.3, entry 1). Second order dependence on [*rac*-LA] was determined with  $k_{app} = 0.110(5) \text{ M}^{-1} \text{ s}^{-1}$  ( $R^2 = 0.993$ ) (Figure 4.17, left). Good agreement between observed and calculated  $M_n$  values for one growing chain per metal centre was observed, followed by a deviation from the

calculated trend at high conversion (> 60%) due to intramolecular transesterification reaction (Figure 4.17, right). MALDI-ToF mass spectrometry spectrum (Figure 4.18) shows the presence of cyclic PLA and  $\Delta(m/z) = 72.0$  Da between each peak envelope. A minor distribution of PLA end capped with  $-\text{OCyMe}$  and  $-\text{OH}$  end groups was also presented.

The ROP initiated by **10** and externally added **24** (Table 4.3, entry 2) was carried out. The ROP results were similar to those obtained from the ROP with *in situ* generated **10** and **24** under analogous conditions. The resultant PLAs were determined to be heterotactically-enriched ( $P_r = 0.83\text{--}0.84$ ). The comparative results of the ROP with and without **24** (Table 4.3) showed the negligible effect of **24** on polymerisation conversion,  $M_n$  and tacticity, indicated that **24** is a poor chain transfer agent. It is worth noting that the  $^{11}\text{B}$  NMR spectrum of the reaction of *in situ* generated **10** and **24** with 15 equiv. of *rac*-LA in  $\text{THF-}d_8$  recorded after 10 min showed signals at 17.8 and  $-6.1$  ppm corresponding to **24** and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively.

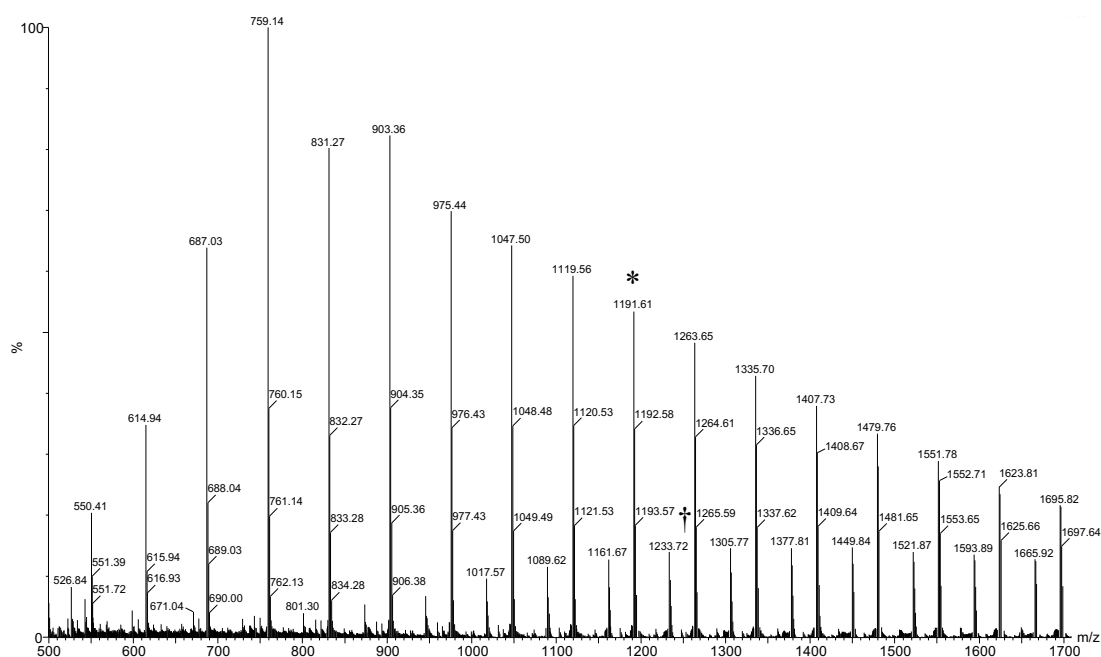
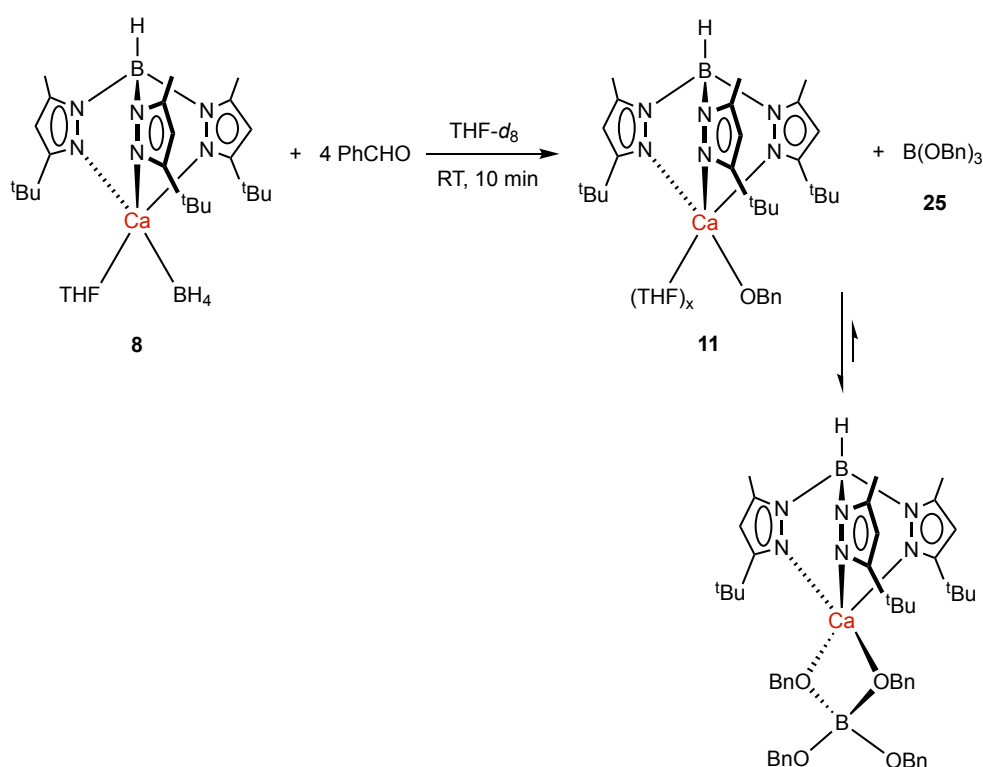


**Figure 4.18** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 4 equiv. of 2-methylcyclohexanone.  $M_n(\text{GPC}) = 2,160 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.78$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{8}]_0:[\text{CyMeO}]_0 = 20:1:4$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0$  Da between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-\text{OCyMe}$  and  $-\text{OH}$  end groups.

### 4.5.3 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$ (**8**) with benzaldehyde

Given the inefficient chain transfer ability of  $\text{B}(\text{OCHPh}_2)_3$  (**23**) and  $\text{B}(\text{OCyMe})_3$  (**24**) in the ROP of *rac*-LA, the use of  $\text{B}(\text{OBn})_3$  (**25**) was investigated whether it could lead to efficient immortal ROP of *rac*-LA. An NMR tube scale reaction of complex **8** with 4 equiv. of benzaldehyde was performed in  $\text{THF-}d_8$  leading to the formation of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and **25** existed in equilibrium with  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$  due to the smaller size of the  $-\text{OBn}$  moiety (Scheme 4.4). The  $^1\text{H}$  NMR spectrum recorded after 10 min showed two singlets corresponding to  $\text{OCH}_2\text{Ph}$  of **25** ( $\delta = 4.97$  ppm), with **11** and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$  ( $\delta = 4.75$  ppm). The quantitative  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at 18.1 and 3.9 ppm corresponding to  $\text{B}(\text{OBn})_3$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$  (ratio = 3:7 by integration), respectively.



**Scheme 4.4** Reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 4 equiv. of benzaldehyde in  $\text{THF-}d_8$ .

Complex **11**, generated *in situ* from **1** and 1 equiv. of benzaldehyde, polymerised 800 equiv. of *rac*-LA in THF at RT to reach 91% conversion in 3 min and showed second order dependence on  $[\textit{rac}\text{-LA}]$  (Table 4.4 entry 3). The presence of **25** resulted in a significant effect on polymerisation rate compared to the ROP without **25** under

analogous conditions. In the presence of 800 equiv. of *rac*-LA, 47% conversion was reached after 20 min, then 64% after 5 h, giving PLA with a moderate *D* value (1.37) (Table 4.4, entry 1). Kinetic analysis showed that the polymerisation did not follow either first or second order dependence on [*rac*-LA].

**Table 4.4** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**) or (Tp<sup>tBu,Me</sup>)Ca(OBn)(THF)<sub>x</sub> (**11**) with additives.<sup>a</sup>

| Entry | Initiator | Additive  | Conv. <sup>b</sup><br>(%) | Time<br>(min) | <i>M</i> <sub>n</sub><br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub><br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>P</i> <sub>r</sub> <sup>f</sup> |
|-------|-----------|-----------|---------------------------|---------------|-----------------------------------------------------------------------|-------------------------------------------------------------------------|-----------------------|------------------------------------|
| 1     | <b>8</b>  | 4 PhCHO   | 64                        | 300           | 23,350                                                                | 18,553                                                                  | 1.37                  | 0.74                               |
| 2     | <b>11</b> | <b>25</b> | 68                        | 300           | 23,470                                                                | 19,706                                                                  | 1.40                  | 0.74                               |
| 3     | <b>11</b> | -         | 91                        | 3             | 83,090                                                                | 105,012                                                                 | 1.39                  | 0.82                               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>: [initiator]<sub>0</sub>: [additive]<sub>0</sub> = 800:1:as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated *M*<sub>n</sub> (g mol<sup>-1</sup>) for –OH and –OBn end groups, *M*<sub>n</sub> (entry 1, 2) = (conv. (%) × 800 × 144.1)/4 + 108.1, *M*<sub>n</sub> (entry 3) = conv. (%) × 800 × 144.1 + 108.1. <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> Measured by <sup>1</sup>H {<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

Plot of *M*<sub>n</sub>(GPC) vs. conversion (%) (Figure 4.19, squares) shows close agreement between measured and calculated *M*<sub>n</sub> values based on two growing polymer chains per metal centre from 20% (20 s) to 47% conversion (20 min) due to an exchange between **25** with the polymeryl chain on Ca *via* tetra-alkoxy borate (Scheme 4.5). As expected, the ROP of *rac*-LA using **11** and externally added **25** gave similar results, reaching 68% conversion after 6 h. Measured *M*<sub>n</sub> values were in close agreement with those calculated for two chains per metal centre (Figure 4.19, diamonds). In contrast, *M*<sub>n</sub>(GPC) values of PLA formed by only **11** were close to those calculated for one chain per metal centre followed by a deviation at high monomer conversion due to transesterification reactions. It is worth noting that the *M*<sub>n</sub>(GPC) data was different from the ROP with (Tp<sup>tBu,Me</sup>)Mg(BH<sub>4</sub>) (**20**) and 4 equiv. of benzaldehyde (section 4.2.3).<sup>29</sup> Good agreement between measured *M*<sub>n</sub> and those calculated for four chains per metal centre was observed indicating a chain transfer ability of **25** and greater chain transfer than propagation rate in the ROP with magnesium initiator.

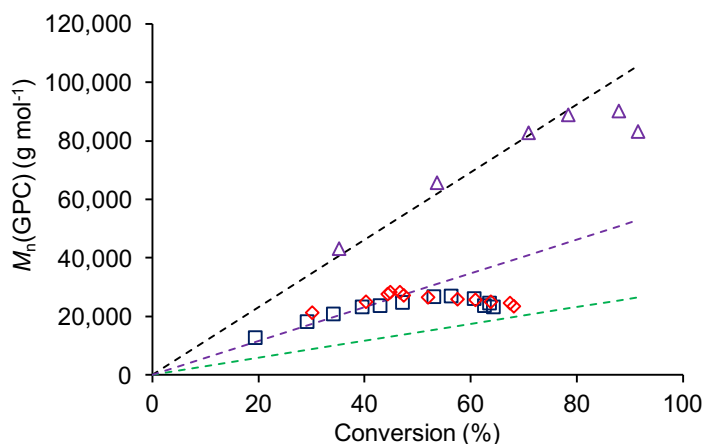
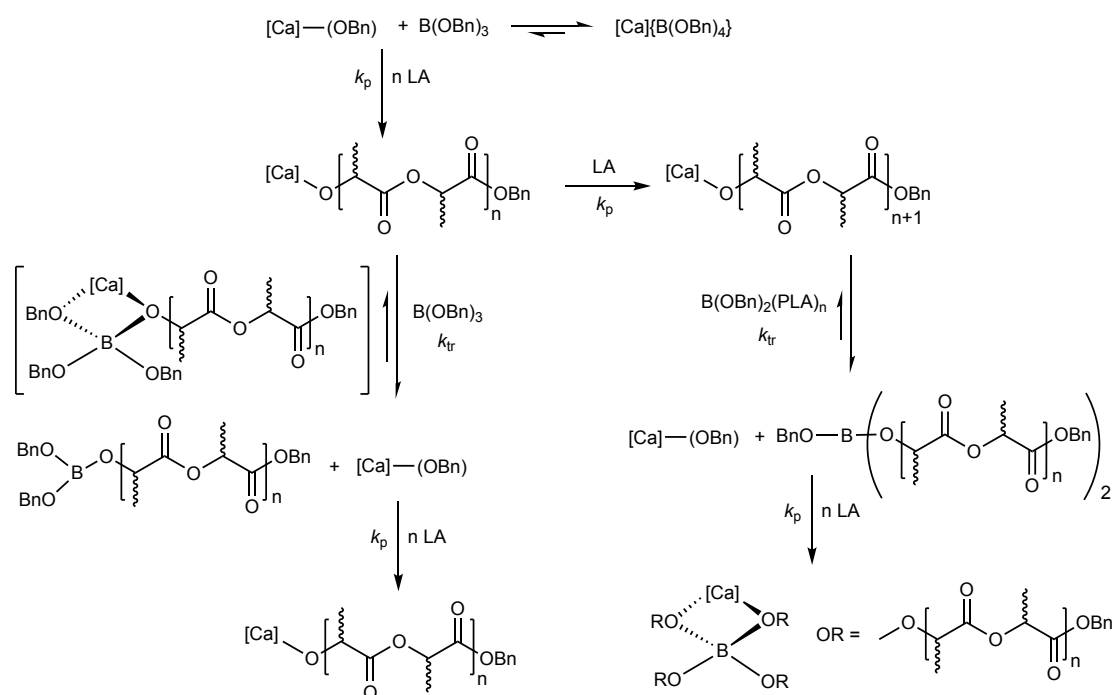


**Figure 4.19** Plots of  $M_n(\text{GPC})$  vs. conversion (%). Conditions: 6 mL THF, RT,  $[\text{rac-LA}]_0 = 0.5$  M. The black, purple and green dashed lines represent  $M_n(\text{calcd})$  for one, two and four PLA chains per metal centre, respectively. Squares:  $[\text{rac-LA}]_0:[\mathbf{8}]_0:[\text{PhCHO}]_0 = 800:1:4$ ,  $D = 1.17\text{--}1.37$ . Diamonds:  $[\text{rac-LA}]_0:[\mathbf{11}]_0:[\mathbf{25}]_0 = 800:1:1$ ,  $D = 1.12\text{--}1.38$ . Triangles:  $[\text{rac-LA}]_0:[\mathbf{11}]_0 = 800:1$ ,  $D = 1.03\text{--}1.41$ .



**Scheme 4.5** The proposed mechanism of the ROP of LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 4 equiv. of benzaldehyde.  $[\text{Ca}] = (\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{THF})_x$ .

It was hypothesised that  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$  was involved in the resting state of the catalyst since a crowded coordination sphere could inhibit *rac*-LA to coordinate to Ca during the initiation step. This resulted in a decrease in concentration of **11** available as active catalyst which led to a decline in polymerisation rate. Despite the inactivity of

some metal centres in the polymerisation, the  $M_n$ (GPC) was observed to be in a close agreement with those calculated for two chains per metal centre due to chain transfer reaction with  $B(OR)_3$  where  $OR = OBn$  or polymeryl chain (Figure 4.19).

Examples of the resting states of the catalyst in the ROP of cyclic esters were reported. Chisholm *et al.* studied the ROP of *rac*-LA using Mg or Zn alkoxide complexes supported by the <sup>Dipp</sup>NacNac ligand. The chelation of polymer chain to Zn *via* four membered ring and the dimeric Mg species where two Mg coordinated to two growing polymer chains were proposed as the resting state of the catalysts during polymerisation.<sup>33</sup> Another example was the use of (<sup>Dipp</sup>NacNac)Mg(OCMe<sub>2</sub>COOEt)(L) (L = py or DMAP) as catalysts for the copolymerisation of *rac*-LA and  $\epsilon$ -CL.<sup>34</sup> Studies of the copolymerisation showed that only *rac*-LA was polymerised, attributed to the chelation of the growing PLA chain to Mg *via* five membered ring as the resting state of the catalyst inhibiting the initiation of  $\epsilon$ -CL.

The slow polymerisation rate from 53% (40 min) until 64% conversion (5 h) could be attributed to the predominance of  $(Tp^{tBu,Me})Ca\{B(OBn)_x(PLA)_{4-x}\}$  ( $x = 0-3$ ) considered as the resting state of the catalyst at the later stages of polymerisation. This hypothesis was supported by an NMR tube scale reaction of *in situ* generated **11** and **25** with 15 equiv. of *rac*-LA in THF-*d*<sub>8</sub> at RT. The <sup>11</sup>B NMR spectrum recorded after 10 min (Figure 4.20, a) shows signals at 18.7 and 3.5 ppm indicating  $B(OR)_3$  and  $B(OR)_4$  ( $OR = OBn$  or polymeryl). However, the <sup>11</sup>B NMR spectrum recorded after 1 h (Figure 4.20, b) shows a signal at 2.8 ppm suggesting a major distribution of  $(Tp^{tBu,Me})Ca\{B(OBn)_x(PLA)_{4-x}\}$  ( $x = 0-3$ ). Moderately heterotactic PLAs with  $P_r = 0.74$  were obtained. The hetero-selectivity was lower than those obtained by using only **11** ( $P_r = 0.82$ ) (Table 4.4) which could attribute to chain transfer or transesterification reactions.



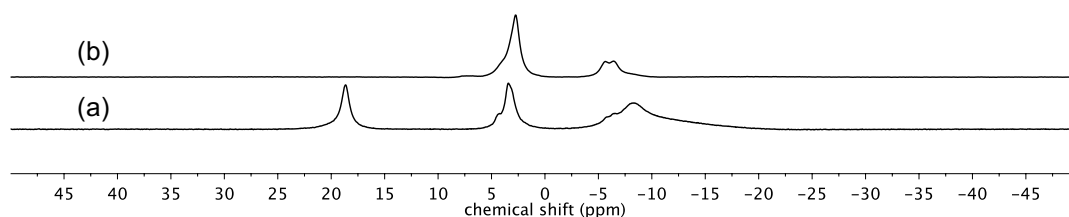


**Figure 4.20**  $^{11}\text{B}$  NMR spectra (THF- $d_8$ , 160.4 MHz, 298 K) of *in situ* generated  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $\text{B}(\text{OBn})_3$  (**25**) with 15 equiv. of *rac*-LA recorded after 10 min (a) and 1 h (b).

MALDI-ToF mass spectrum (Figure 4.21) shows a major distribution of peak envelopes corresponding to PLA with  $-\text{OBn}$  and  $-\text{OH}$  end groups. Cyclic PLA and a separation between peak envelopes of  $\Delta(m/z) = 72.0$  Da were observed due to transesterification reactions.

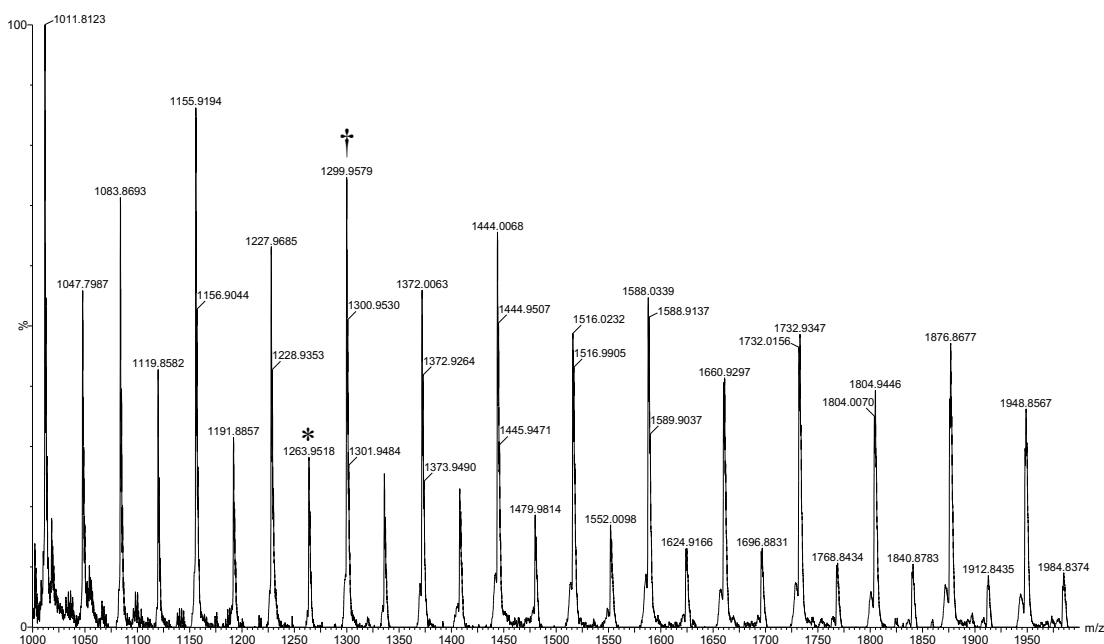


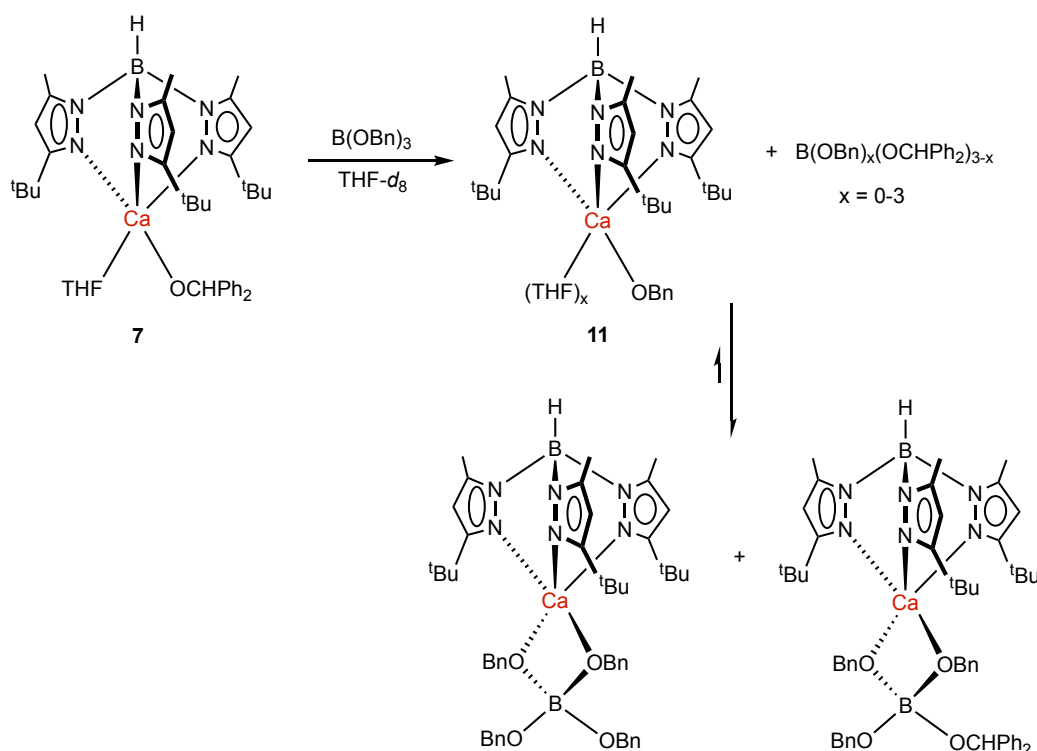
**Figure 4.21** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 4 equiv. of benzaldehyde.  $M_n(\text{GPC}) = 1,670 \text{ g mol}^{-1}$ ,  $\bar{D} = 1.77$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{8}]_0:[\text{PhCHO}]_0 = 20:1:4$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ , 1.0 mL THF at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0$  Da between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-\text{OBn}$  and  $-\text{OH}$  end groups.

The poor chain transfer ability of **23** and **24** in the ROP of *rac*-LA was attributed to the size of  $-\text{OCHPh}_2$  or  $-\text{OCyMe}$  substituents inhibiting the intermolecular exchange with polymeric chain on the metal centre unlike the smaller alkoxy group, **25**. The chain

transfer reaction by **25** resulted in a decrease in ROP rate, poor-controlled  $M_n$  and reduced stereoselectivity.

#### 4.5.4 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$ (**7**) with $\text{B}(\text{OBn})_3$ (**25**)

The role of  $\text{B}(\text{OBn})_3$  (**25**) as a chain transfer agent was further studied by the ROP initiated by  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**). An NMR tube scale reaction of **7** and  $\text{B}(\text{OBn})_3$  was carried out in  $\text{THF}-d_8$  at RT. The  $^1\text{H}$  NMR spectrum recorded after 10 min showed the absence of **7**. Multiple signals in the region of 4.90-5.10 ppm were assigned to methylene protons of  $\text{OCH}_2\text{Ph}$ , indicating the presence of  $\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 1-3$ ). The NMR data suggest that the reaction of **7** and  $\text{B}(\text{OBn})_3$  led to the formation of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) in equilibrium with  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 3-4$ ) and  $\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 0-3$ ) as shown in Scheme 4.6. The quantitative  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at 16.8 and 2.7 ppm corresponding to  $\text{B}(\text{OR})_3$  and coordinated  $\text{B}(\text{OR})_4$  (ratio = 4:6 by integration), respectively.



**Scheme 4.6** The proposed pathway for reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and  $\text{B}(\text{OBn})_3$  (**25**) in  $\text{THF}-d_8$ .

The existence of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 3-4$ ) was confirmed by reacting **7** and **25** in toluene- $d_8$ . The  $^{11}\text{B}$  NMR spectrum recorded after 10 min at RT

showed signals at 4.20 and -7.9 ppm corresponding to  $B(OR)_4$  and the apical B-H of  $Tp^{tBu,Me}$  ligand. The  $^1H$  NMR spectra were recorded at various temperatures (298, 273, 253 and 233 K) as shown in Figure 4.22. Two signals at 4.90 and 4.72 ppm are assigned to methylene protons of  $(Tp^{tBu,Me})Ca\{B(OCH_2Ph)_4\}$  and  $(Tp^{tBu,Me})Ca\{B(OCH_2Ph)_3(OCHPh_2)\}$ , respectively. Whereas the signal at 6.46 ppm corresponds to the methine proton of  $(Tp^{tBu,Me})Ca\{B(OBn)_3(OCHPh_2)\}$  which became pronounced as the temperature was decreased.

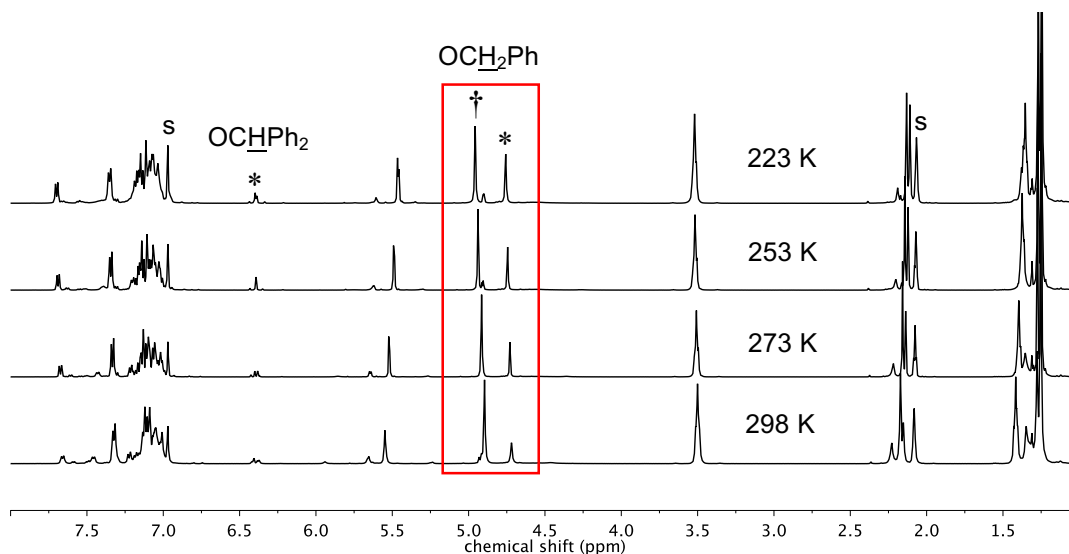


**Figure 4.22** VT  $^1H$  NMR spectra (toluene- $d_8$ , 499.9 MHz) of reaction of  $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$  (**7**) with  $B(OBn)_3$  (**25**) from 223-298 K. “†” denotes  $(Tp^{tBu,Me})Ca\{B(OBn)_4\}$ . “\*” denotes  $(Tp^{tBu,Me})Ca\{B(OBn)_3(OCHPh_2)\}$ . “s” denotes residual protio-solvent.

The ROESY NMR spectrum recorded at 223 K (Figure 4.23) shows a through-space correlation between the signals at 4.72 ppm and 6.46 ppm supporting close proximity between  $-OBn$  and  $-OCHPh_2$  moieties of  $(Tp^{tBu,Me})Ca\{B(OBn)_3(OCHPh_2)\}$ . While the signal at 4.90 ppm corresponding to methylene protons of  $(Tp^{tBu,Me})Ca\{B(OBn)_4\}$  does not interact through space with the signal at 6.46 ppm of  $OCHPh_2$ . Through-space correlations between the *tert*-butyl of  $Tp^{tBu,Me}$  ( $\delta = 1.25$  and  $1.27$  ppm) with methylene protons of the  $-OBn$  moiety of  $(Tp^{tBu,Me})Ca\{B(OBn)_4\}$  and  $(Tp^{tBu,Me})Ca\{B(OBn)_3(OCHPh_2)\}$  ( $\delta = 4.90$  and  $4.72$  ppm) were observed. In contrast, no through-space correlation between the *tert*-butyl of  $Tp^{tBu,Me}$  ( $\delta = 1.25$  and  $1.27$  ppm) and methine proton of the  $-OCHPh_2$  moiety of  $(Tp^{tBu,Me})Ca\{B(OBn)_3(OCHPh_2)\}$  ( $\delta =$

6.46 ppm) was observed, indicated the absence of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  containing bridging  $-\text{OCHPh}_2$  groups between Ca and B. It is worth noting that the ROESY NMR spectrum of **7** in toluene- $d_8$  at RT showed a correlation between the  $-\text{OCHPh}_2$  (6.39 ppm) and the *tert*-butyl of  $\text{Tp}^{\text{tBu,Me}}$  (1.36 ppm).

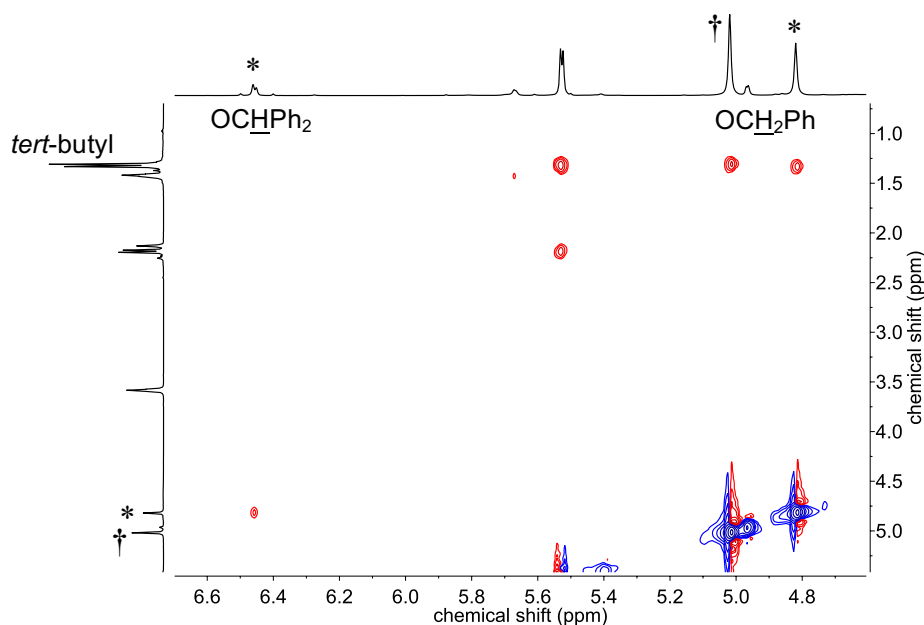


**Figure 4.23** ROESY NMR spectrum (toluene- $d_8$ , 499.9 MHz, 233 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with  $\text{B}(\text{OBn})_3$  (**25**). “†” denotes  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ . “\*” denotes  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ .

As shown in Table 4.5 (entry 2), complex **7** was found to be very active in the ROP of *rac*-LA (90% conversion in 3 min) giving  $M_n$  of PLA consistent with those calculated for one chain per metal centre (Figure 4.25, diamonds). The ROP of *rac*-LA using **7** and **25** was performed under analogous conditions. The addition of **25** affected the polymerisation rate as 90% conversion was reached only after 7 min (Table 4.5, entry 1). Second order dependence on  $[\textit{rac}\text{-LA}]$  was observed with  $k_{\text{app}} = 0.045(1) \text{ M}^{-1}\text{s}^{-1}$  ( $R^2 = 0.996$ ) (Figure 4.24, squares). The slow polymerisation rate could be rationalised by a lower concentration of **11** as active catalyst due to an equilibrium of **11** and the tetraalkoxy borate species  $\text{B}(\text{OR})_4$  postulated as the resting state (Scheme 4.6).

**Table 4.5** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**) with B(ONb)<sub>3</sub> (**25**).<sup>a</sup>

| Entry | Additive  | Conv. <sup>b</sup><br>(%) | Time<br>(min) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|---------------------------|---------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>25</b> | 90                        | 7             | 56,170                                                | 26,046                                                  | 1.44                   | 0.78               |
| 2     | -         | 94                        | 3             | 75,580                                                | 108,547                                                 | 1.57                   | 0.82               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:[initiator]<sub>0</sub>:[additive]<sub>0</sub> = 800:1:as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>),  $M_n$  (entry 1) for –OH and –ONb end groups = (conv. (%) × 800 × 144.1)/4 + 108.1,  $M_n$  (entry 2) for –OH and –OCHPh<sub>2</sub> end groups = conv. (%) × 800 × 144.1 + 184.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

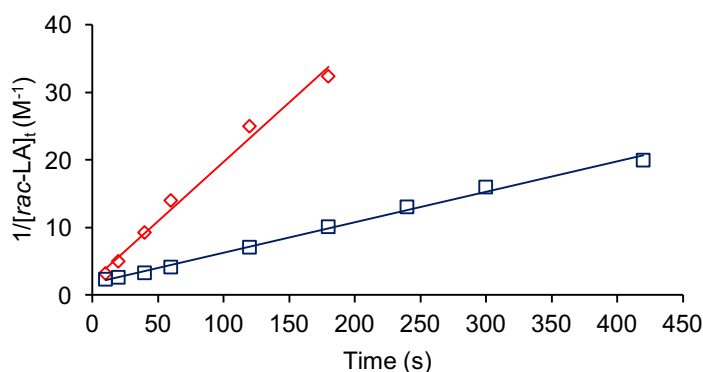


**Figure 4.24** Plots of  $1/[rac\text{-}LA]_t$  vs. time. Conditions: 6 mL THF, RT, [*rac*-LA]<sub>0</sub> = 0.5 M. Squares: [*rac*-LA]<sub>0</sub>:**7**<sub>0</sub>:**25**<sub>0</sub> = 800:1:1 ( $k_{app} = 0.045(1) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.996$ ). Diamonds: [*rac*-LA]<sub>0</sub>:**7**<sub>0</sub> = 800:1 ( $k_{app} = 0.176(9) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.989$ ).

The decreased concentration of **11** also led to the greater  $M_n$ (GPC) values than those calculated for one chain per metal centre at low monomer conversions (<40%) (Figure 4.25, squares). The  $M_n$  values were observed to be significantly lower than those calculated for one chain per metal centre at higher conversions (>40%) due to transesterification reactions and chain transfer reaction by B(OR)<sub>3</sub> (OR = ONb, OCHPh<sub>2</sub> or polymeryl chain) through tetra-alkoxy borate (Scheme 4.7).

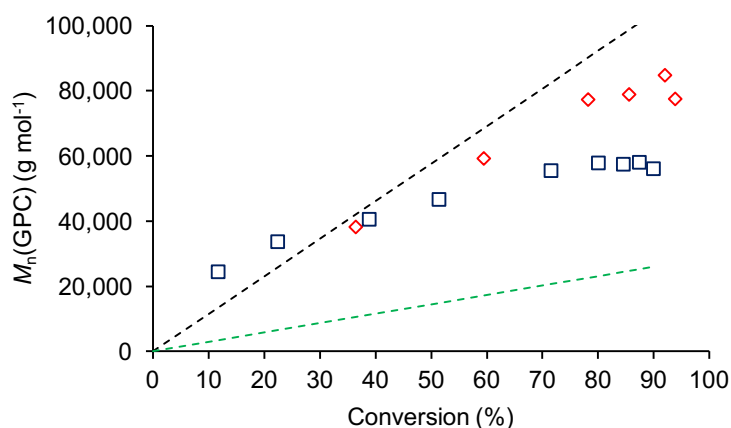
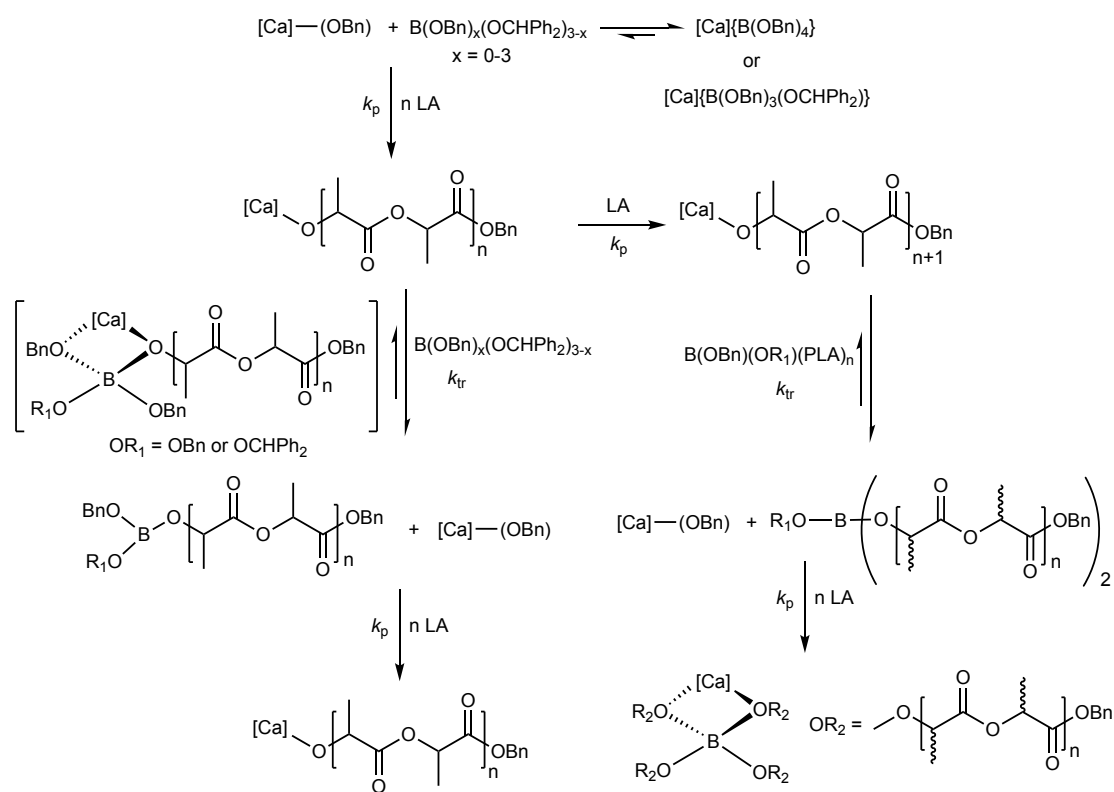


**Figure 4.25** Plots of  $M_n(\text{GPC})$  vs. conversion (%). Conditions: 6 mL THF, RT,  $[\text{rac-LA}]_0 = 0.5$  M. The black and green dashed lines represent  $M_n(\text{calcd})$  for one and four PLA chains per metal centre, respectively. Squares:  $[\text{rac-LA}]_0:[\mathbf{7}]_0:[\mathbf{25}]_0 = 800:1:1$ ,  $D = 1.07\text{--}1.44$ . Diamonds:  $[\text{rac-LA}]_0:[\mathbf{7}]_0 = 800:1$ ,  $D = 1.05\text{--}1.57$ .



**Scheme 4.7** The proposed mechanism for the ROP of LA using  $(\text{Tp}^{\text{tBu,M\acute{e}}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with 1 equiv. of  $\text{B}(\text{OBn})_3$  (**25**).  $[\text{Ca}] = (\text{Tp}^{\text{tBu,M\acute{e}}})\text{Ca}(\text{THF})_x$ .

MALDI-ToF mass spectrum (Figure 4.26) shows PLA with  $-\text{OBn}$  and  $-\text{OH}$  end groups. No PLA terminated with  $-\text{OCHPh}_2$  and  $-\text{OH}$  is observed. A major distribution of peak

envelopes corresponds to cyclic PLA, along with the repeating unit of  $\Delta m/z = 72.0$  Da between peak envelopes reflect transesterification reactions.

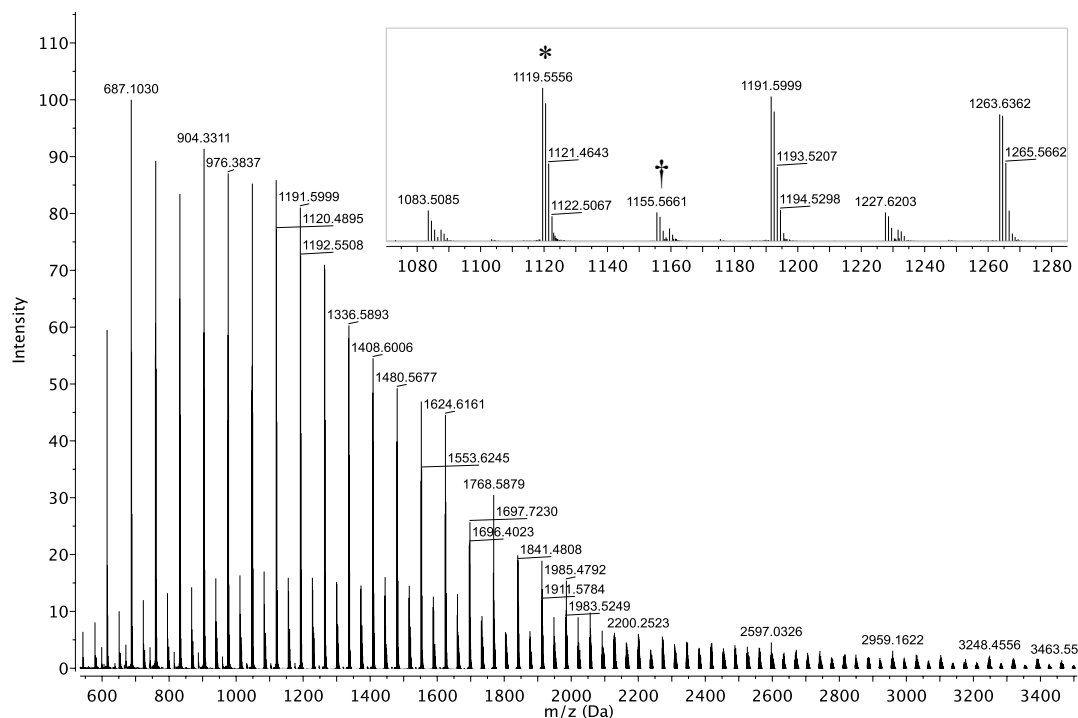


**Figure 4.26** MALDI-ToF MS of PLA synthesised using  $(Tp^{tBu,Me})Ca(OCHPh_2)(THF)$  (**7**) with 1 equiv. of  $B(OBn)_3$  (**25**).  $M_n(GPC) = 2,980 \text{ g mol}^{-1}$ ,  $D = 1.24$ . Conditions:  $[rac\text{-}LA]_0:[7]_0:[25]_0 = 20:1:1$ ,  $[rac\text{-}LA]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $K^+$  dopant.  $\Delta(m/z) = 72.0$  Da between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-OBn$  and  $-OH$  end groups.

#### 4.6 ROP of *rac*- and *meso*-LA using $(Tp^{tBu,Me})Sr(BH_4)(THF)_2$ (**21**)

In general, strontium complexes have been reported to be more active than their calcium congeners in the ROP of cyclic esters.<sup>27, 35-44</sup> However, lower activity was observed in the ROP of *rac*-LA by  $(Tp^{tBu,Me})Sr(BH_4)(THF)_2$  (**21**) than that using  $(Tp^{tBu,Me})Ca(BH_4)(THF)$  (**8**) under analogous conditions. For the ROP of 800 equiv. of *rac*-LA using **21**, 70% conversion was achieved after 1 min then 74% after 5 min (Table 4.10, entry 1), while **8** took 4 min to reach 87% (Table 4.1, entry 1). The similar behaviour reported by Roesky *et al.* showed that  $Ca(BH_4)_2(THF)_2$  (**4.24**) or  $[Cp^*Ca(BH_4)(THF)_2]_2$  (**4.26**) were more active in the ROP of *L*-LA or  $\epsilon$ -CL than the Sr analogues (**4.25** and **4.27**).<sup>27</sup> The kinetic results followed neither first nor second order dependence on  $[rac\text{-}LA]$ . The  $M_n(GPC)$  values were considerably lower than

those calculated for one polymer chain per metal centre due to transesterification reactions (Table 4.6, entry 1). The resulting PLA formed by **21** showed a negligible decrease in hetero-selectivity with  $P_r = 0.72$ , compared to that obtained from **8** ( $P_r = 0.77$ ).

Complex **21** was shown to be more active in the ROP of *meso*-LA than **8**, polymerising 800 equiv. of *meso*-LA (93% conversion) in 10 s. Poor agreement between measured and calculated  $M_n$  values for one chain per metal centre was observed (Table 4.6, entry 2). A negligible decrease in syndio-selectivity was measured ( $P_r = 0.82$ ), compared to PLA formed by **8** ( $P_r = 0.85$ ).

**Table 4.6** Selected data for the ROP of *rac*- and *meso*-LA using (Tp<sup>tBu,Me</sup>)Sr(BH<sub>4</sub>)(THF)<sub>2</sub> (**21**).<sup>a</sup>

| Entry | LA            | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|---------------|---------------------------|-------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <i>rac</i> -  | 75                        | 300         | 50,200                                                | 86,462                                                  | 1.54                   | 0.72               |
| 2     | <i>meso</i> - | 93                        | 10          | 75,580                                                | 107,212                                                 | 1.38                   | 0.82               |

<sup>a</sup> Conditions: [monomer]<sub>0</sub>: [initiator]<sub>0</sub> = 800:1, [monomer]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –LA-H end groups,  $M_n$  (entry 1, 2) = conv. (%) × 800 × 144.1 + 2. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

The end group analysis of PLA formed by **21** is reminiscent of that by **8**, evidenced by MALDI-ToF mass spectrum (Figure 4.27). A major distribution of cyclic PLA and the repeating units of  $\Delta m/z = 72.0$  Da between peak envelopes indicate transesterification reactions. A minor distribution of peak envelopes correspond to PLA with –LA-H and –OH end groups, and  $\alpha,\omega$ -dihydroxytelechelic PLA was also observed.



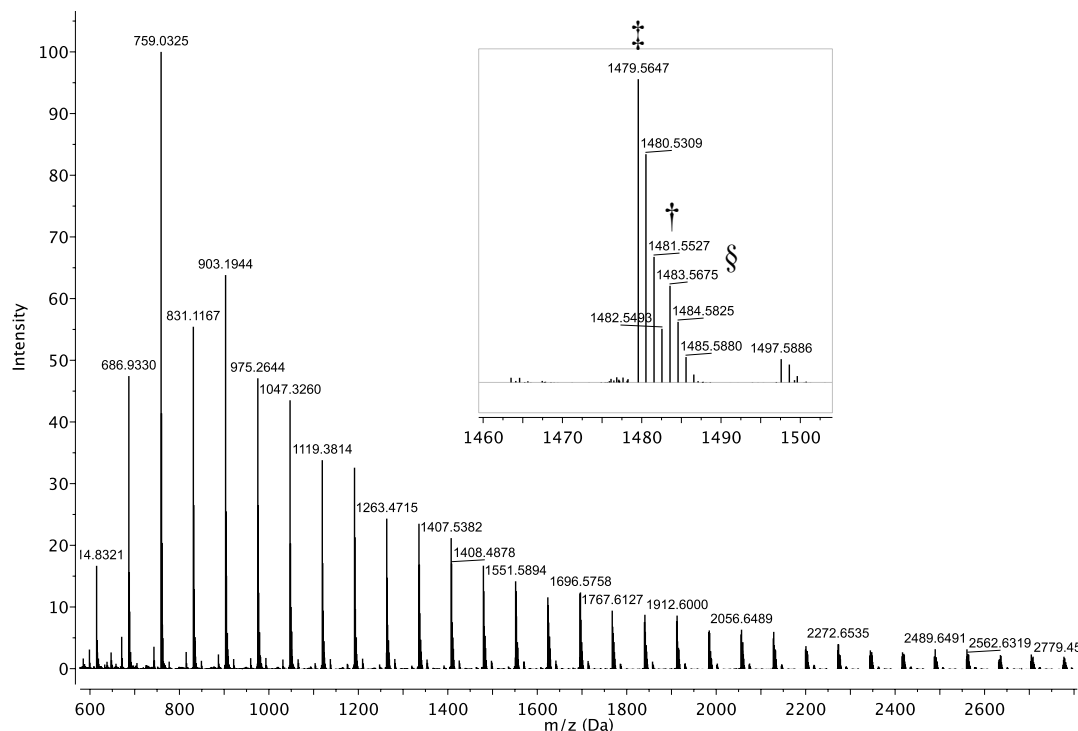


**Figure 4.27** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**).  $M_n(\text{GPC}) = 2,720 \text{ g mol}^{-1}$ ,  $D = 1.73$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{21}]_0 = 20:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “‡” denotes cyclic PLA. “†” denotes PLA with  $-\text{LA}-\text{H}$  and  $-\text{OH}$  end groups. “§” denotes  $\alpha,\omega$ -dihydroxytelechelic PLA.

#### 4.7 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$ (**21**) with benzaldehyde

An NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**) and 4 equiv. of benzaldehyde was performed in  $\text{THF}-d_8$  at RT. The  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at 4.0, -2.8 and -7.1 ppm corresponding to the tetra-coordinated boron of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  or  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$ ,  $\text{Sr}\cdots\text{H}-\text{B}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}$  (**3**) and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  ligand, respectively. The  $^1\text{H}$  NMR spectrum recorded after 10 min (Figure 4.28, a) shows two doublets at 7.23 and 7.36 ppm (integral ratio = 7:3) assigned to *o*- $\text{C}_6\text{H}_5$  protons of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$ , respectively.  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$  was independently synthesised *via* an NMR tube scale reaction of  $\text{Sr}(\text{BH}_4)_2(\text{THF})_2$  and 8 equiv. of benzaldehyde performed in  $\text{THF}-d_8$  at RT for 18 h. The  $^1\text{H}$  NMR spectrum of  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$  (Figure 4.28, b) shows a singlet at 4.70 ppm corresponding to methylene protons  $\text{OCH}_2\text{Ph}$  moiety which

appeared at the same chemical shift of those obtained from  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  (Figure 4.28, a).

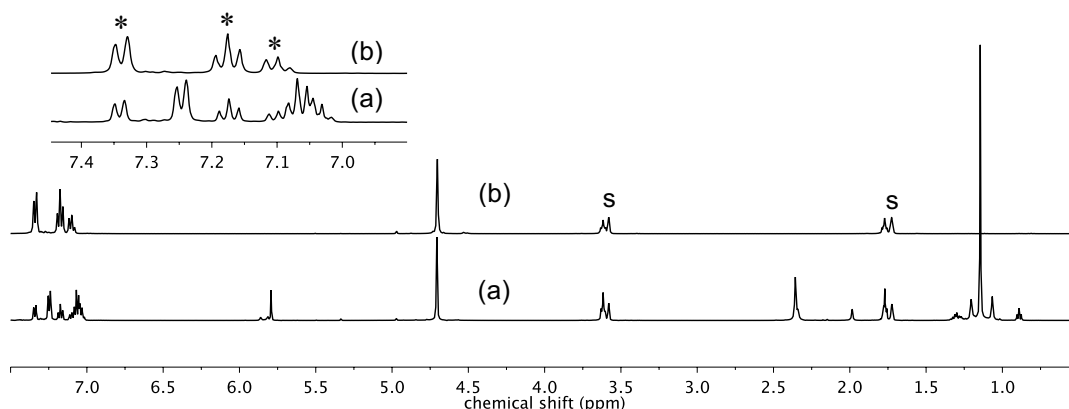
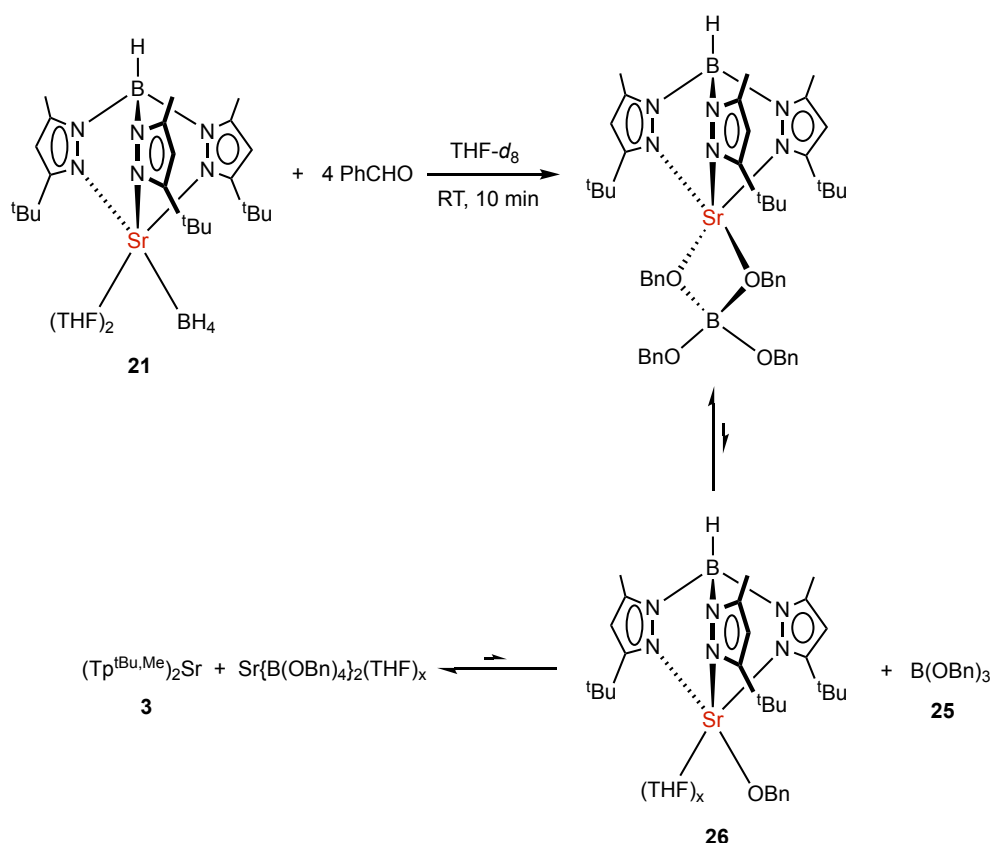


**Figure 4.28**  $^1\text{H}$  NMR spectra ( $\text{THF-}d_8$ , 499.9 MHz, 298K) of (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and (b)  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$ . “s” denotes residual protio-solvent. “\*” denotes  $\text{C}_6\text{H}_5$  protons of  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$ .

The proposed mechanism for the reaction between **21** and 4 equiv. of benzaldehyde in  $\text{THF-}d_8$  is shown in Scheme 4.8. Association and dissociation of  $\text{B}(\text{OBn})_3$  (**25**) to the metal centre occurs resulting in various species including  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ,  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OBn})(\text{THF})_x$  (**26**). **26** is unstable as reported in Chapter Two (section 2.6) and rapidly transforms to  $(\text{Tp}^{\text{tBu,Me}})_2\text{Sr}$  (**3**) and  $\text{Sr}(\text{OBn})_2(\text{THF})_x$ .  $\text{Sr}(\text{OBn})_2(\text{THF})_x$  subsequently coordinates to **25** giving  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$ .

The reaction of **21** with 4 equiv. of benzaldehyde was performed in THF at RT for 10 min, followed by an addition of 800 equiv. of *rac*-LA. Only 15% conversion was observed after 3 h. The measured  $M_n$  value ( $5,300 \text{ g mol}^{-1}$ ) was consistent with that calculated ( $4,431 \text{ g mol}^{-1}$ ) based on four chains per metal centre, and a moderate  $D$  value (1.40) was observed. The slow ROP rate strongly suggested that the resting state of the catalyst during the ROP of *rac*-LA involved the chelation of tetra-alkoxy borate to the metal centre, which led to the suppression of initiation or propagation of the ROP of LA.



**Scheme 4.8** The proposed mechanism of the reaction between  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**) with 4 equiv. of benzaldehyde in  $\text{THF-}d_8$ .

The polymerisation of 800 equiv. of *rac*-LA using *in situ* generated  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$  was carried out under analogous conditions, 12% conversion was reached after 24 h. The low polymerisation rate could be attributed to the presence of  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$  in an aggregated form instead of a simple dinuclear species. The  $M_n$  (GPC,  $3,900 \text{ g mol}^{-1}$ ) was much higher than the  $M_n$  (calcd,  $1,837 \text{ g mol}^{-1}$ ) based on eight chains per metal centre. The broad  $\bar{D}$  value (1.63) was observed. The poor ROP efficiency due to an aggregation of catalysts or polymer growing species was reported. Feijen *et al.* used  $\text{Ca}(\text{OMe})_2$  for the bulk polymerisation of 100 equiv. of *L*-LA or  $\epsilon$ -CL at  $120^\circ\text{C}$ .<sup>45</sup> The full conversion for the ROP of  $\epsilon$ -CL was reached after 10 min whereas 66% conversion was reached after 1.5 h for the ROP of *L*-LA. The resultant polymers showed much higher  $M_n$ (GPC) values than those calculated for two chains per metal centre with moderate  $\bar{D}$  values (1.25-1.43). Tang *et al.* reported the ROP of  $\epsilon$ -CL (100-330 equiv.) with  $\text{Sr}(\text{O}^i\text{Pr})_2$  in toluene at  $40^\circ\text{C}$ .<sup>46</sup> The full conversion was reached after 6 h, giving PCLs with very broad  $\bar{D}$  values (3.37-7.37). The  $M_n$ (GPC) values were also higher than those calculated for two chains per metal centre.

#### 4.8 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$ (**13**) with $\text{B}(\text{OBn})_3$ (**25**)

An NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) and 1 equiv. of  $\text{B}(\text{OBn})_3$  (**25**) was performed in  $\text{THF-}d_8$  at RT. The  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at 4.3, -2.6 and -7.5 ppm corresponding to  $\text{B}(\text{OR})_4$ ,  $\text{Sr}\cdots\text{H-B}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}$  (**3**) and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively. The  $^1\text{H}$  NMR spectrum recorded after 10 min (Figure 4.29, a) shows the absence of **13**.

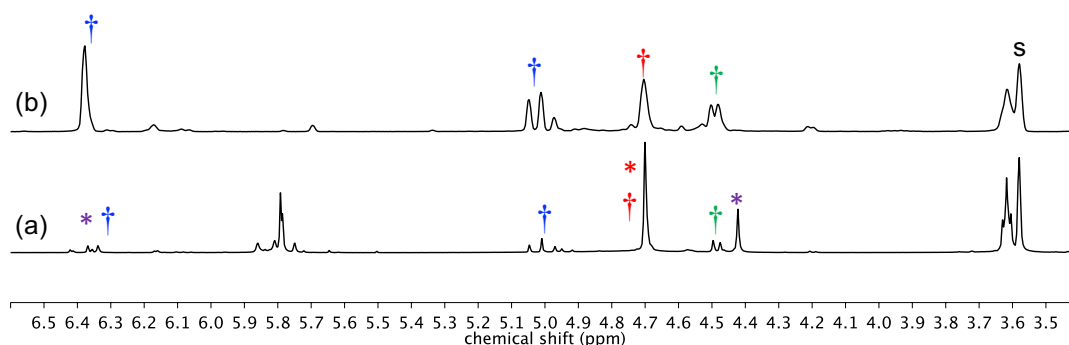
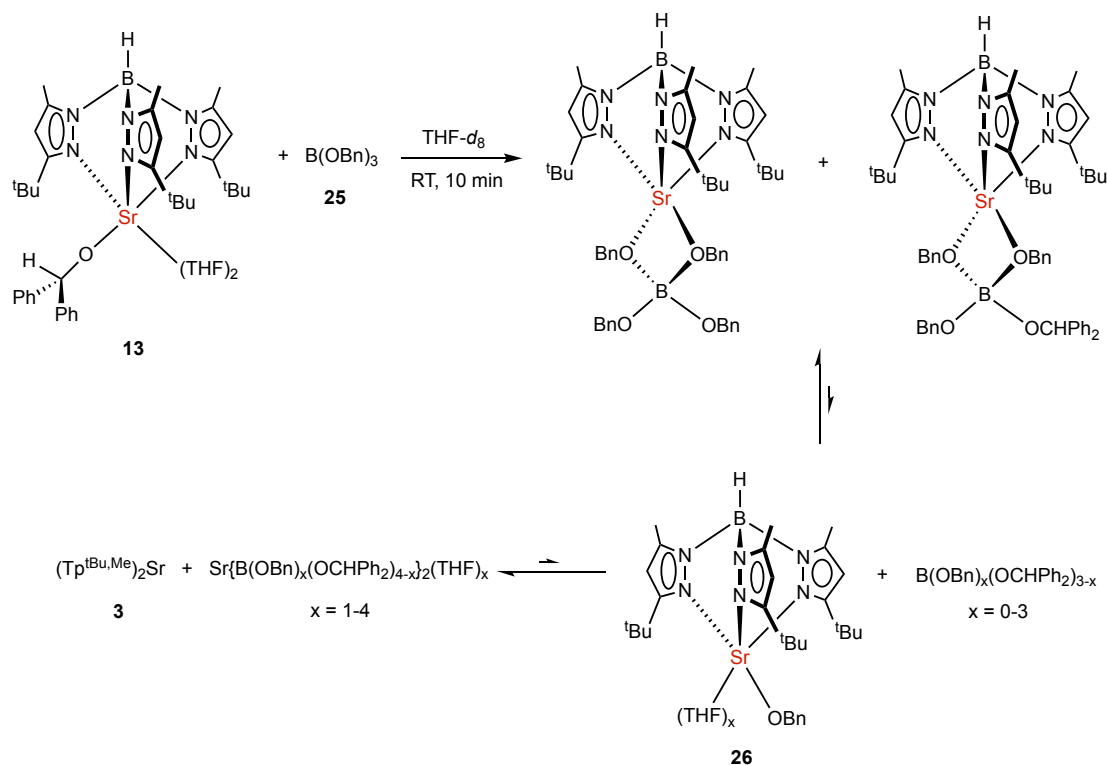


**Figure 4.29**  $^1\text{H}$  NMR spectra ( $\text{THF-}d_8$ , 499.9 MHz, 298K) of (a) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) with 1 equiv. of  $\text{B}(\text{OBn})_3$  (**25**) recorded after 10 min and (b) reaction of  $\text{Sr}(\text{OCHPh}_2)_2(\text{THF})_x$ , 2 equiv. of  $\text{B}(\text{OCHPh}_2)_3$  (**23**) and 3 equiv. of **25** recorded after 1 h. “s” denotes residual protio-solvent.

Two singlets at 4.72 and 4.42 ppm (Figure 4.29, a) are assigned to methylene protons of  $-\text{OCH}_2\text{Ph}$  moiety of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  (\*) and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  (\*) which are analogous to those observed from the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with **25**. A minor signal corresponding to  $\text{Sr}\{\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{4-x}\}_2(\text{THF})_x$  ( $x = 1-3$ , †) was also observed at  $\delta = 4.48$  ppm. An NMR tube scale reaction of  $\text{Sr}(\text{BH}_4)_2(\text{THF})_2$  and 8 equiv. of benzophenone was carried out in  $\text{THF-}d_8$  at RT, giving  $\text{Sr}(\text{OCHPh}_2)_2(\text{THF})_x$  and 2 equiv. of **23**. The addition of 3 equiv. of **25** generated  $\text{Sr}\{\text{B}(\text{OBn})_4\}_2(\text{THF})_x$  (†),  $\text{Sr}\{\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{4-x}\}_2(\text{THF})_x$  ( $x = 1-3$ , †) and  $\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 1-3$ , ‡), evidenced by the  $^1\text{H}$  NMR (Figure 4.29, b). The  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at 18.8, 4.6, -2.3 and -6.8 ppm corresponding to  $\text{B}(\text{OR})_3$ ,  $\text{B}(\text{OR})_4$ ,  $\text{Sr}\cdots\text{H-B}$  of **3** and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively.

The existence of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  were confirmed by the ROESY NMR spectrum of the reaction between **13** and **25** in  $\text{THF-}$

$d_8$  recorded at 253 K. A through-space correlation between  $-\text{OCH}_2\text{Ph}$  (4.36 ppm) and  $-\text{OCHPh}_2$  (6.38 ppm) moieties was observed, supporting the presence of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ . Through-space correlations between *tert*-butyl of  $\text{Tp}^{\text{tBu,Me}}$  ( $\delta = 1.14$  and  $1.16$  ppm) and methylene protons of  $-\text{OBn}$  groups of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  ( $\delta = 4.70$  and  $4.36$  ppm, respectively) were also observed. The proposed mechanism for the reaction of **13** and **25** is illustrated in Scheme 4.9.



**Scheme 4.9** The proposed mechanism for the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) with 1 equiv. of  $\text{B}(\text{OBn})_3$  (**25**) in  $\text{THF-}d_8$ .

Complex **13** was reported in Chapter Two to be a highly active ROP catalyst, 95% conversion (800 equiv. of *rac*-LA) was reached after 10 s (Table 4.7, entry 3). The reaction of **13** and **25** in a 1:1 ratio was performed in THF at RT for 10 min, followed by an addition of 800 equiv. of *rac*-LA. The conversion reached 70% after 5 min and then 77 % after 5 h (Table 4.7, entry 1, 2) which was slower than using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and **25**. The precipitous drop in the ROP rate after 5 min was attributed to the catalyst resting state involving tetra-alkoxy borate species.

**Table 4.7** Selected data for the ROP of *rac*-LA using (Tp<sup>tBu,Me</sup>)Sr(OCHPh<sub>2</sub>)(THF)<sub>2</sub> (**13**) with B(OR)<sub>3</sub> (**25**).<sup>a</sup>

| Entry | Additive  | Conv. <sup>b</sup><br>(%) | Time<br>(min) | $M_n$<br>(GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$<br>(calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|-----------|---------------------------|---------------|-------------------------------------------------------|---------------------------------------------------------|------------------------|--------------------|
| 1     | <b>25</b> | 70                        | 5             | 33,950                                                | 20,282                                                  | 1.50                   | 0.68               |
| 2     | <b>25</b> | 77                        | 300           | 37,230                                                | 22,299                                                  | 1.42                   | 0.65               |
| 3     | -         | 95                        | 0.16          | 69,550                                                | 109,700                                                 | 1.56                   | 0.68               |

<sup>a</sup> Conditions: [*rac*-LA]<sub>0</sub>:[initiator]<sub>0</sub>:[additive]<sub>0</sub> = 800:1:as stated, [*rac*-LA]<sub>0</sub> = 0.5 M, [initiator]<sub>0</sub> = 625 μM, 6.0 mL THF at RT. <sup>b</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 17.4 μL g<sup>-1</sup> and α = 0.736. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>),  $M_n$  (entry 1, 2) for -OH and -OBn end groups = (conv. (%) × 800 × 144.1)/4 + 108.1,  $M_n$  (entry 3) for -OH and -OCHPh<sub>2</sub> end groups = conv. (%) × 800 × 144.1 + 184.1. <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Measured by <sup>1</sup>H{<sup>1</sup>H} NMR (CDCl<sub>3</sub>) analyses.

The  $M_n$ (GPC) values were in close agreement with those calculated for two chains per metal centre from 15% (10 s) to 60% conversion (2 min) (Figure 4.30), suggesting chain transfer ability of B(OR)<sub>3</sub> (OR = -OBn, -OCHPh<sub>2</sub> or polymeryl chain) in the ROP of *rac*-LA using strontium initiator. Afterwards, the  $M_n$ (GPC) values deviated from those calculated for two chains per metal centre from 66% (3 min) to 77% conversion (5 h) due to transesterification reactions

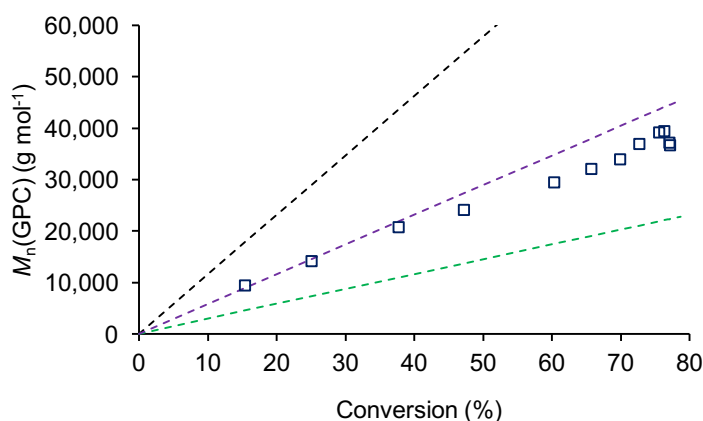


**Figure 4.30** Plot of  $M_n$ (GPC) vs. conversion (%). Conditions: 6 mL THF, RT, [*rac*-LA]<sub>0</sub> = 0.5 M. The black, purple and green dashed lines represent  $M_n$ (calcd) for one, two and four PLA chains per metal centre, respectively. [*rac*-LA]<sub>0</sub>:**[13]**<sub>0</sub>:**[25]**<sub>0</sub> = 800:1:1.  $\bar{D}$  = 1.20-1.42.

MALDI-ToF mass spectrum (Figure 4.31) shows a major distribution of cyclic PLA due to intramolecular transesterification. A minor distribution of peak envelopes was

assigned to PLA terminated with  $-\text{OBn}$  and  $-\text{OH}$  end groups. No PLA terminated with  $-\text{OCHPh}_2$  and  $-\text{OH}$  end groups was observed in the MALDI-ToF or  $^1\text{H}$  NMR spectra.

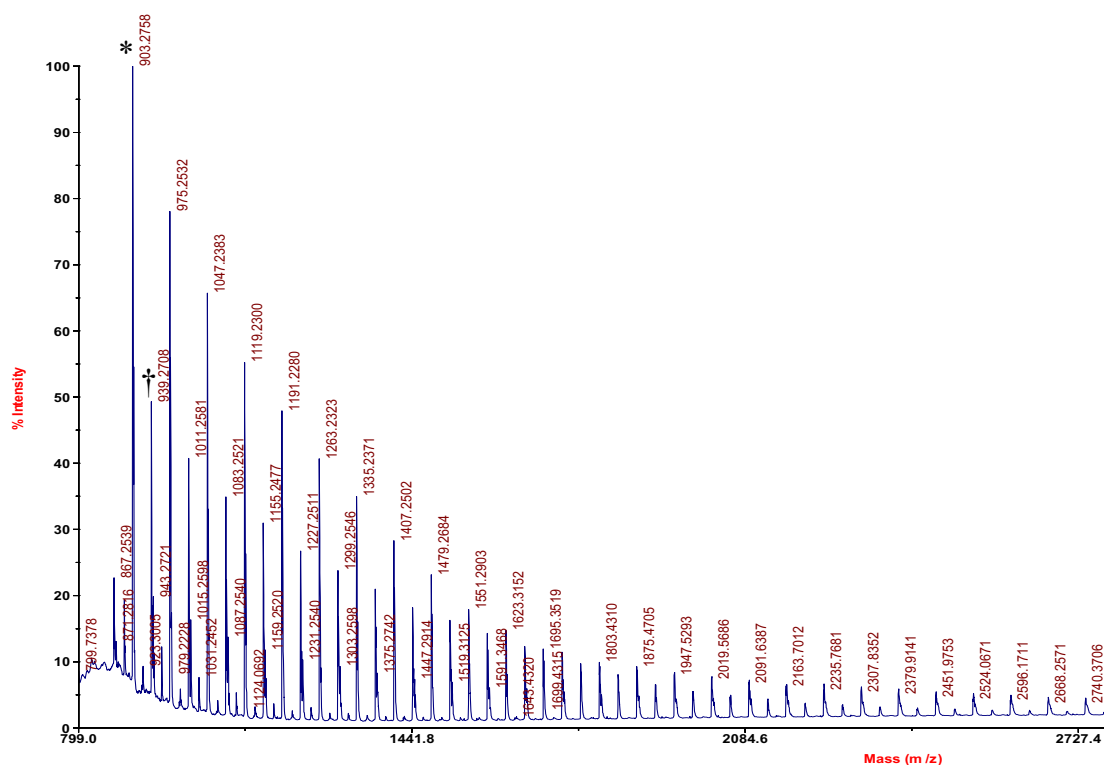


**Figure 4.31** MALDI-ToF MS of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) with 1 equiv. of  $\text{B}(\text{OBn})_3$  (**25**).  $M_n(\text{GPC}) = 1,310 \text{ g mol}^{-1}$ ,  $D = 1.56$ . Conditions:  $[\text{rac-LA}]_0:[\textbf{13}]_0:[\textbf{25}]_0 = 20:1:1$ ,  $[\text{rac-LA}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL THF}$  at RT.  $\text{K}^+$  dopant.  $\Delta(m/z) = 72.0 \text{ Da}$  between peak envelopes. “\*” denotes cyclic PLA. “†” denotes PLA with  $-\text{OBn}$  and  $-\text{OH}$  end groups.

#### 4.9 ROP of *rac*-LA using $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$ (**21**) with benzophenone or 2-methylcyclohexanone

An NMR tube scale reaction of **21** and 4 equiv. of benzophenone was performed in  $\text{THF-}d_8$  at RT, producing  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) and  $\text{B}(\text{OCHPh}_2)_3$  (**23**). The  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at 18.4 and  $-7.5 \text{ ppm}$  corresponding to  $\text{B}(\text{OCHPh}_2)_3$  and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively.

An NMR tube scale reaction of **21** and 4 equiv. of 2-methylcyclohexanone was carried out under the analogous conditions, giving  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCyMe})(\text{THF})_x$  (**27**) and  $\text{B}(\text{OCyMe})_3$  (**24**). Complex **27** was labile and redistributed by the Schlenk equilibrium to form  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}$  (**3**) and  $\text{Sr}(\text{OCyMe})_2(\text{THF})_x$ . The  $^{11}\text{B}$  NMR spectrum recorded after

10 min showed signals at 18.0, -2.6 and -7.3 ppm assigned to **24**,  $\text{Sr} \cdots \text{H-B}$  of **3** and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively.

The polymerisations of 800 equiv. of *rac*-LA using **21** with 4 equiv. of benzophenone or 2-methylcyclohexanone were extremely active, reaching over 90% conversion within 10 s (Table 4.8). The high polymerisation rate was observed due to the absence of tetra-alkoxy borate as ROP initiator and the inefficiency of **23** and **24** as chain transfer agents. The poorly controlled  $M_n(\text{GPC})$  values and a moderate  $D$  value (1.56) were observed due to transesterification reactions. Moderately heterotactic PLAs were obtained with  $P_r = 0.71$ -0.72.

**Table 4.8** Selected data for the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**) with additives.<sup>a</sup>

| Entry | Additive | Conv. <sup>b</sup><br>(%) | Time<br>(s) | $M_n$ obs <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$ calcd <sup>d</sup><br>(g mol <sup>-1</sup> ) | $D$ <sup>e</sup> | $P_r$ <sup>f</sup> |
|-------|----------|---------------------------|-------------|--------------------------------------------------|----------------------------------------------------|------------------|--------------------|
| 1     | 4 PhCOPh | 93                        | 10          | 53,550                                           | 107,394                                            | 1.56             | 0.71               |
| 2     | 4 CyMeO  | 91                        | 10          | 59,390                                           | 105,019                                            | 1.56             | 0.72               |

<sup>a</sup> Conditions:  $[\text{rac-LA}]_0:[\text{initiator}]_0:[\text{additive}]_0 = 800:1$  as stated,  $[\text{rac-LA}]_0 = 0.5$  M,  $[\text{initiator}]_0 = 625$   $\mu\text{M}$ , 6.0 mL THF at RT. <sup>b</sup> Measured by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) analyses. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 17.4$   $\mu\text{L g}^{-1}$  and  $\alpha = 0.736$ . <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>),  $M_n$  (entry 1) for  $-\text{OH}$  and  $-\text{OCHPh}_2$  end groups =  $\text{conv. (\%)} \times 800 \times 144.1 + 184.1$ ,  $M_n$  (entry 2) for  $-\text{OH}$  and  $-\text{OCyMe}$  end groups =  $\text{conv. (\%)} \times 800 \times 144.1 + 114.1$ . <sup>e</sup>  $D = M_w/M_n$ . <sup>f</sup> Measured by  $^1\text{H}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ) analyses.

MALDI-ToF mass spectrum of PLAs formed by ROP of *rac*-LA using **21** and 4 equiv. of benzophenone or 2-methylcyclohexanone showed the presence of PLA with  $-\text{OH}$  and the corresponding alkoxide end groups. Cyclic PLA was also observed as a major distribution due to back-biting. The peak envelopes are separated by  $\Delta m/z = 72.0$  Da reflecting transesterification reactions.

#### 4.10 Summary and conclusions for Chapter Four

This Chapter described the catalytic activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) in the ROP of *rac*-LA in THF at RT. Complex **8** polymerised 800 equiv. of *rac*-LA within 3 min in THF at RT. The kinetic analysis showed second order and first order dependence on concentrations of *rac*-LA and **8**, respectively. The propagation rate constant was calculated, giving  $k_p = 198(13)$   $\text{M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.992$ ). The overall rate law was determined as  $-\text{d}[\text{rac-LA}]/\text{dt} = k_p[\text{rac-LA}]^2[\text{8}]$ ,  $k_p = 198(13)$   $\text{M}^{-2}\text{s}^{-1}$  ( $R^2 = 0.992$ ). The mismatch between measured and calculated  $M_n$  values was observed during high conversions (> 40%) due to intra- and intermolecular transesterifications. Moderate  $D$  values were



obtained in the range of 1.30-1.80. Moderately heterotactic PLAs were formed with  $P_r = ca. 0.74-0.77$  analysed by  $^1\text{H}\{^1\text{H}\}$  NMR spectroscopy. MALDI-ToF mass spectrometry showed three types of PLA including cyclic PLA, PLA with non-opened LA ring ( $-\text{LA-H}$ ) and  $-\text{OH}$  end groups, and  $\alpha,\omega$ -dihydroxytelechelic PLA. Complex **8** was also active for the ROP of 800 equiv. of *meso*-LA, reaching 96% conversion in 1 min. First order dependence on  $[\textit{meso}\text{-LA}]$  was observed giving  $k_{\text{app}} = 0.048(2) \text{ s}^{-1}$  ( $R^2 = 0.996$ ). Syndiotactically-enriched PLA was produced showing  $P_r = 0.85$ .

The mechanistic studies of the ROP of LA initiated by **8** were carried out. The reaction of **8** and 5 equiv. of *L*-LA was performed in  $\text{THF-}d_8$  at 223 K. The presence of the first hydride transfer product  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-H})(\text{THF})_x$  and  $\text{BH}_3(\text{THF})$  was detected after 10 min and characterised by NMR spectroscopy. Deuterium labelling experiments using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) showed the formation of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{LA-D})(\text{THF})_x$  and  $\text{BD}_3(\text{THF})$  analysed by  $^2\text{H}$  NMR spectroscopy. The end-group analysis of PLA with  $-\text{LA-D}$  and  $-\text{OH}$  end groups *via*  $^1\text{H}$  or  $^2\text{H}$  NMR spectroscopy and MALDI-ToF mass spectrometry confirmed the existence of non-opened LA ring ( $-\text{LA-D}$ ) and  $-\text{CHMeCD}_2(\text{OH})$  termini.

The chain transfer ability of *in situ* generated  $\text{B}(\text{OR})_3$  was investigated. The NMR tube scale reactions of **8** with 4 equiv. of benzophenone or 2-methylcyclohexanone produced corresponding alkoxide complexes  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**10**) and borate ester analogues  $\text{B}(\text{OCHPh}_2)_3$  (**23**) and  $\text{B}(\text{OCyMe})_3$  (**24**), respectively. The negligible effect of **23** or **24** on polymerisation rate,  $M_n$  and polymer tacticity was observed, indicating their poor ability as chain transfer agents. The NMR tube scale reaction of **8** with 4 equiv. of benzaldehyde formed  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $\text{B}(\text{OBn})_3$  (**25**) which were in equilibrium with  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ . The presence of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$  was postulated as the resting state of the catalyst. Diminished polymerisation rate and poor control over  $M_n$  and tacticity could be attributed to this.

The ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with **25** also demonstrated the chain transfer nature of **25**. The slow ROP rate ( $k_{\text{app}} = 0.045(1) \text{ M}^{-1}\text{s}^{-1}$ ,  $R^2 = 0.996$ ) was observed compared to those obtained from using only **7**. Poor agreement between measured and calculated  $M_n$  based on one polymer chain per metal centre together with the reduction in stereoselectivity ( $P_r = 0.78$ ) was presented.

The catalytic activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})_2$  (**21**) was also studied. **21** showed high activity in the ROP of *rac*- and *meso*-LA, producing moderately heterotactic PLA ( $P_r = 0.72$ ) and highly syndiotactic PLA ( $P_r = 0.82$ ), respectively. The end group analysis through MALDI-ToF mass spectrometry showed the presence of cyclic PLA, PLA with non-opened LA ring (-LA-H) and -OH end groups, and  $\alpha,\omega$ -dihydroxytelechelic PLA. The polymerisations of *rac*-LA using **21** with 4 equiv. of benzophenone, 2-methylcyclohexanone or benzaldehyde were performed in THF at RT in order to probe the chain transfer ability of borate esters, **23**, **24** and **25** in the ROP of LA with strontium initiators. Over 90% conversion was reached within 10 s from the ROP of *rac*-LA involving **23** or **24**. Whereas the ROP of *rac*-LA involving **25** showed slow polymerisation (15% conversion in 3 h), attributed to the major distribution of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  acting as the resting state of the catalyst. The impact of **25** on polymerisation was also observed from the ROP of *rac*-LA using  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (**13**) with **25** in THF at RT, giving the low ROP rate and close agreement between experimental and calculated  $M_n$  based on two polymer chains per metal centre.

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# **Chapter Five**

**Alkaline earth organohydroborate,  
tetrahydroborate and alkoxide complexes for  
the ROP of *rac*-BBL**

## Chapter Five

### 5.1 Overview

This Chapter will describe catalytic activity and mechanisms of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) for the ROP of *rac*- $\beta$ -butyrolactone (*rac*-BBL). The ROP of *rac*-BBL catalysed by calcium organohydroborate, tetrahydroborate and alkoxide complexes will also be discussed. The use of borate esters as chain transfer agents in the ROP of *rac*-BBL with magnesium and calcium alkoxide initiators will be presented.

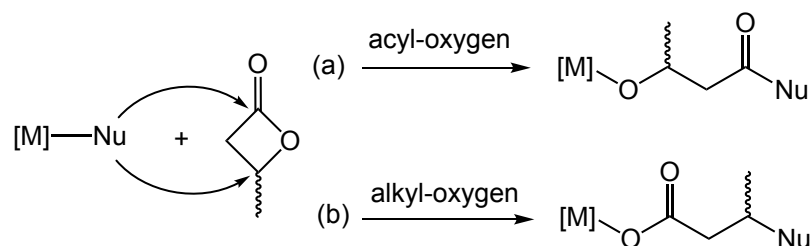
### 5.2 Introduction

#### 5.2.1 $\beta$ -butyrolactone (BBL) and poly(3-hydroxybutyrate) (PHB)

Poly(3-hydroxybutyrate) (PHB) is a biodegradable and biocompatible aliphatic polyester which is naturally produced by bacteria and other living organisms.<sup>1-4</sup> The bacteria-produced PHB is isotactic with all stereocentres in the (*R*) configuration. The low thermostability of isotactic PHB during the melting process limited its rheological studies and processing window.<sup>5</sup> Isotactic PHB is also very brittle due to the high crystallinity ( $T_m = 180\text{ }^\circ\text{C}$ ), which limits its applications in consumer products.<sup>6</sup> Blending with other polymers,<sup>6-8</sup> copolymerisation *via* microbial synthetic routes,<sup>9, 10</sup> or incorporation with different organic and inorganic additives<sup>11-13</sup> have been attempted to improve the mechanical properties of bacterial PHB and broaden its processing ability. However, the high costs of PHB fabrication through biotechnological routes and poor control of molecular weight, *D* and polymer tacticity have restricted the commercialisation of PHB. Rieger *et al.* reported an alternative pathway to synthesise atactic and isotactic PHB from the cobalt-catalysed alternating copolymerisation of propylene oxide and carbon monoxide which are low-cost, industrially available chemicals.<sup>14</sup> The polymerisation mechanism combined a CO insertion with an epoxide ring-opening reaction in a presence of pyridine.

Ring-opening polymerisation (ROP) of  $\beta$ -butyrolactone (BBL) where the relief of ring-strain is the driving force for polymerisation has emerged as the most efficient method to prepare PHB with better control of macromolecular parameters. The polymerisation can proceed *via* different mechanisms such as anionic, coordination-insertion, organo-catalysed, enzymatic and cationic. In general, the ROP of BBL can

proceed *via* two pathways which involves either acyl bond cleavage forming a metal alkoxide species, or alkyl bond cleavage leading to a metal carboxylate species (Scheme 5.1).<sup>15</sup> The ROP of BBL is normally accompanied by side-reactions including inter- and intramolecular transesterifications, chain-transfer, multiple hydrogen transfer reactions or elimination, resulting in poorly-controlled ROP parameters (rate,  $M_n$ ,  $\bar{D}$ ) or the uncontrolled formation of *trans*-crotonate chain ends ( $-\text{CH}=\text{CHMe}$ ).<sup>12, 16-22</sup>

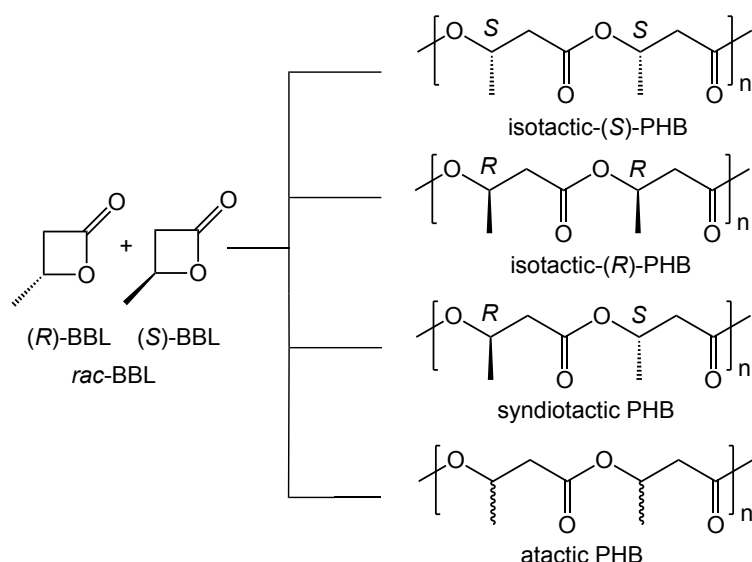


**Scheme 5.1** Acyl-oxygen (a) and alkyl-oxygen (b) cleavages for ROP of BBL. [M] = metal centre. Nu = nucleophile.<sup>21</sup>

The production of isotactic PHB with controlled molecular weights and  $\bar{D}$  can be achieved from the ROP of enantiomeric pure (*R*) or (*S*)-BBL. However, the (*R*) or (*S*)-BBL monomers prepared from carbonylation of the corresponding chiral enantiopure epoxides are relatively expensive.<sup>23, 24</sup> Coates and Dunn reported a one-pot catalytic system to prepare PHB, where (*R*)-BBL was synthesised from a carbonylation of propylene oxide and carbon monoxide with cobalt based catalysts, followed by the subsequent ROP of (*R*)-BBL using (<sup>Dipp</sup>NacNac)Zn(O<sup>i</sup>Pr) as a catalyst.<sup>25</sup>

Unlike bacteria-mediated biosynthesis, which gives only isotactic PHB, controlled ROP of *rac*-BBL provided PHB with different degree of stereoselectivity<sup>26</sup> such as atactic PHB<sup>27, 28</sup> or PHB enriched in isotactic<sup>29-34</sup> and syndiotactic<sup>35, 36</sup> dyads (Scheme 5.2). In general, *rac*-BBL is less readily polymerised than lactide (LA), supported by numerous studies reporting extremely low activity and molecular weight PHB.<sup>21, 37-47</sup>





**Scheme 5.2** Various PHB microstructures from the ROP of *rac*-BBL.<sup>21</sup>

### 5.2.2 Metal complexes as *rac*-BBL ROP catalysts

In 2002, Coates *et al.* reported the synthesis of single-site  $\beta$ -diiminate zinc alkoxide complexes,  $(^{\text{Ar'}}\text{NacNac})\text{Zn}(\text{O}^i\text{Pr})$  ( $\text{Ar}' = 2,6\text{-C}_6\text{H}_3^i\text{Pr}_2$  (**5.1**) and  $2,6\text{-C}_6\text{H}_3\text{Et}_2$  (**5.2**), Figure 5.1) and their activity in the ROP of BBL.<sup>20</sup> Complex **5.1** was active in the ROP of *rac*-BBL ( $[\textit{rac}\text{-BBL}]_0:[\textbf{5.1}]_0 = 200$ ) in  $\text{C}_6\text{D}_6$  at RT, reaching 91% conversion after 70 min. The  $M_n$  values of PHB were in good agreement with those calculated for one chain growing per metal centre, and  $\bar{D}$  values were relatively narrow (*ca.* 1.06–1.13). High molecular weight PHB was achieved by polymerising 2,000 equiv. of *rac*-BBL with **5.1** at RT for 12 h. However, the  $M_n$  of PHB ( $144,000 \text{ g mol}^{-1}$ ) at 90% conversion was rather lower than that calculated ( $172,180 \text{ g mol}^{-1}$ ) for one polymer chain per metal centre, and a  $\bar{D}$  value became broader (1.20). This was attributed to transesterification and other side reactions which degraded PHB after all monomer was consumed (*vide supra*). Kinetic analysis showed first order dependence on **5.1** and *rac*-BBL concentrations. Complex **5.2** was found to be less active than **5.1**, taking over 40 h to polymerise 200 equiv. of *rac*-BBL (95% conversion) at RT to give PHB with a broad  $\bar{D}$  value (1.70) and significantly higher than expected  $M_n$  due to greater propagation than initiation rate. Complex **5.2** is a poor ROP initiator at RT as its preference to exist in a dimeric form in solution inhibits coordination of monomer to the metal centre and therefore suppresses polymerisation. The ROP of *rac*-BBL using **5.1** or **5.2** gave atactic PHB as analysed by  $^{13}\text{C}\text{-}\{^1\text{H}\}$  NMR spectroscopy. The polymer end-group analysis by  $^1\text{H}$  NMR showed PHB terminated with  $\text{-O}^i\text{Pr}$  and –

OH groups obtained from **5.1**, indicating a coordination-insertion mechanism *via* acyl-oxygen bond cleavage.

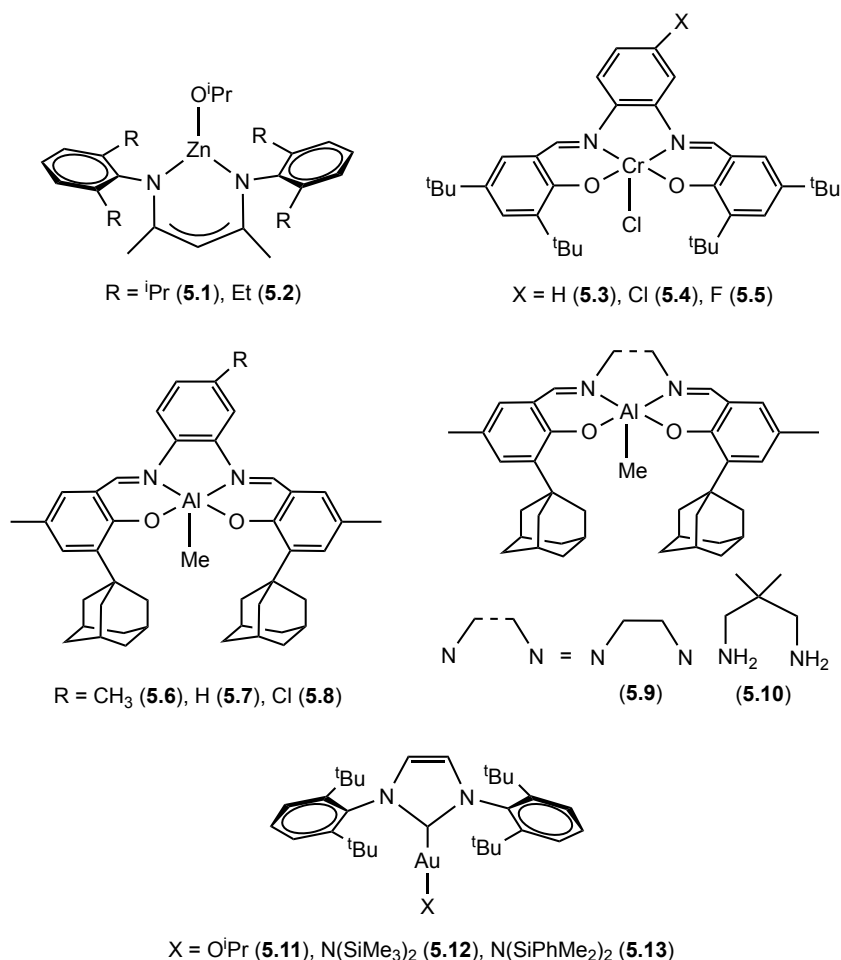


**Figure 5.1** Metal complexes for ROP of *rac*-BBL (**5.1-5.13**).<sup>20, 34, 48, 49</sup>

Le Borgne and Spassky reported an early example of stereoselective ROP of *rac*-BBL through kinetic resolution.<sup>29</sup> Chiral initiators were prepared by the reaction of alkyl metal complexes ( $\text{ZnEt}_2$ ,  $\text{CdMe}_2$  and  $\text{AlEt}_3$ ) with (*R*)-3,3-dimethyl-1,2 butanediol. With the zinc and aluminium initiators, the (*R*)-enantiomer was preferentially incorporated in the polymer chain with a stereoselectivity ratio ( $r_R$ ) of 1.6 and 1.1, respectively. The stereoselectivity ratio ( $r$ ) is the ratio of the polymerisation rate constants of the two enantiomers ( $r = k_{\text{fast}}/k_{\text{slow}}$ ) which is often used to examine the efficiency of a catalyst in a stereoselective polymerisation.<sup>50</sup> On the other hand, predominance for (*S*)-enantiomer incorporation in the polymer chain was observed with the cadmium based initiator giving  $r_S$  of 1.01. Aluminoxane catalysts ( $\text{AlR}_3/\text{H}_2\text{O}$ ) were used in the ROP of *rac*-BBL to form a mixture of PHBs with different tacticity, isolated by fractionation.<sup>32, 51</sup> However, the polymerisation was

very slow and some aluminoxanes required several days reaching full conversion to give a small fraction of isotactic PHB with broad  $D$  values (6.0-7.0).

Rieger *et al.* reported a series of chromium(III) salophen complexes (**5.3**, **5.4** and **5.5**, Figure 5.1) and their catalytic activity in the ROP of *rac*-BBL.<sup>34</sup> All complexes gave moderately isotactic PHBs ( $P_m = 0.63$ - $0.66$ ) with high molecular weights and broad  $D$  values (5.2-9.6). The ROP activity was reported to be influenced by the aryl substituents on the salophen framework. Shaver *et al.* also reported a series of aluminium alkyl complexes supported by salophen (**5.6**, **5.7** and **5.8**) and salen (**5.9** and **5.10**) ligands (Figure 5.1) and their ROP of *rac*-BBL in the presence of BnOH.<sup>49</sup> The salen complexes **5.9** and **5.10** converted 100 equiv. of *rac*-BBL to over 90% conversion after 3.5 h at 100 °C in toluene, giving moderately isotactic PHBs ( $P_m = ca. 0.55$ ) with moderate  $D$  values (1.11-1.37), and close agreement between experimental and calculated  $M_n$  values. Complexes **5.6** and **5.7** showed a much slower rate of ROP than **5.9** and **5.10** under analogous conditions, producing PHB with moderate  $D$  values (1.39-1.42) and poor agreement between experimental  $M_n$  values and those calculated. Complex **5.8** which contains an electron-withdrawing Cl group showed only 47% conversion, affording PHB with a broad  $D$  value (2.21) and experimental  $M_n$  considerably higher than calculated. All salophen complexes (**5.6**-**5.8**) produced slightly syndiotactic PHBs with  $P_r = 0.53$ - $0.55$ .

Thomas *et al.* presented gold(I) alkoxide and amido complexes supported by a N-heterocyclic carbene ligand (NHC), (NHC)Au(X) (X = O<sup>*i*</sup>Pr (**5.11**), N(SiMe<sub>3</sub>)<sub>2</sub> (**5.12**), N(SiPhMe<sub>2</sub>)<sub>2</sub> (**5.13**), Figure 5.1).<sup>48</sup> The initiator activity followed the sequence: **5.11** < **5.12**  $\approx$  **5.13**. For the bulk polymerisation of 100 equiv. of *rac*-BBL at 50 °C, **5.11** converted 46% after 24 h, while **5.12** or **5.13** converted over 75% after 2 h. PHBs formed by all complexes showed good to moderate  $D$  values (1.14-1.57), and experimental  $M_n$  values that were higher than those calculated. The PHB tacticity was not reported. A solvent effect was observed for the ROP using **5.12**, in which reactions performed in polar solvents led to some polymerisation. For [*rac*-BBL]<sub>0</sub>: [**5.12**]<sub>0</sub> = 100, reaction in THF showed the highest activity (66% conversion after 4.5 h). Whereas the ROP in acetonitrile reached 31% conversion after 24 h. No polymerisation was observed in nonpolar solvents such as toluene or CH<sub>2</sub>Cl<sub>2</sub>.

Tin alkoxide complexes were reported to be active in the ROP of *rac*-BBL. However, the polymerisations proceeded very slowly, giving PHB with modest syndiotactic

enchainment. Gross *et al.* carried out the polymerisation of *rac*-BBL catalysed by  $\text{SnBu}_3(\text{OMe})$  at 75 °C to give low molecular weight PHB with modest syndiotacticity ( $P_r = 0.63$ ) after 18 days.<sup>52</sup> The syndioselectivity was slightly improved to  $P_r = 0.70$  when the ROP was conducted at 40 °C (only *ca.* 40% conversion after 55 days). The polymerisation with related alkyltin compounds such as  $\text{SnBu}_2(\text{OMe})_2$ ,  $\text{SnBu}(\text{OMe})_3$ ,  $(\text{Bu}_3\text{Sn})_2\text{O}$ ,  $(\text{Ph}_3\text{Sn})_2\text{O}$  or alkyldistannoxanes were also reported and showed activities comparable to those obtained with  $\text{SnBu}_3(\text{OMe})$ .<sup>35, 36, 53-55</sup> Kricheldorf and Eggerstedt reported the use of dialkyltin oxides ( $\text{Bu}_2\text{SnO}$ ,  $\text{Et}_2\text{SnO}$ ,  $\text{Oct}_2\text{SnO}$  and  $\text{Me}_2\text{SnO}$ ) in the ROP of *rac*-BBL at various temperatures.<sup>56</sup>  $\text{Bu}_2\text{SnO}$  and  $\text{Et}_2\text{SnO}$  showed superior activity to  $\text{Oct}_2\text{SnO}$  and  $\text{Me}_2\text{SnO}$  and produced moderately syndiotactic PHB with  $P_r = 0.58$ -0.72.

In 2006, Carpentier *et al.* presented yttrium amido complexes supported by dianionic alkoxy-amino-bisphenolate ligands (**5.14** and **5.15**, Figure 5.2).<sup>57, 58</sup> The corresponding alkoxide complexes (**5.16** and **5.17**, Figure 5.2) were generated *in situ* from **5.14** or **5.15** with 1 equiv. of  $i\text{PrOH}$ . All complexes converted 200-600 equiv. of *rac*-BBL within 1-60 min at 20 °C in toluene. The ROP of *rac*-BBL with **5.16** or **5.17** was more rapid than those with **5.14** or **5.15**. A strong solvent effect was observed as **5.16** polymerised 200 equiv. of *rac*-BBL in toluene or chlorobenzene to reach 97% conversion within 1 min, whereas polymerisation in THF took 2 h to reach 98% conversion. For ratios of  $[\textit{rac}\text{-BBL}]_0:[\textbf{5.16}]_0$  less than 600, the resultant PHB showed narrow  $D$  values (1.03-1.15) and good agreement between experimental and calculated  $M_n$  values for one growing chain per metal centre. However, the experimental  $M_n$  values were much lower than the those calculated for higher monomer loadings (1,000-2,000). Chain transfer reactions or poor correlation between polystyrene calibration and the actual  $M_n$  of PHB were hypothesised to cause the mismatch in  $M_n$ . Syndiotactically-enriched PHBs were produced with  $P_r = 0.81$ -0.94. At  $[\textit{rac}\text{-BBL}]_0:[\textbf{5.16}]_0 = 400$ , **5.17** showed less stereoselectivity giving syndiotactic PHB with  $P_r = 0.81$  compared to **5.16** ( $P_r = 0.89$ ) under analogous conditions, indicating the effect of ligand substituent on stereocontrol *via* chain-end control. The melting temperature ( $T_m$ ) of PHB analysed by DSC increased with the degree of syndioselectivity. The highest  $T_m$  value obtained from syndiotactic PHB ( $P_r = 0.94$ ) was 183 °C, slightly higher than that of pure isotactic PHB (180 °C).

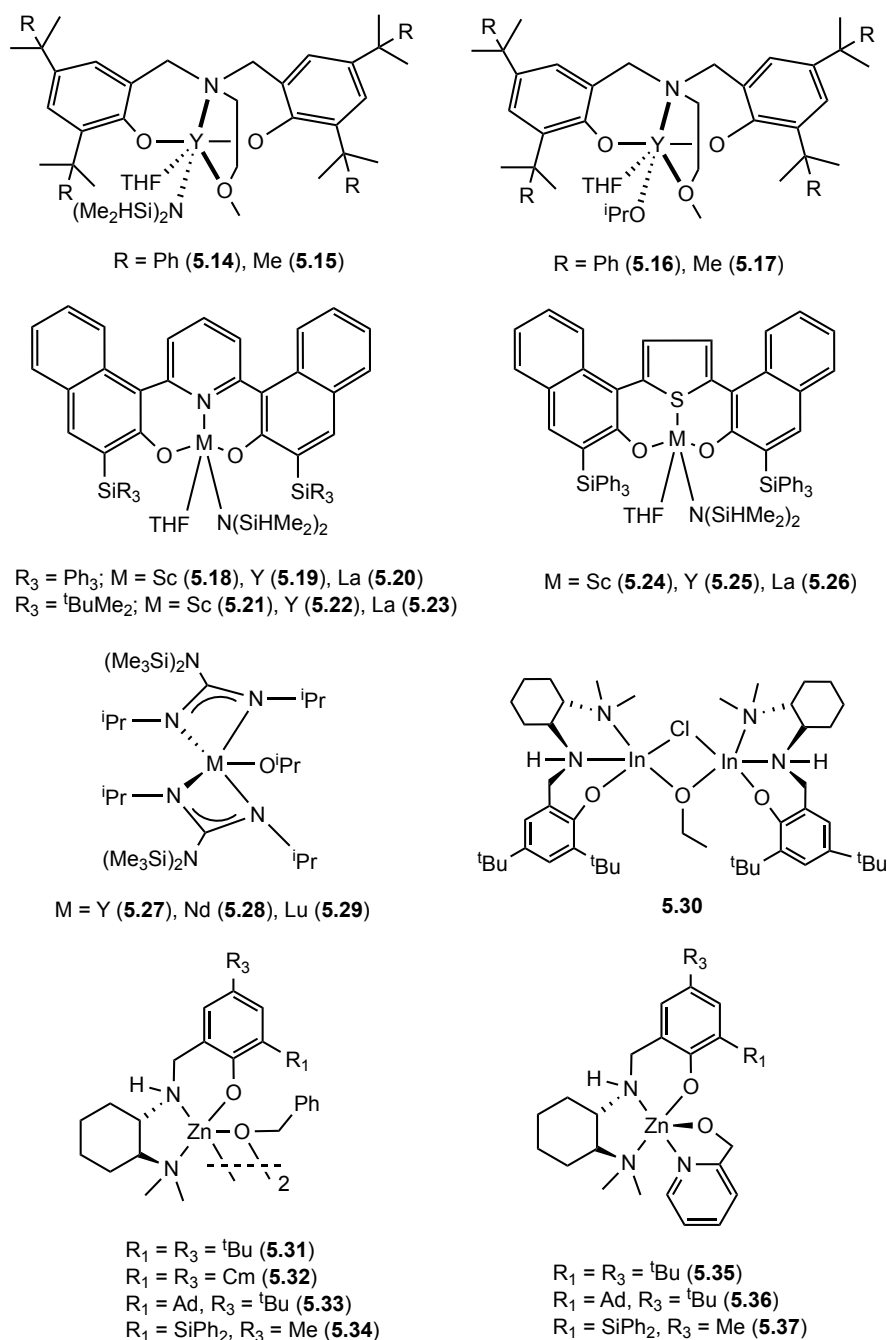


**Figure 5.2** Metal complexes as ROP of *rac*-BBL catalysts (**5.14-5.37**).<sup>33, 37, 58-60</sup>

Later in 2010 from Carpentier, a series of Group 3 metal amido complexes supported by silyl *ortho*-substituted tridentate 2,6-bis(naphtholate)pyridine including  $(\text{ONO}^{\text{SiPh}_3})\text{M}\{\text{N}(\text{SiHMe}_2)_2\}(\text{THF})$  ( $M = \text{Sc}$  (**5.18**),  $\text{Y}$  (**5.19**),  $\text{La}$  (**5.20**)) and  $(\text{ONO}^{\text{Si}^t\text{BuMe}_2})\text{M}\{\text{N}(\text{SiHMe}_2)_2\}(\text{THF})$  ( $M = \text{Sc}$  (**5.21**),  $\text{Y}$  (**5.22**),  $\text{La}$  (**5.23**)), and 2,5-bis(naphtholate)thiophene,  $(\text{OSO}^{\text{SiPh}_3})\text{M}\{\text{N}(\text{SiHMe}_2)_2\}(\text{THF})$  ( $M = \text{Sc}$  (**5.24**),  $\text{Y}$  (**5.25**),  $\text{La}$  (**5.26**)) was prepared by the corresponding pro-ligand  $(\text{OZO}^{\text{SiR}_3})\text{H}_2$  and  $\text{M}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{THF})_x$  precursor (Figure 5.2).<sup>37</sup> Complexes **5.18-5.26** were active

in the ROP of *rac*-LA in THF, affording heterotactically-enriched PLA ( $P_r = 0.65$ - $0.93$ ) with moderate  $\bar{D}$  values ( $1.32$ - $1.82$ ) and good agreement between experimental and calculated  $M_n$  values. Complexes **5.18-5.20** and **5.24-5.26** were also active in the ROP of *rac*-BBL at  $20$ - $50$  °C. Complex **5.26** showed the highest activity, reaching 92% conversion of 300 equiv. of *rac*-BBL after 6 h in toluene at RT. Most of the resulting PHBs showed good agreement between experimental and calculated  $M_n$ . However,  $M_n$  values larger than those calculated were observed at low  $[rac\text{-BBL}]_0:[\text{initiator}]_0$  ratios. Higher stereoselectivity was observed from PHBs prepared in toluene ( $P_r = 0.48$ - $0.87$ ) than those in THF ( $P_r = 0.46$ - $0.57$ ).

Carpentier and Trifonov reported a series of bis(guanidinate) alkoxide Group 3 metal complexes  $\{(\text{Me}_3\text{Si})_2\text{NC}(\text{N}^i\text{Pr})_2\}_2\text{M}(\text{O}^i\text{Pr})$  ( $\text{M} = \text{Y}$  (**5.27**),  $\text{Nd}$  (**5.28**),  $\text{Lu}$  (**5.29**), Figure 5.2).<sup>33</sup> Complexes **5.27** polymerised 100-400 equiv. of *rac*-BBL at  $20$  °C in toluene within 2-8 h, affording syndiotactically-enriched PHBs ( $P_r = ca.$   $0.80$ ) with moderate  $\bar{D}$  values ( $1.18$ - $1.27$ ) and higher than calculated  $M_n$  values. The degree of syndioselectivity was increased slightly to  $P_r = 0.84$  when the ROP was performed in THF. Atactic PHBs were obtained when  $\text{CH}_2\text{Cl}_2$  or hexane were used as a solvent. Complex **5.28** polymerised 100 equiv. of *rac*-BBL at  $20$  °C in toluene to reach 96% conversion within 2 h. Atactic PHB was formed with a narrow  $\bar{D}$  value ( $1.09$ ) and  $M_n$  close to that calculated. Complex **5.29** showed poor activity for the ROP of 100 equiv. of *rac*-BBL under analogous conditions, reaching 27% conversion after 14 h. However, the resultant PHB showed a high degree of syndiotacticity with  $P_r = 0.82$  with a moderate  $\bar{D}$  value ( $1.34$ ) and  $M_n$  close to that calculated.

Mehrkhodavandi *et al.* reported the dinuclear indium complex supported by a chiral diaminophenoxy ligand,  $\{(\text{NNO})\text{InCl}\}_2(\mu\text{-Cl})(\mu\text{-OEt})$  (**5.30**, Figure 5.2) for highly controlled immortal ROP of *rac*-BBL.<sup>60</sup> Complex **5.30** polymerised 200-5,000 equiv. of *rac*-BBL in THF at RT to reach full conversion after 21 h. High molecular weight PHBs were obtained ( $> 300,000 \text{ g mol}^{-1}$ ) with good agreement with calculated values and narrow  $\bar{D}$  values ( $1.02$ - $1.07$ ). The immortal ROP of *rac*-BBL using **5.30** with EtOH or mPEG as chain transfer agents produced PHB with close agreement between experimental and calculated  $M_n$  and very narrow  $\bar{D}$  values ( $1.01$ - $1.07$ ). No stereoselectivity was observed from **5.30**, giving atactic PHB.

Later in 2016, Mehrkhodavandi reported the formation of moderately syndiotactic PHBs from the ROP of *rac*-BBL catalysed by a series of dinuclear and mononuclear

zinc complexes supported by diaminophenolate ancillary ligands (Figure 5.2),  $[(\text{NN}_{\text{H}}\text{OR}_1)\text{Zn}(\text{OBn})]_2$  ( $\text{R}_1 = \text{'Bu}$  (**5.31**), cumyl (**5.32**), adamantyl (**5.33**),  $\text{SiPh}_3$  (**5.34**) and  $(\text{NN}_{\text{H}}\text{OR}_1)\text{Zn}(\text{OCH}_2\text{Pyr})$  ( $\text{R}_1 = \text{'Bu}$  (**5.35**), adamantyl (**5.36**),  $\text{SiPh}_3$  (**5.37**)).<sup>59</sup> Complex **5.31** was highly active in the polymerisation in  $\text{CH}_2\text{Cl}_2$  at RT. Full conversion of 400-3,000 equiv. of *rac*-BBL was reached within 1-30 min to form PHB with high molecular weights (up to  $140,000 \text{ g mol}^{-1}$ ) and moderate *D* values (1.17-1.34). Moderately syndiotactic PHBs were formed with  $P_r = 0.66$ -0.71. Complexes with bulkier substituents (**5.32**, **5.33** and **5.34**) were less active and formed slightly syndiotactic PHBs ( $P_r = 0.57$ -0.65) attributed to the effect of steric environment on the polymerisation activity. Complexes **5.35** and **5.36** showed similar behaviour, full conversion of 400 equiv. of *rac*-BBL being reached after 10 min forming PHBs with good agreement between experimental and calculated  $M_n$  and narrow *D* values (1.04-1.12). Slightly syndiotactic PHBs were obtained with  $P_r = 0.61$ -0.67. A reduction in rate and tacticity was also observed in the ROP using **5.37** as full conversion was reached after 60 min under analogous conditions giving partially syndiotactic PHB ( $P_r = 0.55$ ). The thermorheological properties of the high molecular weight and moderately syndiotactic PHBs showed good thermal stabilities and excellent melt strength demonstrating for the first time that PHB can be a processable thermoplastic.

### 5.2.3 Alkaline earth metal complexes as *rac*-BBL ROP catalysts

Despite the extensive studies of the ROP of *rac*-BBL catalysed by various metal complexes containing aluminium<sup>32, 49, 51, 61</sup>, tin<sup>35, 36, 52-56</sup>, yttrium<sup>37, 46, 57, 58, 62-64</sup>, indium<sup>60, 65</sup>, zinc<sup>39, 59, 66-68</sup>, transition metals<sup>34, 48, 69, 70</sup> and lanthanide metals<sup>22, 33, 37, 71</sup>, the use of alkaline earth metal complexes as ROP of *rac*-BBL catalysts is very rare. Only magnesium-based initiators have been reported for their activity in the polymerisation of *rac*-BBL.<sup>38, 66, 72</sup> To date, the ROP of *rac*-BBL with heavy alkaline earth metal (calcium, strontium or barium) complexes is unreported.

In 2007, Liu *et al.* reported the ROP of *rac*-BBL using dibutylmagnesium as an initiator.<sup>72</sup> Bulk polymerisations of *rac*-BBL with  $\text{Bu}_2\text{Mg}$  were performed at  $100^\circ\text{C}$  for 24 h. For  $[\textit{rac}\text{-BBL}]_0:[\text{Bu}_2\text{Mg}]_0 = 10, 50$  and  $100$ , conversions over 90% were obtained giving PHBs with experimental  $M_n$  greater than those calculated for one growing chain per metal centre with moderate *D* values (1.26-1.36). For [*rac*-

$\text{BBL}]_0:[\text{Bu}_2\text{Mg}]_0 = 200\text{--}400$ , conversions over 75% were reached giving PHBs with experimental  $M_n$  lower than those calculated with moderate  $D$  values (1.38–1.44) due to inter- and intramolecular transesterification reactions. Slightly syndiotactic PHBs were obtained with  $P_r = ca. 0.6$ . The kinetic behaviour was investigated from the ROP of 25, 50 or 100 equiv. of *rac*-BBL in toluene at 80 °C, giving first order dependence on concentrations of *rac*-BBL and  $\text{Bu}_2\text{Mg}$ . The polymer end-group analysis by  $^1\text{H}$  NMR showed PHB end capped by  $-\text{Bu}$  and  $-\text{OH}$  groups indicating a coordination-insertion pathway.

In 2010, Ko *et al.* prepared a magnesium butyl complex supported by a NNN-tridentate anilido-aldimine ligand,  $(\text{AA}^{\text{Pip}})\text{Mg}(\text{Bu})$  (**5.38**, Figure 5.3) by reaction of ((*E*)-2, 6-diisopropyl-N-(2-((2-(piperidin-1-yl)ethylimino)methyl)phenyl)aniline ( $\text{AA}^{\text{Pip}}\text{-H}$ ) and  $\text{Bu}_2\text{Mg}$ .<sup>66</sup> For  $[\text{5.38}]_0 = 0.01\text{ M}$ , **5.38** polymerised 100 equiv. of *rac*-BBL in the presence of 9-anthracenemethanol in toluene at 30 °C to reach 44% conversion after 6 h, whereas 33% conversion was reached after 6 h when THF was used as a solvent under analogous conditions. To improve the activity, the polymerisation was carried out in toluene at 30 °C with  $[\text{5.38}]_0 = 0.04\text{ M}$ . The conversion reached 76% within 16 h, affording PHB with  $M_n$  higher than calculated and a moderate  $D$  value (1.28). Complex **5.38** produced moderately syndiotactic PHBs with  $P_r = 0.60\text{--}0.69$ .

In 2016, Ma *et al.* prepared a series of magnesium silylamido complexes supported by NNO chiral aminophenolate ligands,  $(\text{NNO})\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}$  (**5.39–5.45**, Figure 5.3), and studied their catalytic activity towards the ROP of *rac*-LA and *rac*-BBL.<sup>38</sup> Complexes **5.39–5.45** initiated the ROP of 200 equiv. of *rac*-BBL in toluene at RT, resulting in PHBs with moderate  $D$  values (1.30–1.47) and high molecular weights (23,200–49,600  $\text{g mol}^{-1}$ ) that were much higher than those calculated. All complexes produced moderate syndiotactic PHB with  $P_r = 0.56\text{--}0.73$ . A solvent effect was observed when using **5.40** at RT. In toluene, 90% conversion was reached after 20 h for the ROP of 200 equiv. of *rac*-BBL affording PHB with  $P_r = 0.58$ . In THF, the stereoselectivity was invariant ( $P_r = 0.58$ ) whereas the polymerisation rate decreased (89% conversion in 30 h). The steric hindrance of the aminophenolate ligand also played a role in the catalytic performance for the ROP of *rac*-BBL. The less sterically hindered **5.39** showed the lowest activity (80% conversion within 48 h). The most active initiators are **5.41** and **5.42** featuring sterically demanding substituents



polymerised 200 equiv. of *rac*-BBL to 90% conversion after 19 h. A slight reduced rate was also observed in the ROP using **5.43-5.45** which could be attributed to the presence of bulky substituents in the coordination sphere of magnesium inhibiting the incoming monomer.

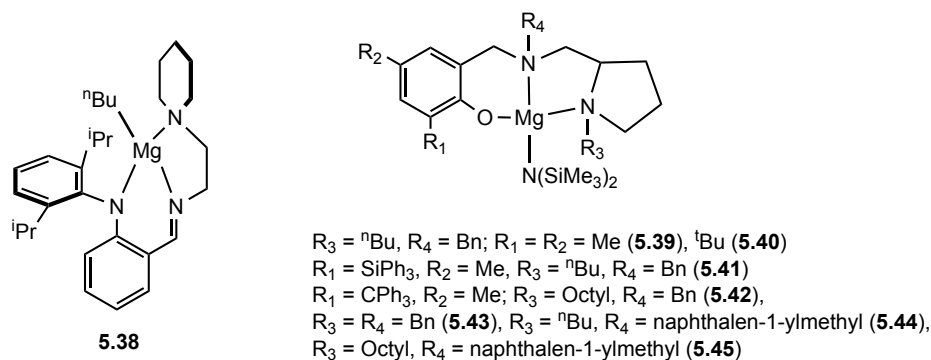
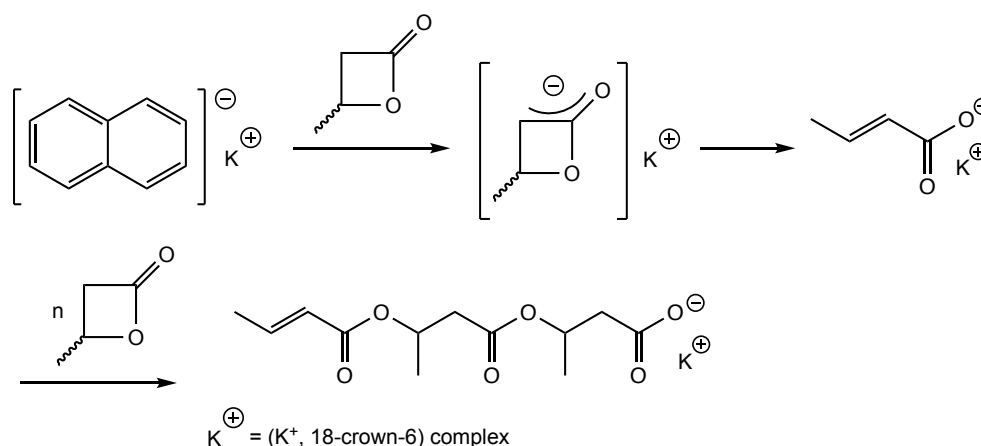


**Figure 5.3** Magnesium complexes as ROP of *rac*-BBL catalysts (**5.38-5.45**).<sup>38, 66</sup>

#### 5.2.4 Anionic ROP of *rac*-BBL

The anionic ROP of the four-membered lactone monomer takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon centre adjacent to the endocyclic ether oxygen followed by acyl-oxygen or alkyl-oxygen cleavages, resulting in alcoholate or carboxylate propagating species, respectively.<sup>15, 73</sup> In 1989, Kricheldorf and Scharnagl reported the anionic ROP of BBL using potassium benzoate, phenolate or *tert*-butylate.<sup>74</sup> The presence of a *trans*-crotonate ( $-\text{CH}=\text{CHMe}$ ) end group was observed from all PHB samples. In 1992, Jedlinski *et al.* reported the anionic ROP of BBL initiated by potassium naphthalenides in the presence of cations coordinated by polydentate ligands such as 18-crown-6 or cryptand.<sup>75</sup> More than 90% conversion of 40-150 equiv. of BBL was reached within 96-200 h. The resultant PHBs showed moderate  $\bar{D}$  values (1.22-1.29) with experimental  $M_n$  in good agreement with those calculated for one growing chain per potassium. Polymer end-group analysis by  $^1\text{H}$  NMR spectroscopy showed unsaturated *trans*-crotonate end groups suggesting carboxylate anions acting as propagating species. The proposed mechanism (Scheme 5.3) showed the formation of the lactone enolate due to  $\alpha$ -proton abstraction with the formation of dihydronaphthalene. The rearrangement of the cyclic enolate led to the corresponding carboxylate anion acting as an anionic initiator by nucleophilic attack on the BBL ring followed by alkyl-oxygen bond cleavage. *Trans*-crotonate end capped PHB was also

observed from the use of potassium hydride in the presence of 18-crown-6 complex<sup>76</sup>, sodium hydride<sup>77</sup> or N-heterocyclic carbene zinc adduct (NHC-Zn(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>)<sup>67</sup> as initiators for anionic ROP of *rac*-BBL.



**Scheme 5.3** Proposed mechanism for the anionic ROP of BBL using potassium naphthalenide.<sup>75</sup>

### 5.2.5 ROP of *rac*-BBL using tetrahydroborate initiators

In 2009, Carpentier and Trifonov prepared a series of yttrium tetrahydroborate and alkoxide complexes supported by dianionic bis(amide) ligand derived from the 1,4-diaza-1,3-butadiene (DAB) ligand, [(DAB)Y(BH<sub>4</sub>)<sub>2</sub>][Li(DME)<sub>3</sub>] (**5.46**) and (DAB)Y(O<sup>t</sup>Bu)(THF)(DME) (**5.47**) (Figure 5.4).<sup>40</sup> The ROP of *rac*-BBL was carried out in toluene at RT. Complex **5.46** polymerised 100 equiv. of *rac*-BBL to 61% conversion after 14 h, while **5.47** took 18 h to reach 67% conversion under analogous conditions. Both complexes produced atactic PHBs with moderate *D* values (1.18–1.25) and *M<sub>n</sub>* values in fair agreement with those calculated for one growing chain per metal centre. A conversion limitation was observed for **5.46**. The ROP of 200 equiv. of *rac*-BBL showed 41% conversion after 20 h, while only 14% conversion was reached after 48 h from the ROP of 500 equiv. of *rac*-BBL.

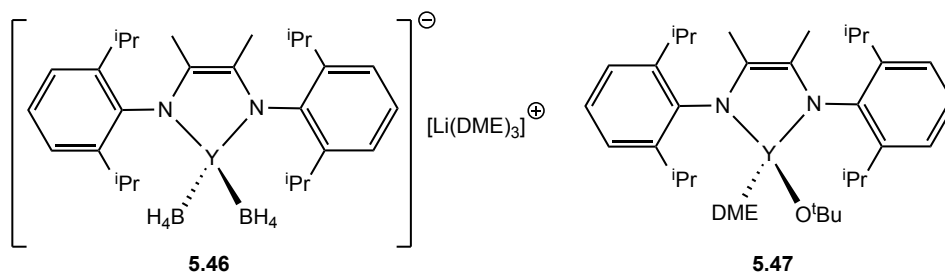


**Figure 5.4** Yttrium tetrahydroborate and alkoxide complexes (**5.46** and **5.47**) as ROP of *rac*-BBL catalysts reported by Carpentier and Trifonov.<sup>40</sup>

In 2010, Gauvin *et al.* reported the grafting of  $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$  (**5.48**) onto non-porous silica dehydroxylated at 700 °C ( $\text{SiO}_2$ -700) affording well-defined bis(tetrahydroborate) surface species,  $\text{SiO}_2$ -**5.48**.<sup>71</sup> Complex **5.48** produced atactic PHB with a moderate  $\bar{D}$  value (1.75), whereas  $\text{SiO}_2$ -**5.48** formed isotactically-enriched PHBs ( $P_m = 0.84$ -0.85). The ROP of 200 equiv. of *rac*-BBL using  $\text{SiO}_2$ -**5.48** was performed in toluene at RT, 75% conversion was reached after 24 h affording highly isotactic PHB ( $P_m = 0.85$ ). The resultant PHB showed a moderate  $\bar{D}$  value (1.18) and experimental  $M_n$  close to that calculated based on one growing polymer chain per metal centre, although the end groups of the PHB were not reported.

Later in 2011, Carpentier and Trifonov reported neodymium tetrahydroborate complexes supported by diamino-bis(phenoxide) (ONNO),  $[(\text{ONNO})\text{Nd}(\mu\text{-BH}_4)\text{Li}(\text{THF})]_2$  (**5.49**) and  $(\text{ONNO})\text{Nd}(\text{BH}_4)(\mu\text{-BH}_4)\text{Li}(\text{THF})_2$  (**5.50**) synthesised by reactions of  $\text{Nd}(\text{BH}_4)_3(\text{THF})_2$  with dilithium diamino-bis(phenolate)s  $\text{Li}_2(\text{ONNO})$  (Figure 5.5).<sup>78</sup> For the ROP of 100 equiv. of *rac*-BBL using **5.49**, 61% or 45% conversion was reached after 12 h when toluene or THF was used as a solvent, respectively, whereas **5.50** showed 24% conversion after 12 h with both solvents under analogous conditions. Both complexes produced atactic PHBs with close agreement between measured  $M_n$  and those calculated for one growing chain per metal centre, with narrow  $\bar{D}$  values (1.07-1.12).

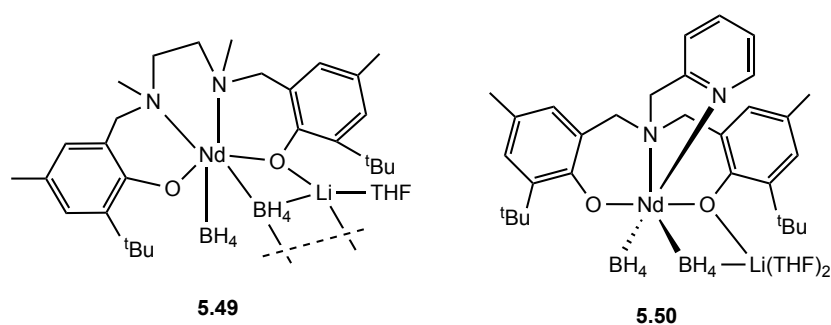
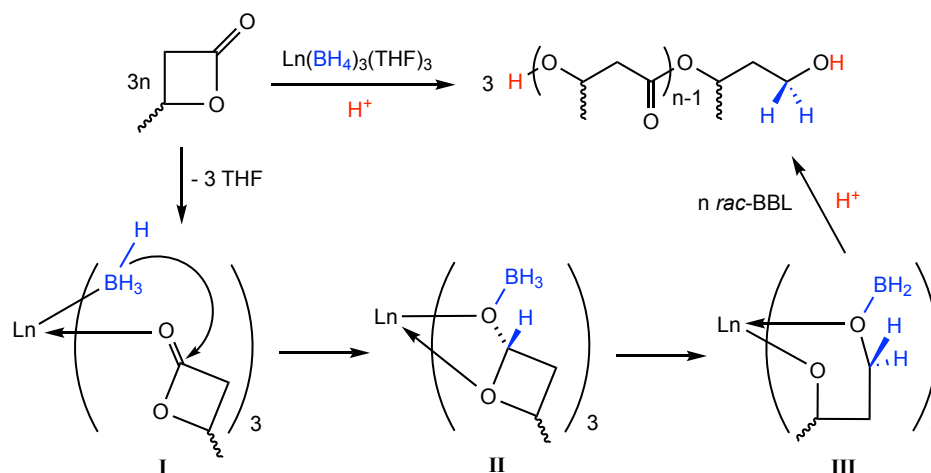


**Figure 5.5** Neodymium tetrahydroborate complexes (**5.49** and **5.50**) as ROP of *rac*-BBL catalysts reported by Carpentier and Trifonov.<sup>78</sup>

In 2013, Guillaume, Maron and Roesky reported the ROP of *rac*-BBL using Ln(BH<sub>4</sub>)<sub>3</sub>(THF)<sub>3</sub> (Ln = La (**5.51**), Nd (**5.52**) and Sm (**5.53**)).<sup>79</sup> The ROP of *rac*-BBL with **5.51-5.53** was carried out in toluene at RT with [*rac*-BBL]<sub>0</sub>: [BH<sub>4</sub>]<sub>0</sub> ratio = 100. All polymerisations reached full conversion after 23 h affording atactic PHBs with narrow *D* values (1.03-1.06) and *M<sub>n</sub>* values in close agreement with those calculated for one growing chain per Ln-BH<sub>4</sub> active site – *i.e.*, three chains per metal centre. An attempt to increase the ROP rate by increasing the temperature from RT to 60 °C was unsuccessful as less than 75% conversion was reached after 18 h under analogous conditions. At higher monomer loadings (200-300), all complexes converted 22-39% of *rac*-BBL after 48-92 h. The formation of α,ω-dihydroxytelechelic PHB was analysed from <sup>1</sup>H NMR and MALDI-ToF MS of low molecular weight PHB formed by **5.52**. Based on the experimental data, the proposed ROP mechanism (Scheme 5.4) showed the replacement of THF by *rac*-BBL during the initiation step giving Ln(BH<sub>4</sub>)<sub>3</sub>(*rac*-BBL)<sub>3</sub> (**I**) followed by hydride migration from BH<sub>4</sub> to the adjacent carbonyl carbon and the BH<sub>3</sub> transfer to the oxygen to form **II**. Then, the second hydride migrated to the same carbon and opened the *rac*-BBL ring affording **III**. The incoming monomers underwent enchainment by a coordination-insertion pathway generating a growing polymer chain on the metal centre terminated with –CHMeCH<sub>2</sub>CH<sub>2</sub>OBH<sub>2</sub>. The formation of α,ω-dihydroxytelechelic PHB was obtained after hydrolysis. DFT studies of the initiation step showed that the formation of alkoxyborane product with –CH<sub>2</sub>OBH<sub>2</sub> end group occurred *via* a kinetically accessible and thermodynamically favourable mechanism, supporting dihydroxy PHB formation.



**Scheme 5.4** Proposed DFT mechanism for the ROP of *rac*-BBL by  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$ .<sup>79</sup>

In the following section, the polymerisation study of *rac*-BBL with  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) as a catalyst is reported together with mechanistic investigations. Complex **22** was synthesised by  $\beta$ -hydride transfer using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{nBu})$  and benzaldehyde in benzene at RT for 4 h, and has previously been reported as a catalyst for the ROP of *rac*-LA.<sup>80</sup> Well-controlled ROP of *rac*-LA was obtained at RT with THF used as a solvent. With  $[\text{rac-LA}]_0:[\text{22}]_0 = 100$ , 86% conversion was reached after 17 h. PLA with a narrow  $\bar{D}$  value (1.10) and close agreement between  $M_n(\text{GPC})$  ( $13,540 \text{ g mol}^{-1}$ ) and that calculated ( $12,500 \text{ g mol}^{-1}$ ) for one chain per metal centre was observed. Moderately heterotactic PLA was produced with  $P_r = 0.61$ .

Preliminary studies of the ROP of *rac*-BBL were carried out by using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**) as a catalyst. Keeping the initial *rac*-BBL concentration constant at 0.5 M, **1** showed no activity with  $[\text{rac-BBL}]_0:[\text{1}]_0 = 800$  either in toluene- $d_8$  or THF- $d_8$  at RT after 90 h. At  $[\text{rac-BBL}]_0:[\text{1}]_0 = 300$ , only 34% conversion was reached after 24 h in toluene- $d_8$ . A solvent effect on the polymerisation rate was observed for ROP with  $[\text{rac-BBL}]_0:[\text{1}]_0 = 100$ . Full conversion was reached within 10 min in toluene- $d_8$ , whereas 53% conversion was observed after 6.5 h in THF- $d_8$  under analogous conditions. Therefore, all polymerisation studies of *rac*-BBL described in the following sections were performed in toluene or toluene- $d_8$  at RT.

### 5.3 ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**)

Kinetic analysis of the ROP of 100 equiv. of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**) in toluene-*d*<sub>8</sub> was carried out by <sup>1</sup>H NMR spectroscopy at RT, reaching 87% conversion after 48 h. First order dependence on *rac*-BBL concentration was observed with  $k_{\text{app}} = 0.0426(6) \text{ h}^{-1}$  ( $R^2 = 0.999$ ), as judged by a linear plot of  $\ln([rac\text{-BBL}]_0/[rac\text{-BBL}]_t)$  vs. time (Figure 5.6).

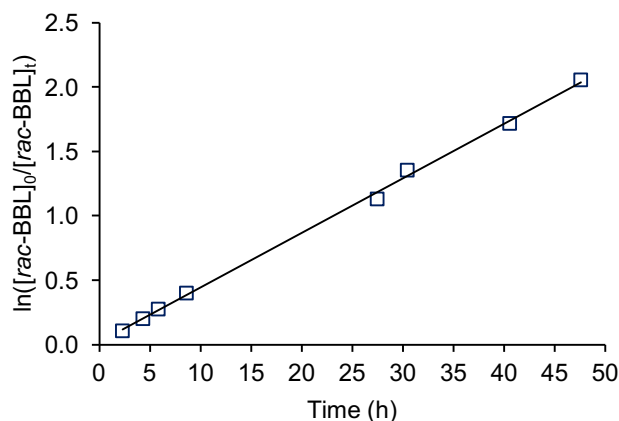


**Figure 5.6** Plot of  $\ln([rac\text{-BBL}]_0/[rac\text{-BBL}]_t)$  vs. time. Conditions: 0.5 mL toluene-*d*<sub>8</sub>, RT,  $[rac\text{-BBL}]_0 = 0.5 \text{ M}$ .  $[rac\text{-BBL}]_0:[\mathbf{22}]_0 = 100:1$ . The ROP of *rac*-BBL shows  $k_{\text{app}} = 0.0426(6) \text{ h}^{-1}$  ( $R^2 = 0.999$ ).

The parallel polymerisation was carried out in toluene (3.0 mL) under analogous conditions including concentrations of *rac*-BBL or **22**, monomer loading, temperature and polymerisation time (Table 5.1, entry 1). The theoretical  $M_n$  value of the isolated PHB was calculated based on monomer conversion (87 %) determined by the <sup>1</sup>H NMR spectrum of the ROP of *rac*-BBL with **22** in toluene-*d*<sub>8</sub> recorded after 48 h (*vide supra*) due to high volatility of *rac*-BBL ( $T_b = 71\text{--}73 \text{ }^\circ\text{C}$ ).<sup>81</sup> The experimental  $M_n$  values determined by <sup>1</sup>H NMR analysis and GPC of the isolated PHB were in good agreement with those calculated for one growing chain per metal centre, together with a very narrow  $\mathcal{D}$  value (1.04). Atactic PHB was formed with  $P_r = 0.52$ . The microstructure of PHB was analysed by <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy. According to the literature, the upfield and downfield signals in the carbonyl region were assigned to the meso (*m*) diad sequences (*R-R* or *S-S*) and the racemic (*r*) diad sequences (*R-S* or *S-R*), respectively.<sup>52</sup> Therefore,  $P_r$  is calculated from the relative integration of the downfield signal to the total carbonyl region (Figure A8).

**Table 5.1** Selected data for the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**).<sup>a</sup>

| Entry | Ratio <sup>b</sup> | Time<br>(h) | $M_n$ (GPC) <sup>c</sup><br>(g mol <sup>-1</sup> ) | $M_n$ (calcd) <sup>d</sup><br>(g mol <sup>-1</sup> ) | $M_n$ (NMR) <sup>e</sup><br>(g mol <sup>-1</sup> ) | $\bar{D}$ <sup>f</sup> | $P_r$ <sup>g</sup> |
|-------|--------------------|-------------|----------------------------------------------------|------------------------------------------------------|----------------------------------------------------|------------------------|--------------------|
| 1     | 100                | 48          | 8,000                                              | 7,597                                                | 7,529                                              | 1.04                   | 0.52               |
| 2     | 20                 | 6           | 1,840                                              | 1,520                                                | 1,615                                              | 1.07                   | <sup>h</sup>       |

<sup>a</sup> Conditions: [*rac*-BBL]<sub>0</sub> = 0.5 M, 3.0 mL toluene at RT. <sup>b</sup> Ratio = [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub>. <sup>c</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 18.32 μL g<sup>-1</sup> and α = 0.69. <sup>d</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OBn end groups,  $M_n$  (entry 1) = 0.87 × [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub> × 86.1 + 108.1,  $M_n$  (entry 2) = 0.82 × [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub> × 86.1 + 108.1. <sup>e</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated PHB by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>, δ = 5.25 ppm) and those of the chain-end methylene protons (OCH<sub>2</sub>Ph, δ = 5.11 ppm). <sup>f</sup>  $\bar{D} = M_w/M_n$ . <sup>g</sup>  $P_r$  is determined by carbonyl region of inverse gated <sup>13</sup>C{<sup>1</sup>H} NMR spectra. <sup>h</sup> Not measured.

The monomer loading was decreased to 20 equiv. of *rac*-BBL (by increasing **22**<sub>0</sub> from 0.005 M to 0.025 M) and the kinetic analysis was monitored by <sup>1</sup>H NMR spectroscopy with decay of *rac*-BBL measured by integration. 82% conversion was reached after 6 h and the reaction followed first order dependence on [*rac*-BBL] with  $k_{app} = 0.2409(6) \text{ h}^{-1}$  ( $R^2 = 0.998$ , Figure A6). The resultant PHB showed good agreement between measured  $M_n$  values from <sup>1</sup>H NMR or GPC with calculated  $M_n$ , and a narrow  $\bar{D}$  value (1.07) (Table 5.1, entry 2). Assuming first order dependence on **22**, the propagation rate constants ( $k_p$ ) for the ROP of *rac*-BBL with **22**<sub>0</sub> = 0.005 and 0.025 M equal to 8.52 and 9.64 M<sup>-1</sup>h<sup>-1</sup>, respectively.

Polymer end-group analysis by MALDI-ToF mass spectrometry (Figure 5.7) showed a major distribution of peak envelopes corresponding to PHB with –OBn and –OH end groups. For instance, the peak envelope centred at 1336.2 Da corresponds to PHB with –OBn and –OH termini containing 14 monomer units with Na<sup>+</sup> [86.1(14) + 108.1 + 23.0]. However, a very minor distribution of peak envelopes corresponding to PHB terminated with –OBn and *trans*-crotonate (–CH=CHMe) end groups was observed. For example, the peak envelope centred at 801.6 Da corresponds to PHB end capped with *trans*-crotonate and –OBn containing 7 monomer units with Na<sup>+</sup> [86.1(7) + 107.1 + 69.0 + 23.0]. The <sup>1</sup>H NMR spectrum of isolated PHB formed using **22** (Figure 5.8) shows signals at 5.11 and 4.18 ppm corresponding to methylene protons of OCH<sub>2</sub>Ph and methine proton of CHMeOH end groups, respectively. The presence of PHB terminated with *trans*-crotonate and –OBn end groups were also observed from the <sup>1</sup>H NMR spectra of crude and isolated PHBs with the relative integration ratios of the protons in the *trans*-crotonate (–CH=CHMe) and the hydroxyl end group (–CHMeOH) = 0.1:1 and 0.05:1, respectively (Figures A4 and A5).

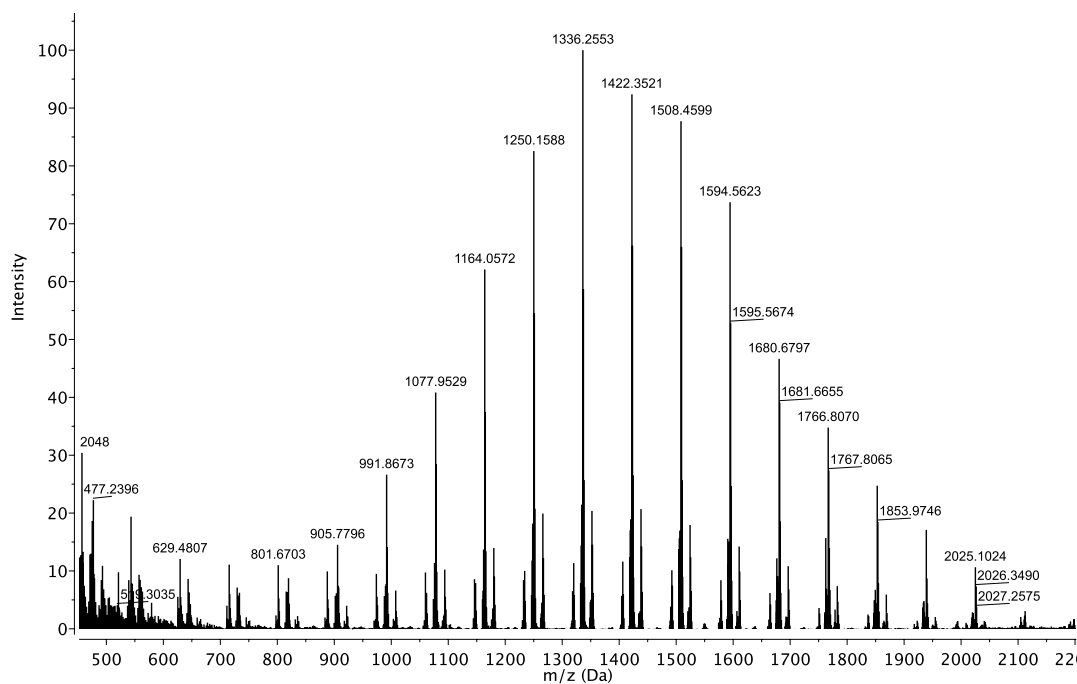


**Figure 5.7** MALDI-ToF MS of PHB synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**).  $M_n(\text{GPC}) = 1,840 \text{ g mol}^{-1}$ ,  $D = 1.07$ . Conditions:  $[\text{rac-BBL}]_0:[\text{22}]_0 = 20:1$ ,  $[\text{rac-BBL}]_0 = 0.5 \text{ M}$ , 1.0 mL toluene at RT.  $\text{Na}^+$  dopant.  $\Delta(m/z) = 86.1 \text{ Da}$  between peak envelopes.

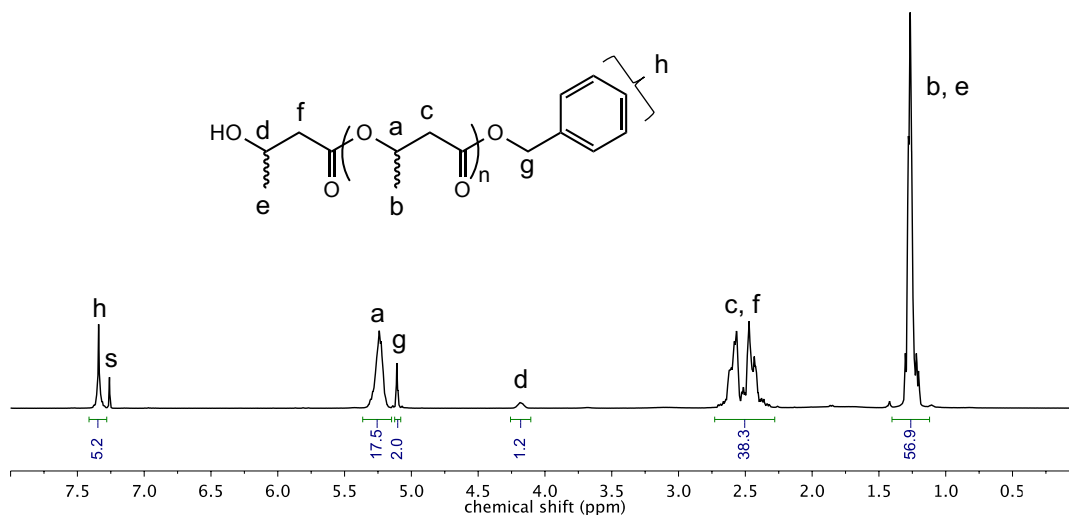


**Figure 5.8**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PHB synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**). Conditions:  $[\text{rac-BBL}]_0:[\text{22}]_0 = 20:1$ ,  $[\text{rac-BBL}]_0 = 0.5 \text{ M}$ , 1.0 mL toluene at RT for 6 h.  $M_n(\text{NMR})$  for  $-\text{OH}$  and  $-\text{OBn}$  end groups =  $1,615 \text{ g mol}^{-1}$  “s” denotes residual protio-solvent.



### 5.4 Mechanistic investigations of ROP of *rac*-BBL using $\text{Tp}^{\text{tBu,Me}}\text{Mg}(\text{OBn})$ (**22**)

As the ROP of *rac*-BBL by metal-based complexes could occur *via* coordination-insertion or anionic mechanism,<sup>20, 82</sup> an NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) with 1 equiv. of *rac*-BBL was carried out in toluene- $d_8$  at RT to investigate the ROP mechanism. The  $^1\text{H}$  NMR spectrum recorded after 4 h (Figure 5.9) shows that all *rac*-BBL monomer was consumed, and the mono-insertion product  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}\}$  (**22.1**) was formed with the absence of signals corresponding to oligomers. This is indicative of a higher initiation than propagation rate for the ROP of *rac*-BBL with **22**.<sup>20</sup> The  $\kappa^2$ -coordination of the initiated chain (**22.1**) indicated in Figure 5.9 was supported by DFT calculations (*vide infra*).

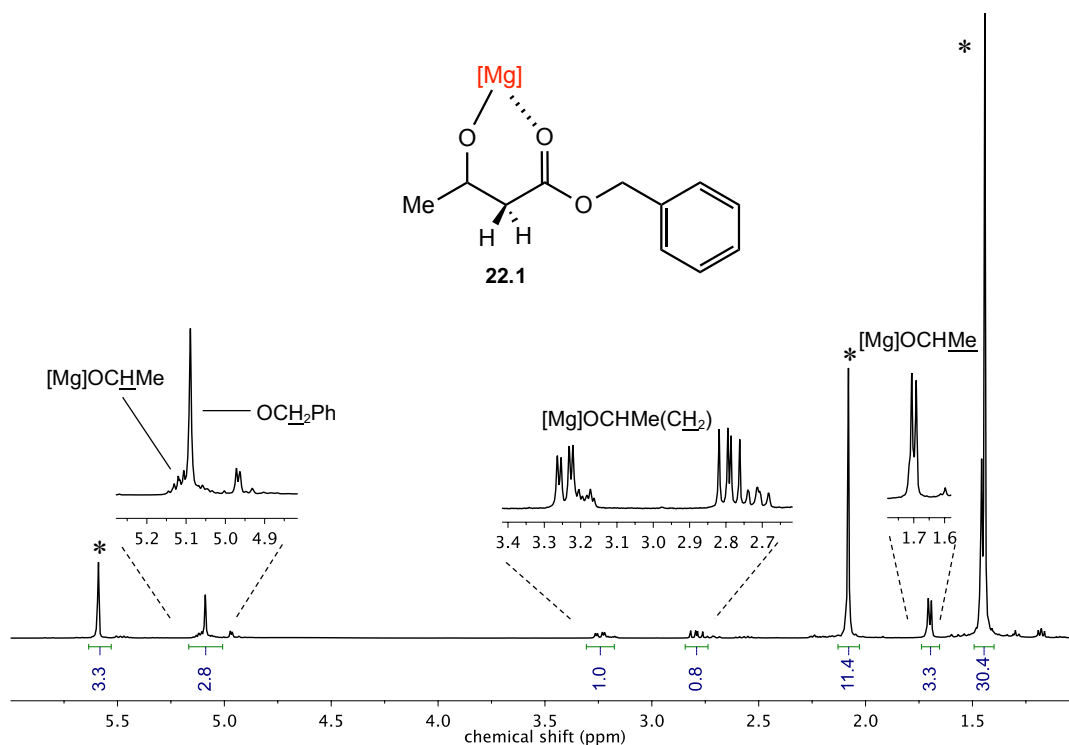


**Figure 5.9**  $^1\text{H}$  NMR spectrum (toluene- $d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) with 1 equiv. of *rac*-BBL recorded after 4 h. “\*” denotes  $\text{Tp}^{\text{tBu,Me}}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}\}$  (**22.1**).  $[\text{Mg}] = (\text{Tp}^{\text{tBu,Me}})\text{Mg}$ .

The  $^{11}\text{B}$  NMR spectrum recorded after 4 h showed a signal at -9.3 ppm corresponding to the apical B-H of the  $\text{Tp}^{\text{tBu,Me}}$  ligand. The ROESY NMR recorded after 4 h showed through-space correlations between *tert*-butyl of the  $\text{Tp}^{\text{tBu,Me}}$  ligand with all protons on the ring-opened *rac*-BBL unit coordinated to Mg, and methylene protons of -OBn

moiety. The  $^1\text{H}$  NMR spectrum of reaction of **22** with 20 equiv. of *rac*-BBL recorded after 4 h (Figure 5.10) shows signals corresponding to the growing polymer chain on the metal centre  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C(O)(BBL)}_{15}\text{OBn}\}$  (**22.2**). The characteristic signals of the ring-opened *rac*-BBL chelating to Mg are also observed which are analogous to those of **22.1**. Therefore, the NMR spectroscopic data strongly suggests that the polymerisation with **22** proceeds *via* coordination-insertion mechanism. The  $\kappa^2$ -coordination of the growing polymer chain in **22.2** is supported by DFT calculations on a model compound (*vide infra*).

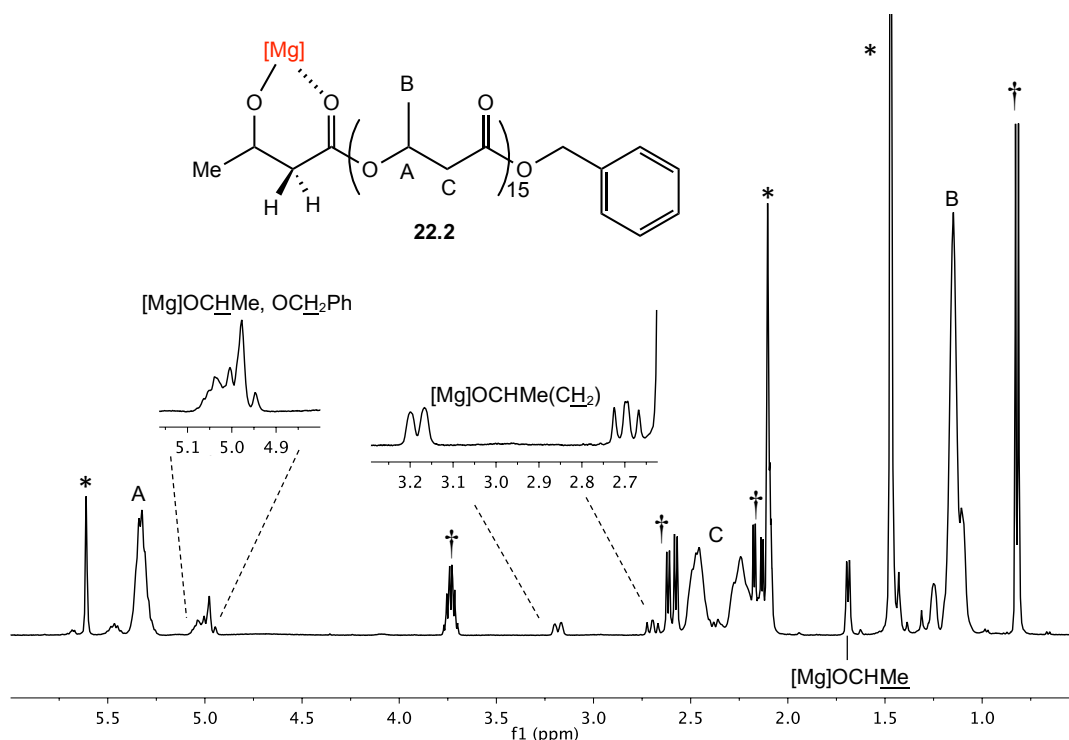


**Figure 5.10**  $^1\text{H}$  NMR spectrum (toluene- $d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) with 20 equiv. of *rac*-BBL recorded after 4 h. “\*” denotes  $\text{Tp}^{\text{tBu,Me}}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C(O)(BBL)}_{15}\text{OBn}\}$  (**22.2**). “+” denotes unreacted *rac*-BBL.  $[\text{Mg}] = (\text{Tp}^{\text{tBu,Me}})\text{Mg}$ .

#### 5.4.1 DFT calculations for the reaction of $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$ (**22**) with (*R*)-BBL

A number of DFT calculations were carried out by Professor Philip Mountford to explore aspects of the reactions of BBL with  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) (discussed later on). The calculations were carried out at the B3PW91 level of theory with corrections for solvent and dispersion effects. Full details are provided in Chapter Six. Throughout this chapter, DFT computed

structures based on experimentally observed species carry a suffix of the type ‘Q’ (denoting quantum chemical calculations). Other DFT species are labelled using letters (‘A’, ‘B’, etc.). Detailed reaction mechanisms have not been calculated, the focus being on the geometries and relative energies of key intermediates, as well as a comparison of computed and experimental  $^{11}\text{B}$  NMR shifts. For simplicity, BBL-derived structures based only on *R*-stereocentres are considered.

Experimentally,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) reacts with 1 equivalent of BBL forming  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}\}$  (**22.1**). Optimisation of the DFT structure of this product (as **22.1Q**) found the geometry illustrated in Figure 5.11 (left). **22.1Q** contains a  $\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}$  moiety coordinated through the alkoxide chain end and the carbonyl oxygen of the internal ester group. The geometry at magnesium is distorted trigonal bipyramidal with the chain end oxygen in an equatorial position and the carbonyl oxygen axial, approximately *trans* to one of the pyrazolyl nitrogens. A four-coordinate analogue of **22.1Q** was also computed, possessing a  $\kappa^1\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}$  ligand. This was found to be  $+2.8\text{ kcal mol}^{-1}$  less stable than **22.1Q**.

Experimentally, the species  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})(\text{BBL})_n\text{OBn}\}$  (**22.2**) with a growing polymeryl chain was observed by NMR spectroscopy. A homologue of this compound was computed containing two opened BBL monomer units, namely  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-}\{\text{OCHMeCH}_2\text{C}(\text{O})\}_2\text{OBn}\}$  (**22.2Q'**) which has the geometry shown in Figure 5.11 (right). Like the first insertion product, **22.1Q**, the nascent growing chain in **22.2Q'** is coordinated in an analogous  $\kappa^2$  manner.

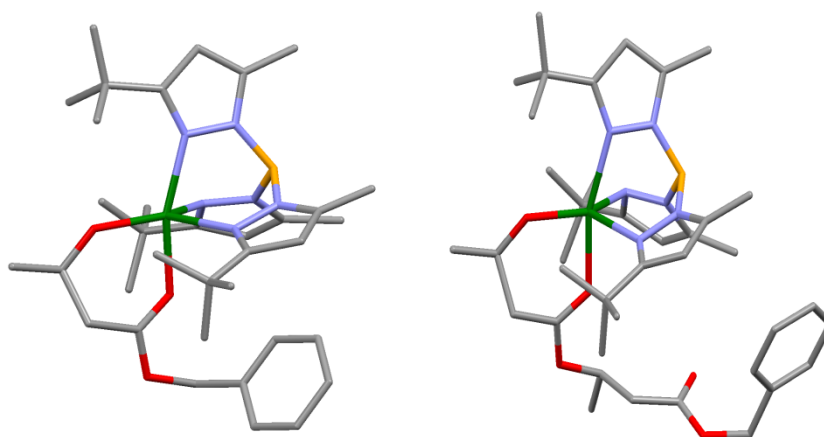


**Figure 5.11.** DFT structures of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C(O)OBn}\}$  (**22.1Q**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-}\{\text{OCHMeCH}_2\text{C(O)}\}_2\text{OBn}\}$  (**22.2Q'**).

The Gibbs free energies ( $\Delta_r G$ ) of the first and second insertion reactions were also computed. For the reaction of **22Q** with BBL to form **22.1Q**,  $\Delta_r G = -6.6 \text{ kcal mol}^{-1}$ , indicating an energetically favourable process as expected. For the second insertion reaction (**22.1Q** + BBL  $\rightarrow$  **22.2Q'**),  $\Delta_r G = -5.0 \text{ kcal mol}^{-1}$ , rather similar to the first insertion. As mentioned, a detailed mechanistic analysis of this reaction (especially with respect to transition state energies) was beyond the scope of this present study.

#### 5.4.2 Side reactions for the ROP of *rac*-BBL using $\text{Tp}^{\text{tBu,Me}}\text{Mg}(\text{OBn})$ (**22**)

As the MALDI-ToF mass spectrum (Figure 5.7) and the  $^1\text{H}$  NMR spectra (Figures A4 and A5) of PHBs showed a minor distribution of PHB terminated with  $-\text{OBn}$  and *trans*-crotonate ( $-\text{CH}=\text{CHMe}$ ), further investigation was carried out to study the effect of variables such as time or temperature on the formation of *trans*-crotonate end group. Previous studies on the ROP of *rac*-BBL by various metal alkoxide complexes such as zinc,<sup>20, 83</sup> aluminium,<sup>18</sup> tin,<sup>17, 84, 85</sup> Group 3 metals (scandium or yttrium)<sup>22, 46</sup> and magnesium<sup>72</sup> have shown similar behaviour. The most common explanation for the formation of the unsaturated end group has been the elimination reaction of polymer chain occurred at the termination step leading to the formation of metal hydroxide species and PHB with a *trans*-crotonate end group. Four mechanisms were proposed for the elimination reaction.<sup>86</sup>

To further support the elimination reaction promoted by **22**, the reaction of **22** with 20 equiv. of *rac*-BBL in toluene- $d_8$  was monitored by  $^1\text{H}$  NMR at 353 K and the spectra were recorded every 5 min for 12 h. Full conversion (99%) of 20 equiv. of *rac*-BBL

to PHB was reached within 1 h. As shown in Figure 5.12, the decay of *rac*-BBL was observed to follow first order dependence on concentration of *rac*-BBL, evidenced by a linear semi-logarithmic plot of  $\ln([rac\text{-BBL}]_0/[rac\text{-BBL}]_t)$  vs. time ( $k_{app} = 4.20(16) \text{ h}^{-1}$ ,  $R^2 = 0.987$ ).

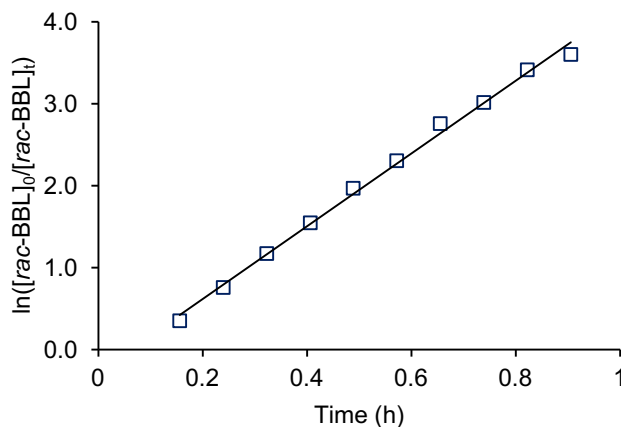


**Figure 5.12** Plot of  $\ln([rac\text{-BBL}]_0/[rac\text{-BBL}]_t)$  vs. time. Conditions: 0.5 mL toluene- $d_8$ , 353 K,  $[rac\text{-BBL}]_0 = 0.5 \text{ M}$ .  $[rac\text{-BBL}]_0:[\mathbf{22}]_0 = 20:1$ . The ROP of *rac*-BBL shows  $k_{app} = 4.20(16) \text{ h}^{-1}$  ( $R^2 = 0.987$ ).

The  $^1\text{H}$  NMR spectrum recorded after 1 h (Figure 5.13, a) showed signals corresponding to the growing polymer chain coordinated to the metal centre (**22.2**) with the absence of any significant amount of *trans*-crotonate end group. The  $^1\text{H}$  NMR spectra recorded after 3.5, 4.5 and 12 h (Figure 5.13, b-d) show the formation of free PHB terminated with a *trans*-crotonate end group, confirmed by a multiplet at 6.83 ppm (\*) assigned to the methine proton of  $\text{CH}=\text{CHMe}$ . In contrast, the signals corresponding to **22.2** were diminished over 12 h confirmed by a disappearance of the doublet at 3.11 ppm (\*) of one methylene proton of  $\text{MgOCHMeCH}_2$  of **22.2** (Figure 5.13, d).

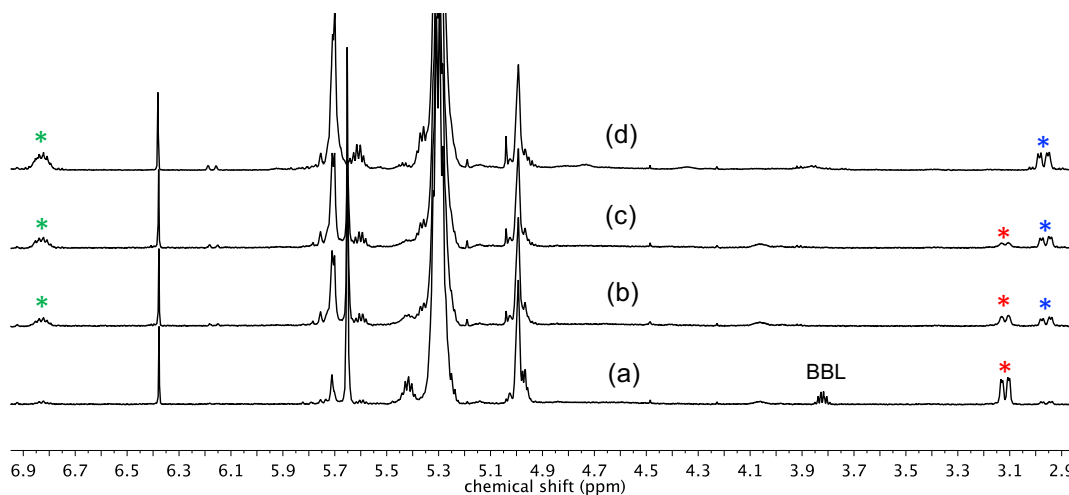


**Figure 5.13**  $^1\text{H}$  NMR spectra (toluene- $d_8$ , 499.9 MHz, 353 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) with 20 equiv. of *rac*-BBL recorded after 1 h (a), 3.5 h (b), 4.5 h (c) and 12 h (d). “\*” denotes the methine proton of  $\text{CH}=\text{CHMe}$ . “\*” denotes one methylene proton of  $\text{MgOCHMeCH}_2$  of **22.2**. “\*” denotes one methylene proton of new species (**22.3**). “BBL” denotes unreacted *rac*-BBL.

The results supported the hypothesis that the polymeryl species undergoes a crotonate elimination reaction *post*-polymerisation, resulting in the formation of PHBs end capped with a *trans*-crotonate group. The formation of magnesium hydroxide species  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OH})$  was anticipated as a result of this elimination reaction.<sup>72</sup> Interestingly, the  $^1\text{H}$  NMR spectrum recorded after 3.5 h (Figure 5.13, b) showed a decreased signal corresponding to the methylene proton of  $\text{MgOCHMeCH}_2$  of **22.2** (\*,  $\delta = 3.11$  ppm) with an increasing signal corresponding to the methylene proton of a new species (**22.3**) formed by the crotonate elimination reaction (\*,  $\delta = 2.94$  ppm). Instead of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OH})$  formed from elimination, the NMR data suggest that a different elimination reaction occurs leading to the formation of a Mg-carboxylic acid species which then rearranges to form the Mg-carboxylate species  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-O}_2\text{CCH}_2\text{CHMeOH}\}$  (**22.3**). DFT calculations in support of the formation of **22.3** as opposed to  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OH})$  are described below. The assignment for **22.3** is described in Figure 5.14 which shows the same  $^1\text{H}$  NMR spectrum as in Figure 5.13 (b) supported by COSY and HSQC. This hypothesis is supported by the PHB depolymerisation by  $\text{CaCl}_2$  or  $\text{MgCl}_2$  reported by Abe *et al.*<sup>87</sup> The Lewis acidity of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  facilitated the  $\beta$ -hydrogen elimination by interacting with carboxyl group yielding oligomers with *trans*-crotonate end group.

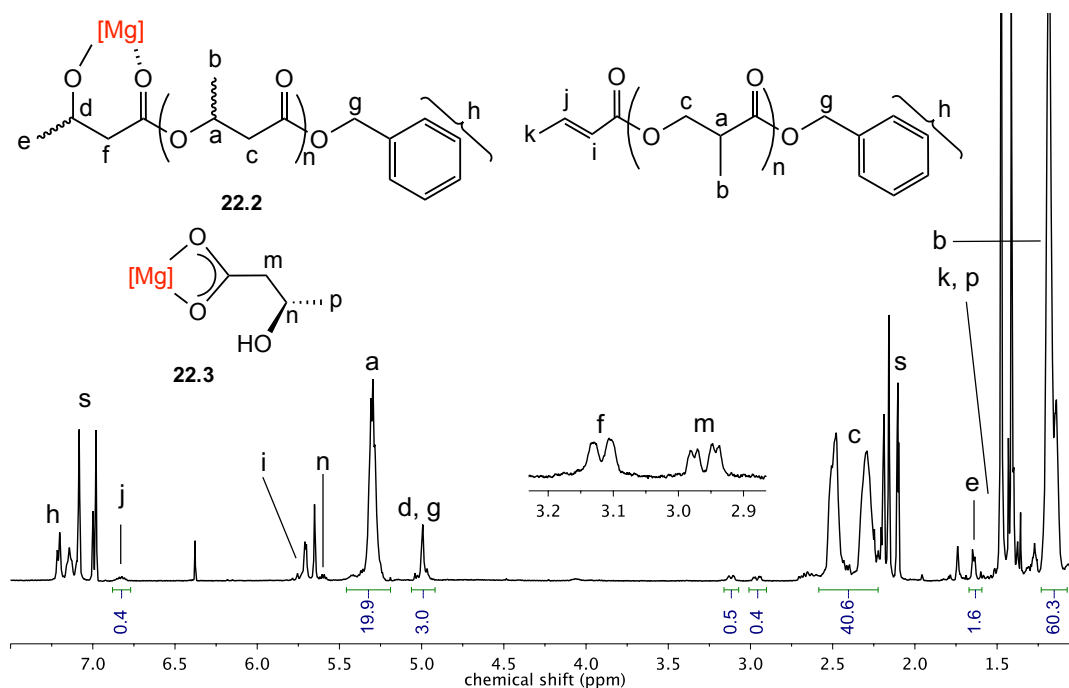


**Figure 5.14**  $^1\text{H}$  NMR spectrum (toluene- $d_8$ , 499.9 MHz, 353 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) with 20 equiv. of *rac*-BBL recorded after 3.5 h. “f” denotes one methylene proton ( $\text{MgOCHMeCH}_2$ ) of the **22.2**. “m” denotes one methylene proton ( $\text{MgO}_2\text{CCH}_2$ ) of **22.3**.  $[\text{Mg}] = (\text{Tp}^{\text{tBu,Me}})\text{Mg}$ . “s” denotes residual protio solvent.

In order to evaluate the formation of the *trans*-crotonate terminated PHB, polymerisations using **22** were carried out in toluene at 80 °C for 1 h and 12 h (Table 5.2, entry 2 and 3). Complex **22** took 6 h to convert 20 equiv. of *rac*-BBL in toluene at RT giving PHB with –OBn and –OH end groups (Table 5.2, entry 1).

**Table 5.2** Selected data for the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**).<sup>a</sup>

| Entry | Temp.<br>(°C) | Time<br>(h) | $M_n(\text{GPC})^b$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{NMR})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | Conv.<br>(%)      | $k_{\text{app}}^h$<br>(h <sup>-1</sup> ) | $R^{2h}$     | Ratio <sup>i</sup> |
|-------|---------------|-------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------|-------------------|------------------------------------------|--------------|--------------------|
| 1     | 25            | 6           | 1,840                                         | 1,520                                           | 1,615                                         | 1.07        | 82 <sup>f</sup>   | 0.2409(6)                                | 0.998        | 0.05:1             |
| 2     | 80            | 1           | 1,940                                         | 1,830                                           | 1,684                                         | 1.10        | > 99 <sup>g</sup> | 4.63(6)                                  | 0.999        | 0.15:1             |
| 3     | 80            | 12          | 1,730                                         | 1,830                                           | 1,820                                         | 1.15        | > 99 <sup>g</sup> | <sup>j</sup>                             | <sup>j</sup> | 1.5:1              |

<sup>a</sup> Conditions: [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub> = 20:1, [*rac*-BBL]<sub>0</sub> = 0.5 M in 3.0 mL toluene. <sup>b</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 18.32 μL g<sup>-1</sup> and α = 0.69. <sup>c</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OBn end groups,  $M_n$  (entry 1-3) = conv. (%) × [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub> × 86.1 + 108.1. <sup>d</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated polymer by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>, δ = 5.25 ppm) and those of the chain-end methylene protons (OCH<sub>2</sub>Ph, δ = 5.11 ppm). <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Condition: [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub> = 20:1, [*rac*-BBL]<sub>0</sub> = 0.5 M in 0.5 mL toluene-*d*<sub>8</sub> in an NMR tube at 298 K for 6 h. <sup>g</sup> Condition: [*rac*-BBL]<sub>0</sub>:**22**<sub>0</sub> = 20:1, [*rac*-BBL]<sub>0</sub> = 0.5 M in 0.5 mL toluene-*d*<sub>8</sub> in an NMR tube at 353 K. Polymerisation was followed to > 99% conversion at 353 K after 1 h and the reaction was continued for 11 h at 353 K. <sup>h</sup> Apparent first order rate constant for consumption of monomer with standard error and  $R^2$  determined by linear regression analysis. <sup>i</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated PHB from the relative integration ratio of vinyl proton of *trans*-crotonate end group (–CH=CHMe, δ = 6.92 ppm) : methine proton adjacent to –OH end group (–CHMeOH, δ = 4.17 ppm). <sup>j</sup> Not measure



Full conversion was reached after 1 h for the ROP of *rac*-BBL with **22** performed in toluene at 80 °C (Table 5.2, entry 2). The resulting PHB showed fair agreement between measured  $M_n$  values from GPC or  $^1\text{H}$  NMR and those calculated for one growing polymer chain per metal centre, and a narrow  $D$  value (1.10).

The  $^1\text{H}$  NMR spectrum of isolated PHB formed using **22** at 80 °C for 1 h showed the presence of *trans*-crotonate chain ends with the relative integration ratio of the protons in the *trans*-crotonate group ( $-\text{CH}=\text{CHMe}$ ) and the hydroxyl end group ( $-\text{CHMeOH}$ ) = 0.15:1 (Table 5.2, entry 2). The ratio is slightly higher than those observed from PHB formed using **22** at RT (0.05:1) (Table 5.2, entry 1). However, when the polymerisation was carried out at 80 °C for an extended period (12 h) (Table 5.2, entry 3), the  $^1\text{H}$  NMR spectrum of the resultant PHB (Figure 5.15) displayed *trans*-crotonate groups with an increased relative integration ratio = 1.5:1.

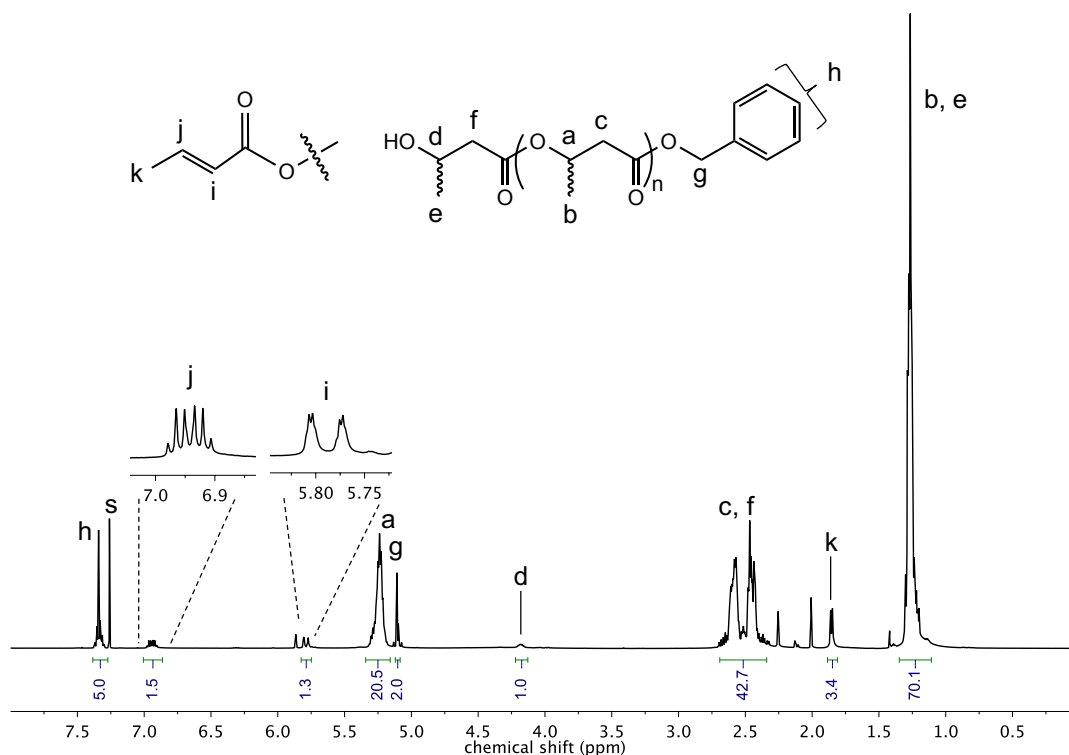


**Figure 5.15**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PHB formed using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**). Conditions:  $[\text{rac-BBL}]_0:[\textbf{22}]_0 = 20:1$ ,  $[\text{rac-BBL}]_0 = 0.5$  M, 1.0 mL toluene at 80 °C for 12 h. “s” denotes residual protio solvent.

The  $M_n$ (GPC) of the resultant PHB was slightly lower than those obtained from PHB quenched after 1 h at 80 °C due to elimination and transesterification reactions. A slight broadening of  $D$  value was also observed ( $D = 1.15$ ). MALDI-ToF mass

spectrum (Figure 5.16) also shows peak envelopes corresponding to PHB terminated with –OBn and *trans*-crotonate end groups. For instance, the peak envelope centred at 1404.4 Da is assigned to PHB with –OBn and *trans*-crotonate containing 14 monomer units and Na<sup>+</sup> [86.1(14) + 107.1 + 69.0 + 23.0]. No cyclic PHB was observed indicated that the intramolecular transesterification reaction was negligible compared to the elimination reaction under these conditions.

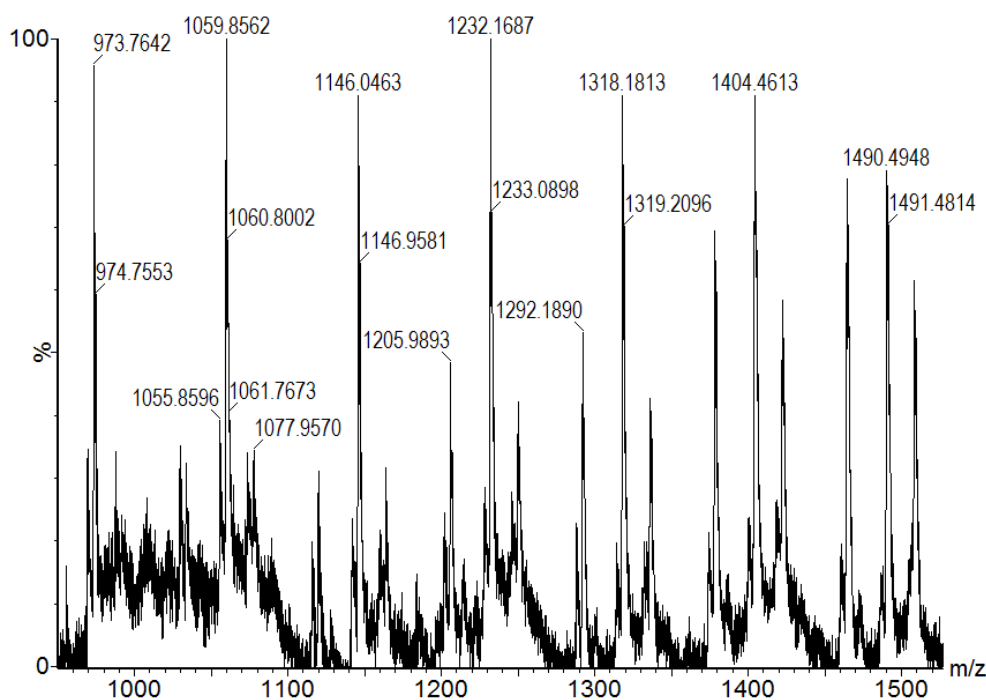
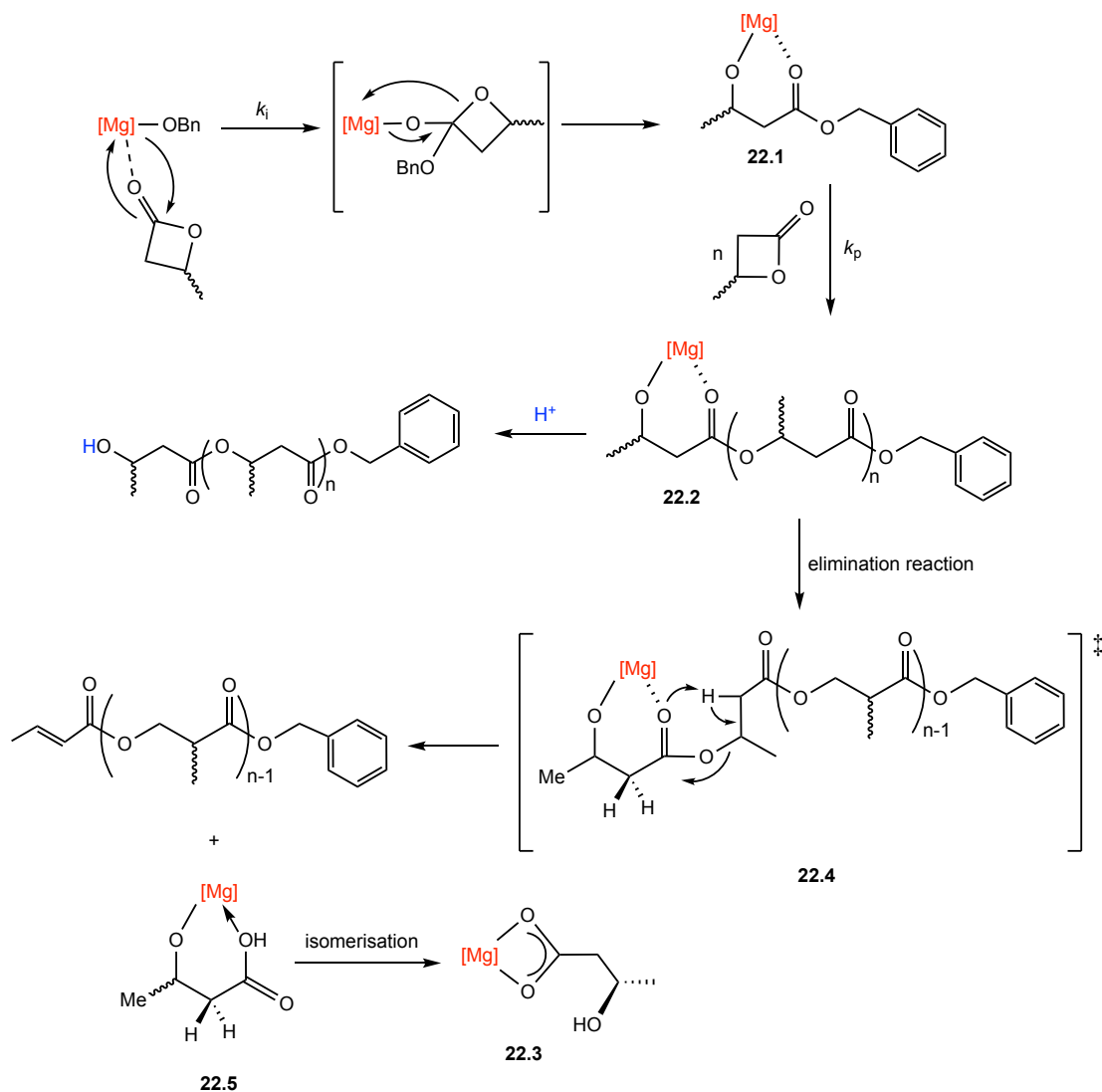


**Figure 5.16** MALDI-ToF MS of PHB formed using (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**).  $M_n(\text{GPC}) = 1,730 \text{ g mol}^{-1}$ ,  $D = 1.15$ . Conditions: [*rac*-BBL]<sub>0</sub>:**[22]**<sub>0</sub> = 20:1, [*rac*-BBL]<sub>0</sub> = 0.5 M, 1.0 mL toluene at 80 °C for 12 h. Na<sup>+</sup> dopant.  $\Delta(m/z) = 86.1 \text{ Da}$  between peak envelopes.

In summary, the ROP of *rac*-BBL using **22** is proposed to operate *via* a coordination-insertion mechanism (Scheme 5.5). The polymerisation proceeds by an insertion of *rac*-BBL monomer into the Mg–OBn bond of **22**, followed by the acyl-oxygen bond cleavage of the *rac*-BBL ring generating the mono-insertion product (Tp<sup>tBu,Me</sup>)Mg{κ<sup>2</sup>-OCHMeCH<sub>2</sub>C(O)OBn} (**22.1**) as the propagating species. Hydrolysis of the Mg-alkoxide bond in **22.2** releases PHB terminated by –OH and –OBn end groups. The formation of PHB with –OBn and *trans*-crotonate end groups and a Mg-carboxylate species (Tp<sup>tBu,Me</sup>)Mg{κ<sup>2</sup>-O<sub>2</sub>CCH<sub>2</sub>CHMeOH} (**22.3**) *via* an intermediate carboxylic acid-alkoxide (**22.5**) could occur after the consumption of all the *rac*-BBL monomer

by elimination reaction *via* the transition state **22.4** under extended polymerisation time and high temperature.



**Scheme 5.5** Proposed mechanism for the ROP of *rac*-BBL initiated by  $(Tp^{tBu,Me})Mg(OBn)$  (**22**).  $[Mg] = (Tp^{tBu,Me})Mg$ .

#### 5.4.3 DFT calculations for the crotonate elimination reactions of **22.2**

As described in the previous section and Scheme 5.5, the  $(Tp^{tBu,Me})Mg\{\kappa^2-OCHMeCH_2C(O)(BBL)_nOBn\}$  (**22.2**) is proposed to undergo an elimination reaction post-polymerisation to form a polymer terminated by *trans*-crotonate and OBn, namely  $BnO(BBL)_{n-1}C(O)CH=CHMe$ , and ultimately a carboxylate complex  $(Tp^{tBu,Me})Mg\{\kappa^2-O_2CCH_2CHMeOH\}$  (**22.3**). A series of DFT calculations was carried out to explore this reaction further.

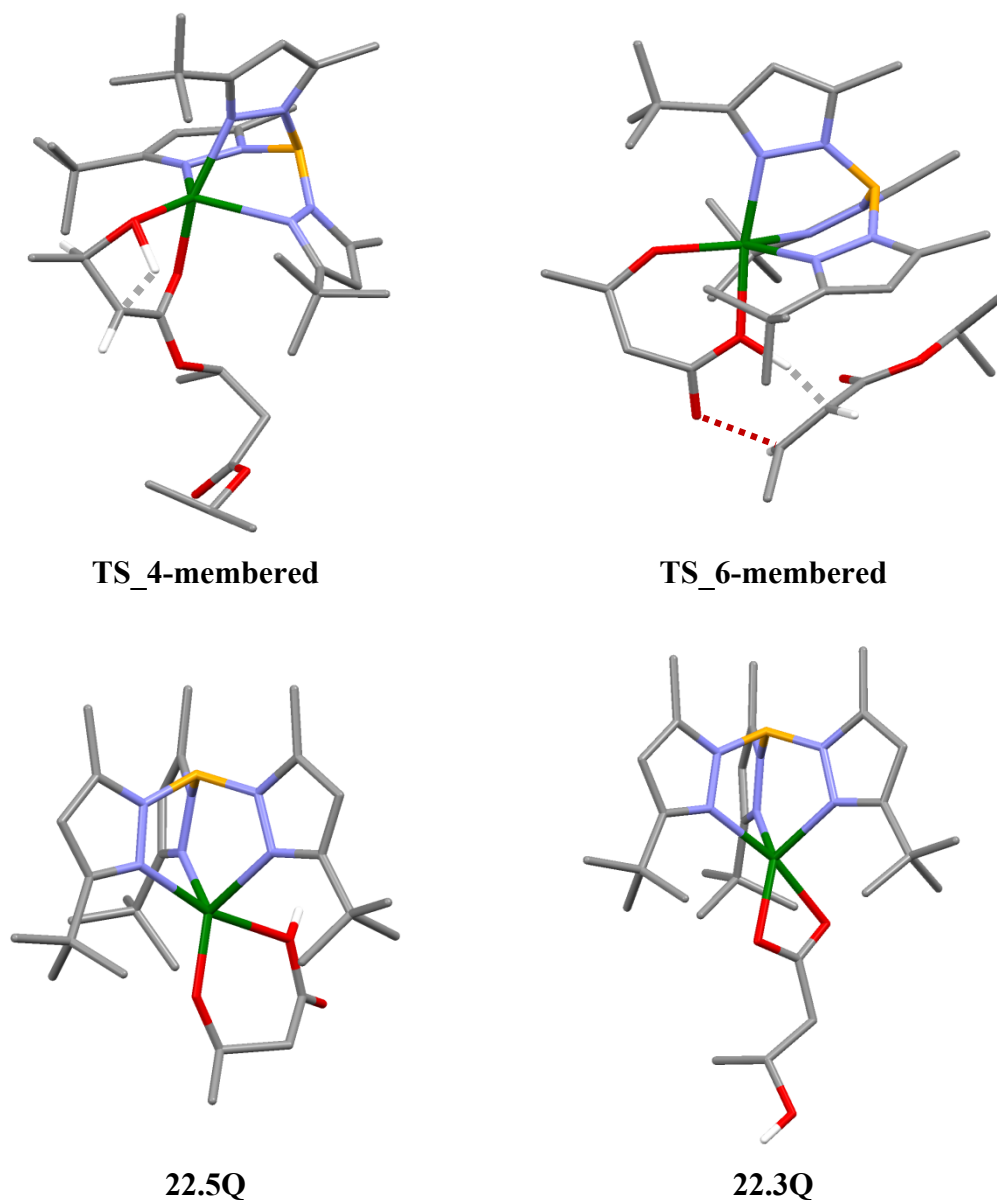


**Figure 5.17.** Top: DFT transition states for crotonate elimination from  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-}\{\text{OCHMeCH}_2\text{C}(\text{O})\}_2\text{O}^i\text{Pr}\}$  (**22.2Q''**). Bottom: first-formed product (**22.5Q**) from **TS\_6-membered** and its more stable isomer **22.3Q**.

The experimental compound **22.2** was modelled by  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-}\{\text{OCHMeCH}_2\text{C}(\text{O})\}_2\text{O}^i\text{Pr}\}$  (**22.2Q''**), the analogue of the DFT model **22.2Q'** used in Section 5.4.1, containing two opened BBL units but terminated by an  $\text{O}^i\text{Pr}$  group to represent the remaining polymeryl chain. Figure 5.17 (top) shows two possible transition states (TS) from **22.2Q''** leading to *trans*-crotonate terminated products. The first TS (labelled **TS\_4-membered**) gives H-atom elimination from the methylene linkage of the last-inserted BBL unit. This leads ultimately to

(Tp<sup>tBu,Me</sup>)Mg(OH) and (in the DFT system) *trans*-<sup>i</sup>PrOC(O)CH<sub>2</sub>OC(O)CH=CHMe. This type of mechanism has been proposed to account for the crotonate end groups found in the ROP of BBL by MgBu<sub>2</sub>.<sup>72</sup> As can be seen in Figure 5.17, **TS\_4-membered** proceeds *via* a rather strained 4-membered ring; the DFT calculations found a very high Gibbs free energy of activation ( $\Delta G^\ddagger = 32.7 \text{ kcal mol}^{-1}$  at 80 °C) which would suggest an extremely slow reaction even at 80 °C, as used in the experiments. The overall Gibbs free energy of reaction for this process is reasonably exergonic ( $\Delta_r G = -3.8 \text{ kcal mol}^{-1}$  at 80 °C) showing that in principle this pathway is at least thermodynamically feasible.

Alternatively, H-atom elimination could occur from the methylene group of the penultimately inserted BBL moiety *via* the transition state **TS\_6-membered** (Figure 5.17). This TS leads (as judged by following the intrinsic reaction coordinate) to the alkoxide-carboxylic acid species **22.5Q** and (in the DFT system) *trans*-<sup>i</sup>PrOC(O)CH=CHMe. This transition state is less strained and features a 6-membered ring which permits simultaneous C–O and C–H cleavage. The calculations for **TS\_6-membered** found a significantly lower Gibbs free energy of activation ( $\Delta G^\ddagger = 26.4 \text{ kcal mol}^{-1}$  at 80 °C) which is thermally accessible at this temperature and would be almost exclusively favoured relative to elimination *via* **TS\_4-membered**.

The Gibbs free energy of reaction for forming **22.5Q** and <sup>i</sup>PrOC(O)CH=CHMe is somewhat endergonic ( $\Delta_r G = 3.9 \text{ kcal mol}^{-1}$  at 80 °C) indicating that this reaction would be thermodynamically unfavourable. However, rearrangement of **22.5Q** to the carboxylate isomer **22.3Q** is exergonic by  $-16.5 \text{ kcal mol}^{-1}$  which drives the crotonate elimination forward, as observed.

### 5.5 Immortal ROP of *rac*-BBL using Tp<sup>(tBu,Me)</sup>Mg(OBn) (**22**) and B(OBn)<sub>3</sub> as chain transfer agent

In previous studies, Carpentier and Guillaume reported the solution and bulk immortal ROP of *rac*-BBL using (DippNacNac)Zn{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5.54**) with BnOH as co-initiator and chain transfer agent.<sup>68</sup> Immortal ROP was achieved with up to 500 equiv. of *rac*-BBL in the presence of 50 equiv. of BnOH in toluene at 90 °C, reaching 96% conversion after 80 min. In a bulk immortal ROP with [*rac*-BBL]:[**5.54**]:[BnOH] = 1,000:1:50 at 90 °C, 97% conversion was reached after 180 min giving PHB with good agreement between measured and calculated  $M_n$  with a narrow  $D$  value (1.12).

Mehrkhodavandi *et al.* also reported the dinuclear zinc complex (**5.31**) for the immortal ROP of *rac*-BBL in the presence of BnOH as chain transfer agent.<sup>59</sup> Polymerisation of 40,000 equiv. of *rac*-BBL with 100 equiv. of BnOH catalysed by **5.31** formed moderately syndiotactic PHB ( $P_r = 0.71$ ) with a very narrow  $\bar{D}$  value (1.02). The efficient chain transfer ability of B(OBn)<sub>3</sub> in the ROP of *rac*-LA using  $\text{Tp}^{(\text{tBu},\text{Me})}\text{Mg}(\text{OBn})$  (**22**) was discussed in Chapter Four (section 4.2.3), giving moderately heterotactic PLA ( $P_r = 0.65$ ) with good agreement between measured and calculated  $M_n$  for four growing polymer chains per metal centre.<sup>80</sup>

In this study, the immortal ROP of *rac*-BBL using **22** and B(OBn)<sub>3</sub> as chain transfer agent was carried out. It is worth noting that in solution, **22** and B(OBn)<sub>3</sub> remained as discrete species. The <sup>11</sup>B NMR spectrum of the reaction between **22** and 1 equiv. of B(OBn)<sub>3</sub> in toluene-*d*<sub>8</sub> recorded after 10 min showed signals at 18.8 and -9.1 ppm corresponding to B(OBn)<sub>3</sub> and the apical B-H of  $\text{Tp}^{(\text{tBu},\text{Me})}$  ligand, respectively. In the absence of B(OBn)<sub>3</sub>, polymerisation of 100 equiv. of *rac*-BBL with **22** in toluene at RT reached 87% conversion after 48 h (Table 5.3, entry 1). The addition of 1 equiv. of B(OBn)<sub>3</sub> into the ROP of *rac*-BBL with **22** showed no significant effect on the polymerisation rate, reaching 86% conversion after 48 h. (Table 5.3, entry 2). First order dependence on *rac*-BBL concentration was observed, giving invariant rate constant ( $k_{\text{app}} = 0.0397(6) \text{ h}^{-1}$ ,  $R^2 = 0.998$ ) compared to the system without B(OBn)<sub>3</sub> ( $k_{\text{app}} = 0.0426(6) \text{ h}^{-1}$ ,  $R^2 = 0.999$ ) (Figure 5.18). The  $M_n(\text{NMR})$  value of PHB showed close agreement with that calculated for four growing chains per metal centre (Table 5.3, entry 2). However, the  $M_n(\text{GPC})$  value was double that calculated, and a moderate  $\bar{D}$  (1.20) value was observed. The results suggest the poor ability of B(OBn)<sub>3</sub> as chain transfer agent with the higher propagation rate than chain transfer rate ( $k_p \gg k_{tr}$ ). The immortal ROP of *rac*-BBL using **22** and B(OBn)<sub>3</sub> is proposed to proceed *via* tetra-alkoxy borate transition state during the chain transfer step. The *in situ* generated **22** and B(OBn)<sub>3</sub> obtained by reacting  $(\text{Tp}^{(\text{tBu},\text{Me})})\text{Mg}(\text{BH}_4)$  (**20**) with 4 equiv. of benzaldehyde, was also used in the ROP of *rac*-BBL.

**Table 5.3** Selected data for the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**) and (Tp<sup>tBu,Me</sup>)Mg(BH<sub>4</sub>) (**20**) with additives.<sup>a</sup>

| Entry | Initiator | Additives             | $M_n(\text{GPC})^b$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{NMR})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | Conv. <sup>f</sup><br>(%) | $k_{\text{app}}^g$<br>(h <sup>-1</sup> ) | $R^2g$ | $P_r^h$      |
|-------|-----------|-----------------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------|---------------------------|------------------------------------------|--------|--------------|
| 1     | <b>22</b> | -                     | 8,000                                         | 7,597                                           | 7,529                                         | 1.04        | 87                        | 0.0426(6)                                | 0.999  | 0.52         |
| 2     | <b>22</b> | B(OBn) <sub>3</sub>   | 4,620                                         | 1,958                                           | 2,798                                         | 1.20        | 86                        | 0.0397(6)                                | 0.998  | 0.53         |
| 3     | <b>20</b> | 5 PhCHO               | 4,410                                         | 2,066                                           | 2,951                                         | 1.25        | 91                        | 0.0498(9)                                | 0.998  | 0.53         |
| 4     | <b>22</b> | 3 B(OBn) <sub>3</sub> | 1,190                                         | 830                                             | 1,167                                         | 1.24        | 91                        | 0.0472(14)                               | 0.994  | <sup>i</sup> |

<sup>a</sup> Conditions: [*rac*-BBL]<sub>0</sub>: [initiator]<sub>0</sub>: [additive]<sub>0</sub> = 100:1: as stated, [*rac*-BBL]<sub>0</sub> = 0.5 M in 3.0 mL toluene at RT for 48 h. <sup>b</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 18.32 μL g<sup>-1</sup> and α = 0.69. <sup>c</sup> Calculated  $M_n$  (g mol<sup>-1</sup>) for –OH and –OBn end groups,  $M_n$  (entry 1) = conv. (%) × [*rac*-BBL]<sub>0</sub>: [**22**]<sub>0</sub> × 86.1 + 108.1,  $M_n$  (entry 2, 3) = (conv. (%) × [*rac*-BBL]<sub>0</sub>: [initiator]<sub>0</sub> × 86.1)/4 + 108.1,  $M_n$  (entry 4) = (conv. (%) × [*rac*-BBL]<sub>0</sub>: [**22**]<sub>0</sub> × 86.1)/12 + 108.1. <sup>d</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated PHB by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>, δ = 5.25 ppm) and those of the chain-end methylene protons (OCH<sub>2</sub>Ph, δ = 5.11 ppm). <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Condition: [*rac*-BBL]<sub>0</sub>: [initiator]<sub>0</sub>: [additive]<sub>0</sub> = 100:1: as stated, [*rac*-BBL]<sub>0</sub> = 0.5 M in 0.5 mL toluene-*d*<sub>8</sub> in an NMR tube at RT for 48 h. Conversion (%) was measured by <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>) analyses. <sup>g</sup> Apparent first order rate constant for consumption of monomer with standard error and  $R^2$  determined by linear regression analysis. <sup>h</sup>  $P_r$  is determined by carbonyl region of inverse gated <sup>13</sup>C{<sup>1</sup>H} NMR spectra. <sup>i</sup> Not measured.

Under analogous conditions, 91% conversion was reached after 48 h giving first order rate constant ( $k_{\text{app}} = 0.0498(9) \text{ h}^{-1}$ ,  $R^2 = 0.998$ ) (Table 5.3, entry 3). The resultant PHB showed poor agreement between  $M_n(\text{GPC})$  and calculated value for four chains per metal centre with a moderate  $D$  value (1.25).

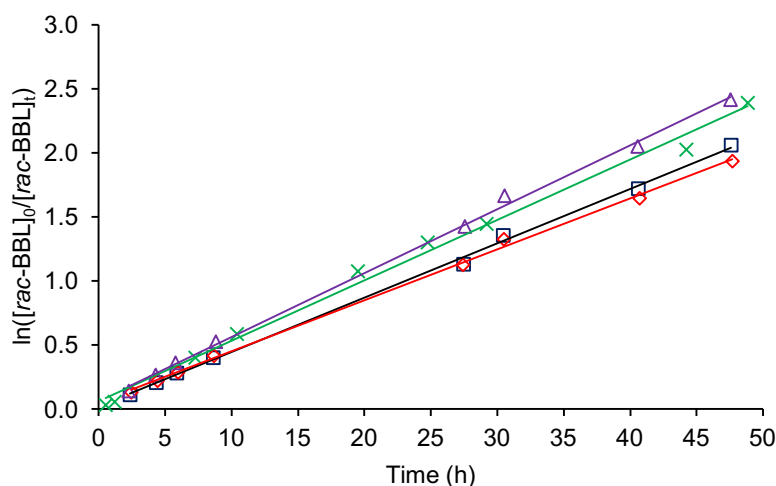


**Figure 5.18** Plots of  $\ln([rac\text{-BBL}]_0/[rac\text{-BBL}]_t)$  vs. time. Condition: 0.5 mL toluene- $d_8$ , RT,  $[rac\text{-BBL}]_0 = 0.5 \text{ M}$ . Squares:  $[rac\text{-BBL}]_0:[\mathbf{22}]_0 = 100:1$  ( $k_{\text{app}} = 0.0426(6) \text{ h}^{-1}$ ,  $R^2 = 0.999$ ). Diamonds:  $[rac\text{-BBL}]_0:[\mathbf{22}]_0:[\text{B}(\text{OBn})_3]_0 = 100:1:1$  ( $k_{\text{app}} = 0.0397(6) \text{ h}^{-1}$ ,  $R^2 = 0.998$ ). Triangles:  $[rac\text{-BBL}]_0:[\mathbf{20}]_0:[\text{PhCHO}]_0 = 100:1:4$  ( $k_{\text{app}} = 0.0498(9) \text{ h}^{-1}$ ,  $R^2 = 0.998$ ). Crosses:  $[rac\text{-BBL}]_0:[\mathbf{22}]_0:[\text{B}(\text{OBn})_3]_0 = 100:1:3$  ( $k_{\text{app}} = 0.0472(14) \text{ h}^{-1}$ ,  $R^2 = 0.994$ ).

An additional ROP experiment was performed where  $[rac\text{-BBL}]_0:[\mathbf{22}]_0:[\text{B}(\text{OBn})_3]_0 = 100:1:3$ , 91% conversion was reached after 48 h under analogous conditions (Table 5.3, entry 4). First order dependence on  $[rac\text{-BBL}]$  was found with  $k_{\text{app}} = 0.0472(14) \text{ h}^{-1}$  ( $R^2 = 0.994$ ) (Figure 5.18, Crosses). The resultant PHB showed the measured  $M_n$  values from GPC or NMR higher than those calculated for twelve polymer chains per metal centre (Table 5.3, entry 4), indicating the greater propagation than chain-transfer reaction rate. The polymerisation studies suggest the negligible effect of  $\text{B}(\text{OBn})_3$  on the rate due to the comparable  $k_{\text{app}}$  values measured from the ROP with and without  $\text{B}(\text{OBn})_3$ . A chain transfer effect is observed from the mismatch between  $M_n(\text{GPC})$  values and those calculated for one chain per metal centre, indicating an exchange between  $\text{B}(\text{OBn})_3$  and polymeric chain on the metal centre.



### 5.6 ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(BH<sub>4</sub>) (**20**)

A kinetic analysis of the ROP of 100 equiv. of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(BH<sub>4</sub>) (**20**) in toluene-*d*<sub>8</sub> was carried out by <sup>1</sup>H NMR spectroscopy at RT, reaching 87% conversion after 72 h. The reaction followed first order dependence on *rac*-BBL concentration with  $k_{\text{app}} = 0.0277(5) \text{ h}^{-1}$  ( $R^2 = 0.996$ ) (Figure 5.19). The resultant PHB synthesised from a parallel experiment under analogous conditions (Table 5.4, entry 1) showed  $M_n$  values analysed by GPC or NMR moderately higher than those calculated for one chain per metal centre, with a moderate  $\bar{D}$  value (1.18). Atactic PHB was formed with  $P_r = 0.53$ .

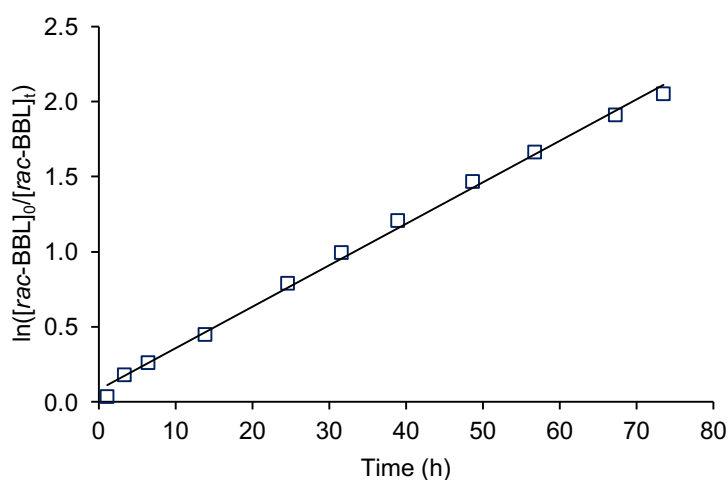


**Figure 5.19** Plot of  $\ln([rac-BBL]_0/[rac-BBL]_t)$  vs. time. Conditions: 0.5 mL toluene-*d*<sub>8</sub>, RT,  $[rac-BBL]_0 = 0.5 \text{ M}$ .  $[rac-BBL]_0:[\mathbf{20}]_0 = 100:1$ . The ROP of *rac*-BBL shows  $k_{\text{app}} = 0.0280(5) \text{ h}^{-1}$  ( $R^2 = 0.996$ ).

In order to determine the end groups of low molecular weight PHB formed using **20**, the ROP of *rac*-BBL with  $[rac-BBL]_0:[\mathbf{20}]_0 = 20:1$  (by increasing  $[\mathbf{20}]_0$  from 0.005 M to 0.025 M) was carried out under analogous conditions. The kinetic analysis was performed in toluene-*d*<sub>8</sub> at RT, reaching 86% conversion after 10 h (Table 5.4, entry 2). First order dependence on *rac*-BBL concentration was observed with  $k_{\text{app}} = 0.1701(2) \text{ h}^{-1}$  ( $R^2 = 0.998$ , Figure A7). The measured  $M_n$  values from GPC or <sup>1</sup>H NMR were slightly higher than those calculated for one chain per metal centre. A moderate  $\bar{D}$  value (1.23) was observed which is larger than that observed from (Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**) ( $\bar{D} = 1.04$ ).

**Table 5.4** Selected data for ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Mg(BH<sub>4</sub>) (**20**) and (Tp<sup>tBu,Me</sup>)Mg(BD<sub>4</sub>) (**20-d<sub>4</sub>**).<sup>a</sup>

| Entry | Initiator               | $[rac\text{-BBL}]_0$<br>: $[\text{initiator}]_0$ | Time<br>(h) | $M_n(\text{GPC})^b$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{NMR})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | Conv. <sup>f</sup><br>(%) | $k_{\text{app}}^g$<br>(h <sup>-1</sup> ) | $R^2g$ | $P_r^h$      |
|-------|-------------------------|--------------------------------------------------|-------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------|---------------------------|------------------------------------------|--------|--------------|
| 1     | <b>20</b>               | 100                                              | 72          | 8,920                                         | 7,503                                           | 9,859                                         | 1.18        | 87                        | 0.0280(5)                                | 0.996  | 0.53         |
| 2     | <b>20</b>               | 20                                               | 10          | 1,830                                         | 1,485                                           | 1,858                                         | 1.23        | 86                        | 0.1701(2)                                | 0.998  | <sup>i</sup> |
| 3     | <b>20-d<sub>4</sub></b> | 20                                               | 10          | 2,090                                         | 1,470                                           | 1,898                                         | 1.14        | 85                        | 0.1597(5)                                | 0.999  | <sup>i</sup> |

<sup>a</sup> Conditions:  $[rac\text{-BBL}]_0 = 0.5$  M in 3.0 mL toluene at RT. <sup>b</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 18.32$  μL g<sup>-1</sup> and  $\alpha = 0.69$ . <sup>c</sup> Calculated  $M_n$  (g mol<sup>-1</sup>),  $M_n$  (entry 1, 2) for –OH and –CH<sub>2</sub>CH<sub>2</sub>OH = conv. (%)  $\times [rac\text{-BBL}]_0 : [\text{initiator}]_0 \times 86.1 + 4$ ,  $M_n$  (entry 3) for –OH and –CH<sub>2</sub>CD<sub>2</sub>OH = conv. (%)  $\times [rac\text{-BBL}]_0 : [\text{initiator}]_0 \times 86.1 + 6$ . <sup>d</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated PHB by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>,  $\delta = 5.25$  ppm) and those of the chain-end methylene protons (CH<sub>2</sub>CH<sub>2</sub>OH,  $\delta = 1.86$  ppm). <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Condition:  $[rac\text{-BBL}]_0 = 0.5$  M in 0.5 mL toluene-*d*<sub>8</sub> in an NMR tube at RT. Conversion (%) was measured by <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>) analyses. <sup>g</sup> Apparent first order rate constant for consumption of monomer with standard error and  $R^2$  determined by linear regression analysis. <sup>h</sup>  $P_r$  is determined by carbonyl region of inverse gated <sup>13</sup>C{<sup>1</sup>H} NMR spectra. <sup>i</sup> Not measured.

Assuming first order dependence on **[20]**, the propagation rate constants ( $k_p$ ) for the ROP of *rac*-BBL with  $[20]_0 = 0.005$  and  $0.025$  M equal to  $5.60$  and  $6.80$   $\text{M}^{-1}\text{h}^{-1}$ , respectively. Values of  $k_{\text{app}}$  and  $k_p$  obtained from the ROP of *rac*-BBL using **20** are slightly lower than those obtained from **22**. This presumably suggests that less proportion of **20** was involved in the catalytic cycle than **22**, leading to poorer agreement between  $M_n$  (GPC) values and those calculated ( $M_n(\text{GPC}) > M_n(\text{calcd})$ ) compared to those observed from **22**.

Polymer end group analysis by  $^1\text{H}$  NMR showed the presence of PHB with  $-\text{OH}$  and  $-\text{OCHMeCH}_2\text{CH}_2\text{OH}$  end groups, which is consistent with the NMR observation of PHB formed using  $\text{La}(\text{BH}_4)_3(\text{THF})_3$  reported by Guillaume *et al.*<sup>79</sup> As shown in Figure 5.20 (a), signals at  $4.12$  and  $1.85$  ppm are assigned to methylene protons of  $-\text{CH}_2\text{CH}_2\text{OH}$  and  $-\text{CH}_2\text{CH}_2\text{OH}$ , respectively. The chain-end assignment is confirmed by deuterium labelling experiments using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BD}_4)$  (**20-*d*<sub>4</sub>**). Complex **20-*d*<sub>4</sub>** converted 20 equiv. of *rac*-BBL after 10 h under analogous conditions affording PHB with a measured  $M_n$  value higher than that calculated with a moderate  $D$  (1.14). First order rate constant ( $k_{\text{app}} = 0.1597(5) \text{ h}^{-1}$ ,  $R^2 = 0.999$ , Figure A7) was effectively the same as that determined from using **20** (Table 5.4, entry 3). The  $^1\text{H}$  NMR spectrum of PHB formed using **20-*d*<sub>4</sub>** (Figure 5.20, b) shows no signal at  $4.12$  ppm assigned to methylene protons ( $-\text{CH}_2\text{CH}_2\text{OH}$ ), indicating replacement of these protons by deuterium.

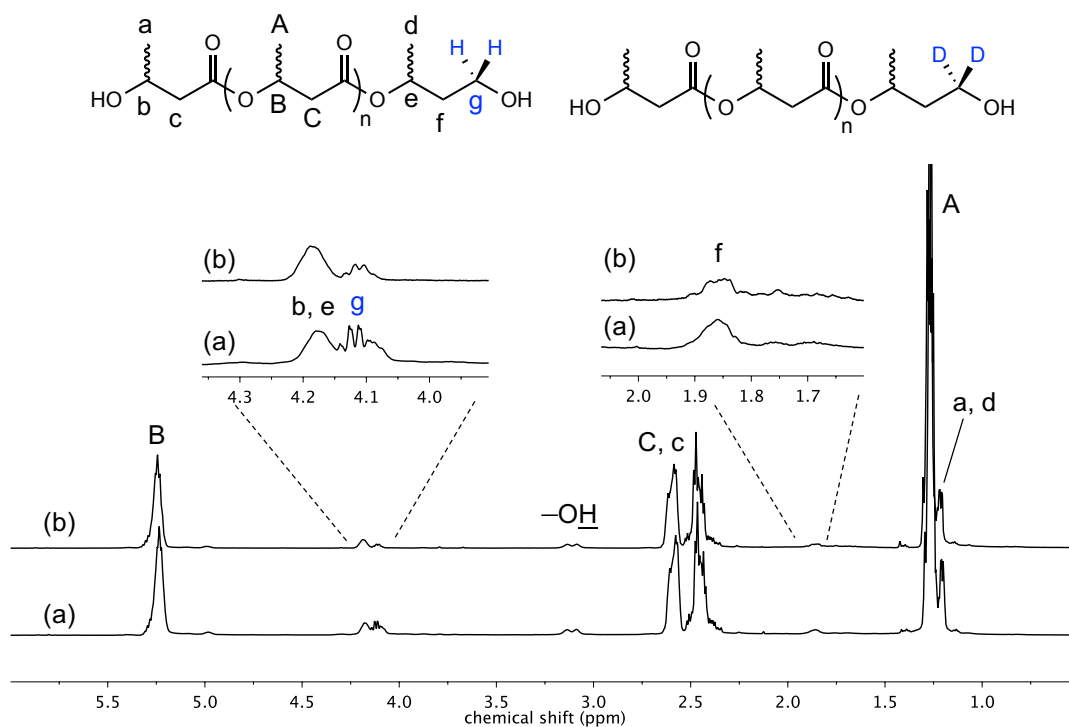


**Figure 5.20**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PHBs obtained by the large scale polymerisations of (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) or (b)  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BD}_4)$  (**20-d<sub>4</sub>**) with 20 equiv. of *rac*-BBL.

The  $^2\text{H}$  NMR in protio- $\text{CHCl}_3$  (Figure 5.21) shows signal at 4.13 ppm corresponding to  $-\text{CH}_2\text{CD}_2\text{OH}$  indicating the deuterium migration from the  $\text{BD}_4$  group of **20-d<sub>4</sub>** to the carbonyl carbon of *rac*-BBL.

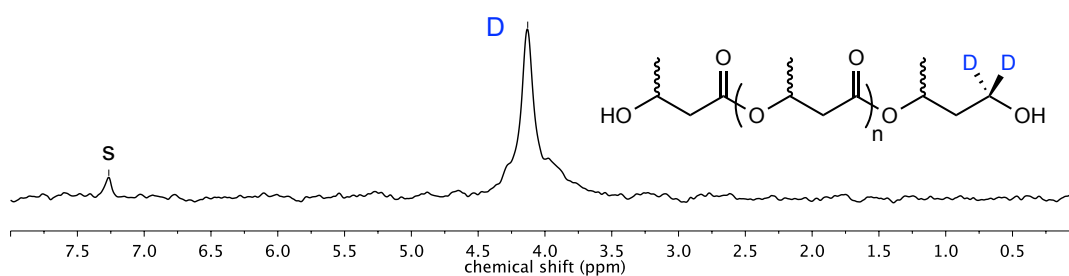


**Figure 5.21**  $^2\text{H}$  NMR spectrum ( $\text{CHCl}_3$ , 76.7 MHz, 298 K) of isolated PHB obtained by the polymerisation of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BD}_4)$  (**20-d<sub>4</sub>**) with 20 equiv. of *rac*-BBL. “s” denotes residual  $\text{CDCl}_3$ .

### 5.7 Mechanistic investigations of the ROP of *rac*-BBL using $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$ (**20**)

Guillaume *et al.* proposed the alkoxyborane species  $\text{Ln}(\text{OCHMeCH}_2\text{CH}_2\text{OBH}_2)_3$  as an initiator for the ROP of *rac*-BBL using  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$  (Scheme 5.4).<sup>79</sup> In order to probe for an analogous alkoxy borane species,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2\}$  (**A**), an NMR tube scale reaction of **20** with 2 equiv. of *rac*-BBL was carried out in toluene- $d_8$  at RT. The  $^{11}\text{B}$  NMR spectrum recorded after 10 min showed signals at -9.4 and -37.7 corresponding to the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$  and the coordinated  $\text{BH}_4$  of **20**, respectively. A doublet corresponding to a  $\text{BH}(\text{OR})_2$  species was also observed at 25.8 ppm, in conjunction with two singlets at 18.1 and 2.1 ppm assigned to  $\text{B}(\text{OR})_3$  and  $\text{B}(\text{OR})_4$  species, respectively, on the basis of the chemical shifts.<sup>88</sup> The  $^{11}\text{B}$  NMR spectrum recorded after 1 h (Figure 5.22, a) shows signals at 18.1, 2.1 and -9.4 ppm corresponding to  $\text{B}(\text{OR})_3$  and  $\text{B}(\text{OR})_4$  species as well as the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively. An NMR tube scale reaction of **20** and 1 equiv. of *rac*-BBL was also carried out under analogous conditions. The  $^{11}\text{B}$  NMR spectrum recorded after 1 h showed the same resonances as depicted in Figure 5.22 (a).

An additional NMR tube scale experiment was performed by reacting **20** with 20 equiv. of *rac*-BBL in toluene- $d_8$  at RT. The  $^{11}\text{B}$  NMR spectrum recorded after 10 h (Figure 5.22, b) shows only two signals at 18.1 and -9.4 ppm corresponding to a  $\text{B}(\text{OR})_3$  species and the apical B-H of  $\text{Tp}^{\text{tBu,Me}}$ , respectively. An attempt to detect **A** at low temperature was unsuccessful as no reaction was observed from the VT  $^1\text{H}$  NMR spectra of reaction of **20** and 2 equiv. of *rac*-BBL in toluene- $d_8$  from 223-283 K.

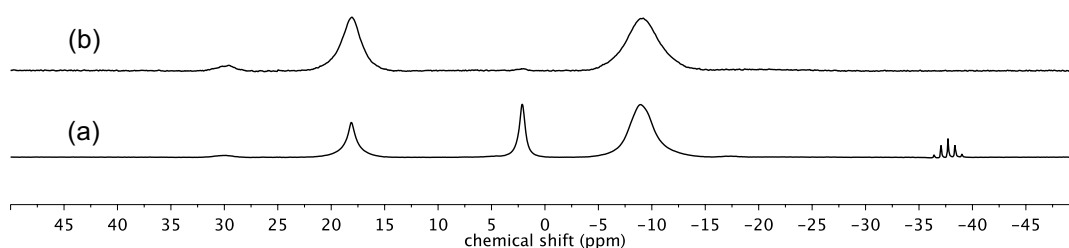
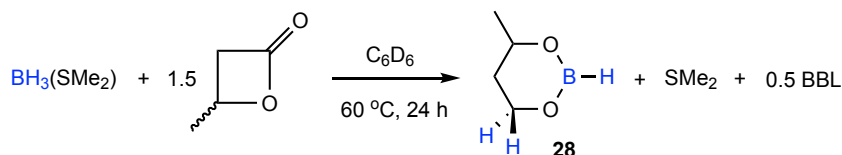


**Figure 5.22**  $^{11}\text{B}$  NMR spectrum (toluene- $d_8$ , 160.4 MHz, 298 K) of (a) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and 2 equiv. of *rac*-BBL recorded after 1 h and (b) reaction of **20** and 20 equiv. of *rac*-BBL recorded after 10 h.

DFT calculations (*vide infra*) on the hypothetical species **A** suggested that the  $\text{--OBH}_2$  resonance should appear at *ca.* 56.5 ppm in the  $^{11}\text{B}$  NMR spectrum, consistent with this species not being formed. For confirmation of the reliability of the computational method, the DFT chemical shifts for **20Q** were -8.4 and -38.6 ppm in good agreement with experimental values (-9.4 and -37.7 ppm).

A ring-opened and reduced *rac*-BBL was tentatively assigned as the  $(\text{OR})_n$  moieties of  $\text{BH}(\text{OR})_2$ ,  $\text{B}(\text{OR})_3$  or  $\text{B}(\text{OR})_4$ . An explanatory experiment was carried out on the NMR tube scale, namely the reaction of  $\text{BH}_3(\text{SMe}_2)$  and *rac*-BBL in a 1:1.5 molar ratio in  $\text{C}_6\text{D}_6$  at 60 °C (Equation 5.1), giving the reduced hydride transfer product 4-methyl-1, 3, 2-dioxaborinane (**28**). An analogous reaction of  $\text{BH}_3(\text{SMe}_2)$  with 2-methyl-2,4-pentanediol (1:1.2 molar ratio) to form 4,4,6-trimethyl-1,3,2-dioxaborinane has been reported.<sup>89</sup>



**Equation 5.1**

The  $^{11}\text{B}$  NMR spectrum recorded after 24 h shows a doublet at 25.8 ppm and a quartet at -19.4 ppm corresponding to  $\text{HB}(\text{OR})_2$  (**28**) and unreacted  $\text{BH}_3(\text{SMe}_2)$ , respectively. The  $^1\text{H}$  NMR spectrum (Figure 5.23) shows **28**,  $\text{SMe}_2$ , unreacted *rac*-BBL and  $\text{BH}_3(\text{SMe}_2)$ . Compound **28** is highly volatile, and attempts to isolate it from the starting materials and side products on a preparative scale were unsuccessful.

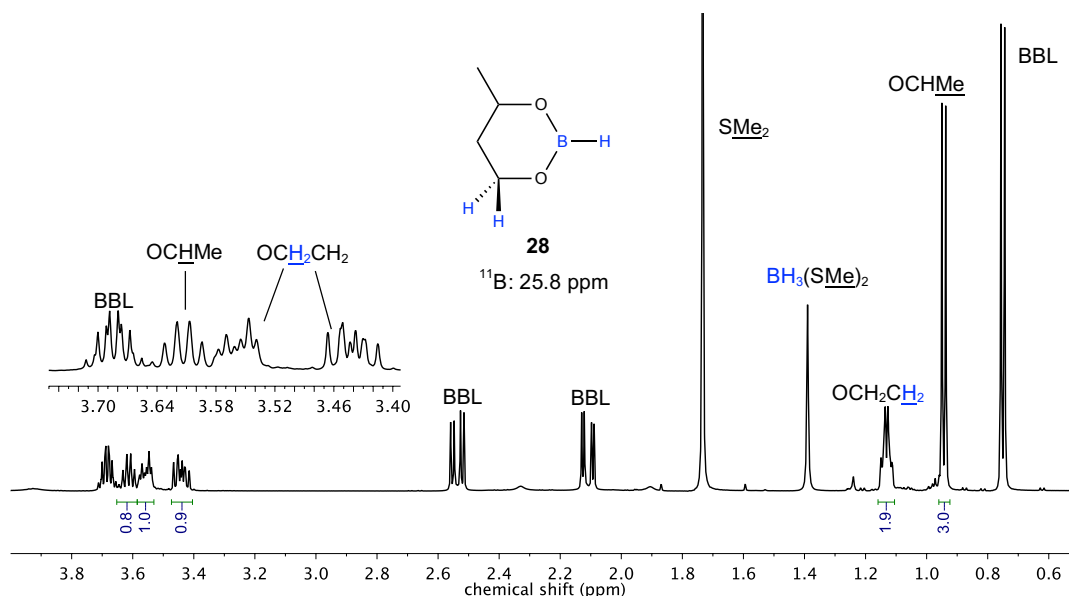


**Figure 5.23**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of reaction of  $\text{BH}_3(\text{SMe}_2)$  with *rac*-BBL in 1:1.5 molar ratio in  $\text{C}_6\text{D}_6$  at 60 °C for 24 h. “BBL” denotes unreacted *rac*-BBL.

The solvent-free reaction of  $\text{BH}_3(\text{SMe}_2)$  and *rac*-BBL in a 1:1 molar ratio was performed at 60 °C for 24 h in an attempt (unsuccessful) to isolate **28**. The  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ ) spectrum of the mixture showed a doublet ( $\delta = 25.8$  ppm) and a quartet ( $\delta = 19.4$  ppm) corresponding to **28** and  $\text{BH}_3(\text{SMe}_2)$ , respectively. A broad singlet was observed at 18.2 ppm assigned to the two inequivalent boron atoms of a  $\text{B}(\text{OR})_3$  species 2,2'-(butane-1, 3-diylbis(oxy))bis(4-methyl-1, 3, 2-dioxaborinane (**29**). The  $^{11}\text{B}$  NMR signal at 18.2 ppm of **29** is effectively identical to that observed from the reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and 20 equiv. of *rac*-BBL in toluene- $d_8$  at RT (18.1 ppm, Figure 5.22, b). The  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , Figure 5.24) shows signals corresponding to **28**, **29**,  $\text{SMe}_2$  and unreacted  $\text{BH}_3(\text{SMe}_2)$ . The formation of **28** and **29** is supported by the ESI-HRMS  $m/z = 100.0438$  and 286.1863 Da ( $m/z(\text{calcd})$  for **28** and **29** = 100.0696 and 286.1759 Da), respectively. The DFT computed chemical shift for **28** was 29.6 ppm referenced to that computed for  $\text{BH}_3(\text{SMe}_2)$  at -19.4 ppm. A model DFT compound *R, R, R*-**29Q** gave DFT chemical shifts of 20.1 and 20.7 ppm which compare well with those for **29** at *ca.* 18.2 ppm.

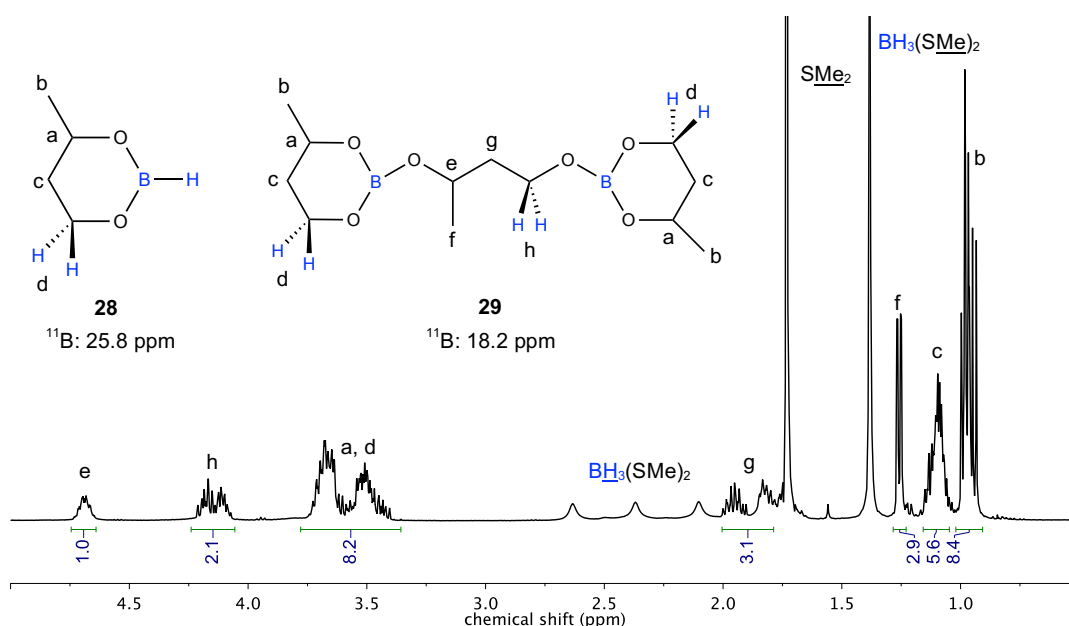


**Figure 5.24**  $^1\text{H}$  NMR spectrum ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K) of the solvent-free reaction of  $\text{BH}_3(\text{SMe}_2)$  and *rac*-BBL at 60 °C for 24 h, forming **28** and **29**.

Examination of the  $^1\text{H}$  NMR spectrum (Figure 5.25, b) of **20** with 20 equiv. of *rac*-BBL (Table 5.4, entry 2) recorded after 10 h shows signals corresponding to the chelating unit of a ring-opened BBL coordinated to the metal centre (\* and \*), which are identical to those observed from  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C(O)(BBL)}_n\text{OBn}\}$  (**22.2**, Figure 5.10). As shown in Figure 5.25 (b), a multiplet at 4.85 ppm is assigned to the methine proton  $\text{C(O)OCHMe}$  (\*) of the penultimate ring-opened BBL group. Broad signals in the region of 3.4–3.8 ppm are tentatively assigned to  $\text{OBOCH}_2$  (\* and †) and  $\text{OBOCHMe}$  (\*) of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{CO(BBL)}_n\text{OCHMeCH}_2\text{CH}_2\text{OBO}_2\text{C}_4\text{H}_8\}$  (**E**). These are in turn reminiscent of **28** and **29** (Figure 5.25, a). The assignment for these methylene and methine protons is supported by COSY, HSQC, HSQC-TOCSY and deuterium labelling experiments using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BD}_4)$  (**20-d<sub>4</sub>**). The  $^1\text{H}$  NMR spectrum for the reaction of **20-d<sub>4</sub>** and 20 equiv. of *rac*-BBL (Figure 5.25, c) shows diminished signals between 3.4–4.2 ppm, while the  $^2\text{H}$  NMR spectrum (Figure 5.25, d) shows the expected broad signals between 3.2–4.5 ppm.



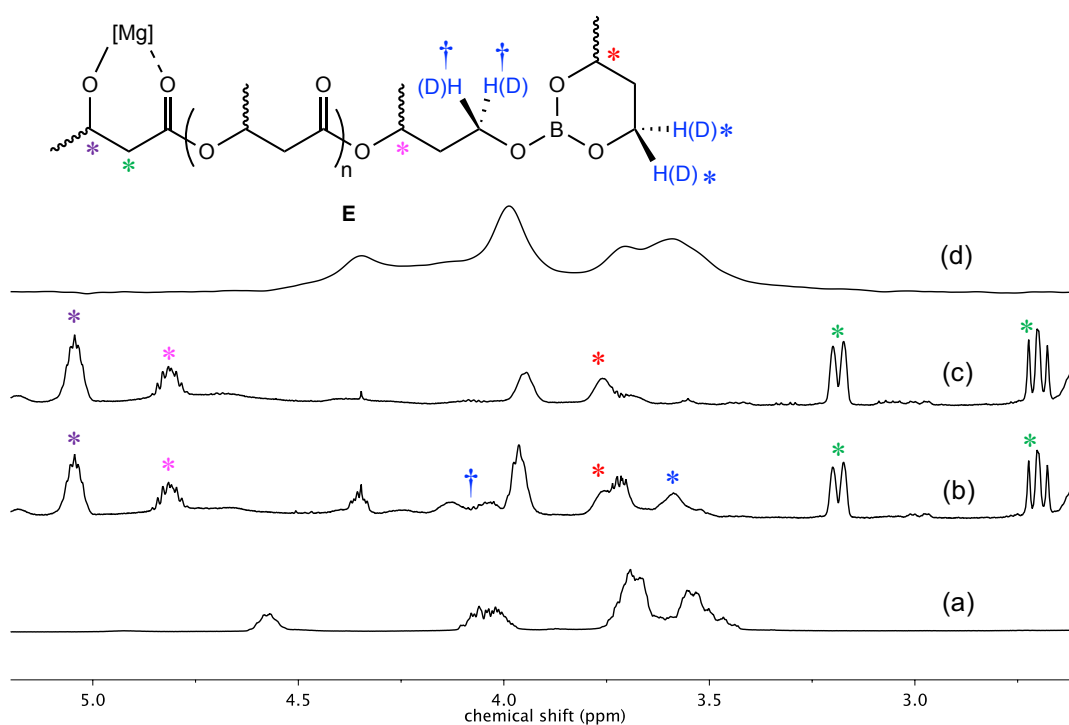
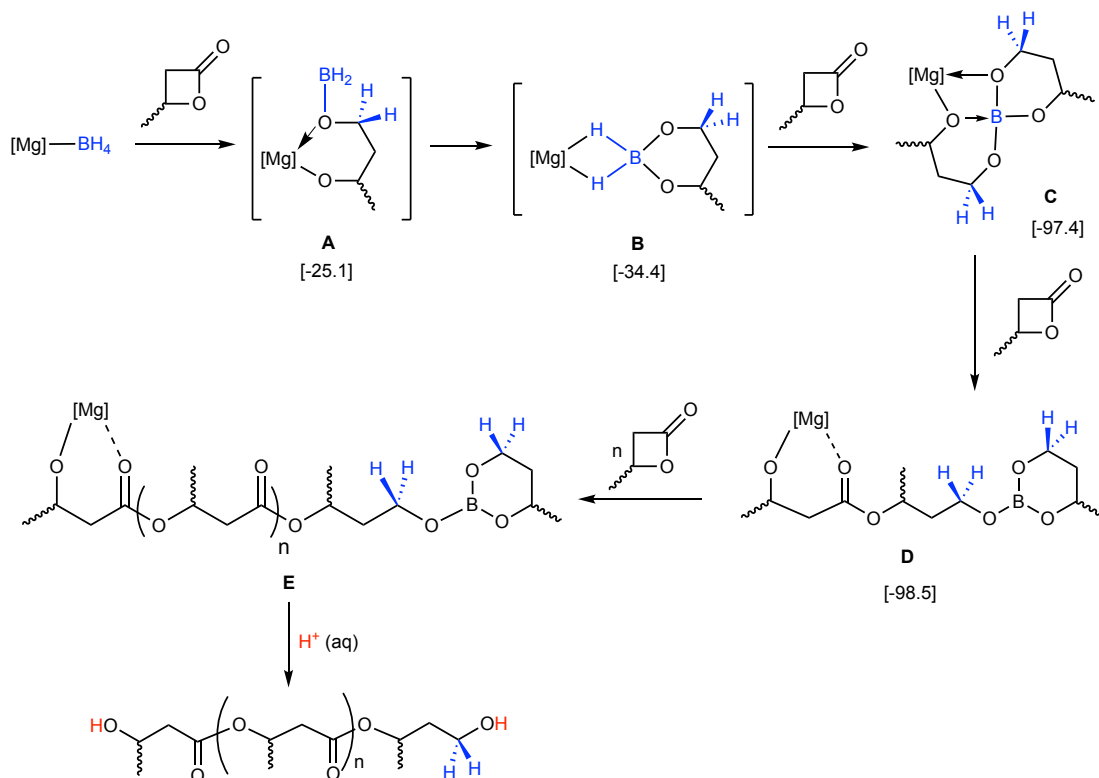


**Figure 5.25**  $^1\text{H}$  NMR spectra (toluene- $d_8$ , 499.9 MHz, 298 K) of (a) **28** and **29**, (b) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and 20 equiv. of *rac*-BBL at RT recorded after 10 h, and (c) reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BD}_4)$  (**20-d<sub>4</sub>**) and 20 equiv. of *rac*-BBL recorded after 10 h.  $^2\text{H}$  NMR spectrum (toluene, 76.7 MHz, 298 K) of (d) reaction of **20-d<sub>4</sub>** and 20 equiv. of *rac*-BBL recorded after 18 h. “\*” and “\*” denote the chelating unit on the metal centre of **E**. “\*” denotes C(O)OCHMe of **E**. “\*” and “†” denote OBOCH<sub>2</sub> of **E**. “\*” denotes OBOCHMe of **E**.  $[\text{Mg}] = (\text{Tp}^{\text{tBu,Me}})\text{Mg}$ .

The mechanism for the ROP of *rac*-BBL using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) is proposed in Scheme 5.6. Two hydrides from the BH<sub>4</sub> group of **20** transfer to the carbonyl carbon of *rac*-BBL and followed by an acyl-oxygen bond cleavage to form  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2\}$  (**A**). Intermediate **A** is subsequently redistributed, generating  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{(\mu\text{-H})_2\text{BO}_2\text{C}_4\text{H}_8\}$  (**B**). Two hydrides of **B** migrate to the carbonyl carbon of *rac*-BBL and open the ring to form tetra-alkoxy borate containing species  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\kappa^2\text{-BO}_4\text{C}_8\text{H}_{16})$  (**C**), supported by the  $^{11}\text{B}$  NMR signal at 2.1 ppm observed from the reaction of **20** and 2 equiv. of *rac*-BBL (Figure 5.22, a). The incoming monomer coordinates to the metal centre of **C** acting as ROP initiator and followed by the insertion of *rac*-BBL into the Mg–O bond of **C** via acyl-oxygen bond cleavage. In the propagation step, the growing polymer chain on the metal centre is

produced with  $-\text{CHMeCH}_2\text{CH}_2\text{OBO}_2\text{C}_4\text{H}_8$  end group (**D**), supported by the  $^{11}\text{B}$  NMR signal at 18.1 ppm observed from the reaction of **20** and 20 equiv. of *rac*-BBL (Figure 5.22, b). The Mg–O and O–B bonds of **E** are hydrolysed, giving  $\alpha,\omega$ -dihydroxytelechelic PHB. The presence of  $-\text{CHMeCH}_2\text{CH}_2\text{OH}$  end group was confirmed by NMR spectroscopy. The  $M_n(\text{GPC})$  value of PHB formed using **20** supports the proposed mechanism as they are consistent with calculated values for one chain per metal centre, together with moderate  $\bar{D}$  values (1.18–1.23) (Table 5.4).



**Scheme 5.6** Proposed mechanism for the ROP of *rac*-BBL using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**).  $[\text{Mg}] = (\text{Tp}^{\text{tBu,Me}})\text{Mg}$ . Values in brackets are DFT Gibbs free energies ( $\text{kcal mol}^{-1}$ , 298 K) for the reaction of **20** with (*R*)-BBL.

### 5.8 DFT calculations for the reaction of $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$ (**20**) with BBL

The experimental results summarised in Scheme 5.6 for the ROP of *rac*-BBL using the magnesium borohydride compound **20** are a variation on the mechanism proposed by Guillaume and Maron for  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$  as presented in Scheme 5.4 above.<sup>79</sup> Both mechanisms proceed *via* double-hydride transfer from  $\text{BH}_4$  to ring-open BBL and produce a  $(\text{L})\text{M}\{\kappa^2\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2\}$  species (**A** ( $\text{M} = \text{Mg}$ ) or **III** ( $\text{M} = \text{Ln}$ )) which eventually accounts in both systems for the observed polymer end groups.

In the case of  $\text{Ln}(\text{BH}_4)_3(\text{THF})_3$  propagation is assumed to proceed without further modification of the  $-\text{OBH}_2$  chain end, whereas for **20** the data suggest that this first-formed terminus is able to ring-open an additional BBL monomer to form a  $-\text{OBO}_2\text{C}_4\text{H}_8$  end group which is observed in a transient intermediate **C**, and then in the propagating chain of **D**. Some aspects of the DFT calculations performed on this system have been described above; in this section addition details are given and comparisons made with the DFT studies of the BBL polymerisation starting from  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) described in Section 5.4.1.

The structure of the proposed initial product **A** is shown in Figure 5.26 and resembles that computed (Figure 5.11) for the experimentally observed  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}\}$  (**22.1**) formed from **22**. Thus **A** has a trigonal bipyramidal geometry at magnesium and the alkoxide oxygen lies in an equatorial site with the dative bond from the  $-\text{CH}_2\text{OBH}_2$  oxygen coordinated axially. An isomer of **A** with a  $\kappa^1\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2$  moiety was 3.7 kcal mol<sup>-1</sup> less stable (*cf.* the  $\kappa^1$  analogue of **22.1** which was 2.8 kcal mol<sup>-1</sup> less stable). As mentioned, the <sup>11</sup>B chemical shift for the  $-\text{CH}_2\text{OBH}_2$  boron was 56.5 ppm (in the expected range for  $\text{H}_2\text{BOR}$  systems). The <sup>11</sup>B shift for the boron atom of the  $\text{Tp}^{\text{tBu,Me}}$  ligand was computed as -8.1 ppm in good agreement with the usual values of *ca.* -8 to -10 ppm for this almost invariant resonance.

The isomer of **A** formed by migration of the alkoxide oxygen to the  $-\text{CH}_2\text{OBH}_2$  boron, namely  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{(\mu\text{-H})_2\text{BO}_2\text{C}_4\text{H}_8\}$  (**B**), is also shown in Figure 5.26. Although it has not been computed, the transition state(s) from **A** to **B** are expected to be low in energy. Compound **B** contains a  $\kappa^2\text{-H}_2\text{BO}_2\text{C}_4\text{H}_8$  moiety and is -9.3 kcal mol<sup>-1</sup> more stable than **A**. The computed <sup>11</sup>B NMR shift for the new moiety is -2.4 ppm while that for the  $\text{Tp}^{\text{tBu,Me}}$  ligand is effectively unchanged. Although **B** could be a suitable candidate for the transient intermediate observed experimentally (<sup>11</sup>B NMR singlet at 2.1 ppm), the computed chemical shift of -2.4 ppm for **B** is not in as good agreement as that for **C** (2.3 ppm, *vide infra*) and, importantly, would appear as a triplet in the proton-coupled <sup>11</sup>B NMR spectrum.

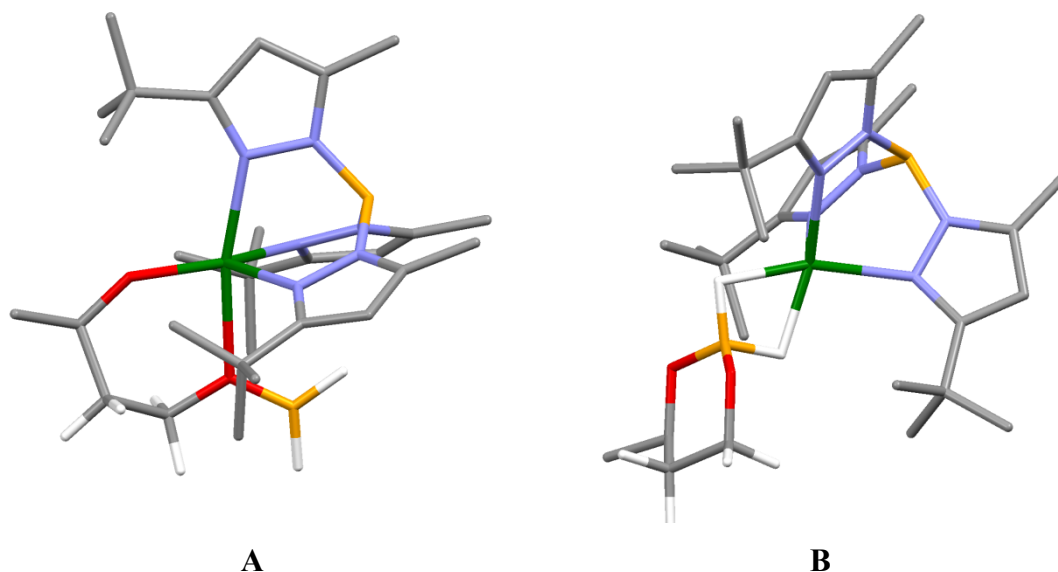


**Figure 5.26.** DFT structures of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2\}$  (**A**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{(\mu\text{-H})_2\text{BO}_2\text{C}_4\text{H}_8\}$  (**B**). Selected H atoms omitted.

The computed Gibbs free energies of formation of **A** ( $\Delta_r G = -25.1 \text{ kcal mol}^{-1}$ ) and **B** ( $\Delta_r G = -34.4 \text{ kcal mol}^{-1}$ ) from **20Q** and BBL are considerably more exergonic than for the formation of **22.1** from the benzyloxide species **22**. Although not directly comparable due to the differing DFT methodology and elimination of THF in their case, Guillaume and Maron reported  $\Delta_r G = -36.5 \text{ kcal mol}^{-1}$  for the reaction of  $\text{La}(\text{BH}_4)_3(\text{THF})_3$  with BBL to form  $\text{La}(\text{BH}_4)_2\{\kappa^2\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2\}(\text{THF})_2$  and THF.<sup>79</sup> The more favourable  $\Delta_r G$  in the case of **20Q** compared to **22** (formation of **22.1Q**) is not readily attributed to any single factor, and will be due to a balance of the various bond energy terms.

The experimentally observed intermediate at 2.1 ppm in the  $^{11}\text{B}$  NMR spectrum upon reaction of **20Q** with 2 equiv. of BBL is proposed to be  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\kappa^2\text{-BO}_4\text{C}_8\text{H}_{16})$  (**C**) which was computed by DFT (Figure 5.27, left). The transformation of **B** to **C** is considerably exergonic ( $\Delta_r G = -63.0 \text{ kcal mol}^{-1}$  from **B** and BBL;  $\Delta_r G = -97.4 \text{ kcal mol}^{-1}$  from **20Q** and 2 equiv. of BBL). The computed  $^{11}\text{B}$  NMR chemical shift of 2.3 ppm is in very good agreement with experiment (2.1 ppm). An alternative isomer of **C** with a geometry analogous to **A** and **22.1Q** was also computed as **C\_alt** which has a three-coordinate  $\text{B}(\text{OR})_3$  moiety. This isomer is  $5.7 \text{ kcal mol}^{-1}$  less stable than **C**, and has a computed  $^{11}\text{B}$  NMR shift of 20.7 ppm. Yet another isomer of **C/C\_alt** (not shown in Figure 5.27) but possessing a  $\kappa^1\text{-OCHMeCH}_2\text{CH}_2\text{OBO}_2\text{C}_4\text{H}_8$  ligand was 8.6

kcal mol<sup>-1</sup> less stable than **C** with a <sup>11</sup>B NMR shift of 21.4 ppm, typical of three-coordinate B(OR)<sub>3</sub> moieties.

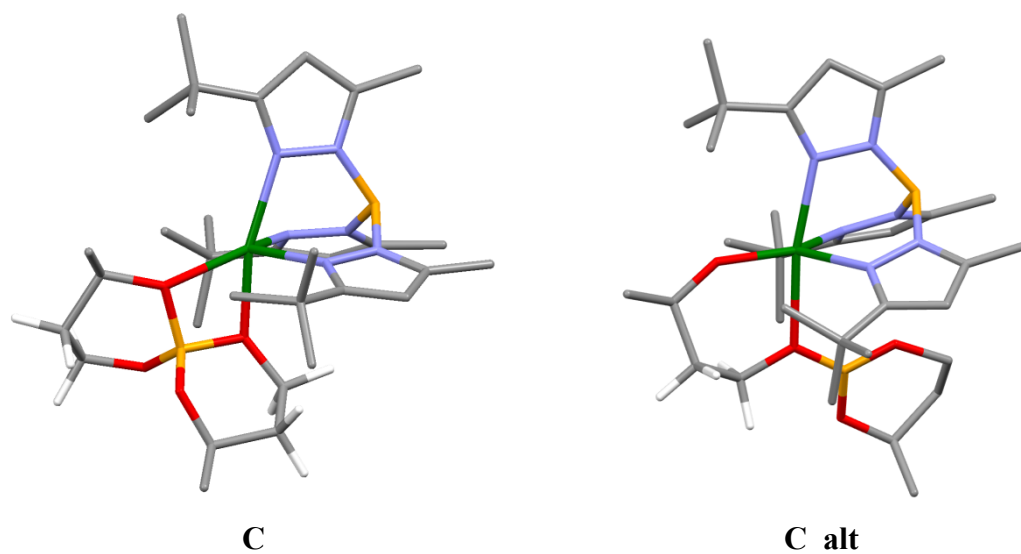


**Figure 5.27.** DFT structures of (Tp<sup>tBu,Me</sup>)Mg(κ<sup>2</sup>-BO<sub>4</sub>C<sub>8</sub>H<sub>16</sub>) (**C**) and its isomer **C\_alt** with a three-coordinate B(OR)<sub>3</sub> moiety. Selected H atoms omitted.

From **C** propagation proceeds in the usual manner *via* insertion into the Mg-OCHMeR. The first insertion product (Tp<sup>tBu,Me</sup>)Mg{κ<sup>2</sup>-OCHMeCH<sub>2</sub>C(O)-OCHMeCH<sub>2</sub>CH<sub>2</sub>OBO<sub>2</sub>C<sub>4</sub>H<sub>8</sub>} (**D**) is shown in Figure 5.28 and is analogous to that computed for (Tp<sup>tBu,Me</sup>)Mg{κ<sup>2</sup>-{OCHMeCH<sub>2</sub>C(O)}<sub>2</sub>OBn} (**22.2Q'**) (Figure 5.11) which is formed from **22.1Q**. The reaction of **C** with BBL to form **D** is only slightly exergonic (Δ<sub>r</sub>G = -1.1 kcal mol<sup>-1</sup>), and less favourable than for **22.1Q** with BBL giving **22.2Q'** (Δ<sub>r</sub>G = -5.0 kcal mol<sup>-1</sup>), probably due to the need to disrupt the favourable central B(OR)<sub>4</sub> moiety of **C**. From **D**, however, the energetics of propagation (as judged experimentally from the similar apparent propagation rate constants for **22** and **20**) are expected to be comparable. Consistent with the observed <sup>11</sup>B NMR chain end chemical shift of 18.1 for the propagating species **E** in Scheme 5.6, the computed value for **D** was 20.0 ppm.

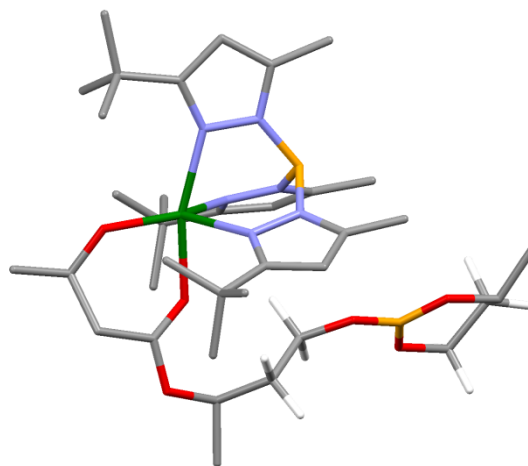


**Figure 5.28.** DFT structure of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C(O)-OCHMeCH}_2\text{CH}_2\text{OBO}_2\text{C}_4\text{H}_8\}$  (**D**). Selected H atoms omitted.

In summary, the DFT calculations for the reactions of **20** with successive equivalents of BBL, when coupled with the experimental NMR data and compared with the previous details DFT study by Guillaume and Maron, provide good support for the mechanism proposed in Scheme 5.6.

### 5.9 ROP of *rac*-BBL using calcium organohydroborate and tetrahydroborate complexes

The catalytic activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**),  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d**) for the ROP of *rac*-BBL was investigated. All polymerisations were carried out in toluene at RT. The results are summarised in Table 5.5.

With  $[\textit{rac}\text{-BBL}]_0:[\textbf{14}]_0 = 100$  or 20, **14** is extremely active for the ROP of *rac*-BBL, reaching full conversion after 20 s (Table 5.5, entry 1 and 2). The monomer conversion was determined by  $^1\text{H}$  NMR analysis in  $\text{CDCl}_3$  of crude polymer from the relative intensity of the methine proton of PHB and that of aromatic protons of 1,4-dimethoxybenzene as internal standard. The resultant PHBs formed using **14** showed moderate *D* values (1.30-1.41). The  $M_n(\text{GPC})$  values are considerably higher than those calculated for one chain per metal centre. These indicate the greater propagation than initiation rate since the hydride transfer step is required to generate the metal alkoxide species acting as ROP initiator. Isotactically-enriched PHB was produced with  $P_m = 0.83$  (Table 5.5, entry 1).

**Table 5.5** Selected data for the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>} (THF) (**14**), (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**) and (Tp<sup>tBu,Me</sup>)Ca(BD<sub>4</sub>)(THF) (**8-d<sub>4</sub>**).<sup>a</sup>

| Entry | Initiator              | $[rac\text{-BBL}]_0$<br>: $[\text{initiator}]_0$ | Time<br>(s) | $M_n(\text{GPC})^b$<br>(g mol <sup>-1</sup> ) | $M_n(\text{calcd})^c$<br>(g mol <sup>-1</sup> ) | $M_n(\text{NMR})^d$<br>(g mol <sup>-1</sup> ) | $\bar{D}^e$ | $k_{\text{app}}^f$<br>(M <sup>-1</sup> min <sup>-1</sup> ) | $R^{2f}$     | $P_m^g$      |
|-------|------------------------|--------------------------------------------------|-------------|-----------------------------------------------|-------------------------------------------------|-----------------------------------------------|-------------|------------------------------------------------------------|--------------|--------------|
| 1     | <b>14</b>              | 100                                              | 20          | 13,740                                        | 8,613                                           | 16,912                                        | 1.41        | <sup>h</sup>                                               | <sup>h</sup> | 0.83         |
| 2     | <b>14</b>              | 20                                               | 10          | 6,340                                         | 1,726                                           | 6,951                                         | 1.30        | <sup>h</sup>                                               | <sup>h</sup> | <sup>h</sup> |
| 3     | <b>8</b>               | 100                                              | 3600        | 19,240                                        | 8,613                                           | 19,425                                        | 1.74        | 1.10(2)                                                    | 0.995        | 0.83         |
| 4     | <b>8</b>               | 20                                               | 600         | 13,850                                        | 1,726                                           | 10,420                                        | 1.72        | <sup>h</sup>                                               | <sup>h</sup> | <sup>h</sup> |
| 5     | <b>8-d<sub>4</sub></b> | 100                                              | 3600        | 19,910                                        | 8,615                                           | 18,954                                        | 1.95        | 0.98(3)                                                    | 0.985        | 0.84         |
| 6     | <b>8-d<sub>4</sub></b> | 20                                               | 600         | 18,200                                        | 1,728                                           | 17,308                                        | 1.86        | <sup>h</sup>                                               | <sup>h</sup> | <sup>h</sup> |

<sup>a</sup> Conditions:  $[rac\text{-BBL}]_0 = 0.5$  M in 3.0 mL toluene at RT, conversion >99%. <sup>b</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters,  $K = 18.32$  μL g<sup>-1</sup> and  $\alpha = 0.69$ . <sup>c</sup> Calculated  $M_n$  (g mol<sup>-1</sup>),  $M_n$  (entry 1-4) for –OH and –CHMeCH<sub>2</sub>CH<sub>2</sub>OH end groups =  $[rac\text{-BBL}]_0 \cdot [\text{initiator}]_0 \times 86.1 + 4$ ,  $M_n$  (entry 5, 6) for –OH and –CHMeCH<sub>2</sub>CD<sub>2</sub>OH end groups =  $[rac\text{-BBL}]_0 \cdot [\text{initiator}]_0 \times 86.1 + 6$ . <sup>d</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated polymer by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>,  $\delta = 5.25$  ppm) and those of the chain-end methylene protons (CH<sub>2</sub>CH<sub>2</sub>OH,  $\delta = 1.86$  ppm). <sup>e</sup>  $\bar{D} = M_w/M_n$ . <sup>f</sup> Condition:  $[rac\text{-BBL}]_0 = 0.5$  M in 0.5 mL toluene-*d*<sub>8</sub> in an NMR tube at RT. Polymerisation was followed to 95% conversion. Apparent second order rate constant for consumption of monomer with standard error and  $R^2$  determined by linear regression analysis. <sup>g</sup>  $P_m$  is determined by carbonyl region of inverse gated <sup>13</sup>C{<sup>1</sup>H} NMR spectra. <sup>h</sup> Not measured.

Complex **8** was less active in the ROP of *rac*-BBL than **14**, although more active than the analogous magnesium complex (Tp<sup>tBu,Me</sup>)Mg(BH<sub>4</sub>) (**20**) as full conversion was reached after 1 h while complex **20** took 72 h to reach 87% conversion under analogous conditions. With [*rac*-BBL]<sub>0</sub>:**[8]**<sub>0</sub> = 100 in toluene-*d*<sub>8</sub> at RT, a short induction period was observed in the initial stages of polymerisation. After 10 min, the polymerisation demonstrated second order dependence on [*rac*-BBL] with  $k_{app} = 1.10(2) \text{ M}^{-1}\text{min}^{-1}$  ( $R^2 = 0.995$ , Figure 5.29).

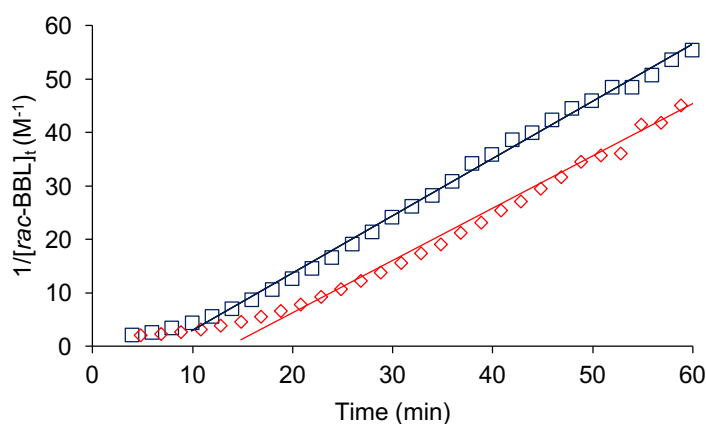


**Figure 5.29** Second order plot of  $1/[rac\text{-BBL}]_t$  vs. time. Conditions: 0.5 mL toluene-*d*<sub>8</sub>, RT, [*rac*-BBL]<sub>0</sub> = 0.5 M. Squares: [*rac*-BBL]<sub>0</sub>:**[8]**<sub>0</sub> = 100:1 ( $k_{app} = 1.10(2) \text{ M}^{-1}\text{min}^{-1}$ ,  $R^2 = 0.995$ ). Diamonds: [*rac*-BBL]<sub>0</sub>:**[8-d<sub>4</sub>]**<sub>0</sub> = 100:1 ( $k_{app} = 0.98(3) \text{ M}^{-1}\text{min}^{-1}$ ,  $R^2 = 0.985$ ).

The <sup>11</sup>B NMR spectrum of **8** with 100 equiv. of *rac*-BBL in toluene-*d*<sub>8</sub> at RT recorded after 1 h showed signals at 2.2 ppm corresponding to B(OR)<sub>4</sub> as well as minor signals at -7.5 and -32.3 ppm corresponding to the apical B-H of Tp<sup>tBu,Me</sup> and BH<sub>4</sub> ligand of **8**, respectively. The signals of unreacted **8** indicated that not all **8** initiated the ROP of *rac*-BBL leading to  $M_n$  (GPC) values much higher than those calculated for one chain per metal centre and broad  $\bar{D}$  values (1.72-1.74) (Table 5.5). The inefficiency of **8** was confirmed by an NMR tube scale reaction of **8** and 20 equiv. of *rac*-BBL in toluene-*d*<sub>8</sub> at RT. The <sup>1</sup>H NMR recorded after 10 min showed full conversion of *rac*-BBL. However, the <sup>11</sup>B NMR spectrum recorded after 10 min showed signals corresponding to unreacted **8** (-7.5 and -32.3 ppm) and B(OR)<sub>4</sub> (2.2 ppm). The slow polymerisation ROP rate is attributed to the presence of (Tp<sup>tBu,Me</sup>)Ca{B(OR)<sub>4</sub>} (OR = polymeric chain), a resting state of the catalyst. Similar behaviour was observed from



the ROP of *rac*-LA using **8** and 4 equiv. of benzaldehyde in THF as described in Chapter Four (section 4.5.3). In contrast, the  $^{11}\text{B}$  NMR spectrum of **14** with 20 equiv. of *rac*-BBL in toluene- $d_8$  at RT recorded after 5 min showed only signals at 56.6 and -5.6 ppm corresponding to (OR)BC $_8$ H $_{14}$  species and the apical B-H of Tp<sup>tBu,Me</sup>, respectively. No resonances corresponding to unreacted **14** or B(OR) $_4$  were observed. As shown in Figure 5.29, the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Ca(BD $_4$ )(THF) (**8-d<sub>4</sub>**) also followed second order dependence on [*rac*-BBL] with  $k_{\text{app}} = 0.98(3) \text{ M}^{-1}\text{min}^{-1}$  ( $R^2 = 0.985$ ) comparable with that measured from **8**. Poor agreement between  $M_n(\text{GPC})$  and  $M_n(\text{calcd})$  with broad  $\bar{D}$  values (1.86-1.95) were observed (Table 5.5). Assuming first order dependence on [**8**] or [**8-d<sub>4</sub>**], the propagation rate constants ( $k_p$ ) for the ROP of *rac*-BBL with [**8**] or [**8-d<sub>4</sub>**] equal to 220 and 196  $\text{M}^{-2}\text{min}^{-1}$ , respectively. Isotactically-enriched PHBs with  $P_m = 0.83$ -0.84 were produced from **8** or **8-d<sub>4</sub>**.

Polymer end group analysis by  $^1\text{H}$  NMR spectroscopy of PHBs formed by 20 equiv. of *rac*-BBL with **8** or **14** showed  $\alpha,\omega$ -dihydroxytelechelic PHB, and PHB with *trans*-crotonate and  $-\text{CHMeCH}_2\text{CH}_2\text{OH}$  end groups. Due to the significantly higher reactivity of calcium complexes (**8** or **14**) than magnesium complexes (**20** or **22**), extensive elimination reaction occur at the post-polymerisation stages leading to the formation of the double bond of the *trans*-crotonate unit.

As mentioned in the proposed mechanism for the ROP by **20** (Scheme 5.6),  $\alpha,\omega$ -dihydroxytelechelic PHB was formed by migration of two hydrides from the BH $_4$  group to BBL followed by the ring-opening of BBL. The assignment of  $-\text{CHMeCH}_2\text{CH}_2\text{OH}$  end group was confirmed by deuterium labelling experiments using **8-d<sub>4</sub>**. The  $^1\text{H}$  NMR spectrum of PHB formed using **8-d<sub>4</sub>** (Figure 5.30, b) shows no signal at 4.11 ppm corresponding to the methylene protons of  $-\text{CHMeCH}_2\text{CH}_2\text{OH}$  end group, which is observed for PHB formed using **8** (Figure 5.30, a). While the  $^2\text{H}$  NMR spectrum (Figure 5.30, c) shows a broad signal between 4.0-4.3 ppm assigned to  $-\text{CHMeCH}_2\text{CD}_2\text{OH}$ . Complex **8-d<sub>4</sub>** showed similar ROP behaviour compared to **8**, giving comparable  $k_{\text{app}}$  values,  $M_n(\text{GPC})$  and tacticity (Table 5.5, entry 7 and 8).

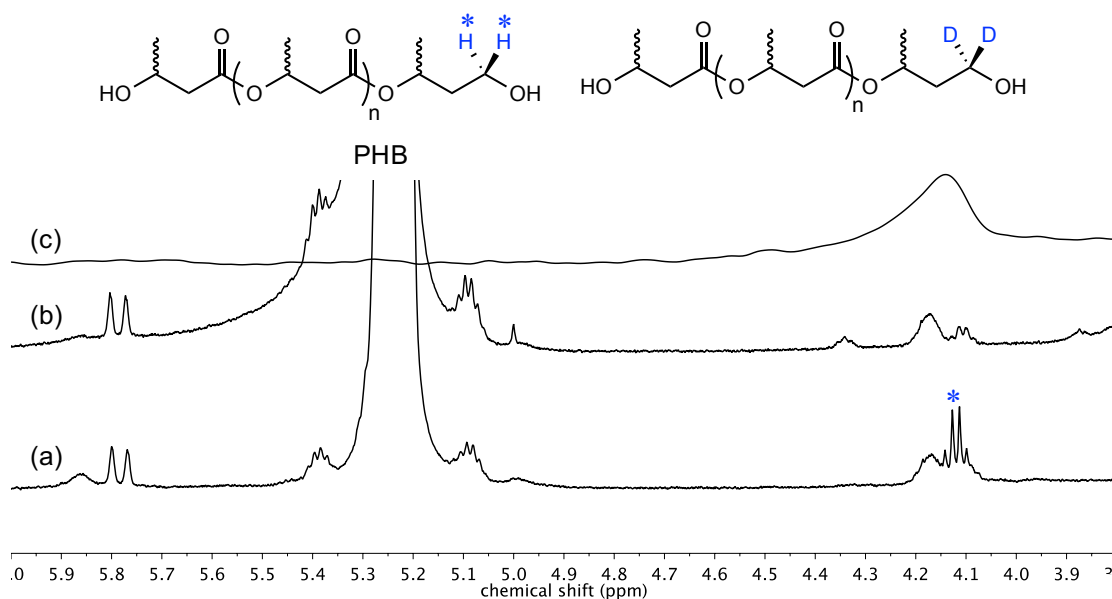


**Figure 5.30**  $^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PHBs formed by 20 equiv. of *rac*-BBL with (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) or (b)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**).  $^2\text{H}$  NMR spectrum ( $\text{CHCl}_3$ , 76.7 MHz, 298 K) of (c) PHB formed by 20 equiv. of *rac*-BBL and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**).

### 5.10 ROP of *rac*-BBL using $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$ (**10**)

$(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) was active in the ROP of *rac*-BBL, reaching full conversion within 20 s (Table 5.6). The polymerisation rate is comparable to that obtained from  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**). However, better control of  $M_n$  and  $D$  values were observed. The polymerisation of 100 equiv. of *rac*-BBL initiated by **10** in toluene at RT produced PHB with good agreement between  $M_n$  analysed by GPC or  $^1\text{H}$  NMR and those calculated for one chain per metal centre. A relatively narrow  $D$  value (1.14) was observed. Isotactically-enriched PHB ( $P_m = 0.83$ ) was obtained.

**Table 5.6** Selected data for the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF) (**10**).<sup>a</sup>

| Entry | [ <i>rac</i> -BBL] <sub>0</sub> : <b>10</b> <sub>0</sub> | Time<br>(s) | <i>M</i> <sub>n</sub> (GPC) <sup>b</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (NMR) <sup>d</sup><br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>e</sup> | <i>P</i> <sub>m</sub> <sup>f</sup> | Ratio <sup>g</sup> |
|-------|----------------------------------------------------------|-------------|--------------------------------------------------------------------|----------------------------------------------------------------------|--------------------------------------------------------------------|-----------------------|------------------------------------|--------------------|
| 1     | 100                                                      | 20          | 9,690                                                              | 8,723                                                                | 9,936                                                              | 1.14                  | 0.83                               | 1:1                |
| 2     | 20                                                       | 10          | 3,350                                                              | 1,836                                                                | 3,076                                                              | 1.30                  | <sup>h</sup>                       | 0.8:1              |

<sup>a</sup> Conditions: [*rac*-BBL]<sub>0</sub> = 0.5 M in 3.0 mL toluene at RT, conversion >99%. <sup>b</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 18.32 μL g<sup>-1</sup> and α = 0.69. <sup>c</sup> Calculated *M*<sub>n</sub> (g mol<sup>-1</sup>) for –OH and –OCyMe end groups = [*rac*-BBL]<sub>0</sub>: [initiator]<sub>0</sub> × 86.1 + 114.1 <sup>d</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated polymer by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>, δ = 5.25 ppm) and those of methine proton of –OCyMe end group (OCHCHMe, δ = 4.40 ppm). <sup>e</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>f</sup> *P*<sub>m</sub> is determined by carbonyl region of inverse gated <sup>13</sup>C{<sup>1</sup>H} NMR spectra. <sup>g</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses from the relative integration ratio of vinyl proton of *trans*-crotonate end group (MeCH=CH, δ 6.92 ppm) : methine proton adjacent to –OH end group (HOCHMe, δ 4.14 ppm). <sup>h</sup> Not measured.

With  $[rac\text{-BBL}]_0:[\mathbf{10}]_0 = 20:1$  (Table 5.6),  $M_n(\text{GPC})$  values are double those calculated for one chain per metal centre and  $D = 1.30$  which is broader than that obtained when  $[rac\text{-BBL}]_0:[\mathbf{10}]_0 = 100:1$  ( $D = 1.14$ ). These indicated the greater propagation than initiation rate for the ROP which become more apparent at lower monomer loadings. The  $^1\text{H}$  NMR spectrum (Figure 5.31) of isolated PHB formed using  $\mathbf{10}$  showed the presence of a *trans*-crotonate end group, characteristic of elimination reaction post polymerisation. The relative ratio of protons in the *trans*-crotonate ( $-\text{CH}=\text{CHMe}$ ) and  $-\text{CHMeOH}$  end groups is 0.8:1 (Figure 5.31), which is comparable to that obtained from the ROP using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  ( $\mathbf{22}$ ) at 80 °C for 12 h (Table 5.2, entry 3).

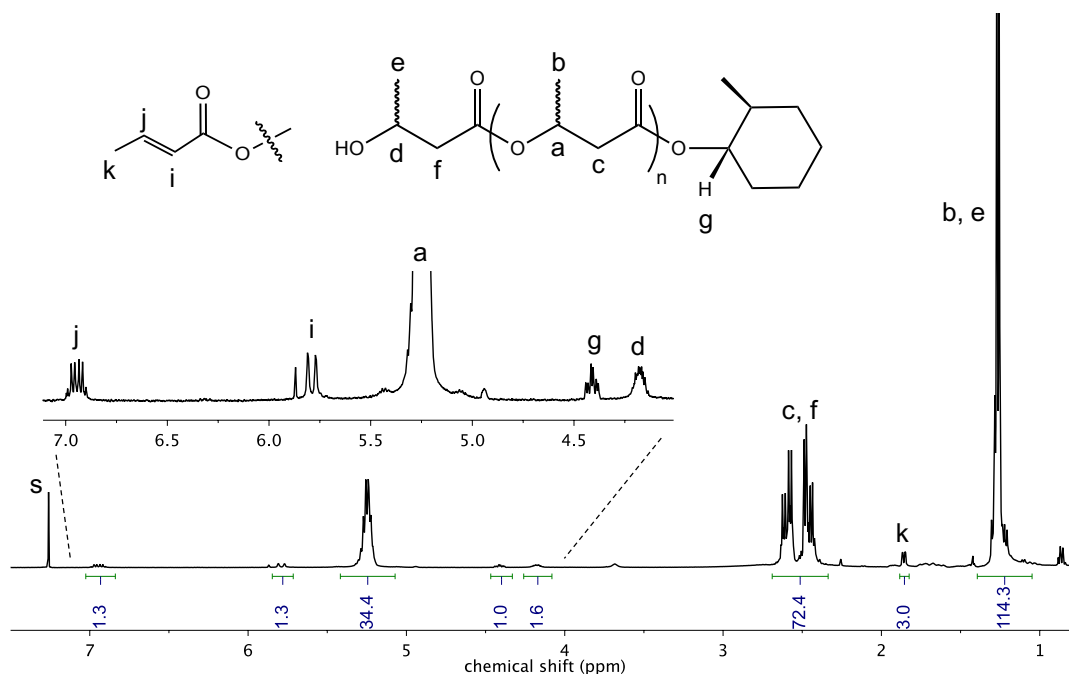


**Figure 5.31**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PHB formed using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  ( $\mathbf{10}$ ). Conditions:  $[rac\text{-BBL}]_0:[\mathbf{10}]_0 = 20:1$ ,  $[rac\text{-BBL}]_0 = 0.5$  M, 1.0 mL toluene at RT for 20 s.  $M_n(\text{NMR}) = 3,076$  g mol $^{-1}$ . “s” denotes residual protio solvent.

MALDI-ToF mass spectrum of PHB formed using  $\mathbf{10}$  (Figure 5.32) shows peak envelopes corresponding to PHB with  $-\text{OCyMe}$  and *trans*-crotonate end groups as a major distribution, and PHB with  $-\text{OCyMe}$  and  $-\text{OH}$  end groups as a minor distribution. For example, a peak envelope centred at 1238.0 Da corresponds to PHB containing 12 BBL units with  $-\text{OCyMe}$  and *trans*-crotonate end groups and  $\text{Na}^+$   $[86.1(12) + 113.1 + 69.0 + 23.0]$ . Whereas another peak envelope centred at 1256.1

Da corresponds to PHB containing 13 BBL units with –OCyMe and –OH end groups and  $\text{Na}^+$   $[86.1(12) + 114.1 + 23.0]$ .

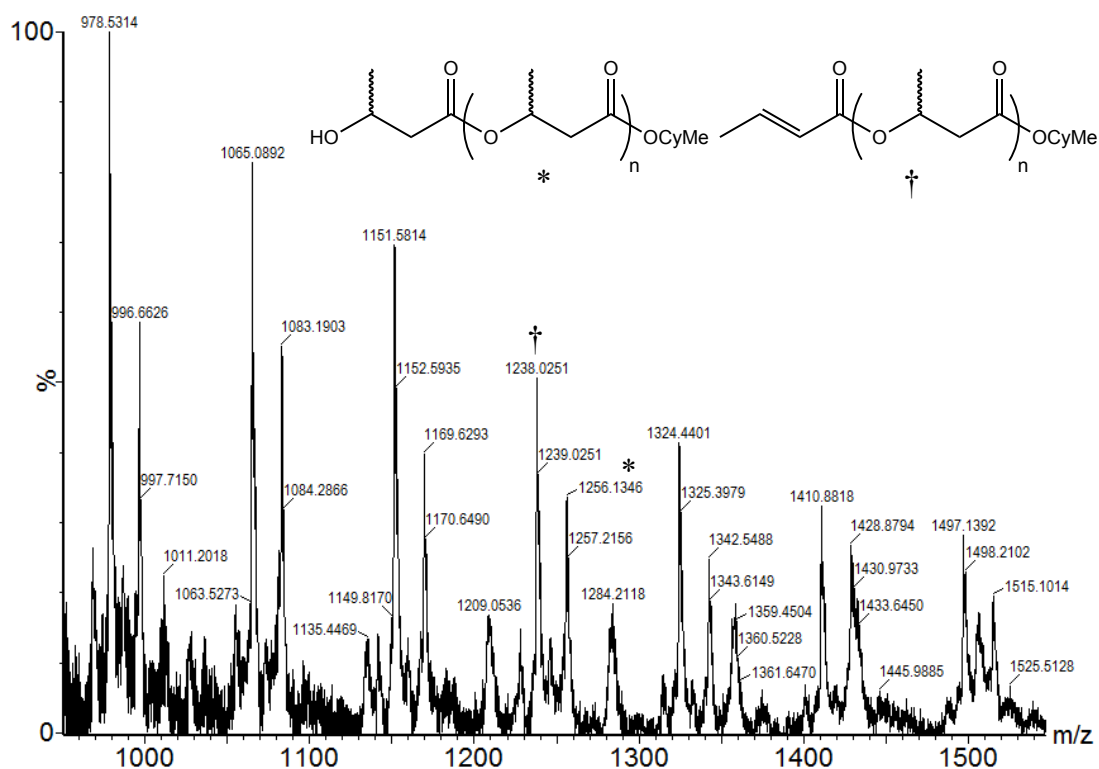


**Figure 5.32** MALDI-ToF MS of PHB synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**).  $M_n(\text{GPC}) = 3,350 \text{ g mol}^{-1}$ ,  $D = 1.30$ . Conditions:  $[\text{rac-BBL}]_0:[\textbf{10}]_0 = 20:1$ ,  $[\text{rac-BBL}]_0 = 0.5 \text{ M}$ ,  $1.0 \text{ mL}$  toluene at RT.  $\text{Na}^+$  dopant.  $\Delta(m/z) = 86.1 \text{ Da}$  between peak envelopes. “\*” denotes PHB with –OCyMe and –OH end groups. “†” denotes PHB with –OCyMe and *trans*-crotonate end groups.

### 5.11 Immortal ROP of *rac*-BBL using calcium alkoxide complexes and borate esters as chain transfer agents

The use of borate esters  $\text{B}(\text{OR})_3$  as chain transfer agents in the ROP of *rac*-BBL with calcium alkoxide complexes was examined.  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) was reacted with 4 equiv. of 2-methylcyclohexanone or benzaldehyde giving  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) with  $\text{B}(\text{OCyMe})_3$  (**24**) or  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) with  $\text{B}(\text{OBn})_3$  (**25**), respectively. The polymerisation results are summarised in Table 5.7.

**Table 5.7** Selected data for the ROP of *rac*-BBL using (Tp<sup>tBu,Me</sup>)Ca(BH<sub>4</sub>)(THF) (**8**) with additives.<sup>a</sup>

| Entry | Additives | [ <i>rac</i> -BBL] <sub>0</sub><br>:[ <b>8</b> ] <sub>0</sub> | Time<br>(s) | <i>M</i> <sub>n</sub> (GPC) <sup>b</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (calcd) <sup>c</sup><br>(g mol <sup>-1</sup> ) | <i>M</i> <sub>n</sub> (NMR)<br>(g mol <sup>-1</sup> ) | <i>D</i> <sup>f</sup> | <i>P</i> <sub>m</sub> <sup>g</sup> | Ratio <sup>h</sup> |
|-------|-----------|---------------------------------------------------------------|-------------|--------------------------------------------------------------------|----------------------------------------------------------------------|-------------------------------------------------------|-----------------------|------------------------------------|--------------------|
| 1     | 4 CyMeO   | 100                                                           | 20          | 8,430                                                              | 2,266                                                                | 9,998 <sup>d</sup>                                    | 1.13                  | 0.83                               | 0.8:1              |
| 2     | 4 PhCHO   | 200                                                           | 60          | 8,860                                                              | 4,412                                                                | 6,509 <sup>e</sup>                                    | 1.39                  | 0.83                               | 0.2:1              |
| 3     | 4 PhCHO   | 100                                                           | 20          | 5,040                                                              | 2,260                                                                | 3,637 <sup>e</sup>                                    | 1.36                  | 0.84                               | 0.2:1              |
| 4     | 4 PhCHO   | 20                                                            | 10          | 2,930                                                              | 539                                                                  | 1,865 <sup>e</sup>                                    | 1.30                  | <sup>i</sup>                       | 0.3:1              |

<sup>a</sup> Conditions: [*rac*-BBL]<sub>0</sub> = 0.5 M in 3.0 mL toluene at RT, conversion >99%. <sup>b</sup> Molecular weights (g mol<sup>-1</sup>) determined by GPC in THF at 30 °C using Mark-Houwink parameters, K = 18.32 μL g<sup>-1</sup> and α = 0.69. <sup>c</sup> Calculated *M*<sub>n</sub> (g mol<sup>-1</sup>), *M*<sub>n</sub> (entry 1) for –OH and –OCyMe end groups = ([*rac*-BBL]<sub>0</sub>:[initiator]<sub>0</sub> × 86.1)/4 + 114.1, *M*<sub>n</sub> (entry 2-4) for –OH and –OBn end groups = ([*rac*-BBL]<sub>0</sub>:[initiator]<sub>0</sub> × 86.1)/4 + 108.1. <sup>d</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated polymer by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>, δ = 5.25 ppm) and those of methine proton of –OCyMe end group (OCHCHMe, δ = 4.40 ppm). <sup>e</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses of isolated polymer by using the relative intensities of the signals of the PHB main-chain methine protons (OCHMeCH<sub>2</sub>, δ = 5.25 ppm) and those of methylene protons of –OBn end group (OCH<sub>2</sub>Ph, δ = 5.11 ppm). <sup>f</sup> *D* = *M*<sub>w</sub>/*M*<sub>n</sub>. <sup>g</sup> *P*<sub>m</sub> is determined by carbonyl region of inverse gated <sup>13</sup>C{<sup>1</sup>H} NMR spectra. <sup>h</sup> Measured by <sup>1</sup>H NMR (CDCl<sub>3</sub>) analyses from the relative integration ratio of vinyl proton of *trans*-crotonate end group (MeCH=CH, δ 6.92 ppm) : methine proton of –OH end group (HOCHMe, δ 4.17 ppm). <sup>i</sup> Not measured.

Similar to the results obtained from the ROP of *rac*-LA using **10** with B(OCyMe)<sub>3</sub> (**24**) described in Chapter Four, the bulky borate ester (**24**) was inefficient chain transfer agent. The presence of **24** had a negligible effect on rate and  $M_n$  compared to the results obtained from the ROP using only **10** (Table 5.6). With 100 equiv. of *rac*-BBL, full conversion was reached after 20 s (Table 5.7, entry 1). The  $M_n$  values of PHBs analysed by GPC or <sup>1</sup>H NMR were consistent with those calculated for one growing chain per metal centre, with a relatively narrow  $\bar{D}$  (1.13).

On the other hand, the ROP involving the less sterically hindered borate ester B(OBn)<sub>3</sub> (**25**) showed a chain transfer effect on the molecular weights. As shown in Table 5.7 (entry 2-4), the  $M_n$  values measured by <sup>1</sup>H NMR or GPC were double those calculated for four growing chains per metal centre, suggesting the greater propagation than chain transfer rate. Surprisingly, only moderate  $\bar{D}$  values (1.36-1.39) were obtained. The tacticity was not affected by the chain transfer reaction as isotactically-enriched PHBs with  $P_m = 0.83$ -0.84 were obtained for all the systems.

It is noteworthy that PHBs formed by the ROP involving **25** showed less formation of *trans*-crotonate end group than those formed by the ROP involving **24**, evidenced by the integration ratio of *trans*-crotonate and –OH chain ends (Table 5.7) and MALDI-ToF MS (*vide infra*). This could be attributed to an exchange between growing polymer chain and **25** by chain transfer reaction which suppresses the degradation of PHB on the metal centre.

MALDI-ToF mass spectrum of PHB synthesised by using **8** and 4 equiv. of benzaldehyde (Figure 5.33) shows a major distribution of peak envelopes corresponding to PHB with –OH and –OBn end groups. Peak envelopes corresponding to PHB with *trans*-crotonate and –OBn end groups were observed as a minor distribution. For example, the peak envelope centred at 1336.0 Da corresponds to –OH and –OBn terminated PHB containing 14 BBL units with Na<sup>+</sup> [86.1(14) + 108.1 + 23.0]. Another peak envelope centred at 1318.0 Da is assigned to *trans*-crotonate and –OBn terminated PHB containing 13 BBL units with Na<sup>+</sup> [86.1(13) + 69.0 + 107.1 + 23.0].

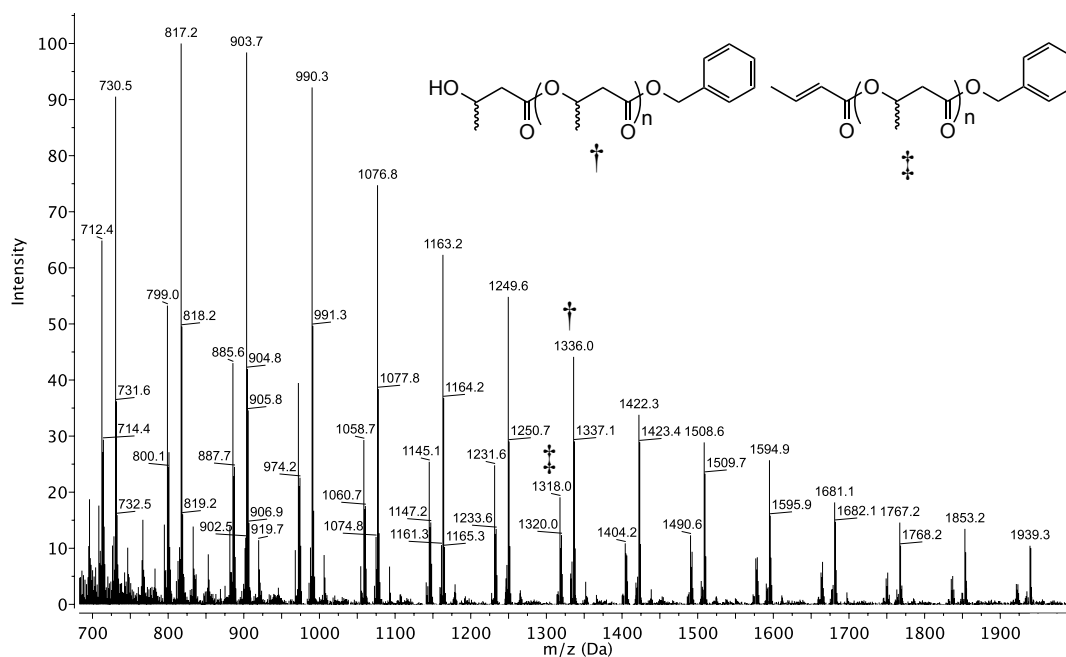


**Figure 5.33** MALDI-ToF MS of PHB synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and 4 equiv. of benzaldehyde.  $M_n(\text{GPC}) = 2,930 \text{ g mol}^{-1}$ ,  $D = 1.30$ . Conditions:  $[\text{rac-BBL}]_0:[\textbf{8}]_0:[\text{PhCHO}]_0 = 20:1:4$ ,  $[\text{rac-BBL}]_0 = 0.5 \text{ M}$ , 1.0 mL toluene at RT.  $\text{Na}^+$  dopant.  $\Delta(m/z) = 86.1 \text{ Da}$  between peak envelopes. “†” denotes PHB with  $-\text{OBn}$  and  $-\text{OH}$  end groups. “‡” denotes PHB with  $-\text{OBn}$  and *trans*-crotonate end groups.

## 5.12 Summary and Conclusions for Chapter Five

$(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**) was active in the ROP of *rac*-BBL in toluene at RT. With  $[\text{rac-BBL}]_0:[\textbf{22}]_0 = 100$  and 20, conversions over 82% were reached after 48 h and 6 h, respectively. First order dependence on *rac*-BBL concentration was determined. The resulting PHBs showed good agreement between measured  $M_n$  from GPC or  $^1\text{H}$  NMR and those calculated for one chain per metal centre with narrow  $D$  values (1.04–1.07). Atactic PHBs were formed with  $P_r = 0.48$ . The polymer end group analysis by  $^1\text{H}$  NMR and MALDI-ToF MS showed PHB terminated with  $-\text{OH}$  and  $-\text{OBn}$  groups with a very minor distribution of PHB with  $-\text{OBn}$  and *trans*-crotonate end groups. To investigate the formation of the *trans*-crotonate group, the polymerisation of 20 equiv. of *rac*-BBL with **22** was performed in toluene- $d_8$  at 80 °C for 12 h. Full conversion was reached after 1 h. The  $^1\text{H}$  NMR spectra recorded after 1 h until 12 h showed the formation of *trans*-crotonate end capped PHB and Mg carboxylate species  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-O}_2\text{CCH}_2\text{CHMeOH}\}$  (**22.3**) via crotonate elimination reaction post-polymerisation of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C(O)(BBL)}_n\text{OBn}\}$  (**22.2**). PHB with



*trans*-crotonate and –OBn termini was characterised from  $^1\text{H}$  NMR and MALDI-ToF analyses.

DFT calculations using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-}\{\text{OCHMeCH}_2\text{C}(\text{O})\}_2\text{O}^i\text{Pr}\}$  (**22.2Q''**) as a model for **22.2** show that an elimination is thermally accessible *via* the transition state **TS\_6-membered** to form the alkoxide carboxylic species (**22.5Q**) and *trans*- $^i\text{PrOC}(\text{O})\text{CH}=\text{CHMe}$  (in the DFT system). The subsequent crotonate elimination reaction involves a rearrangement of **22.5Q** to the carboxylate isomer **22.3Q** which is exergonic by  $-16.5\text{ kcal mol}^{-1}$ .

The mechanism for the ROP of *rac*-BBL with **22** is proposed to operate *via* a coordination-insertion mechanism. The mono-insertion product  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}\}$  (**22.1**) acting as propagating species was observed from the reaction of **22** and 1 equiv. of *rac*-BBL in toluene- $d_8$ . DFT calculations for **22** with (*R*)-BBL show that the first and second insertion reactions, leading to an –OBn terminated growing polymer chain, are thermodynamically favourable. PHB end capped with –OH and –OBn groups is formed after hydrolysis. The elimination at the termination stage leads to PHB terminated with *trans*-crotonate and –OBn groups for prolonged polymerisation time and high temperature.

The immortal ROP of *rac*-BBL with **22** and  $\text{B}(\text{OBn})_3$  as a chain transfer agent was performed. With  $[\textit{rac}\text{-BBL}]_0:[\textbf{22}]_0:[\text{B}(\text{OBn})_3]_0 = 100:1:1$  or  $100:1:3$ , conversions over 85% were achieved after 48 h. The resultant PHBs showed moderate  $\bar{D}$  values (1.20–1.25) and good agreement between measured  $M_n$  and those calculated for two chains per metal centre, indicating the chain transfer ability of  $\text{B}(\text{OBn})_3$  and the greater propagation rate than chain transfer rate.

The catalytic activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) in the ROP of *rac*-BBL was studied. With  $[\textit{rac}\text{-BBL}]_0:[\textbf{20}]_0 = 100$  and 20, conversions over 85% were reached after 72 h and 10 h, respectively. First order dependence on *rac*-BBL concentration was determined. Good agreement between measured  $M_n$  and those calculated for one chain per metal centre with moderate  $\bar{D}$  values (1.18–1.23) were observed. Atactic PHBs were produced with  $P_r = 0.47$ . The presence of –OH and – $\text{CH}_2\text{CH}_2\text{OH}$  end groups confirmed by NMR spectroscopy was consistent with that reported by Guillaume *et al.*<sup>79</sup> Deuterium labelling experiments using  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BD}_4)$  (**20**) also showed the formation of –OH and – $\text{CH}_2\text{CD}_2\text{OH}$  end capped PHB, analysed by  $^1\text{H}$  and

$^2\text{H}$  NMR spectroscopy. The second hydride transfer products (**28** and **29**) synthesised by reaction of  $\text{BH}_3(\text{SMe}_2)$  and *rac*-BBL displayed the cyclic borate esters,  $\text{HB}(\text{OR})_2$  and  $\text{B}(\text{OR})_3$  ( $\text{OR}$  = ring-opened BBL), characterised by NMR and ESI-HRMS. The proposed mechanism for the ROP of *rac*-BBL using **20** begins with two-hydride migration from  $\text{BH}_4$  group of **20** to the carbonyl carbon of *rac*-BBL.  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{CH}_2\text{OBH}_2\}$  (**A**) is generated and subsequently redistributed to form  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{(\mu\text{-H})_2\text{BO}_2\text{C}_4\text{H}_8\}$  (**B**). Two hydrides of **B** then migrate to the carbonyl carbon of *rac*-BBL to produce tetra alkoxy borate species,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BO}_4\text{C}_8\text{H}_{16})$  (**C**), acting as an initiator. The growing polymer chain terminated with  $-\text{CHMeCH}_2\text{CH}_2\text{OBO}_2\text{C}_4\text{H}_8$  group (**D** or **E**) is formed on the metal centre in the propagation step. PHB with  $-\text{OH}$  and  $-\text{CHMeCH}_2\text{CH}_2\text{OH}$  end groups is obtained after hydrolysis.

DFT calculations show computed  $^{11}\text{B}$  NMR chemical shifts of 2.3 and 20.0 ppm for  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\kappa^2\text{-BO}_4\text{C}_8\text{H}_{16})$  (**C**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{-OCHMeCH}_2\text{CH}_2\text{OBO}_2\text{C}_4\text{H}_8\}$  (**D**), respectively. These are consistent with experimentally observed  $^{11}\text{B}$  NMR signals at 2.1 and 18.1 ppm. The Gibbs free energies also show that ROP of *rac*-BBL with **20** via the formation of **C** and **D** is exergonic ( $-97.4$  and  $-98.5$  kcal mol $^{-1}$ ).

The polymerisation activity of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) was also examined. **14** was highly active for the ROP of **20** and **100** equiv. of *rac*-BBL, reaching full conversion within 10-20 s. Complex **8** was less active, converting **20** and **100** equiv. of *rac*-BBL after 10 and 60 min, respectively. Second order dependence on  $[\textit{rac}\text{-BBL}]$  was determined. Poor control over molecular weights and moderate  $D$  values (1.30-1.74) were observed. The measured  $M_n$  values were considerably higher than those calculated for one chain per metal centre, indicating greater propagation than initiation rate. Complexes **14** and **8** gave PHB with  $-\text{OH}$  and  $-\text{CH}_2\text{CH}_2\text{OH}$  end groups, and PHB with *trans*-crotonate and  $-\text{CH}_2\text{CH}_2\text{OH}$  end groups.  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BD}_4)(\text{THF})$  (**8-d<sub>4</sub>**) was used to confirm the existence of  $-\text{CH}_2\text{CH}_2\text{OH}$  end group. PHB with  $-\text{CH}_2\text{CD}_2\text{OH}$  end group was obtained from **8-d<sub>4</sub>**. All complexes gave isotactically-enriched PHBs with  $P_m = 0.83\text{-}0.84$ .

(Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF) (**10**) showed comparable ROP rates to **14** and **8**. Close agreement between measured  $M_n$  values with those calculated for one chain per metal centre and moderate  $D$  values (1.14-1.30) were observed. PHB terminated with –OH and –OCyMe, and PHB terminated with *trans*-crotonate and –OCyMe were observed from NMR spectroscopy and MALDI-ToF mass spectrometry. The immortal ROP of *rac*-BBL with calcium alkoxide initiator and B(OR)<sub>3</sub> as chain transfer agents was investigated. The chain transfer reaction was not observed from the ROP involving B(OCyMe)<sub>3</sub> (**24**) as the substituent is too large to exchange with the polymer chain on the metal centre. The resultant PHBs showed good agreement between measured and calculated  $M_n$  for one chain per metal centre and a relatively narrow  $D$  value (1.13). In contrast, the ROP involving B(OBn)<sub>3</sub> (**25**) gave PHBs with measured  $M_n$  consistent with those calculated for two chains per metal centre and moderate  $D$  values (1.30-1.39). All PHBs showed isotactic enrichment with  $P_m = 0.83$ -0.84.

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# **Chapter Six**

**Experimental details and characterising data**

## Chapter Six

### 6.1 General methods and implementation

All air and moisture sensitive manipulations were carried out using Schlenk line or glove box techniques under an atmosphere of argon or dinitrogen. THF and toluene were pre-dried over activated 4 Å molecular sieves before refluxing in potassium (THF) and sodium (toluene) followed by distillation. Pentane, hexane and benzene were degassed by sparging with dinitrogen and dried by passing through a column of activated alumina.<sup>1</sup> Deuterated solvents were dried over sodium ( $C_6D_6$  and toluene- $d_8$ ), potassium (THF- $d_8$ ) and  $P_2O_5$  ( $CD_2Cl_2$ ), distilled at reduced pressure and stored under argon in Teflon valve ampoules.  $CDCl_3$  was used as received for air-stable polymer samples.

NMR samples were prepared in a glove box in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves.  $^1H$ ,  $^2H$ ,  $^{13}C\{^1H\}$ ,  $^{11}B$  and  $^{11}B\{^1H\}$  NMR spectra were recorded on Bruker Advance III 400, Bruker Advance III 500 spectrometers at ambient temperature unless stated otherwise.  $^1H$  and  $^{13}C\{^1H\}$  spectra were referenced internally to residual protio-solvent ( $^1H$ ) or solvent ( $^{13}C$ ) resonances, and are reported relative to tetramethylsilane ( $\delta = 0$  ppm).  $^2H$  NMR spectra were referenced to the natural abundance deuterium resonance of the protio-solvent. Chemical shifts are quoted in  $\delta$  (ppm) and coupling constants ( $J$ ) in Hz. Assignments were confirmed using two dimensional  $^1H$ - $^1H$  (COSY, TOCSY and ROESY),  $^{13}C$ - $^1H$  (HSQC, HMBC and HSQC-TOCSY).  $^1H\{^1H\}$  (homonuclear decoupled) NMR experiments were performed with a Bruker Advance III 500 spectrometers at ambient temperature. The tacticity of PLA was analysed by  $^1H\{^1H\}$  NMR spectroscopy. In this thesis,  $P_r$  values were calculated from integration obtained from  $^1H\{^1H\}$  NMR spectra as described in Chapter One. Alternatively, the probability of a particular tetrad can be calculated using Bernoullian statistics. Peak deconvolution, using Mestrenova software package, was used to improve accuracy in the determination. These two methods gave the same  $P_r$  values for each PLA. The Quantitative  $^{13}C\{^1H\}$  NMR was used to determine the microstructure of PHB samples with relaxation delay 1.5 s.  $P_r$  and  $P_m$  values of PHB samples were calculated from diad sequences in the carbonyl region (169.0-169.3 ppm).

IR spectra were recorded on a Thermo Scientific Nicolet iS5 FTIR spectrometer. Samples were prepared in a glove box as Nujol mulls between NaCl plates or as a

solution (10 mg in 0.5 mL THF) in a NaCl cell. IR data are reported in wavenumbers within the range 4,000-400  $\text{cm}^{-1}$ . Mass spectra were recorded by the departmental service of University of Oxford. Elemental analysis was carried out by the Elemental Analysis Service at the London Metropolitan University.

MALDI-ToF MS analysis was performed on a Waters MALDI microTOF MX mass spectrometre equipped with a 337 nm nitrogen laser and an accelerating voltage of 25kV was applied. The polymer samples were dissolved in THF at a concentration of 1.0  $\text{mg mL}^{-1}$ . The cationising agent used was potassium trifluoroacetate (Fluka, >99%) for PLA samples and sodium chloride for PHB samples dissolved in THF at a concentration of 5  $\text{mg mL}^{-1}$ . The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methy-2-propenylidene]malononitrile (DCTB) (Fluka) for PLA samples and 2,5-dihydroxybenzoic acid (DHB) for PHB samples and was dissolved in THF at a concentration of 40.0  $\text{mg mL}^{-1}$ . Solutions of matrix, cationising agent and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI plate and left to dry. The spectra were recorded in positive reflectron mode. External instrument calibration was performed using a mixture of standard peptides. Data was analysed with MassLynx and MestReNova.

Polymer molecular weights ( $M_n$ ,  $M_w$  and  $\bar{D}$ ) were determined by GPC using a Polymer Laboratories PL-GPC50 Plus instrument equipped with a Polymer Laboratories PLgel Mixed-D column (300 mm length, 7.5 mm diameter) and a refractive index (RI) detector. THF (Fisher, HPLC grade, stabilised with BHT, 2.5 ppm) was used as an eluent at 30 °C with a flow rate of 1.0  $\text{mL min}^{-1}$ . Samples were dissolved in THF (Fisher, HPLC grade, stabilised with BHT, 2.5 ppm) at a concentration of 2.0  $\text{mg mL}^{-1}$  and filtered before injection. Linear polystyrenes (Polymer Laboratories) were used as primary calibration standards and the appropriate Mark-Houwink corrections for polylactide (PLA) ( $K = 17.4 \mu\text{L g}^{-1}$  and  $\alpha = 0.736$ ) and polyhydroxybutyrate (PHB) ( $K = 18.32 \mu\text{L g}^{-1}$  and  $\alpha = 0.69$ ) in THF at 30 °C were applied to calculate the experimental molecular weights.<sup>2-4</sup>

## 6.2 Literature preparations and reagent purification

( $\text{Tp}^{\text{tBu,Me}}$ )Ca(HBEt<sub>3</sub>)(THF) (**1**), ( $\text{Tp}^{\text{tBu,Me}}$ )Sr(HBEt<sub>3</sub>)(THF)<sub>2</sub> (**2**), ( $\text{Tp}^{\text{tBu,Me}}$ )<sub>2</sub>Sr (**3**), ( $\text{Tp}^{\text{tBu,Me}}$ )Ca(BH<sub>4</sub>)(THF) (**8**), ( $\text{Tp}^{\text{tBu,Me}}$ )Ca(BD<sub>4</sub>)(THF) (**8-d**), ( $\text{Tp}^{\text{tBu,Me}}$ )Ca{( $\mu$ -H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**), ( $\text{Tp}^{\text{tBu,Me}}$ )Mg(BH<sub>4</sub>) (**20**), ( $\text{Tp}^{\text{tBu,Me}}$ )Sr(BH<sub>4</sub>)(THF)<sub>2</sub> (**21**), and

(Tp<sup>tBu,Me</sup>)Mg(OBn) (**22**) were prepared according to or adapted from literature procedures.<sup>5, 6</sup> *Rac*-, *L*- and *D*-LA were provided by Purac and used as received. Crude *meso*-LA was provided by Uhde Inventa-Fisher which was purified by repeated recrystallisation from isopropanol at -30 °C, followed by recrystallisation from toluene and sublimed twice under reduced pressure. *Rac*-BBL purchased from Sigma Aldrich was stirred with CaH<sub>2</sub> for five days and distilled under *vacuo* and followed by freeze-pump-thaw degassing. *Rac*-, *L*-, *D*- and *meso*-LA and *rac*-BBL were stored in a glove box. Benzophenone and 9-borabicyclo[3.3.1]nonane dimer purchased from Sigma Aldrich were used as received. Benzylalcohol (Sigma Aldrich), isopropanol (Sigma Aldrich), 2-methylcyclohexanone (Sigma Aldrich) and 2-methylcyclohexanol (Sigma Aldrich) were dried over calcium hydride for a day at RT, distilled under reduced pressure and degassed prior to use.<sup>7</sup> Benzaldehyde (Sigma Aldrich) was purified by literature procedures and distilled prior to use.<sup>7</sup> Purified 1,4-dimethoxybenzene was dried under *vacuo* and stored in a glove box. B(OBn)<sub>3</sub> purchased from Sigma Aldrich and stored in a glove box was used without further purification. BH<sub>3</sub>(SMe<sub>2</sub>) (Sigma Aldrich) was freshly distilled under reduced pressure prior to use. Other purified liquid reagents were stored under argon in glass ampoules fitted with J. Young Teflon valves. Other commercially available reagents were used as received.

### 6.3 X-ray data collection and processing parameters

Crystals were mounted on glass fibres using perfluoropolyether oil and cooled rapidly in a stream of cold dinitrogen using an Oxford Cryosystems Cryostream unit.<sup>5</sup> Diffraction data were measured using an Enraf-Nonius KappaCCD diffractometer or Agilent Technologies Supernova diffractometer using Mo- $\kappa\alpha$  or Cu- $\kappa\alpha$ , respectively. As appropriate, absorption and decay corrections were applied to the data and equivalent reflections merged.<sup>8, 9</sup> The structures were solved using SIR92<sup>10</sup> or Superflip<sup>11</sup> and further refinements and all other crystallographic calculations were performed using the CRYSTALS program suite.<sup>12</sup> Other details of the structure solution and refinements are given in the CD Appendix.

### 6.4 Computational Details.

Geometry optimizations for all systems were performed with the Gaussian09 package (rev. D.01)<sup>13</sup> at the B3PW91 level of hybrid density functional theory in the gas phase with all atoms represented by the def2-svp basis set.<sup>14</sup> Dispersion was taken into

account both at the optimization and single point stages using Grimme's d3(bj) corrections<sup>15</sup> as implemented in Gaussian09. In addition, the solvent (treated as benzene) influence was taken into consideration in the single point calculations on the gas-phase optimised geometry with SCRF calculations within the SMD model. Gibbs free energies and enthalpies were obtained by summing the SMD energy and the gas-phase Gibbs or enthalpy contribution at 298.15 K obtained from the geometry optimisations, and the d3(bj) correction. NMR chemical shifts were computed using the GIAO method<sup>16, 17</sup> as implemented in Gaussian09 at the B3PW91 level. All atoms were described with the pcSseg-2 NMR basis sets of Jensen.<sup>18</sup> The <sup>11</sup>B NMR shifts are referenced with respect to the experimental value of -19.3 ppm for BH<sub>3</sub>(SMe<sub>2</sub>). The Cartesian coordinates for the following structures are provided as a separate file.

### 6.5 Experimental details and characterising data for Chapter Two

**(Tp<sup>tBu,Me</sup>)<sub>2</sub>Ca (4).** A solution of (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (5) in benzene was stored at 4 °C for a week, yielding 4 as colourless crystals.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.96 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 5.80 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 2.29 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 2.21 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 1.28 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 1.17 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 163.6 (3-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 162.8 (3-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 146.7 (5-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 145.6 (5-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 104.4 (4-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 103.9 (4-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 32.5 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 32.3 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 31.3 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 30.8 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 14.0 (N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 12.6 (N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): -1.6 (d, <sup>1</sup>J<sub>B-H</sub> = 90.1 MHz, B-H-Ca of Tp<sup>tBu,Me</sup>) and -7.2 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

**(Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (5).** To a solid mixture of K(Tp<sup>tBu,Me</sup>) (0.50 g, 1.08 mmol), CaI<sub>2</sub> (0.32 g, 1.08 mmol) and K[N(SiMe<sub>3</sub>)<sub>2</sub>] (0.22 g, 1.08 mmol) was added THF (20 mL). The solution was stirred 18 h. The solvent was removed *in vacuo* and the product was extracted into benzene (40 mL). The solution was concentrated to about 10 mL and stored at 4 °C, yielding 5 as colourless crystals. Yield: 0.15 g (23 %).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.66 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 2.14 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 1.40 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 0.36 (18H, s, N(SiMe<sub>3</sub>)<sub>2</sub>) ppm, B-H of Tp<sup>tBu,Me</sup> not observed. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 163.3 (3-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 146.5 (5-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 103.0 (4-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 32.4

(N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 31.7 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 13.4 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 6.0 (N(SiMe<sub>3</sub>)<sub>2</sub>) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): -8.0 (s, B-H of Tp<sup>tBu,Me</sup>) ppm. IR (NaCl plates, Nujol mull, cm<sup>-1</sup>): 1541 (s), 1337 (m), 1234 (m), 1177 (m), 1067 (s), 1015 (s), 879 (s), 818 (s), 782 (m), 768 (m), 644 (m). EI-MS : *m/z* = 463.3038 Da (100%), [(Tp<sup>tBu,Me</sup>)Ca]<sup>+</sup>. Anal. found (calcd. For C<sub>30</sub>H<sub>58</sub>BCa<sub>7</sub>Si<sub>2</sub>): C, 57.62 (57.75); H, 9.46 (9.37); N, 15.59 (15.72) %.

**NMR tube scale reaction of Ca(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> with 8 equiv. of benzophenone.** In a glove box, a THF-*d*<sub>8</sub> solution (0.5 mL) of Ca(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> (1.5 mg, 0.007 mmol) in J. Young NMR tube was treated with benzophenone (10.5 mg, 0.057 mmol) at RT. The <sup>1</sup>H and <sup>11</sup>B NMR spectra recorded after 18 h showed quantitative conversion to Ca(OCHPh<sub>2</sub>)<sub>2</sub>(THF)<sub>x</sub> (**6**) and 2 equiv. of B(OCHPh<sub>2</sub>)<sub>3</sub> (**23**).

<sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 499.9 MHz, 298 K): 7.43 (8H, br, *o*-C<sub>6</sub>H<sub>5</sub> of **6**), 7.22-7.12 (60H, m, C<sub>6</sub>H<sub>5</sub> of **23**), 7.07 (8H, t, <sup>3</sup>*J* = 7.1 Hz, *m*-C<sub>6</sub>H<sub>5</sub> of **6**), 6.98 (4H, t, <sup>3</sup>*J* = 7.2 Hz, *p*-C<sub>6</sub>H<sub>5</sub> of **6**), 6.38 (6H, s, B(OCHPh<sub>2</sub>)<sub>3</sub>), 6.04 (2H, s, Ca(OCHPh<sub>2</sub>)(THF)<sub>x</sub>) ppm. <sup>11</sup>B NMR (THF-*d*<sub>8</sub>, 160.4 MHz, 298 K) : 18.2 (s, B(OCHPh<sub>2</sub>)<sub>3</sub>) ppm.

**(Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF) (**7**).** To a solid mixture of (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**, 0.46 g, 0.73 mmol) and benzophenone (0.14 g, 0.80 mmol) was added THF (20 mL). The solution was stirred for 15 min. The solvent was removed *in vacuo* and the product was recrystallised from THF:pentane (1:5 v/v) at -30 °C, yielding **7** as colourless crystals. Yield: 0.27 g (47 %).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 7.79 (4H, d, <sup>3</sup>*J* = 7.2 Hz, *o*-C<sub>6</sub>H<sub>5</sub>), 7.34 (4H, t, <sup>3</sup>*J* = 7.6 Hz, *m*-C<sub>6</sub>H<sub>5</sub>), 7.34 (2H, m, *p*-C<sub>6</sub>H<sub>5</sub>), 6.49 (1H, s, OCHPh<sub>2</sub>), 5.70 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 3.25 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>), 2.24 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.38 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.22 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>) ppm, B-H of Tp<sup>tBu,Me</sup> not observed. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 162.3 (3-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 153.2 (*i*-C<sub>6</sub>H<sub>5</sub>), 144.5 (5-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 128.1 (*o*-C<sub>6</sub>H<sub>5</sub>), 127.4 (*m*-C<sub>6</sub>H<sub>5</sub>), 125.1 (*p*-C<sub>6</sub>H<sub>5</sub>), 102.1 (4-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 81.5 (OCHPh<sub>2</sub>), 67.7 (OCH<sub>2</sub>CH<sub>2</sub>), 31.7 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 30.9 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 25.2 (OCH<sub>2</sub>CH<sub>2</sub>), 13.1 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): -8.3 (s, B-H of Tp<sup>tBu,Me</sup>) ppm. IR (NaCl plates, Nujol mull, cm<sup>-1</sup>): 2546(w), 1595(w), 1538 (s), 1361(s), 1339 (m), 1240(w), 1194(m), 1173(s), 1134(s), 1068 (s), 1038 (m), 986(w), 882(w), 768(s), 702 (m), 676 (w), 646 (m), 601 (w). EI-

MS:  $m/z$  = 463.2913 Da (100%),  $[(\text{Tp}^{\text{tBu,Me}})\text{Ca}]^+$ . Anal. found (calcd. For  $\text{C}_{41}\text{H}_{59}\text{BCa}\text{N}_6\text{O}_2$ ): C, 68.67 (68.51); H, 8.38 (8.27); N, 11.61 (11.69) %.

**NMR tube scale synthesis of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{S-lactate})$  (**9**).** In a glove box, a THF- $d_8$  solution (0.2 mL) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{N}(\text{SiMe}_3)_2\}$  (**5**, 12 mg, 0.019 mmol) and a THF- $d_8$  solution (0.3 mL) of *S*-methyl lactate (1.8  $\mu\text{L}$ , 0.019 mmol) were prepared in separate J. Young NMR tubes. Outside a glove box, the two J. Young NMR tubes were cooled down at 195 K using acetone/dry ice bath. The solution of *S*-methyl lactate in the J. Young NMR tube was transferred *via* cannula to the the solution of **5** in another J. Young NMR tube. The  $^1\text{H}$  NMR spectrum recorded at 223 K after 10 min showed quantitative conversion to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{S-lactate})$  (**9**). Complex **9** was stabilised and fully characterised *via* NMR spectroscopy at 223 K.

$^1\text{H}$  NMR (THF- $d_8$ , 500.0 MHz, 223 K) 5.78 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 4.78 (1H, q,  $^3J$  = 5.2 Hz,  $\text{OCHMe}$ ), 3.75 (3H, s,  $\text{MeOCO}$ ), 2.37 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 1.32 (3H, s,  $\text{OCHMe}$  overlapping with 27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 0.04 (18 H,  $(\text{N}(\text{SiMe}_3)_2)$  ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.7 MHz, 223 K): 192.5 ( $\text{MeOCO}$ ), 162.5 ( $3\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 144.5 ( $5\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 102.6 ( $4\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 73.2 ( $\text{OCHMe}$ ), 53.0 ( $\text{MeOCO}$ ), 32.4 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.1 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 25.2 ( $\text{OCHMe}$ ), 13.9 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 2.6 ( $(\text{N}(\text{SiMe}_3)_2)$  ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 223 K): -9.8 (s,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

***trans*-( $\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**).** A solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBET}_3)(\text{THF})$  (**1**, 0.57 g, 0.90 mmol) in THF (20 mL) was treated with 2-methylcyclohexanone (110  $\mu\text{L}$ , 0.90 mmol). The solution was stirred for 15 min. The solvent was removed *in vacuo* and the product was recrystallised from THF:pentane (1:5 v/v) at -30 °C, yielding *trans*-**10** as colourless crystals. Yield: 0.28 g (48 %).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 5.72 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 3.67 (1H, ddd,  $^3J$  = 11.1, 7.5, 4.0 Hz,  $\text{OCH}$ ), 3.29 (4H, m,  $\text{OCH}_2\text{CH}_2$ ), 2.35 (1H, m,  $\text{OCHCH}_2$ ), 2.26 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 2.04 (1H, m,  $\text{OCHMeCH}_2$ ), 2.01 (1H, m,  $\text{CHMeCH}_2\text{CH}_2$ ), 1.88 (1H, m,  $\text{CHMeCH}_2$ ), 1.71 (1H, m,  $\text{OCHMeCH}_2$ ), 1.54 (1H, m,  $\text{OCHCH}_2$ , overlapping with 1H, m,  $\text{CHMeCH}_2$ ), 1.48 (1H, m,  $\text{CHMe}$ , overlapping with 3H, m,  $\text{CHMe}$ ), 1.45 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 1.40 (1H, m,  $\text{CHMeCH}_2\text{CH}_2$ ), 1.21 (4H, m,  $\text{OCH}_2\text{CH}_2$ ) ppm,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$  not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 162.8 ( $3\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 144.9 ( $5\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 102.5 ( $4\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 79.9 ( $\text{OCH}$ ), 68.3

(OCH<sub>2</sub>CH<sub>2</sub>), 44.8 (OCHCHMe), 42.0 (OCHCH<sub>2</sub>), 35.4 (CHMeCH<sub>2</sub>CH<sub>2</sub>), 32.2 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 31.5 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 27.9 (CHMeCH<sub>2</sub>), 27.2 (OCHCH<sub>2</sub>CH<sub>2</sub>), 25.6 (OCH<sub>2</sub>CH<sub>2</sub>), 21.2 (CHMe), 13.5 ((N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): -7.9 (s, B-H of Tp<sup>tBu,Me</sup>) ppm. IR (NaCl plates, Nujol mull, cm<sup>-1</sup>): 1540 (s), 1363 (m), 1340 (w), 1242 (w), 1184 (s), 1069 (s), 983 (w), 782 (m), 668 (m), 674 (m). EI-MS: *m/z* = 463.3027 Da (100%), [(Tp<sup>tBu,Me</sup>)Ca]<sup>+</sup> Anal. found (calcd. For C<sub>35</sub>H<sub>61</sub>BCaN<sub>6</sub>O<sub>2</sub>): C, 64.98 (64.79); H, 9.57 (9.48); N, 12.87 (12.95) %.

**Alternative NMR tube scale synthesis of *cis* and *trans* (Tp<sup>tBu,Me</sup>)Ca(OCyMe) (10).**

In a glove box, a C<sub>6</sub>D<sub>6</sub> solution (0.5 mL) of (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**, 12 mg, 0.019 mmol) in a J. Young NMR tube was treated with a mixture of *cis* and *trans* 2-methylcyclohexanol (2.3 μL, 0.019 mmol) at RT. The <sup>1</sup>H NMR spectrum recorded after 10 min showed quantitative conversion to *cis*- and *trans*-**10** with a 1:1 integral ratio.

Data for *cis*-(Tp<sup>tBu,Me</sup>)Ca(OCyMe) (**10**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.67 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 4.34 (1H, dt, <sup>3</sup>*J* = 5.7, 2.7 Hz, OCH), 2.20 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.89 (1H, m, CHMe), 2.04-1.73 (5H, m, CH<sub>2</sub> of CyMe), 1.66-1.50 (3H, m, CH<sub>2</sub> of CyMe), 1.42 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.25 (3H, d, <sup>3</sup>*J* = 6.3 Hz, CHMe) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 163.2 (3-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 145.2 (5-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 102.5 (4-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 79.4 (OCH), 39.1 (OCHCHMe), 36.8 (CH<sub>2</sub> of CyMe), 30.5 (CH<sub>2</sub> of CyMe), 27.5 (CH<sub>2</sub> of CyMe), 26.8 (CH<sub>2</sub> of CyMe), 17.8 (CHMe), 13.4 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH) ppm.

Data for *trans*-(Tp<sup>tBu,Me</sup>)Ca(OCyMe) (**10**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.67 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 3.56 (1H, td, <sup>3</sup>*J* = 9.4, 4.1 Hz, OCH), 2.20 (1H, m, CH<sub>2</sub> of CyMe), 2.04-1.73 (3H, m, CH<sub>2</sub> of CyMe), 1.66-1.50 (3H, m, CH<sub>2</sub> of CyMe), 1.42 (1H, m, CHMe overlapping with 27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.32 (3H, d, <sup>3</sup>*J* = 6.3 Hz, CHMe), 1.25 (1H, m, CH<sub>2</sub> of CyMe) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 163.2 (3-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 145.2 (5-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 102.5 (4-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 73.7 (OCH), 43.9 (OCHCHMe), 40.8 (CH<sub>2</sub> of CyMe), 35.0 (CH<sub>2</sub> of CyMe), 25.6 (CH<sub>2</sub> of CyMe), 22.8 (CH<sub>2</sub> of CyMe), 20.6 (CHMe), 13.4 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH) ppm.

Common data: <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): -8.7 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

**NMR tube scale synthesis of (Tp<sup>tBu,Me</sup>)Ca(OBn)(THF)<sub>x</sub> (11).** In a glove box, a THF-*d*<sub>8</sub> solution of (Tp<sup>tBu,Me</sup>)Ca(HBEt<sub>3</sub>)(THF) (**1**, 12 mg, 0.019 mmol) in a J. Young NMR



tube was treated with benzaldehyde (1.5  $\mu$ L, 0.019 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to **11**.

$^1\text{H}$  NMR (THF- $d_8$ , 499.9 MHz, 298 K): 7.37 (2H, d,  $^3J = 7.5$  Hz, *o*-C<sub>6</sub>H<sub>5</sub>), 7.16 (2H, t,  $^3J = 7.5$  Hz, *m*-C<sub>6</sub>H<sub>5</sub>), 7.00 (1H, t,  $^3J = 7.2$  Hz, *p*-C<sub>6</sub>H<sub>5</sub>), 5.78 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 5.07 (2H, s, OCH<sub>2</sub>Ph), 2.37 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.34 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.05 (6H, q,  $^3J = 7.4$  Hz, free B(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 0.91 (6H, t,  $^3J = 7.4$  Hz, free B(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.7 MHz, 298 K): 162.7 (3-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 151.8 (*i*-C<sub>6</sub>H<sub>5</sub>), 145.2 (5-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 127.7 (*o*-C<sub>6</sub>H<sub>5</sub>), 126.9 (*m*-C<sub>6</sub>H<sub>5</sub>), 125.0 (*p*-C<sub>6</sub>H<sub>5</sub>), 102.4 (4-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 69.9 (OCH<sub>2</sub>Ph), 32.5 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 31.1 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 17.9 (free B(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 13.4 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 8.57 (free B(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): 73.3 (s, BEt<sub>3</sub>), -8.5 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

**Alternative NMR tube scale synthesis of (Tp<sup>tBu,Me</sup>)Ca(OBn)(THF)<sub>x</sub> (11).** In a glove box, a THF- $d_8$  solution of (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**, 12 mg, 0.019 mmol) in a J. Young NMR tube was treated with benzylalcohol (1.5  $\mu$ L, 0.019 mmol) at RT. The  $^1\text{H}$  NMR spectrum recorded after 10 min showed quantitative conversion to **11**, with resonances identical to those described above.

**NMR tube scale synthesis of (Tp<sup>tBu,Me</sup>)Ca(O<sup>i</sup>Pr)(THF)<sub>x</sub> (12).** In a glove box, a THF- $d_8$  solution of (Tp<sup>tBu,Me</sup>)Ca{N(SiMe<sub>3</sub>)<sub>2</sub>} (**5**, 12 mg, 0.019 mmol) in a J. Young NMR tube was treated with <sup>i</sup>PrOH (1.5  $\mu$ L, 0.019 mmol) at RT. The  $^1\text{H}$  NMR spectrum recorded after 10 min showed quantitative conversion to **12**.

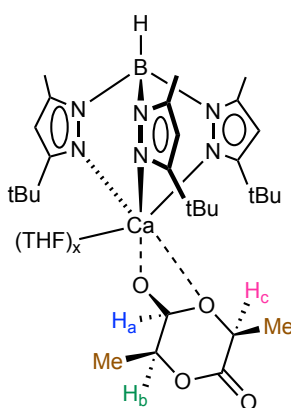
$^1\text{H}$  NMR (THF- $d_8$ , 499.9 MHz, 298 K): 5.76 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 4.15 (1H, hept,  $^3J = 5.9$  Hz, OCHMe<sub>2</sub>), 2.36 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.35 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.04 (6H, d,  $^3J = 5.9$  Hz, OCHMe<sub>2</sub>), 0.05 (18H, s, HN(SiMe<sub>3</sub>)<sub>2</sub>) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): -8.2 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

**(Tp<sup>tBu,Me</sup>)Sr(OCHPh<sub>2</sub>)(THF)<sub>2</sub> (13).** To a solid mixture of (Tp<sup>tBu,Me</sup>)Sr(HBEt<sub>3</sub>)(THF)<sub>2</sub> (**2**, 1.00 g, 1.31 mmol) and benzophenone (0.27 g, 1.50 mmol) was added THF (20 mL). The solution was stirred for 15 min. The solvent was removed *in vacuo* and the product was precipitated out in THF:pentane (1:5 v/v) at -70 °C, yielding **13** as a white powder. Yield: 0.77 g (67 %).

$^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 7.77 (4H, d,  $^3J = 7.5$  Hz, *o*-C<sub>6</sub>H<sub>5</sub>), 7.34 (4H, t,  $^3J = 7.5$  Hz, *m*-C<sub>6</sub>H<sub>5</sub>), 7.17 (2H, m, *p*-C<sub>6</sub>H<sub>5</sub>), 6.49 (1H, s, OCHPh<sub>2</sub>), 5.71 (3H, s,

$\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 3.36 (8H, m,  $\text{OCH}_2\text{CH}_2$ ), 2.24 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.33 (27H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.28 (8H, m,  $\text{OCH}_2\text{CH}_2$ ) ppm, B-H of  $\text{Tp}^{t\text{Bu},\text{Me}}$  not observed.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 162.3 (3- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 154.4 (*i*- $\text{C}_6\text{H}_5$ ), 145.3 (5- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 127.3 (*o*- $\text{C}_6\text{H}_5$ ), 127.3 (*m*- $\text{C}_6\text{H}_5$ ), 125.3 (*p*- $\text{C}_6\text{H}_5$ ), 102.3 (4- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 81.8 ( $\text{OCHPh}_2$ ), 67.9 ( $\text{OCH}_2\text{CH}_2$ ), 32.2 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.2 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 25.6 ( $\text{OCH}_2\text{CH}_2$ ), 13.5 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): -7.4 (s, B-H of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 1540 (m), 1337 (m), 1240 (w), 1204 (w), 1177 (w), 1129 (w), 1064(m), 980 (w), 779(m), 763 (w), 699(s). EI-MS:  $m/z = 511.2449$  Da (100%),  $[(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}]^+$  Anal. found (calcd. For  $\text{C}_{45}\text{H}_{67}\text{BSrN}_6\text{O}_3$ ): C, 64.37 (64.46); H, 8.16 (8.05); N, 9.97 (10.02) %.

**NMR tube scale synthesis of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$ .** In a glove box, a THF- $d_8$  solution (0.2 mL) of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**, 15 mg, 0.024 mmol) and a THF- $d_8$  solution (0.3 mL) of *L*-LA (17 mg, 0.120 mmol) were prepared in separate J. Young NMR tubes. Outside a glove box, the two J. Young NMR tubes were cooled down at 195 K using acetone/dry ice bath. The solution of *L*-LA in the J. Young NMR tube was transferred *via* cannula to the the solution of **1** in another J. Young NMR tube. The  $^1\text{H}$  NMR spectrum recorded at 223 K after 10 min showed quantitative conversion to  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$ . The intermediate was stabilised and fully characterised *via* NMR spectroscopy at 223 K.

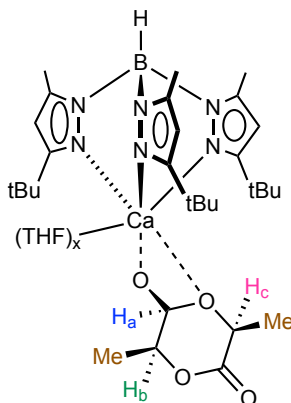


$^1\text{H}$  NMR (THF- $d_8$ , 500.0 MHz, 223 K) 5.85 (3H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 5.53 (1H, d,  $^3J = 1.6$  Hz,  $\text{H}_a$ ), 4.28 (1H, q,  $^3J = 7.2$  Hz,  $\text{H}_c$ ), 4.23 (1H, app q,  $^3J = 7.2, 5.3$  Hz,  $\text{H}_b$ ), 2.39 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.36 (6H, d,  $^3J = 6.5$  Hz,  $\text{CH}_b\text{Me}$  overlapping  $\text{CH}_c\text{Me}$ ), 1.33 (27H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 0.76 (9H, t,  $^3J = 7.7$  Hz, free  $\text{B}(\text{CH}_2\text{CH}_3)_3$ ), 0.45 (6H, q,  $^3J = 7.7$  Hz,

free  $\text{B}(\text{CH}_2\text{CH}_3)_3$  ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 125.7 MHz, 223 K): 168.7 ( $\text{O}\text{C}\text{OCH}_c\text{Me}$ ), 162.2 ( $3\text{-N}_2\text{C}_3^t\text{BuMeH}$ ), 145.3 ( $5\text{-N}_2\text{C}_3^t\text{BuMeH}$ ), 102.6 ( $4\text{-N}_2\text{C}_3^t\text{BuMeH}$ ), 98.1 ( $\text{OCH}_a$ ), 81.3 ( $\text{CH}_b$ ), 70.0 ( $\text{CH}_c$ ), 32.5 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.0 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 18.7 ( $\text{CH}_b\text{Me}$ ), 15.0 ( $\text{CH}_c\text{Me}$ ), 13.8 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 13.6 (free  $\text{B}(\text{CH}_2\text{CH}_3)_3$ ), 10.2 (free  $\text{B}(\text{CH}_2\text{CH}_3)_3$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 223 K): 25.7 (s,  $\text{BEt}_3$ ), -10.3 (s,  $\text{B-H}$  of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.

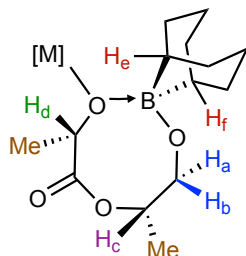
## 6.6 Experimental details and characterising data for Chapter Three

**NMR tube scale synthesis of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$  (14.1) and  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{OCHMeC}(\text{O})\text{OCHMeCH}_2\text{O}(\text{BC}_8\text{H}_{14})\}$  (14.3).** In a glove box, a  $\text{THF}-d_8$  solution (0.2 mL) of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**, 15 mg, 0.024 mmol) and a  $\text{THF}-d_8$  solution (0.3 mL) of *L*-LA (17 mg, 0.120 mmol) were prepared in separate J. Young NMR tubes. Outside a glove box, the two J. Young NMR tubes were cooled down at 195 K using acetone/dry ice bath. The solution of *L*-LA in the J. Young NMR tube was transferred *via* cannula to the the solution of **14** in another J. Young NMR tube. The intermediates **14.1** and **14.3** were stabilised and fully characterised *via* NMR spectroscopy at 223 K.



Data for  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{L-LA-H})(\text{THF})_x$  (**14.1**).  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 500.0 MHz, 223 K): 5.85 (3H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 5.53 (1H, d,  $^3J = 1.9$  Hz,  $\text{H}_a$ ), 4.28 (1H, q,  $^3J = 6.8$  Hz,  $\text{H}_c$ ), 4.21 (1H, app q,  $^3J = 6.3, 5.5$  Hz,  $\text{H}_b$ ), 2.39 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.79 (2H, m,  $\text{H}_\gamma$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 1.69 (4H, m,  $\text{H}_\beta$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 1.49 (4H, m,  $\text{H}_\beta$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 1.36 (6H, d,  $^3J = 6.7$  Hz,  $\text{CH}_b\text{Me}$  overlapping  $\text{CH}_c\text{Me}$ ), 1.35 (2H, m,  $\text{H}_\gamma$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 1.33 (27H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 0.88 (2H, s,  $\text{H}_\alpha$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 125.7 MHz, 223 K): 168.7 ( $\text{O}\text{C}\text{OCH}_c\text{Me}$ ), 162.0 ( $3\text{-N}_2\text{C}_3^t\text{BuMeH}$ ), 145.3 ( $5\text{-N}_2\text{C}_3^t\text{BuMeH}$ ), 102.7 ( $4\text{-N}_2\text{C}_3^t\text{BuMeH}$ ), 98.1 ( $\text{OCH}_a$ ), 81.3 ( $\text{CH}_b$ ), 70.0 ( $\text{CH}_c$ ), 32.5 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.0 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 18.7 ( $\text{CH}_b\text{Me}$ ), 15.0 ( $\text{CH}_c\text{Me}$ ), 13.8 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 13.6 (free  $\text{B}(\text{CH}_2\text{CH}_3)_3$ ), 10.2 (free  $\text{B}(\text{CH}_2\text{CH}_3)_3$ ) ppm.

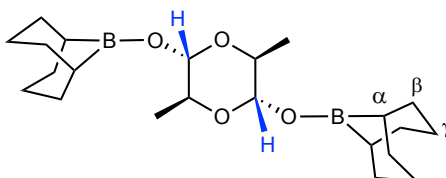
$\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 98.1 ( $\text{OCH}_a$ ), 81.2 ( $\text{CH}_b$ ), 70.3 ( $\text{CH}_c$ ), 33.2 ( $\text{CH}_\beta$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 32.5 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.0 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 28.5 ( $\text{CH}_\gamma$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 23.7 ( $\text{CH}_\alpha$  of  $(\text{HBC}_8\text{H}_{14})(\text{THF})$ ), 18.8 ( $\text{CH}_b\text{Me}$ ), 15.0 ( $\text{CH}_c\text{Me}$ ), 13.7 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 223 K): -8.3 (s,  $\text{B-H}$  of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.



Data for  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{OCHMeC}(\text{O})\text{OCHMeCH}_2\text{O}(\text{BC}_8\text{H}_{14})\}$  (**14.3**).  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 500.0 MHz, 223 K): 5.96 (3H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$  overlapping with 1H, s,  $\text{H}_b$ ), 4.39 (1H, q,  $^3J = 7.1$  Hz,  $\text{H}_d$ ), 3.85 (1H, m,  $\text{H}_c$  overlapping with 1H, m,  $\text{H}_a$ ), 2.42 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 2.00-1.50 (10H, m,  $\text{CH}_2$  of  $\text{BC}_8\text{H}_{14}$ ), 1.41 (3H, d,  $^3J = 6.8$  Hz,  $\text{CH}_d\text{Me}$ ), 1.31 (27H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$  overlapping with 2H, s,  $\text{CH}_2$  of  $\text{BC}_8\text{H}_{14}$ ), 1.04 (3H, d,  $^3J = 6.2$  Hz,  $\text{CH}_c\text{Me}$ ), 0.66 (1H, s,  $\text{H}_e$  of  $\text{BC}_8\text{H}_{14}$ ), 0.53 (1H, s,  $\text{H}_f$  of  $\text{BC}_8\text{H}_{14}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 125.7 MHz, 223 K): 168.7 ( $\text{OCOCH}_c\text{Me}$ ), 162.0 (3- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 146.2 (5- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 103.6 (4- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 76.5 ( $\text{OCH}_2\text{CH}_c\text{Me}$ ), 70.9 ( $\text{CH}_d$ ), 62.6 ( $\text{CH}_c$ ), 33.2, 33.1, 32.9 and 32.8 ( $\text{CH}_2$  of  $\text{BC}_8\text{H}_{14}$ ), 32.7 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 30.9 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 27.5 and 27.4 ( $\text{CH}_2$  of  $\text{BC}_8\text{H}_{14}$ ), 24.3 ( $\text{CH}_f$  of  $\text{BC}_8\text{H}_{14}$ ), 23.8 ( $\text{CH}_e$  of  $\text{BC}_8\text{H}_{14}$ ), 22.6 ( $\text{CH}_d\text{Me}$ ), 22.3 ( $\text{CH}_c\text{Me}$ ), 13.9 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 223 K): 3.8 (s,  $\text{O}_2\text{B}(\text{C}_8\text{H}_{14})$ ), -8.3 (s,  $\text{B-H}$  of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.

**(3,6-dimethyl-1,4-dioxane-2,5-diyl)bis(oxy)bis(9-borabicyclo[3.3.1]nonane) (15).**

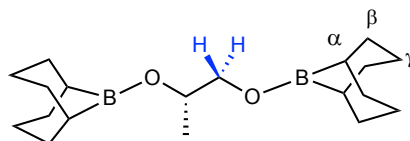
To a solid mixture of *L*-LA (0.12 g, 0.82 mmol) and  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  (0.20 g, 0.82 mmol) was added benzene (20 mL). The solution was stirred at 60 °C for 18 h. The solvent was removed *in vacuo* to give colourless oil. Yield: 0.23 g (72%).



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 5.51 (2H, d,  $^3J = 3.5$  Hz,  $\text{OCH}$ ), 5.41-5.39 (1H, m,  $\text{OCH}$ ), 5.32 (1H, d,  $^3J = 4.3$  Hz,  $\text{OCH}$ ), 5.21 (1H, d,  $^3J = 6.8$  Hz,  $\text{OCH}$ ), 4.34 (1H, qd,  $^3J = 4.4, 6.4$  Hz,  $\text{CHMe}$ ), 4.27-4.18 (1H, m,  $\text{CHMe}$ ), 4.04 (1H, qd,  $^3J = 4.4, 6.4$  Hz,

CHMe), 2.0-1.6 (8H, m,  $\underline{H}_\beta$  overlapping with 2H, m,  $\underline{H}_\gamma$ ), 1.6-1.4 (2H, m,  $\underline{H}_\alpha$  overlapping with 2H, m,  $\underline{H}_\gamma$ ), 1.31 (3H, d,  $^3J = 6.5$  Hz, CHMe), 1.26 (3H, d,  $^3J = 6.4$  Hz, CHMe), 1.23 (3H, d,  $^3J = 6.3$  Hz, CHMe), 1.17-1.13 (3H, d,  $^3J = 6.6$  Hz, CHMe), 1.09 (3H, d,  $^3J = 6.4$  Hz, CHMe) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 105.9, 105.6, 102.2, 97.7 and 97.4 (OCH), 80.6, 77.3, 72.6, 72.0 and 67.5 (OCHCHMe), 33.9-33.6 ( $\underline{\text{CH}}_\beta$ ), 25.0 ( $\underline{\text{CH}}_\alpha$ ), 23.7-23.5 ( $\underline{\text{CH}}_\gamma$ ), 18.0, 17.9, 17.4, 15.6 and 14.3 (OCHCHMe) ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): 58.7 (s, OB( $\text{C}_8\text{H}_{14}$ )) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 1774 (m), 1740 (s), 1487 (m), 1403 (m), 1332 (s, B-O st), 1315 (s, B-O st), 1286 (s), 1236 (m), 1164 (m), 1146 (m), 1114 (m), 1079 (m), 1049 (w), 1021 (w), 994 (w), 933 (w), 900 (s), 878 (w), 678 (s). ESI-HRMS:  $m/z$  found (calcd for  $\text{C}_{22}\text{H}_{38}\text{B}_2\text{O}_4\text{NH}_4$ ,  $[\text{M}+\text{NH}_4]^+$ ): 406.3307 Da (406.3302 Da).

**(propane-1,2-diyl)bis(oxy)bis(9-borabicyclo[3.3.1]nonane (16).** To a solid mixture of *L*-LA (0.12 g, 0.82 mmol) and  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  (0.40 g, 1.64 mmol) was added benzene (20 mL). The solution was stirred at 60 °C for 18 h. The solvent was removed *in vacuo* to give colourless oil. Yield: 0.25 g (96%).



$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 4.39 (1H, m, OCHMe), 3.91 (1H, dd,  $^3J = 10.7$ , 7.4 Hz, OCHMeCH $\underline{\text{H}}_2$ ), 3.73 (1H, dd,  $^3J = 10.7$ , 3.9 Hz, OCHMeCH $\underline{\text{H}}_2$ ), 2.0-1.6 (8H, m,  $\underline{H}_\beta$  overlapping with 2H, m,  $\underline{H}_\gamma$ ), 1.6-1.4 (2H, m,  $\underline{H}_\alpha$  overlapping with 2H, m,  $\underline{H}_\gamma$ ), 1.08 (3H, d,  $^3J = 6.4$  Hz, OCHMe) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 71.6 (OCHMe), 70.7 (OCHMeCH $\underline{\text{H}}_2$ ), 33.9-33.5 ( $\underline{\text{CH}}_\beta$ ), 24.8 ( $\underline{\text{CH}}_\alpha$ ), 24.3-23.7 ( $\underline{\text{CH}}_\gamma$ ), 19.6 (OCHMe) ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): 56.8 (s, OB( $\text{C}_8\text{H}_{14}$ )) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 1741 (s), 1486 (w), 1333 (s, B-O st), 1315 (s, B-O st), 1285 (s), 1236 (s), 1179 (s), 1142 (s), 1113 (m), 1078 (s), 1050 (s), 1022 (s), 987 (m), 932 (m), 899 (s), 878 (m), 848 (m), 821 (m), 698 (m), 677 (s). ESI-HRMS:  $m/z$  found (calcd for  $\text{C}_{19}\text{H}_{34}\text{B}_2\text{O}_2$ ,  $[\text{M}]^+$ ): 316.2741 Da (316.2745 Da).

**9-(benzhydryloxy)-9-borabicyclo[3.3.1]nonane ( $\text{BC}_8\text{H}_{14}$ )(OCHPh $_2$ ) (17).** To a solid mixture of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  (0.10 g, 0.41 mmol) and benzophenone (0.15 g, 0.82 mmol) was added benzene (20 mL). The solution was stirred at 60 °C for 18 h. The solvent

was removed *in vacuo* and the product was washed with cold pentane to give **17** as white powder. Yield: 0.11 g (88%).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 7.43 (4H, d,  $^3J = 7.7$  Hz, *o*- $\text{C}_6\text{H}_5$ ), 7.17 (4H, m, *m*- $\text{C}_6\text{H}_5$ ), 7.06 (2H, t,  $^3J = 7.4$  Hz, *p*- $\text{C}_6\text{H}_5$ ), 6.29 (1H, s,  $\text{OCHPh}_2$ ), 1.85 (2H, m,  $\text{H}_\gamma$ ), 1.83 (4H, m,  $\text{H}_\beta$ ), 1.75 (4H, m,  $\text{H}_\beta$ ), 1.59 (2H, s,  $\text{H}_\alpha$ ), 1.28 (2H, m,  $\text{H}_\gamma$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K) 144.3 (*i*- $\text{C}_6\text{H}_5$ ), 128.2 (*m*- $\text{C}_6\text{H}_5$ ), 127.2 (*p*- $\text{C}_6\text{H}_5$ ), 126.7 (*o*- $\text{C}_6\text{H}_5$ ), 79.7 ( $\text{OCHPh}_2$ ), 33.5 ( $\text{CH}_\beta$ ), 25.1 ( $\text{CH}_\alpha$ ), 23.3 ( $\text{CH}_\gamma$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): 58.0 (s,  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$ ) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 1400 (m), 1334 (m), 1315 (m), 1282 (m), 1171 (m), 1140 (m), 1078 (m), 756 (m), 737 (m), 699 (m), 676 (w), 668 (w). ESI-HRMS:  $m/z$  found (calcd for  $\text{C}_{21}\text{H}_{25}\text{BO}$ ,  $[\text{M}]^+$ ): 304.2010 Da (304.1998 Da).

***cis*-, *trans*-9-(2-methylcyclohexyloxy)-9-borabicyclo[3.3.1]nonane) *cis*- and *trans*-( $\text{BC}_8\text{H}_{14}$ )(OCyMe) (**18**).** To a solid mixture of  $(\mu\text{-H})_2(\text{BC}_8\text{H}_{14})_2$  (0.10 g, 0.41 mmol) and 2-methylcyclohexanone (0.09 g, 0.82 mmol) was added benzene (20 mL). The solution was stirred at 60 °C for 18 h. The solvent was removed *in vacuo* to give **18** as colourless oil. Yield: 0.09 (94%).

Data for *cis*-( $\text{BC}_8\text{H}_{14}$ )(OCyMe) (**18**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 4.10 (1H, dt,  $^3J = 5.0, 2.6$  Hz,  $\text{OCH}$ ), 1.92 (2H, m,  $\text{H}_\gamma$ ), 1.87 (8H, m,  $\text{H}_\beta$ ), 1.80 (1H, m,  $\text{OCHCH}_2$ ), 1.69 (1H, m,  $\text{CH}_2$  of CyMe), 1.64 (1H, m,  $\text{CHMeCH}_2$ ), 1.60 (1H, m,  $\text{CH}_2$  of CyMe overlapping with 2H, m,  $\text{H}_\alpha$ ), 1.49 (1H, m,  $\text{OCHCH}_2$ ), 1.42 (1H, m,  $\text{CHMe}$  overlapping with 2H, m,  $\text{H}_\gamma$ ), 1.34 (1H, m,  $\text{CH}_2$  of CyMe overlapping with 1H, m,  $\text{CHMeCH}_2$ ), 1.17 (1H, m,  $\text{CH}_2$  of CyMe), 0.92 (3H, d,  $^3J = 6.8$ ,  $\text{CHMe}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K) 79.9 ( $\text{OCH}$ ), 36.2 ( $\text{CHMe}$ ), 35.8 ( $\text{OCHCH}_2$ ), 33.9-33.6 ( $\text{CH}_\beta$  and  $\text{CH}_2$  of CyMe), 29.3 ( $\text{CHMeCH}_2$ ), 25.4 ( $\text{CH}_2$  of CyMe), 25.1 ( $\text{CH}_\alpha$ ), 23.8 ( $\text{CH}_\gamma$ ), 18.0 ( $\text{CHMe}$ ) ppm.

Data for *trans*-( $\text{BC}_8\text{H}_{14}$ )(OCyMe) (**18**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 3.60 (1H, td,  $^3J = 10.0, 4.4$  Hz,  $\text{OCH}$ ), 1.92 (2H, m,  $\text{H}_\gamma$ ), 1.87 (8H, m,  $\text{H}_\beta$  overlapping with 1H,  $\text{CH}_2$  of CyMe), 1.75 (1H, m,  $\text{OCHCH}_2$ ), 1.60 (2H, m,  $\text{H}_\alpha$  overlapping with 1H,  $\text{CH}_2$  of CyMe), 1.57 (1H, m,  $\text{CHMe}$  overlapping with 1H, m,  $\text{CHMeCH}_2$ ), 1.47 (1H, m,  $\text{CH}_2$  of CyMe), 1.42 (2H, m,  $\text{H}_\gamma$ ), 1.34 (1H, m,  $\text{OCHCH}_2$ ), 1.10 (1H, m,  $\text{CH}_2$  of CyMe), 0.98 (3H, d,  $^3J = 6.3$ ,  $\text{CHMe}$ ), 0.86 (1H, m,  $\text{CHMeCH}_2$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K) 74.4 ( $\text{OCH}$ ), 39.2 ( $\text{CHMe}$ ), 33.9-33.6 ( $\text{CH}_\beta$ ,  $\text{CHMeCH}_2$  and  $\text{CH}_2$  of

CyMe), 25.9 ( $\underline{\text{CH}}_2$  of CyMe), 25.1 ( $\underline{\text{CH}}_\alpha$ ), 23.8 ( $\underline{\text{CH}}_\gamma$ ), 20.9 ( $\text{OCH}\underline{\text{CH}}_2$ ), 19.2 ( $\text{CH}\underline{\text{Me}}$ ) ppm.

Common data:  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): 55.8 (s,  $(\underline{\text{BC}}_8\text{H}_{14})(\text{OCyMe})$ ) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 1579 (w), 1412 (m), 1401 (m), 1333 (s), 1317 (s), 1287 (s), 1238 (m), 1215 (m), 1178 (m), 1138 (m), 1112 (m), 1076 (m), 1051 (m), 1022 (s), 986 (s), 974 (m), 901 (s), 846 (m), 678 (s). ESI-HRMS:  $m/z$  found (calcd for  $\text{C}_{15}\text{H}_{27}\text{BO}$ ,  $[\text{M}]^+$ ): 234.2156 Da (234.2155 Da).

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (14) and 2 equiv. of benzophenone.** In a glove box, a THF- $d_8$  solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (14, 12.00 mg, 0.018 mmol) in a J. Young NMR tube was treated with benzophenone (6.64 mg, 0.036 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})_x$  (7) and  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (17).

Data for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})_x$  (7).  $^1\text{H}$  NMR (THF- $d_8$ , 499.9 MHz, 298 K): 7.42 (4H, m,  $o\text{-C}_6\text{H}_5$ ), 7.14 (4H, t,  $^3J = 7.4$  Hz,  $m\text{-C}_6\text{H}_5$ ), 7.00 (2H, t,  $^3J = 6.5$  Hz,  $p\text{-C}_6\text{H}_5$ ), 6.06 (1H, s,  $\text{OCHPh}_2$ ), 5.76 (3H, s,  $\text{N}_2\text{C}_3\text{tBuMeH}$ ), 3.62 (4H, m,  $\text{OCH}_2\text{CH}_2$ ), 2.36 (9H, s,  $\text{N}_2\text{C}_3\text{tBuMeH}$ ), 1.77 (4H, m,  $\text{OCH}_2\text{CH}_2$ ), 1.27 (27H, s,  $\text{N}_2\text{C}_3\text{tBuMeH}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.7 MHz, 298 K): 163.0 (3- $\text{N}_2\text{C}_3\text{tBuMeH}$ ), 145.5 ( $i\text{-C}_6\text{H}_5$ ), 145.2 (5- $\text{N}_2\text{C}_3\text{tBuMeH}$ ), 128.1 ( $o\text{-C}_6\text{H}_5$ ), 127.5 ( $m\text{-C}_6\text{H}_5$ ), 125.7 ( $p\text{-C}_6\text{H}_5$ ), 102.6 (4- $\text{N}_2\text{C}_3\text{tBuMeH}$ ), 81.5 ( $\text{OCHPh}_2$ ), 68.5 ( $\text{OCH}_2\text{CH}_2$ ), 32.7 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.6 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 26.6 ( $\text{OCH}_2\text{CH}_2$ ), 13.8 ( $\text{N}_2\text{C}_3\text{tBuMeH}$ ) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): -8.8 (s,  $\underline{\text{B-H}}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

Data for  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (17).  $^1\text{H}$  NMR (THF- $d_8$ , 499.9 MHz, 298 K): 7.42 (4H, m,  $o\text{-C}_6\text{H}_5$ ), 7.28 (4H, t,  $^3J = 7.6$  Hz,  $m\text{-C}_6\text{H}_5$ ), 7.19 (2H, t,  $^3J = 7.4$  Hz,  $p\text{-C}_6\text{H}_5$ ), 6.36 (1H, s,  $\text{OCHPh}_2$ ), 1.85 (2H, m,  $\text{H}_\gamma$ ), 1.79 (4H, m,  $\text{H}_\beta$ ), 1.73 (2H, m,  $\text{H}_\alpha$ ), 1.67 (4H, m,  $\text{H}_\beta$ ), 1.27 (2H, m,  $\text{H}_\gamma$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.7 MHz, 298 K): 140.0 ( $i\text{-C}_6\text{H}_5$ ), 129.2 ( $m\text{-C}_6\text{H}_5$ ), 128.1 ( $o\text{-C}_6\text{H}_5$ ), 127.5 ( $p\text{-C}_6\text{H}_5$ ), 80.4 ( $\text{OCHPh}_2$ ), 34.1 ( $\underline{\text{CH}}_\beta$ ), 25.2 ( $\underline{\text{CH}}_\alpha$ ), 24.2 ( $\underline{\text{CH}}_\gamma$ ) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): 57.8 (s,  $(\underline{\text{BC}}_8\text{H}_{14})(\text{OCHPh}_2)$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (14) and 1 equiv. of benzophenone.** In a glove box, a THF- $d_8$  solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (14, 12.00 mg, 0.018 mmol) in a J. Young NMR tube was treated with benzophenone (3.32 mg, 0.018 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})_x$  (7) and  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (17).

H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**, 12.00 mg, 0.018 mmol) in a J. Young NMR tube was treated with benzophenone (3.28 mg, 0.018 mmol) at RT. The <sup>1</sup>H NMR spectrum recorded after 10 min showed signals corresponding to (Tp<sup>tBu,Me</sup>)Ca(OCHPh<sub>2</sub>)(THF)<sub>x</sub> (**7**), (BC<sub>8</sub>H<sub>14</sub>)(OCHPh<sub>2</sub>) (**17**) and unreacted **14** in a 1:1:1 ratio, which were identical to those described above.

**NMR tube scale reaction of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**) and 2 equiv. of 2-methylcyclohexanone.** In a glove box, a C<sub>6</sub>D<sub>6</sub> solution of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**, 12.00 mg, 0.018 mmol) in a J. Young NMR tube was treated with 2-methylcyclohexanone (4.40 μL, 0.036 mmol) at RT. The <sup>1</sup>H and <sup>11</sup>B NMR spectra recorded after 10 min showed quantitative conversion to *trans*-(Tp<sup>tBu,Me</sup>)Ca(OCyMe)(THF)<sub>x</sub> (**10**) and *trans*-(BC<sub>8</sub>H<sub>14</sub>)(OCyMe) (**18**).

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.72 (6H, s, N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H), 3.60 (1H, td, <sup>3</sup>J = 10.1, 4.7 Hz, OCH of **18**), 3.51 (1H, td, <sup>3</sup>J = 9.5, 4.4 Hz, OCH of **10**), 3.31 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>), 2.34 (1H, m, CH<sub>2</sub> of OCyMe), 2.25 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H overlapping with 1H, m, CH(CH<sub>2</sub>) of CyMe, **10**), 2.0-1.6 (11H, CH<sub>2</sub> of CyMe overlapping with 8H, m, H<sub>β</sub> and 2H, m, H<sub>γ</sub>), 1.6-1.4 (2H, m, H<sub>α</sub> overlapping with 2H, m, H<sub>γ</sub>), 1.57 (1H, m, CHMe of **18**), 1.46 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H overlapping with CH<sub>2</sub> of CyMe), 1.41 (1H, m, CHMe of **10**), 1.40 (3H, m, CHMe of **10** overlapping with 1H, m, CH<sub>2</sub> of CyMe), 1.35 (1H, m, CH<sub>2</sub> of CyMe), 1.25 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>), 0.98 (3H, CHMe of **18**), 0.84 (1H, m, CH<sub>2</sub> of CyMe) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 162.8 (3-N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H), 144.9 (5-N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H), 102.5 (4-N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H), 80.0 (OCH of **18**), 79.5 (OCH of **10**), 68.3 (OCH<sub>2</sub>CH<sub>2</sub>), 44.3 (CHMe of **10**), 41.3 (CH<sub>2</sub> of CyMe), 39.2 (CHMe of **18**), 35.8, 35.3 (CH<sub>2</sub> of CyMe), 33.9, 33.6 (CH<sub>β</sub>), 32.2 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 31.5 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 27.7, 27.0 (CH<sub>2</sub> of CyMe), 25.6 (CH<sub>α</sub>), 25.4 (OCH<sub>2</sub>CH<sub>2</sub>), 24.3-23.7 (CH<sub>γ</sub> overlapping with CH<sub>2</sub> of CyMe), 20.9 (CHMe of **10**), 19.2 (CHMe of **18**) 13.5 (N<sub>2</sub>C<sub>3</sub><sup>tBuMe</sup>H) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): 55.8 (s, (BC<sub>8</sub>H<sub>14</sub>)(OCyMe)), -8.1 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

**NMR tube scale reaction of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**) and 2 equiv. of benzaldehyde.** In a glove box, a THF-*d*<sub>8</sub> solution of (Tp<sup>tBu,Me</sup>)Ca{(μ-H)<sub>2</sub>BC<sub>8</sub>H<sub>14</sub>}(THF) (**14**, 15.0 mg, 0.023 mmol) in a J. Young NMR tube was treated with benzaldehyde (4.65 μL, 0.046 mmol) at RT. The <sup>1</sup>H and <sup>11</sup>B NMR spectra recorded



after 10 min showed quantitative conversion to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**).

Data for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**).  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 499.9 MHz, 298 K): 7.36 (2H, d,  $^3J = 7.6$  Hz,  $o\text{-C}_6\text{H}_5$ ), 7.16 (2H, t,  $^3J = 7.6$  Hz,  $m\text{-C}_6\text{H}_5$ ), 7.01 (1H, t,  $^3J = 7.3$  Hz,  $p\text{-C}_6\text{H}_5$ ), 5.78 (6H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 5.04 (2H, s,  $\text{OCH}_2\text{Ph}$ ), 3.62 (4H, m,  $\text{OCH}_2\text{CH}_2$ ), 2.37 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 1.95-1.75 (4H, m,  $\text{OCH}_2\text{CH}_2$ ), 1.34 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 125.7 MHz, 298 K): 163.0 (3- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 145.6 (5- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 141.2 ( $i\text{-C}_6\text{H}_5$ ), 128.0 ( $m\text{-C}_6\text{H}_5$ ), 127.2 ( $o\text{-C}_6\text{H}_5$ ), 125.3 ( $p\text{-C}_6\text{H}_5$ ), 102.7 (4- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 70.4 ( $\text{OCH}_2\text{Ph}$ ), 67.2 ( $\text{OCH}_2\text{CH}_2$ ), 32.8 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.4 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 24.3 ( $\text{OCH}_2\text{CH}_2$ ), 13.7 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 298 K): -8.1 (s,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

Data for  $(\text{BC}_8\text{H}_{14})(\text{OBn})$  (**19**).  $^1\text{H}$  NMR ( $\text{THF}-d_8$ , 499.9 MHz, 298 K): 7.33-7.20 (5H, m,  $\text{C}_6\text{H}_5$ ), 5.08 (2H, s,  $\text{OCH}_2\text{Ph}$ ), 1.95-1.75 (8H, m,  $\text{H}_\beta$ ), 1.72 (2H, br. s,  $\text{H}_\alpha$ ), 1.34 (4H, m,  $\text{H}_\gamma$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 125.7 MHz, 298 K): 138.4 ( $i\text{-C}_6\text{H}_5$ ), 129.2, 128.2 and 127.5 ( $\text{C}_6\text{H}_5$ ), 68.5 ( $\text{OCH}_2\text{Ph}$ ), 34.2 ( $\text{CH}_\beta$ ), 25.7 ( $\text{CH}_\alpha$ ), 24.3 ( $\text{CH}_\gamma$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 298 K): 57.2 (s,  $(\text{BC}_8\text{H}_{14})(\text{OBn})$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**).** A mixture of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**, 12 mg, 0.015 mmol) with  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**, 4.62 mg, 0.015 mmol) in  $\text{THF}-d_8$  (0.5 mL) was transferred to a J. Young NMR tube. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 18 h at RT showed signals corresponding to **7** and **17**.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  (**18**).** A mixture of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**, 12 mg, 0.015 mmol) with  $(\text{BC}_8\text{H}_{14})(\text{OCyMe})$  (**18**, 3.50 mg, 0.015 mmol) in  $\text{THF}-d_8$  (0.5 mL) was transferred to a J. Young NMR tube. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 18 h at RT showed signals corresponding to **7** and **18**.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) with  $(\text{BC}_8\text{H}_{14})(\text{OCH}_2\text{Ph})$  (**19**).** A mixture of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**, 12 mg, 0.015 mmol) with  $(\text{BC}_8\text{H}_{14})(\text{OCH}_2\text{Ph})$  (**19**, 3.42 mg, 0.015 mmol) in  $\text{THF}-d_8$  (0.5 mL) was transferred to a J. Young NMR tube. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 18 h

at RT showed signals corresponding to **7**, **19**,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $(\text{BC}_8\text{H}_{14})(\text{OCHPh}_2)$  (**17**), which were identical to those described above.

## 6.7 Experimental details and characterising data for Chapter Four

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and 4 equiv. of benzophenone.** In a glove box, a THF- $d_8$  solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**, 12.0 mg, 0.020 mmol) in a J. Young NMR tube was treated with benzophenone (15.66 mg, 0.086 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})_x$  (**7**) and  $\text{B}(\text{OCHPh}_2)_3$  (**23**).

Data for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})_x$  (**7**).  $^1\text{H}$  NMR (THF- $d_8$ , 499.9 MHz, 298 K): 7.44 (4H, d,  $^3J = 7.5$  Hz, *o*-C<sub>6</sub>H<sub>5</sub>), 7.14 (4H, m, *m*-C<sub>6</sub>H<sub>5</sub>), 7.00 (2H, t,  $^3J = 7.3$  Hz, *p*-C<sub>6</sub>H<sub>5</sub>), 6.10 (1H, s, OCHPh<sub>2</sub>), 5.77 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 3.62 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>), 2.36 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.76 (2H, m, OCH<sub>2</sub>CH<sub>2</sub>), 1.34 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 1.22 (4H, m, OCH<sub>2</sub>CH<sub>2</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.7 MHz, 298 K): 163.0 (3-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 154.2 (*i*-C<sub>6</sub>H<sub>5</sub>), 145.1 (5-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 128.2 (*o*-C<sub>6</sub>H<sub>5</sub>), 128.0 (*m*-C<sub>6</sub>H<sub>5</sub>), 125.6 (*p*-C<sub>6</sub>H<sub>5</sub>), 102.7 (4-N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 82.4 (OCHPh<sub>2</sub>), 68.4 (OCH<sub>2</sub>CH<sub>2</sub>), 32.7 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 31.6 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 26.6 (OCH<sub>2</sub>CH<sub>2</sub>), 13.8 (N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): -8.6 (s, B-H of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

Data for  $\text{B}(\text{OCHPh}_2)_3$  (**23**).  $^1\text{H}$  NMR (THF- $d_8$ , 499.9 MHz, 298 K): 7.25-7.15 (30H, m, C<sub>6</sub>H<sub>5</sub>), 6.39 (3H, s, OCHPh<sub>2</sub>) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.7 MHz, 298 K): 145.5 (*i*-C<sub>6</sub>H<sub>5</sub>), 129.1 (*o*-C<sub>6</sub>H<sub>5</sub>), 127.8 (*m*-C<sub>6</sub>H<sub>5</sub>), 127.3 (*p*-C<sub>6</sub>H<sub>5</sub>), 78.3 (OCHPh<sub>2</sub>) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): 19.1 (s, B(OCHPh<sub>2</sub>)<sub>3</sub>) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and 4 equiv. of 2-methylcyclohexanone.** In a glove box, a C<sub>6</sub>D<sub>6</sub> solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**, 12.00 mg, 0.020 mmol) in a J. Young NMR tube was treated with 2-methylcyclohexanone (10.4  $\mu\text{L}$ , 0.086 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to *trans*- $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})_x$  (**10**) and *cis*- and *trans*-B(OCyMe)<sub>3</sub> (**24**).

Data for *trans*- $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})_x$  (**10**).  $^1\text{H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.72 (6H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 3.53 (2H, td,  $^3J = 9.3$ , 4.0 Hz, OCH of CyMe), 3.36 (8H, m, OCH<sub>2</sub>CH<sub>2</sub>), 2.26 (18H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH), 2.21 (2H, m, CH(CH<sub>2</sub>) of CyMe), 1.88 (6H, m, CH<sub>2</sub> of CyMe), 1.46 (54H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH overlapping with 2H, m, CHMe),

1.41 (6H, m,  $\underline{\text{CH}_2}$  of CyMe), 1.34 (6H, d,  $^3J = 5.1$  Hz,  $\underline{\text{CHMe}}$ ), 1.27 (8H, m,  $\text{OCH}_2\underline{\text{CH}_2}$ ), 1.26 (2H, m,  $\underline{\text{CH}_2}$  of CyMe) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 162.7 (3- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 144.9 (5- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 102.5 (4- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 79.2 ( $\text{OCH}$ ), 68.2 ( $\text{OCH}_2\text{CH}_2$ ), 43.9 ( $\underline{\text{CHMe}}$ ), 40.6, 35.1, 33.9, 26.8 ( $\underline{\text{CH}_2}$  of CyMe), 32.2 ( $\text{N}_2\text{C}_3\underline{\text{C}}(\text{Me}_3)\text{MeH}$ ), 31.5 ( $\text{N}_2\text{C}_3\underline{\text{C}}(\text{Me}_3)\text{MeH}$ ), 20.6 ( $\underline{\text{CHMe}}$ ), 13.6 ( $\text{N}_2\text{C}_3^t\text{Bu}\underline{\text{MeH}}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 298 K): -8.9 (s,  $\underline{\text{B-H}}$  of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.

Data for *cis*- $\text{B}(\text{OCyMe})_3$  (**24**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 4.45 (3H, m,  $\text{OCH}$ ), 1.92 (6H, m,  $\underline{\text{CH}_2}$ ), 1.77 (3H, m,  $\underline{\text{CH}_2}$ ), 1.73 (3H, m,  $\underline{\text{CH}_2}$ ), 1.49 (2H, m,  $\underline{\text{CHMe}}$ ), 1.40 (6H, m,  $\underline{\text{CH}_2}$ ), 1.26 (6H, m,  $\underline{\text{CH}_2}$ ), 1.03 (9H, m,  $\underline{\text{CHMe}}$ ) of *cis* ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 71.6-71.4 ( $\text{OCH}$  of *cis*), 36.5 ( $\underline{\text{CHMe}}$  of *cis*), 33.9, 33.0, 29.7, 27.5 ( $\underline{\text{CH}_2}$  of CyMe), 18.6-18.3 ( $\underline{\text{CHMe}}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 298 K): 18.2 (s,  $\underline{\text{B}}(\text{OCyMe})_3$ ) ppm.

Data for *trans*- $\text{B}(\text{OCyMe})_3$  (**24**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 3.91 (3H, pd,  $^3J = 10.0$ , 4.3 Hz,  $\text{OCH}$  of *trans*), 2.20 (3H, m,  $\underline{\text{CH}_2}$ ), 1.62 (6H, m,  $\underline{\text{CH}_2}$ ), 1.52 (2H, m,  $\underline{\text{CHMe}}$ ), 1.46 (9H, m,  $\underline{\text{CH}_2}$ ), 1.12 (9H, m,  $\underline{\text{CHMe}}$  overlapping with 3H, m,  $\underline{\text{CH}_2}$ ), 0.94 (3H, m,  $\underline{\text{CH}_2}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 77.3-77.0 ( $\text{OCH}$ ), 39.7 ( $\underline{\text{CHMe}}$ ), 33.9, 33.0, 29.7, 27.5 ( $\underline{\text{CH}_2}$  of CyMe), 19.4-19.2 ( $\underline{\text{CHMe}}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 298 K): 18.2 (s,  $\underline{\text{B}}(\text{OCyMe})_3$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and 4 equiv. of benzaldehyde.** In a glove box, a  $\text{THF}-d_8$  solution of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**, 12.00 mg, 0.020 mmol) in a J. Young NMR tube was treated with benzaldehyde (8.80  $\mu\text{L}$ , 0.086 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}(\text{OBn})(\text{THF})_x$  (**11**) and  $\text{B}(\text{OBn})_3$  (**25**) and  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ .

$^1\text{H}$  NMR ( $\text{THF}-d_8$ , 499.9 MHz, 298 K): 7.40-7.11 (5H, m,  $\text{C}_6\text{H}_5$  of **11** and  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ ), 7.33-7.20 (15H, m,  $\text{C}_6\text{H}_5$  of  $\text{B}(\text{OBn})_3$ ), 5.82 (6H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 4.97 ( $\text{OCH}_2\text{Ph}$  of  $\text{B}(\text{OBn})_3$ ), 4.75 ( $\text{OCH}_2\text{Ph}$  of **11** and  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ ), 3.62 (4H, m,  $\text{OCH}_2\text{CH}_2$  of **11**), 2.38 (9H, s,  $\text{N}_2\text{C}_3^t\text{Bu}\underline{\text{MeH}}$ ), 1.77 (8H, m,  $\text{OCH}_2\underline{\text{CH}_2}$  of **11**), 1.28 (27H, s,  $\text{N}_2\text{C}_3^t\text{Bu}\underline{\text{MeH}}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{THF}-d_8$ , 125.7 MHz, 298 K): 163.6 (3- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 145.5 (5- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 144.2 (*i*- $\text{C}_6\text{H}_5$  of **11** and  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ ), 141.0 (*i*- $\text{C}_6\text{H}_5$  of  $\text{B}(\text{OBn})_3$ ), 128.9, 128.6, 128.1,

127.8, 127.4 and 126.9 ( $\text{C}_6\text{H}_5$  of **11** and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$  overlapping with  $\text{C}_6\text{H}_5$  of  $\text{B}(\text{OBn})_3$ ), 103.1 ( $4\text{-N}_2\text{C}_3^{\text{tBuMeH}}$ ), 66.5 ( $\text{OCH}_2\text{CH}_2$  of **11**), 66.2 ( $\text{OCH}_2\text{Ph}$  of  $\text{B}(\text{OBn})_3$ ), 65.2 ( $\text{OCH}_2\text{Ph}$  of **11** and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ ), 32.6 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.7 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 26.4 ( $\text{OCH}_2\text{CH}_2$  of **11**), 13.8 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{THF}-d_8$ , 160.4 MHz, 298 K): 18.7 (s,  $\text{B}(\text{OBn})_3$ ), -3.9 (s,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ ), -7.9 (s,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**) and  $\text{B}(\text{OBn})_3$  (**25**).** In a glove box, a toluene- $d_8$  solution (0.2 mL) of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**, 12.0 mg, 0.015 mmol) and a toluene- $d_8$  solution (0.3 mL) of  $\text{B}(\text{OBn})_3$  (**25**, 4.60  $\mu\text{L}$ , 0.015 mmol) were prepared in separate J. Young NMR tubes. Outside a glove box, the two J. Young NMR tubes were cooled down at 195 K using acetone/dry ice bath. The solution of **25** in the J. Young NMR tube was transferred *via* cannula to the the solution of **7** in another J. Young NMR tube. The  $^1\text{H}$  NMR spectrum recorded after 10 min at 253 K showed signals corresponding to  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ .

Data for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ .  $^1\text{H}$  NMR (toluene- $d_8$ , 500.0 MHz, 253 K): 7.68 (4H, d,  $^3J = 7.3$  Hz,  $o\text{-C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ ), 7.27-6.98 ( $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ), 6.39 (1H, s,  $\text{OCHPh}_2$ ), 5.50 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 4.74 (6H, s,  $\text{OCH}_2\text{Ph}$ ), 2.15 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 1.27 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 125.7 MHz, 253 K): 162.8 (3- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 149.2 (5- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 143.4 ( $i\text{-C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ), 142.7 ( $i\text{-C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ), 130-125 ( $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ), 102.9 (4- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 77.5 ( $\text{OCHPh}_2$ ), 65.6 ( $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ), 32.5 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.6 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 13.9 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{11}\text{B}$  NMR (toluene- $d_8$ , 160.4 MHz, 253 K): 4.4 (s,  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCHPh}_2)(\text{OBn})_3\}$ ), -7.8 (s,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

Data for  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OBn})_4\}$ .  $^1\text{H}$  NMR (toluene- $d_8$ , 500.0 MHz, 253 K): 7.34 (8H, d,  $^3J = 7.4$  Hz,  $o\text{-C}_6\text{H}_5$ ), 7.27-6.98 ( $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_4\}$ ), 5.49 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 4.93 (8H, s,  $\text{OCH}_2\text{Ph}$ ), 2.13 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 1.25 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 125.7 MHz, 253 K): 162.7 (3-

$\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 146.1 (5- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 143.4 (*i*- $\text{C}_6\text{H}_5$ ), 130-125 ( $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{CaB}(\text{OCH}_2\text{Ph})_4$ ), 102.8 (4- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 65.6 ( $\text{OCH}_2\text{Ph}$ ), 32.4 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.5 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 13.8 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{11}\text{B}$  NMR (toluene- $d_8$ , 160.4 MHz, 253 K): 4.4 (s,  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Ca}\{\text{B}(\text{OCH}_2\text{Ph})_4\}$ ), -7.8 (s, B-H of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}(\text{BH}_4)(\text{THF})$  (21) and 4 equiv. of benzaldehyde.** In a glove box, a THF- $d_8$  solution of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}(\text{BH}_4)(\text{THF})$  (21, 12.00 mg, 0.017 mmol) in a J. Young NMR tube was treated with benzaldehyde (7.45  $\mu\text{L}$ , 0.073 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min demonstrated quantitative conversion to  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ .

$^1\text{H}$  NMR (THF- $d_8$ , 500.0 MHz, 298 K): 7.34 (16H, d,  $^3J = 7.3$  Hz, *o*- $\text{C}_6\text{H}_5$  of  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 7.25 (8H, d,  $^3J = 7.0$  Hz, *o*- $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ), 7.17 (16H, t,  $^3J = 7.4$  Hz, *m*- $\text{C}_6\text{H}_5$  of  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 7.11 (8H, m, *p*- $\text{C}_6\text{H}_5$  of  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 7.09-7.00 (12H, m, *m*- $\text{C}_6\text{H}_5$  and *p*- $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ), 5.79 (3H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 4.71 (8H, s,  $\text{OCH}_2\text{Ph}$ ), 2.36 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.14 (27H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.8 MHz, 298 K): 163.4 (3- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) 146.7 (5- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 144.7, 144.3 (*i*- $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 128.8, 128.6 (*m*- $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 128.2, 127.9 (*o*- $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 127.0, 126.8 (*p*- $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 103.5 (4- $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 65.7, 65.0 ( $\text{OCH}_2\text{Ph}$  of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_4\}(\text{THF})_x$ ), 32.9 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.7 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 14.0 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 298 K): 4.0 (s,  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ), -7.1 (br. s, B-H of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (13) with  $\text{B}(\text{OBn})_3$  (25).**

In a glove box, a THF- $d_8$  solution of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_2$  (13, 12.0 mg, 0.014 mmol) in a J. Young NMR tube was treated with  $\text{B}(\text{OBn})_3$  (25, 4.60  $\mu\text{L}$ , 0.015 mmol) at RT. The  $^1\text{H}$  NMR spectrum recorded after 10 min showed signals corresponding to  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ ,  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ,  $\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 1-4$ ) and  $\text{B}(\text{OCH}_2\text{Ph})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 0-3$ ).

$^1\text{H}$  NMR (THF- $d_8$ , 500.0 MHz, 298 K): 7.58-6.89 ( $\text{C}_6\text{H}_5$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ,  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_4\}$ ,  $\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 1-4$ ) and  $\text{B}(\text{OCH}_2\text{Ph})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 0-3$ )), 6.34 (m,  $\text{OCHPh}_2$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ ,  $\text{Sr}\{\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 1-3$ ) and  $\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 1-3$ ), 5.79 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ), 5.10-4.90 (3H, m,  $\text{B}(\text{OCH}_2\text{Ph})_x(\text{OCHPh}_2)_{3-x}$  ( $x = 1-3$ ), 4.70 (8H, s,  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_4\}$  and  $\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_4\}_2$ ), 4.50 ( $\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 1-3$ )), 4.43 (6H, s,  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OCH}_2\text{Ph})_3(\text{OCHPh}_2)\}$ ), 2.36-2.33 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ), 1.16-1.15 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$  of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$  and  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$ ) ppm.

$^{11}\text{B}$  NMR (THF- $d_8$ , 160.4 MHz, 253 K): 4.3 (s,  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_3(\text{OCHPh}_2)\}$ ,  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}\{\text{B}(\text{OBn})_4\}$  and  $\text{Sr}\{\text{B}(\text{OBn})_x(\text{OCHPh}_2)_{4-x}\}$  ( $x = 1-4$ )), -7.3 (s,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})$  (**21**) with 4 equiv. of benzophenone.** In a glove box, a THF- $d_8$  solution of  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{BH}_4)(\text{THF})$  (**21**, 12.00 mg, 0.017 mmol) in a J. Young NMR tube was treated with benzophenone (13.30 mg, 0.073 mmol) at RT. The  $^1\text{H}$  and  $^{11}\text{B}$  NMR spectra recorded after 10 min showed quantitative conversion to  $(\text{Tp}^{\text{tBu,Me}})\text{Sr}(\text{OCHPh}_2)(\text{THF})_x$  (**13**) and  $\text{B}(\text{OCHPh}_2)_3$  (**23**).

$^1\text{H}$  NMR (THF- $d_8$ , 500.0 MHz, 298 K): 7.38 (4H, d,  $^3J = 7.2$  Hz,  $o\text{-C}_6\text{H}_5$  of **13**), 7.22-7.14 (30H, m,  $\text{C}_6\text{H}_5$  of **23**), 7.12 (4H, t,  $^3J = 7.6$  Hz,  $m\text{-C}_6\text{H}_5$  of **13**), 6.98 (2H, t,  $^3J = 7.3$  Hz,  $p\text{-C}_6\text{H}_5$  of **13**), 6.38 (3H, s,  $\text{B}(\text{OCHPh}_2)_3$ ), 6.04 (1H, s,  $\text{OCHPh}_2$  of **13**), 5.78 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 3.62 (8H, m,  $\text{OCH}_2\text{CH}_2$ ), 2.33 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 1.82 (8H, m,  $\text{OCH}_2\text{CH}_2$ ), 1.26 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (THF- $d_8$ , 125.8 MHz, 298 K): 162.4 (3- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 155.0 ( $i\text{-C}_6\text{H}_5$  of **13**), 146.0 (5- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 145.0 ( $i\text{-C}_6\text{H}_5$  of  $\text{B}(\text{OCHPh}_2)_3$ ), 129.1 ( $\text{C}_6\text{H}_5$  of **23**), 128.1 ( $o\text{-C}_6\text{H}_5$  of **13**), 127.9 ( $m\text{-C}_6\text{H}_5$  of **13**), 127.8 ( $\text{C}_6\text{H}_5$  of **23**), 127.3 ( $\text{C}_6\text{H}_5$  of **23**), 125.5 ( $p\text{-C}_6\text{H}_5$  of **13**), 102.8 (4- $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 82.3 ( $\text{OCHPh}_2$  of **13**), 78.3 ( $\text{OCHPh}_2$  of **23**), 68.4 ( $\text{OCH}_2\text{CH}_2$ ), 33.0 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 31.5 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ), 26.6 ( $\text{OCH}_2\text{CH}_2$ ), 14.0 ( $\text{N}_2\text{C}_3^{\text{tBuMeH}}$ ) ppm.  $^{11}\text{B}$  NMR (THF- $d_8$ , 160.5 MHz, 298 K): 16.8 (s,  $\text{B}(\text{OCHPh}_2)_3$ ), -9.2 (s,  $\text{B-H}$  of  $\text{Tp}^{\text{tBu,Me}}$ ) ppm.

**NMR tube scale reaction of (Tp<sup>tBu,Me</sup>)Sr(BH<sub>4</sub>)(THF) (21) with 4 equiv. of 2-methylcyclohexanone.** In a glove box, a THF-*d*<sub>8</sub> solution of (Tp<sup>tBu,Me</sup>)Sr(BH<sub>4</sub>)(THF) (**21**, 12.00 mg, 0.017 mmol) in a J. Young NMR tube was treated with 2-methylcyclohexanone (8.86  $\mu$ L, 0.073 mmol) at RT. The <sup>1</sup>H and <sup>11</sup>B NMR spectra recorded after 10 min showed quantitative conversion to *trans*-(Tp<sup>tBu,Me</sup>)Sr(OCyMe)(THF)<sub>x</sub> (**27**) and *cis*- and *trans*-B(OCyMe)<sub>3</sub> (**24**).

<sup>1</sup>H NMR (THF-*d*<sub>8</sub>, 499.9 MHz, 298 K): 5.78 (6H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 4.27 (3H, m, OCH of **24**, *cis*), 3.68 (3H, m, OCH of **24**, *trans*), 3.62 (8H, m, OCH<sub>2</sub>CH<sub>2</sub>), 3.08 (2H, m, OCH of **27**), 2.34 (18H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 1.99-1.33 (16H, m, CH<sub>2</sub> of CyMe), 1.82 (4H, m, CHCH<sub>2</sub> of **27**), 1.56 (3H, m, CHMe of **24**, *cis*), 1.38 (3H, m, CHMe of **24**, *trans*), 1.31 (54H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 1.30-0.90 (8H, m, CH<sub>2</sub> of CyMe), 1.07 (4H, m, CHCH<sub>2</sub> of **27**), 0.99 (2H, m, CHMe of **27** overlapping with 6H, m, CHMe of **27**), 0.92 (9H, m, CHMe of **24**, *trans*), 0.88 (9H, m, CHMe of **24**, *cis*) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-*d*<sub>8</sub>, 125.7 MHz, 298 K): 162.4 (3-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) 145.8 (5-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 102.7 (4-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 80.3 (OCH of **27**), 77.8, 77.7 and 77.5 (OCH of **24**, *trans*), 72.2, 72.1 and 72.0 (OCH of **24**, *cis*), 45.4 (CHMe of **27**), 42.3 (CHCH<sub>2</sub> of CyMe), 40.3 (CHMe of **24**, *trans*), 37.3 (CHMe of **24**, *cis*), 35.7, 34.6, 33.7 (CH<sub>2</sub> of CyMe), 33.0 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 31.7 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 30.2, 28.1, 27.4, 26.8, 26.5, 26.1 and 21.6 (CH<sub>2</sub> of CyMe), 21.6 (CHMe of **27**), 40.3 (CHMe of **24**, *trans*), 37.3 (CHMe of **24**, *cis*), 13.9 (N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) ppm. <sup>11</sup>B NMR (THF-*d*<sub>8</sub>, 160.4 MHz, 298 K): 17.8 (s, B(OCyMe)<sub>3</sub>), -7.4 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

## 6.8 Experimental details and characterising data for Chapter Five

**(Tp<sup>tBu,Me</sup>)Mg(BD<sub>4</sub>) (20-*d*<sub>4</sub>)** To a solid mixture of (Tp<sup>tBu,Me</sup>)Mg(I) (0.60 g, 1.04 mmol) and Na(BD<sub>4</sub>) (0.13 g, 3.12 mmol) was added THF (20 mL). The solution was stirred at RT for 18h. The solvent was removed *in vacuo* and the product was extracted into benzene (40 mL). The solvent was removed *in vacuo* to give a white powder. The product was washed with cold pentane (3 x 5 mL). Yield: 0.30 g (62 %).

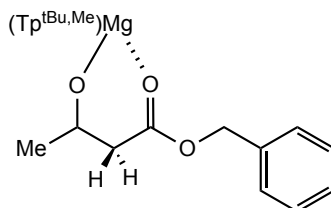
<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 499.9 MHz, 298 K): 5.65 (3H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 2.07 (9H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 1.48 (27H, s, N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) ppm. <sup>2</sup>H NMR (C<sub>6</sub>H<sub>6</sub>, 76.8 MHz, 298 K): 0.87 (q, BD<sub>4</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 167.6 (3-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) 145.0 (5-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 104.3 (4-N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH), 32.1 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 32.3 (N<sub>2</sub>C<sub>3</sub>C(Me<sub>3</sub>)MeH), 13.3 (N<sub>2</sub>C<sub>3</sub><sup>tBu</sup>MeH) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): -

9.1 (s, B-H of  $\text{Tp}^{\text{tBu,Me}}$ ), -38.2 (br. s,  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\underline{\text{B}}\text{D}_4)$ ) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 2570 (m), 2359 (s), 2341 (s), 1828 (m), 1652 (m), 1542 (s, B-D<sub>b</sub> of  $\text{BD}_4$ ), 1190 (s), 1068 (s), 1021 (s), 769 (m), 722 (m), 649 (s).

**$(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{I})$**  To a solid mixture of  $\text{K}(\text{Tp}^{\text{tBu,Me}})$  (1.00 g, 2.13 mmol) and  $\text{MgI}_2$  (0.79 g, 2.84 mmol) was added THF (20 mL). The solution was stirred at RT for 18h. The solvent was removed *in vacuo* and the product was extracted into benzene (40 mL). The solvent was removed *in vacuo* to give a white powder. The product was washed with cold pentane (3 x 5 mL). Yield: 0.77 (63 %).

$^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 499.9 MHz, 298 K): 5.63 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ), 2.07 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ), 1.59 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 165.6 (3- $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ) 145.2 (5- $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ), 104.0 (4- $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ), 32.3 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 32.0 ( $\text{N}_2\text{C}_3\text{C}(\underline{\text{Me}}_3)\text{MeH}$ ), 13.0 ( $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ) ppm. IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 1542 (s), 1365 (m), 1301 (m), 1240 (m), 1187 (s), 1175 (m), 1067 (m), 1022 (m), 986 (m), 850 (m), 766 (s), 670 (w), 668 (w), 648 (s). EI-MS:  $m/z$  = 447.3151 Da (100%) of  $[(\text{Tp}^{\text{tBu,Me}})\text{Mg}]^+$ . Anal. found (calcd. For  $\text{C}_{24}\text{H}_{40}\text{BMgN}_6\text{I}$ ): C, 50.07 (50.16); H, 7.15 (7.02); N, 14.56 (14.63) %.

**NMR tube scale synthesis of the mono-insertion product  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})\text{OBn}\}$  (**22.1**).** In a glove box, a J. Young NMR tube was charged with  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**, 13.6 mg, 0.025 mmol) and *rac*-BBL (2  $\mu\text{L}$ , 0.025 mmol) in toluene- $d_8$  (0.5 mL) at RT. The  $^1\text{H}$  NMR spectrum recorded after 4 h showed quantitative conversion to **22.1**.

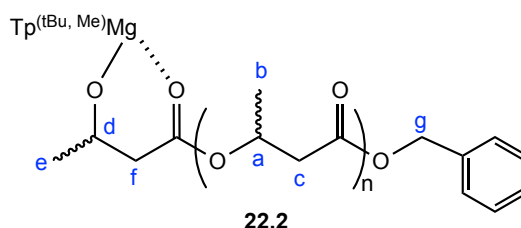


$^1\text{H}$  NMR (toluene- $d_8$ , 500.0 MHz, 298 K): 7.26 (2H, d,  $^3J$  = 6.9 Hz,  $o\text{-C}_6\text{H}_5$ ), 7.08 (2H, m,  $m\text{-C}_6\text{H}_5$ ), 7.02 (1H, m,  $p\text{-C}_6\text{H}_5$ ), 5.59 (3H, s,  $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ), 5.12 (1H, m,  $\text{OCHMe}$ ), 5.09 (2H, s,  $\text{OCH}_2\text{Ph}$ ), 3.25 (1H, dd,  $^3J$  = 13.2, 4.1 Hz,  $\text{OCHMeCH}_2$ ), 2.79 (1H, dd,  $^3J$  = 13.0, 9.5 Hz,  $\text{OCHMeCH}_2$ ), 2.08 (9H, s,  $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ), 1.70 (3H, d,  $^3J$  = 5.8 Hz,  $\text{OCHMe}$ ), 1.44 (27H, s,  $\text{N}_2\text{C}_3^{\text{tBu}}\text{MeH}$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR (toluene- $d_8$ , 125.7 MHz, 298 K): 144.8 ( $i\text{-C}_6\text{H}_5$ ), 129.2 ( $o\text{-C}_6\text{H}_5$ ), 129.0 ( $m\text{-C}_6\text{H}_5$ ), 128.4 ( $p\text{-C}_6\text{H}_5$ ), 103.3 (4-

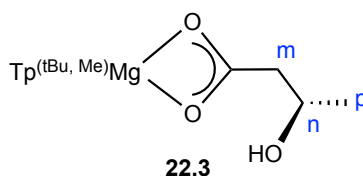


$\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 67.3 ( $\text{OCHMe}$ ), 66.0 ( $\text{OCH}_2\text{Ph}$ ), 50.0 ( $\text{OCHMeCH}_2$ ), 32.4 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 31.5 ( $\text{N}_2\text{C}_3\text{C}(\text{Me}_3)\text{MeH}$ ), 28.2 ( $\text{OCHMe}$ ), 13.2 ( $\text{N}_2\text{C}_3^t\text{BuMeH}$ ) ppm.  $^{11}\text{B}$  NMR (toluene- $d_8$ , 160.4 MHz, 298 K): -9.3 (s, B-H of  $\text{Tp}^{t\text{Bu},\text{Me}}$ ) ppm.

**NMR tube scale reaction of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Mg}(\text{OBn})$  (**22**) and 20 equiv. of *rac*-BBL.** In a glove box, a J. Young NMR tube was charged with  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Mg}(\text{OBn})$  (**22**, 6.94 mg, 0.0125 mmol) and *rac*-BBL (20.4  $\mu\text{L}$ , 0.25 mmol) in toluene- $d_8$  (0.5 mL) at RT. The reaction was monitored by  $^1\text{H}$  NMR spectroscopy at 353 K and the spectra were recorded every 5 min for 12 h. The  $^1\text{H}$  NMR spectrum recorded after 3.5 h showed a presence of  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})(\text{BBL})_n\text{OBn}\}$  (**22.2**) and  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Mg}\{\kappa^2\text{-O}_2\text{CCH}_2\text{CHMeOH}\}$  (**22.3**) and PHB terminated with  $\text{-OBn}$  and *trans*-crotonate end groups. The  $^{11}\text{B}$  NMR spectrum was recorded after 12 h showed signals corresponding to **22.3**. To clarify the chemical shift assignments, diagrams showing a concise atom labelling scheme of **22.2**, **22.3** and PHB terminated with  $\text{-OBn}$  and *trans*-crotonate end groups are accompanied.

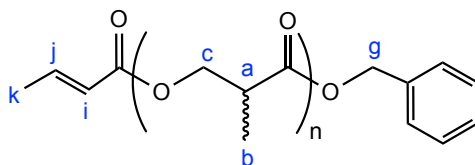


Data for  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Mg}\{\kappa^2\text{-OCHMeCH}_2\text{C}(\text{O})(\text{BBL})_n\text{OBn}\}$  (**22.2**).  $^1\text{H}$  NMR (toluene- $d_8$ , 500.0 MHz, 353 K): 7.25-7.10 (5H, m,  $\text{C}_6\text{H}_5$ ), 5.65 (3H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 5.32 (nH, m,  $\text{H}_a$ ), 4.97 (1H, m,  $\text{H}_d$  overlapping with 2H, m,  $\text{H}_g$ ), 3.10 (1H, m,  $\text{H}_f$ ), 2.60-2.21 (2nH, m,  $\text{H}_c$ ), 2.16 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.63 (3H, m,  $\text{H}_e$ ), 1.46 (27H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.17 (3nH, m,  $\text{H}_b$ ) ppm.



Data for  $(\text{Tp}^{t\text{Bu},\text{Me}})\text{Mg}\{\kappa^2\text{-O}_2\text{CCH}_2\text{CHMeOH}\}$  (**22.3**).  $^1\text{H}$  NMR (toluene- $d_8$ , 500.0 MHz, 353 K): 5.70 (3H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 5.60 (1H, m,  $\text{H}_n$ ), 2.98 (1H, dd,  $^3J = 16.7$ , 5.8 Hz,  $\text{H}_m$ ), 2.70 (1H, m,  $\text{H}_m$ ), 2.19 (9H, s,  $\text{N}_2\text{C}_3^t\text{BuMeH}$ ), 1.43 (3H, m,  $\text{H}_p$  overlapping

with 27H, s, N<sub>2</sub>C<sub>3</sub><sup>t</sup>BuMeH) ppm. <sup>11</sup>B NMR (toluene-*d*<sub>8</sub>, 160.4 MHz, 298 K): -8.8 (s, B-H of Tp<sup>tBu,Me</sup>) ppm.

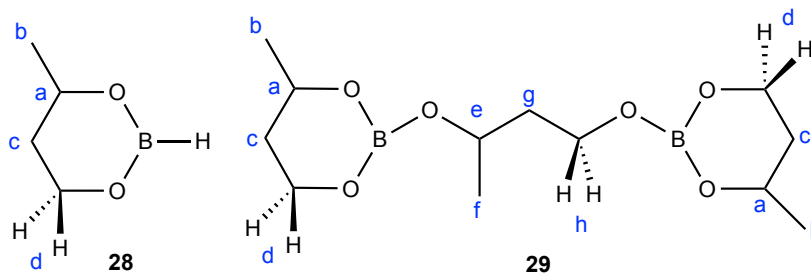


Data for PHB terminated with -OBn and *trans*-crotonate groups. <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 500.0 MHz, 353 K): 7.25-7.10 (5H, m, C<sub>6</sub>H<sub>5</sub>), 6.84 (1H, m, H<sub>j</sub>), 5.70 (1H, m, H<sub>i</sub>), 5.30 (nH, m, H<sub>a</sub>), 4.97 (2H, m, H<sub>g</sub>), 2.58-2.23 (2nH, m, H<sub>c</sub>), 1.43 (3H, m, H<sub>k</sub>), 1.17 (3nH, m, H<sub>b</sub>) ppm.

**NMR tube scale synthesis of 4-methyl-1, 3, 2-dioxaborinane (28).** In a glove box, a C<sub>6</sub>D<sub>6</sub> solution (0.25 mL) of *rac*-BBL (10 μL, 0.12 mmol) was prepared in a J. Young NMR tube. Outside a glove box, BH<sub>3</sub>(SMe<sub>2</sub>) (7.6 μL, 0.08 mmol) was added in the C<sub>6</sub>D<sub>6</sub> solution of *rac*-BBL using Schlenk line. The solution was heated at 60 °C for 24 h. The <sup>1</sup>H NMR spectrum recorded after 24 h showed signals corresponding to **28** and unreacted *rac*-BBL.

<sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500.0 MHz, 298 K): 3.61 (1H, q, <sup>3</sup>*J* = 6.3 Hz, OCHMe), 3.56 (1H, dt, <sup>3</sup>*J* = 11.3, 4.1 Hz, OCH2CH<sub>2</sub>), 3.44 (1H, ddd, <sup>3</sup>*J* = 11.4, 7.6, 6.1 Hz, OCH2CH<sub>2</sub>), 1.13 (2H, dddt, <sup>3</sup>*J* = 7.2, 5.5, 4.4, 1.5 Hz, OCH<sub>2</sub>CH2), 0.94 (3H, d, <sup>3</sup>*J* = 6.1 Hz, OCHMe) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.7 MHz, 298 K): 67.1 (OCHMe), 60.7 (OCH2CH<sub>2</sub>), 34.5 (OCH<sub>2</sub>CH2), 22.7 (OCHMe) ppm. <sup>11</sup>B NMR (C<sub>6</sub>D<sub>6</sub>, 160.4 MHz, 298 K): 25.8 (d, <sup>1</sup>*J*<sub>B-H</sub> = 170.8 MHz, HB(OR)<sub>2</sub> of **28**) ppm.

**Independent synthesis of 4-methyl-1, 3, 2-dioxaborinane (28) and 2,2'-(butane-1, 3-diylbis(oxy))bis(4-methyl-1, 3, 2-dioxaborinane) (29).** In a glove box, a J. Young NMR tube was charged with *rac*-BBL (0.1 mL, 1.23 mmol). Outside a glove box, BH<sub>3</sub>(SMe<sub>2</sub>) (0.13 mL, 1.23 mmol) was added in the the J. Young tube containing *rac*-BBL *via* Schlenk line. The solvent-free reaction was heated at 60 °C for 24 h to give a mixture of **28** and **29**. The final product was colourless oil and characterised without further purification due to its low boiling point. To clarify the chemical shift assignments of a mixture of **28** and **29**, a diagram showing a concise atom labelling scheme of **28** and **29** is accompanied.



Data for 4-methyl-1, 3, 2-dioxaborinane (**28**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500.0 MHz, 298 K): 3.75-3.40 (3H,  $\text{H}_a$  and  $\text{H}_d$ ), 1.10 (2H, m,  $\text{H}_c$ ), 0.97 (3H,  $\text{H}_b$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 68.3 ( $\underline{\text{CH}}_a$ ), 61.7 ( $\underline{\text{C}}(\text{H}_d)_2$ ), 34.3 ( $\underline{\text{C}}(\text{H}_c)_2$ ), 22.7 ( $\underline{\text{C}}(\text{H}_b)_3$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): 25.8 (d,  $^1J_{\text{B-H}} = 171.9$  MHz,  $\underline{\text{HB}}(\text{OR})_2$  of **28**) ppm. ESI-HRMS:  $m/z$  found (calcd for  $\text{C}_4\text{H}_9\text{BO}_2$ ,  $[\text{M}]^+$ ): 100.0438 Da (100.0696 Da).

Data for 2,2'-(butane-1, 3-diylbis(oxy))bis(4-methyl-1, 3, 2-dioxaborinane) (**29**).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 500.0 MHz, 298 K): 4.69 (1H, m,  $\text{H}_e$ ), 4.14 (2H, m,  $\text{H}_h$ ), 3.75-3.40 (6H,  $\text{H}_a$  and  $\text{H}_d$ ), 2.00-1.75 (2H,  $\text{H}_g$ ), 1.26 (3H, dd,  $^3J = 6.2, 1.5$  Hz,  $\text{H}_f$ ), 1.10 (4H, m,  $\text{H}_c$ ), 0.97 (6H,  $\text{H}_b$ ) ppm.  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 125.7 MHz, 298 K): 68.3 ( $\underline{\text{CH}}_a$ ), 66.0 ( $\underline{\text{CH}}_e$ ), 61.7 ( $\underline{\text{C}}(\text{H}_d)_2$ ), 60.7 ( $\underline{\text{C}}(\text{H}_h)_2$ ), 40.8 ( $\underline{\text{C}}(\text{H}_g)_2$ ), 34.3 ( $\underline{\text{C}}(\text{H}_c)_2$ ), 22.7 ( $\underline{\text{C}}(\text{H}_b)_3$ ) ppm.  $^{11}\text{B}$  NMR ( $\text{C}_6\text{D}_6$ , 160.4 MHz, 298 K): 18.2 (br. s,  $\underline{\text{B}}(\text{OR})_3$  moiety) ppm. ESI-HRMS:  $m/z$  found (calcd for  $\text{C}_{12}\text{H}_{24}\text{B}_2\text{O}_6$ ,  $[\text{M}]^+$ ): 286.1863 Da (286.1759 Da).

Common data: IR (NaCl plates, Nujol mull,  $\text{cm}^{-1}$ ): 2404 (s), 2273 (s), 1420 (m), 1327 (s), 1281 (s), 1207 (m), 1170 (m), 1093 (s), 915 (s), 888 (s), 761 (m), 664 (s).

## 6.9 General procedures for ROP of LA (Chapters Two, Three and Four)

**General procedure for the polymerisation of *rac*-, *L*-, and *meso*-LA.** In a glove box, a stock solution of catalyst (18.75  $\mu\text{mol}$ ) in THF (5.0 mL) was prepared. The stock solution of catalyst (3.75  $\mu\text{mol}$ , 1.0 mL) was added into a stirred THF solution of LA (0.432 g, 3.0 mmol, 5.0 mL) at RT.  $[\text{LA}]_0:[\text{initiator}]_0 = 800$  or as specified. Aliquots (ca. 0.1 mL) were taken at appropriate time intervals and quenched inside a glove box with degassed, wet THF (ca. 0.2 mL). The volatiles were evaporated to give PLA. The monomer to polymer % conversion was determined using  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ ), and measured by integration of the  $\underline{\text{CHMe}}$  resonances of the unreacted monomer and PLA. Aliquots were recovered for GPC and MALDI-ToF MS analyses. The polymer was isolated by addition of pentane to a concentrated THF solution of PLA to yield a precipitate which was washed with pentane and dried under vacuum.

**General procedure for the polymerisation of *rac*-LA with additives.** In a glove box, a stock solution of catalyst (18.75  $\mu\text{mol}$ ) and additive in THF (5.0 mL) was prepared. The stock solution of catalyst (3.75  $\mu\text{mol}$ , 1.0 mL) and additive was added into a stirred THF solution of LA (0.432 g, 3.0 mmol, 5.0 mL) at RT.  $[\text{LA}]_0:[\text{initiator}]_0 = 800$  or as specified. Aliquots (*ca.* 0.1 mL) were taken at appropriate time intervals and quenched inside a glove box with degassed, wet THF (*ca.* 0.2 mL). The volatiles were evaporated to give PLA. The monomer to polymer % conversion was determined using  $^1\text{H}$  NMR spectroscopy ( $\text{CDCl}_3$ ) and measured by integration of the  $\text{CHMe}$  resonances of the unreacted monomer and PLA. Aliquots were recovered for GPC and MALDI-ToF MS analyses. The polymer was isolated by addition of pentane to a concentrated THF solution of PLA to yield a precipitate which was washed with pentane and dried under vacuum.

#### 6.10 General procedures for ROP of *rac*-BBL (Chapter Five)

**General procedure for the polymerisation of *rac*-BBL.** In a glove box, a solution of *rac*-BBL (0.129 g, 1.5 mmol) in toluene (1.0 mL) was added rapidly in one portion to a stirred toluene solution of catalyst (0.0015 or 0.075 mmol, 2.0 mL) at RT.  $[\text{rac-BBL}]_0:[\text{initiator}]_0 = 100$  or 20. The polymerisation was quenched inside a glove box with degassed, wet THF (*ca.* 1.0 mL). The volatiles were evaporated to give crude PHB. The crude PHB was then dissolved in THF and isolated upon precipitation in pentane, filtered and dried under vacuum. The crude and isolated PHB samples were analysed by NMR spectroscopy, GPC and MALDI-ToF mass spectrometry. Monomer conversion was calculated from  $^1\text{H}$  NMR spectrum of a parallel NMR tube scale experiment carried out in toluene- $d_8$  under analogous conditions (*vide infra*) by using the integration (Int.) ratio =  $\text{Int.}_{\text{PHB}}/[\text{Int.}_{\text{PHB}}+\text{Int.}_{\text{BBL}}]$  of the methine hydrogen ( $\delta = 5.25$  ppm for PHB and  $\delta = 4.66$  for BBL). The  $M_n(\text{NMR})$  of PHB samples were determined by  $^1\text{H}$  NMR analysis in  $\text{CDCl}_3$  from the relative intensity of the resonances of PHB methine protons ( $-\text{OCHMeCH}_2$ ,  $\delta = 5.25$  ppm) and those of the chain ends.

**General procedure for the polymerisation of *rac*-BBL with additive.** In a glove box, a solution of *rac*-BBL (0.129 g, 1.5 mmol) in toluene (1.0 mL) was added rapidly in one portion to a stirred toluene solution of catalyst (0.0015 or 0.075 mmol, 2.0 mL) and additive at RT.  $[\text{rac-BBL}]_0:[\text{initiator}]_0 = 100$  or 20. The polymerisation was quenched inside a glove box with degassed, wet THF (*ca.* 1.0 mL). The volatiles were evaporated

to give PHB. The crude PHB was then dissolved in THF and isolated upon precipitation in pentane, filtered and dried under vacuum. The crude and isolated PHB samples were analysed by NMR spectroscopy, GPC and MALDI-ToF mass spectrometry. Monomer conversion was calculated from  $^1\text{H}$  NMR spectrum of a parallel NMR tube scale experiment carried out in toluene- $d_8$  under analogous conditions (*vide infra*) by using the integration (Int.) ratio =  $\text{Int.}_{\text{PHB}}/[\text{Int.}_{\text{PHB}}+\text{Int.}_{\text{BBL}}]$  of the methine hydrogen ( $\delta = 5.25$  ppm for PHB and  $\delta = 4.66$  for BBL). The  $M_n(\text{NMR})$  of PHB samples were determined by  $^1\text{H}$  NMR analysis in  $\text{CDCl}_3$  from the relative intensity of the resonances of PHB methine protons ( $-\text{OCHMeCH}_2$ ,  $\delta = 5.25$  ppm) and those of the chain ends.

**General procedure for the kinetic analyses of the ROP of *rac*-BBL with various catalysts.** In a glove box, a stock solution of catalyst (0.05 mmol, 0.4 mL, toluene- $d_8$ ) was prepared. The stock solution of catalyst (0.0125 mmol, 0.1 mL, toluene- $d_8$ ) was added into a J. Young NMR tube charged with toluene- $d_8$  (0.4 mL). A volume of *rac*-BBL (10  $\mu\text{L}$ , 0.25 mmol) was measured using a microlitre syringe (Hamilton 50  $\mu\text{L}$ ) and added into a solution of catalyst in toluene- $d_8$  (0.5 mL) in the J. Young NMR tube.  $[\text{rac-BBL}]_0:[\text{initiator}]_0 = 20$ . A blank toluene- $d_8$  was injected to an NMR probe set at RT, locked and shimmed. Then, the experimental sample was injected to the NMR probe and arrayed  $^1\text{H}$  NMR spectra was set to run every 120 seconds (number of scans = 4). The polymerisation kinetics was calculated from decay of intensity of the methine proton ( $\text{CHMe}$ ) of *rac*-BBL. The apparent rate constant ( $k_{\text{app}}$ ) was obtained from a linear plot of  $\ln([\text{rac-BBL}]_0/[\text{rac-BBL}]_t)$  vs. time.

## 6.11 References for Chapter Six

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# Appendix

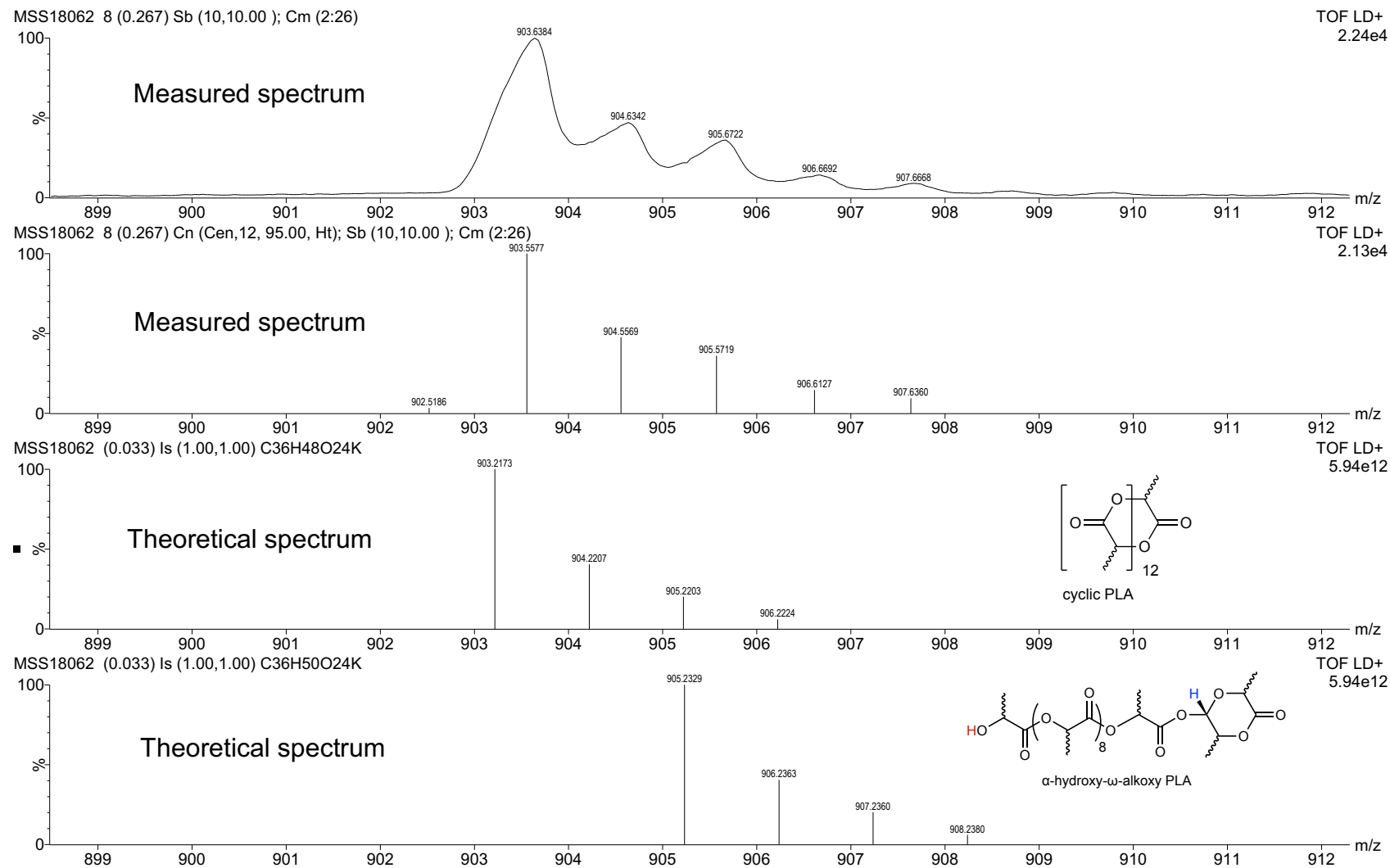


**Figure A1** MALDI-ToF mass spectra of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**).



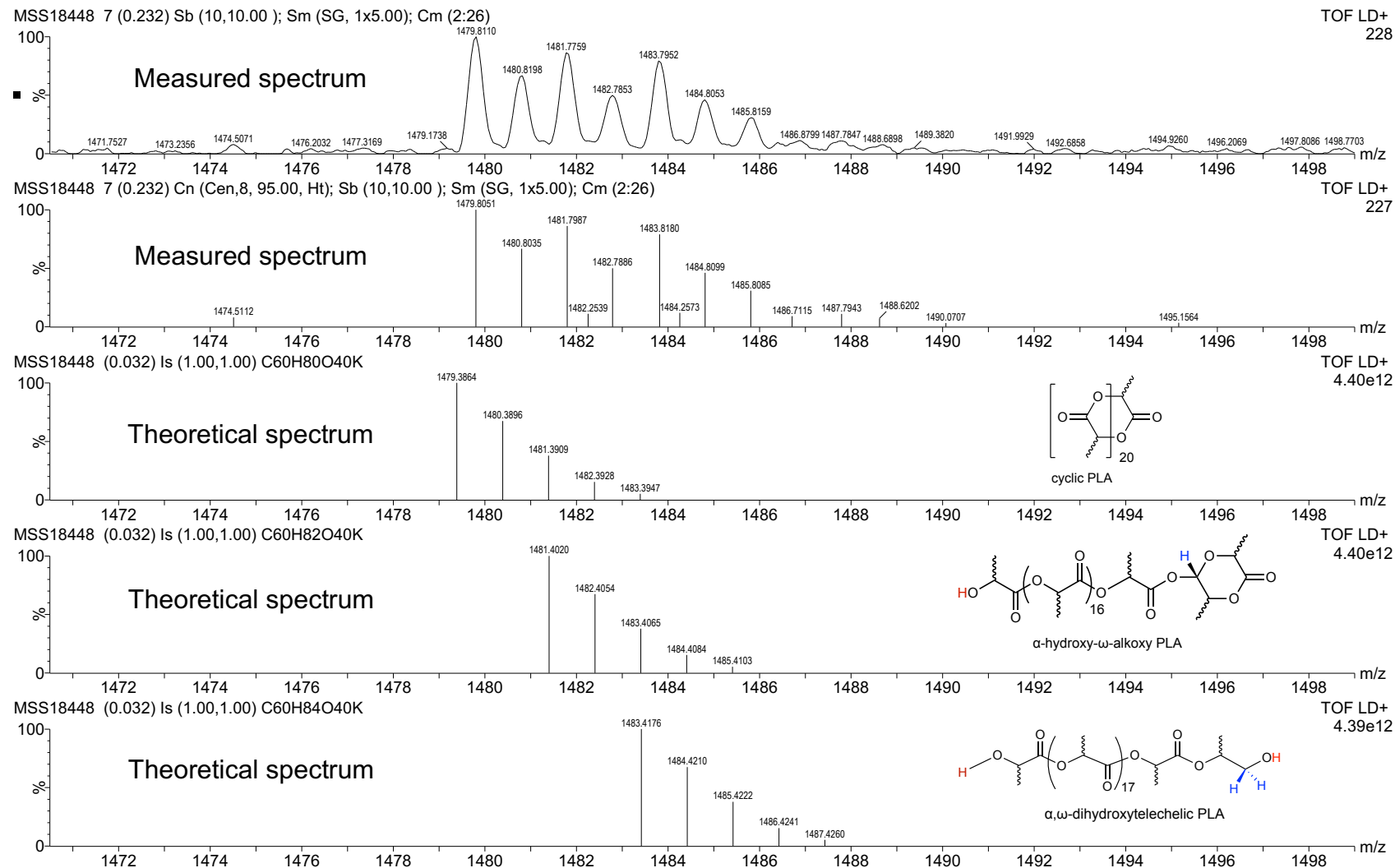


**Figure A2** MALDI-ToF mass spectra of PLA synthesised using  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**).

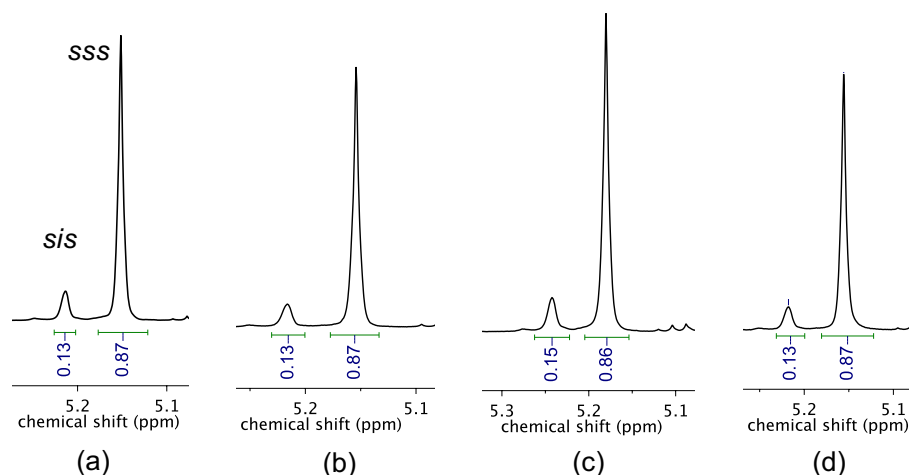


**Figure A3**  $^1\text{H}\{^1\text{H}\}$  NMR spectra ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of syndiotactically-enriched PLAs ( $P_r = 0.86\text{--}0.87$ ) synthesised from the ROP of 800 equiv. of *meso*-LA with (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{HBEt}_3)(\text{THF})$  (**1**), (b)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**), (c)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) and (d)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCHPh}_2)(\text{THF})$  (**7**).

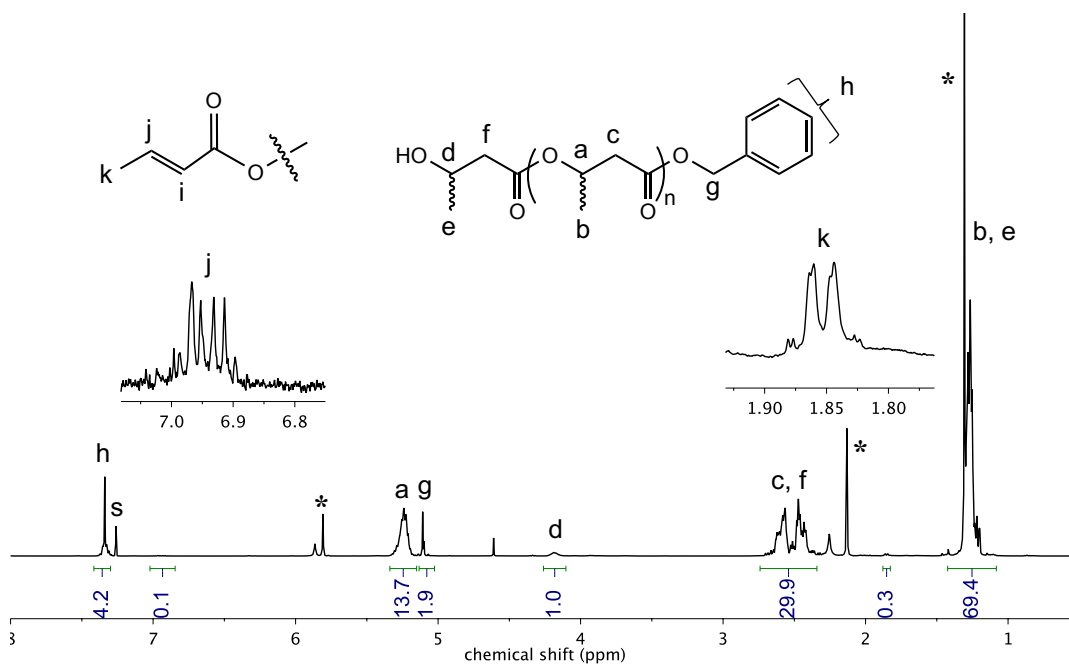


**Figure A4**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of crude PHB synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**). Conditions:  $[\text{rac-BBL}]_0:[\text{22}]_0 = 20:1$ ,  $[\text{rac-BBL}]_0 = 0.5\text{ M}$ , 1.0 mL toluene at RT for 6 h.  $M_n(\text{NMR})$  for  $-\text{OH}$  and  $-\text{OBn}$  terminated PHB = 1,288  $\text{g mol}^{-1}$  “s” denotes residual protio-solvent. “\*” denotes  $\text{Tp}^{\text{tBu,Me}}$  ligand.

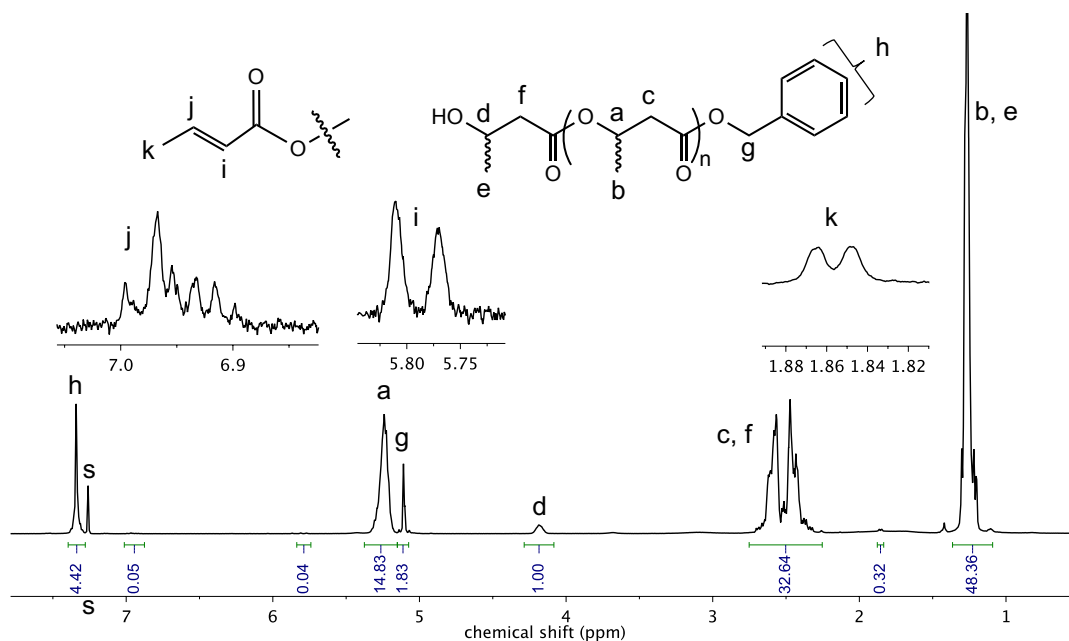


**Figure A5**  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ , 499.9 MHz, 298 K) of isolated PHB synthesised by  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**). Conditions:  $[\text{rac-BBL}]_0:[\mathbf{22}]_0 = 20:1$ ,  $[\text{rac-BBL}]_0 = 0.5$  M, 1.0 mL toluene at RT for 6 h.  $M_n(\text{NMR})$  for  $-\text{OH}$  and  $-\text{OBn}$  terminated PHB =  $1,615$  g  $\text{mol}^{-1}$  “s” denotes residual protio-solvent.

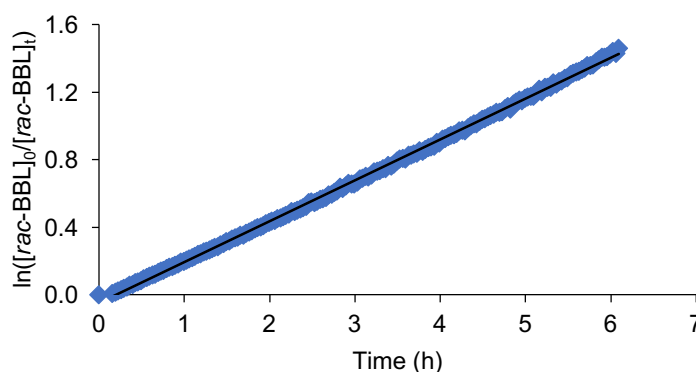


**Figure A6** ROP of *rac*-BBL with  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{OBn})$  (**22**). Plot of  $\ln([\text{rac-BBL}]_0/[\text{rac-BBL}]_t)$  vs. time. Conditions: 0.5 mL toluene- $d_8$ , RT,  $[\text{rac-BBL}]_0 = 0.5$  M.  $[\text{rac-BBL}]_0:[\mathbf{22}]_0 = 20:1$ .  $k_{\text{app}} = 0.2409(6)$   $\text{h}^{-1}$  ( $R^2 = 0.998$ ).

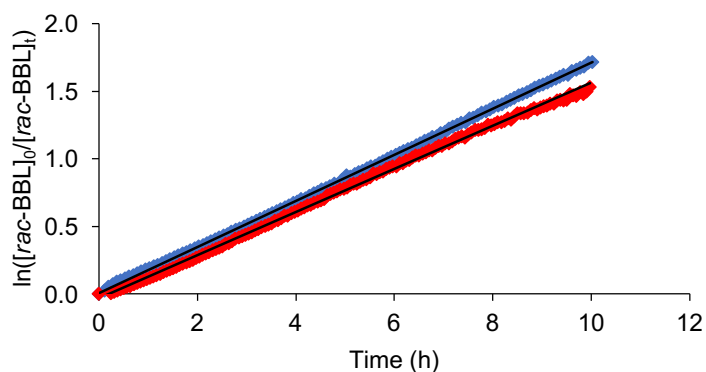


**Figure A7** Plots of  $\ln([rac-BBL]_0/[rac-BBL]_t)$  vs. time. Conditions: 0.5 mL toluene- $d_8$ , RT,  $[rac-BBL]_0:[cat.]_0 = 20:1$ ,  $[rac-BBL]_0 = 0.5$  M. Blue: ROP of *rac*-BBL with  $(Tp^{tBu,Me})Mg(BH_4)$  (**20**),  $k_{app} = 0.1701(2) \text{ h}^{-1}$  ( $R^2 = 0.998$ ). Red: ROP of *rac*-BBL with  $(Tp^{tBu,Me})Mg(BD_4)$  (**20-d<sub>4</sub>**),  $k_{app} = 0.1597(5) \text{ h}^{-1}$  ( $R^2 = 0.999$ ).

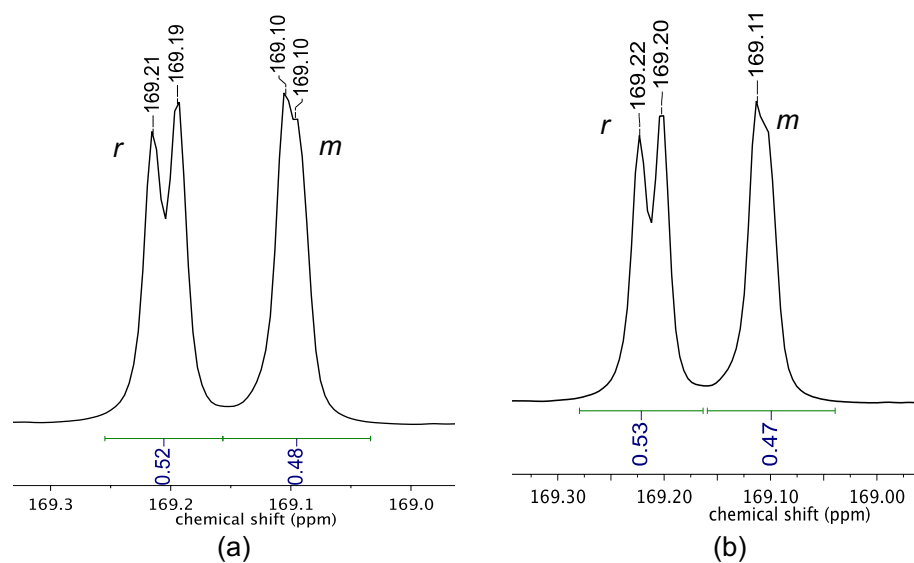


**Figure A8** Inverse gated  $^{13}C\{^1H\}$  NMR spectra ( $CDCl_3$ , 125.7 MHz, 298 K) of atactic PHBs ( $P_r = 0.47$ - $0.48$ ) synthesised from the ROP of 100 equiv. of *rac*-BBL with  $(Tp^{tBu,Me})Mg(OBn)$  (**22**, Left) or  $(Tp^{tBu,Me})Mg(BH_4)$  (**20**, Right) in toluene at RT.

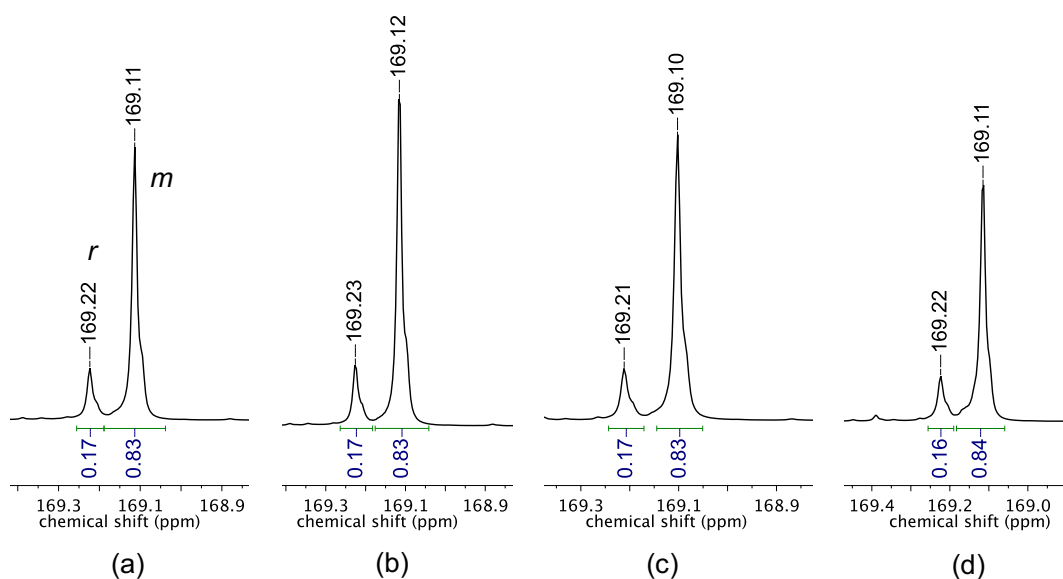


**Figure A9** Inverse gated  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra ( $\text{CDCl}_3$ , 125.7 MHz, 298 K) of isotactically-enriched PHBs ( $P_m = 0.83\text{--}0.84$ ) synthesised from the ROP of 100 equiv. of *rac*-BBL with (a)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**), (b)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**), (c)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{OCyMe})(\text{THF})$  (**10**) and (d)  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}(\text{BH}_4)(\text{THF})$  (**8**) with 4 equiv. of benzaldehyde in toluene at RT.

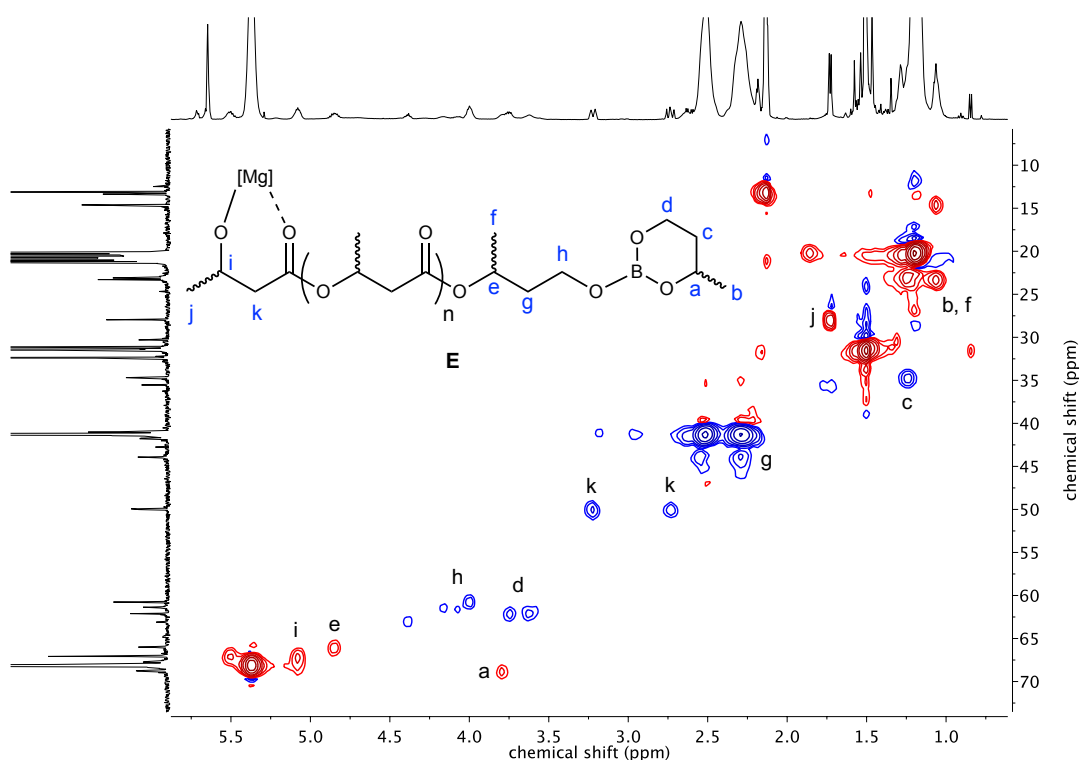


**Figure A10** HSQC NMR spectrum (toluene- $d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and 20 equiv. of *rac*-BBL at RT recorded after 10 h.

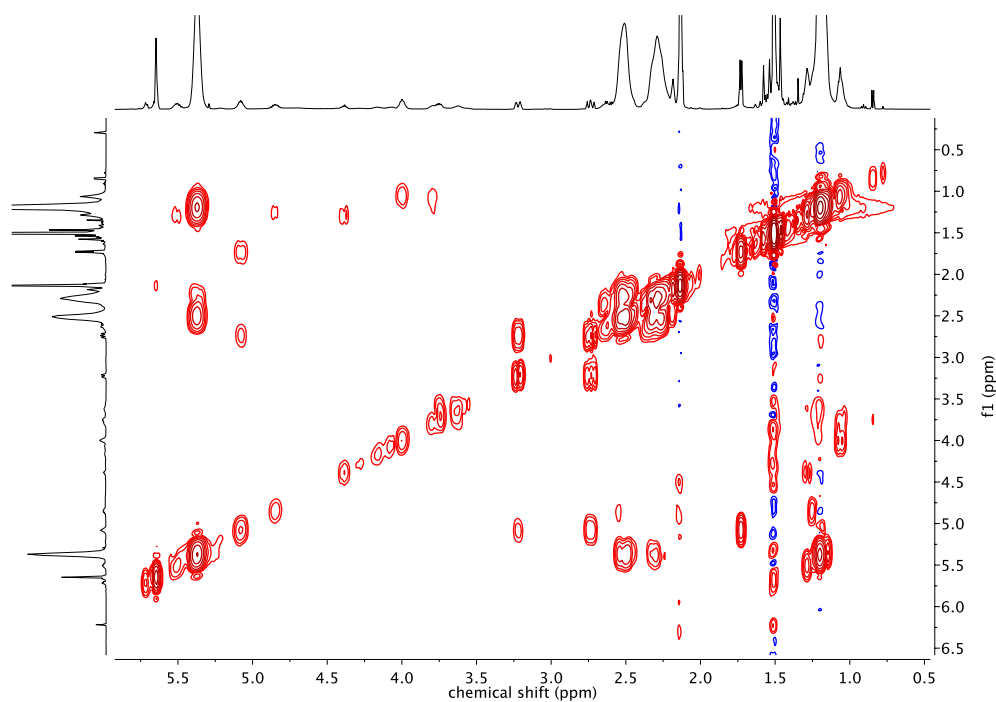


**Figure A11** COSY NMR spectrum (toluene- $d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and 20 equiv. of *rac*-BBL at RT recorded after 10 h.

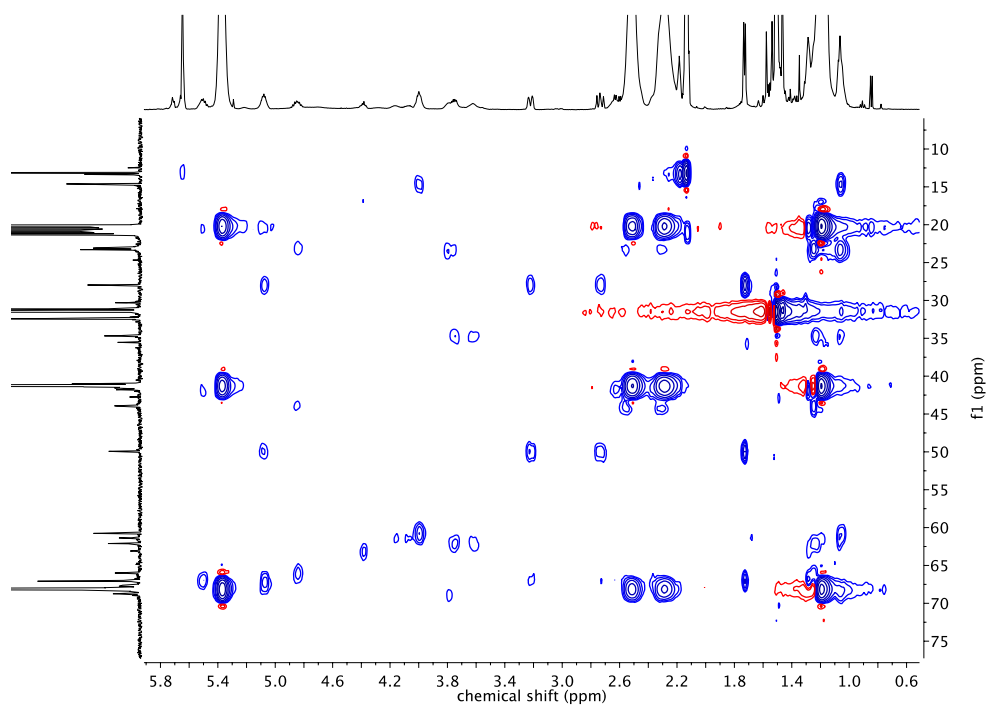


**Figure A12** HSQC-TOCSY NMR spectrum (toluene- $d_8$ , 499.9 MHz, 298 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Mg}(\text{BH}_4)$  (**20**) and 20 equiv. of *rac*-BBL at RT recorded after 10 h.

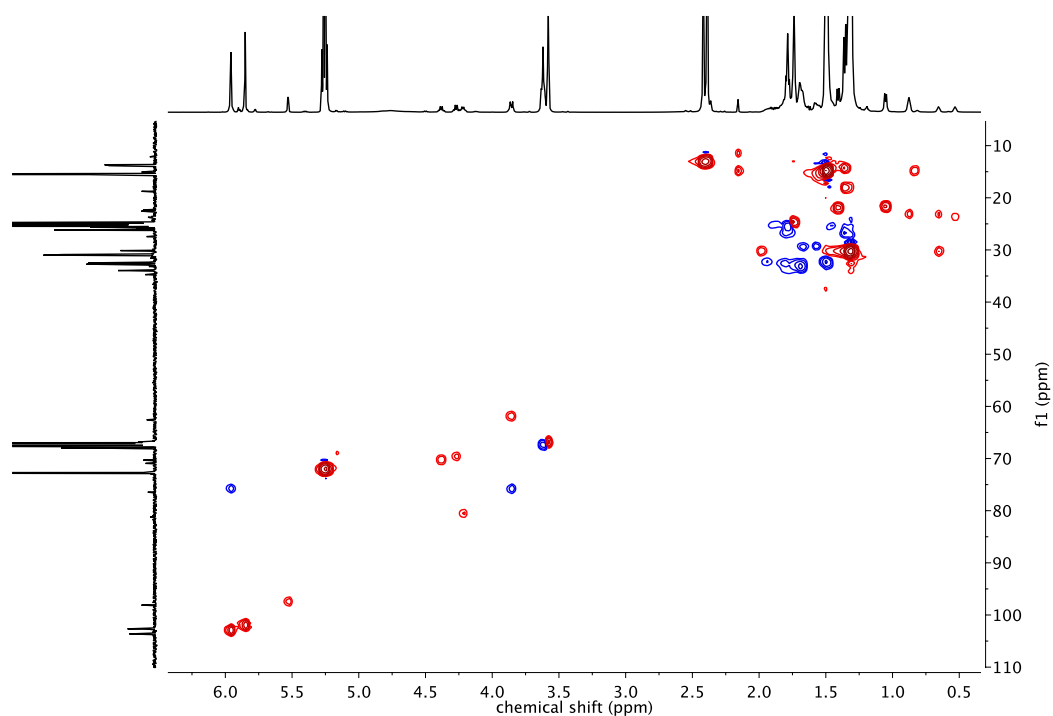


**Figure A13** HSQC NMR spectrum (THF- $d_8$ , 499.9 MHz, 223 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) and 5 equiv. of *L*-LA.

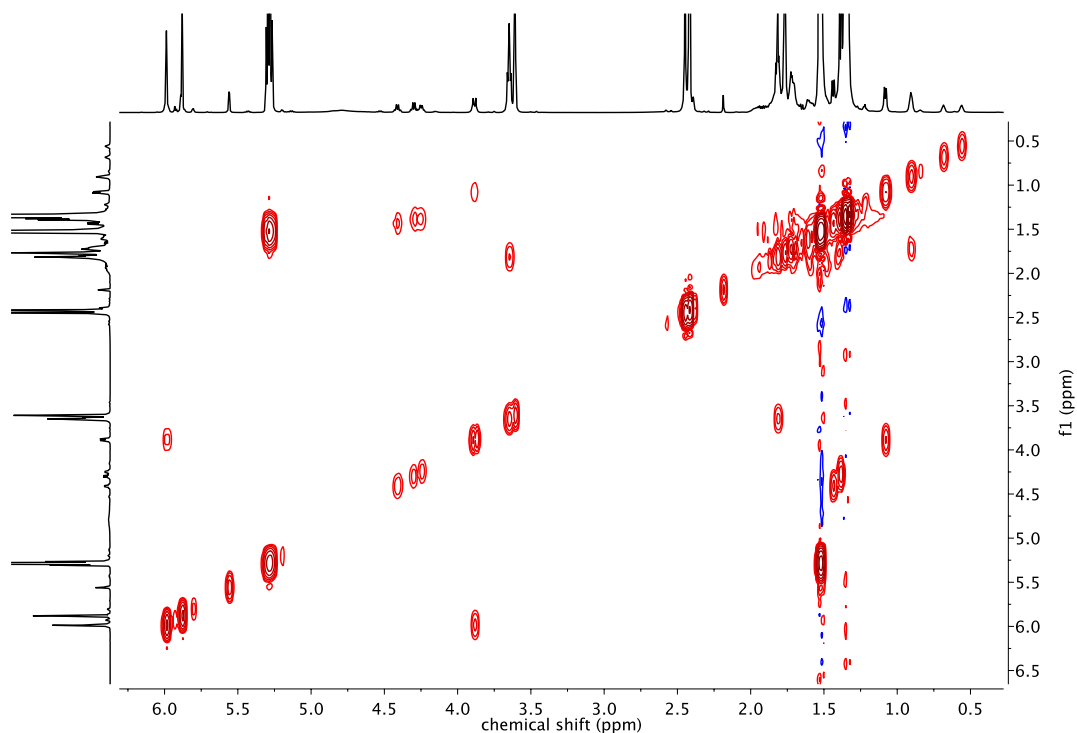


**Figure A14** COSY NMR spectrum (THF- $d_8$ , 499.9 MHz, 223 K) of reaction of  $(\text{Tp}^{\text{tBu,Me}})\text{Ca}\{(\mu\text{-H})_2\text{BC}_8\text{H}_{14}\}(\text{THF})$  (**14**) and 5 equiv. of *L*-LA.

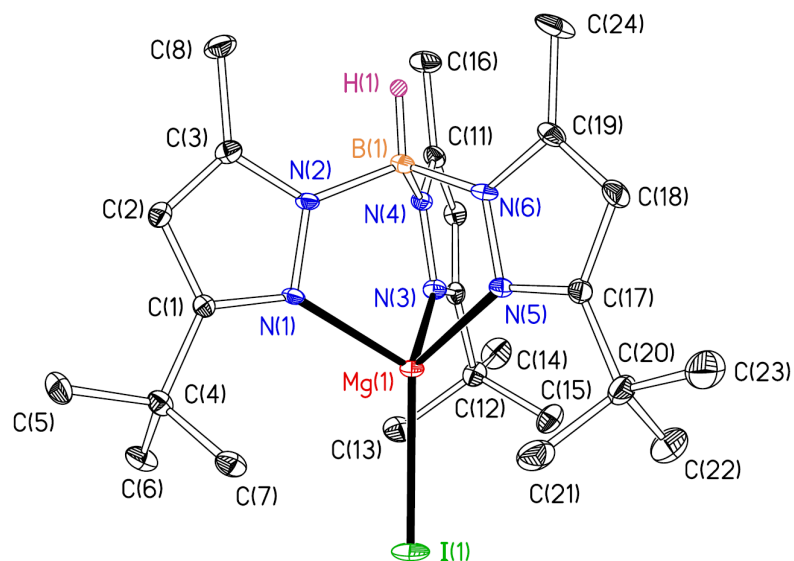
**A15 Additional crystallographic structure for (Tp<sup>tBu,Me</sup>)Mg(I)**

**Figure A15** Displacement ellipsoid plot of (Tp<sup>tBu,Me</sup>)Mg(I). H atoms are omitted. Ellipsoids are drawn at 35% probability level.

**Table A1** Selected bond lengths (Å) and angles (°) for (Tp<sup>tBu,Me</sup>)Mg(I).

|                 |           |                 |           |
|-----------------|-----------|-----------------|-----------|
| Mg(1)-N(1)      | 2.101(2)  | Mg(1)-N(3)      | 2.119(2)  |
| Mg(1)-N(5)      | 2.081(2)  | Mg(1)-I(1)      | 2.6669(8) |
| N(1)-Mg(1)-N(3) | 98.16(9)  | N(3)-Mg(1)-N(5) | 94.04(9)  |
| N(1)-Mg(1)-N(5) | 89.89(9)  | N(1)-Mg(1)-I(1) | 120.70(7) |
| N(3)-Mg(1)-I(1) | 119.82(7) | N(5)-Mg(1)-I(1) | 126.69(7) |