Exploring coordination chemistry and reactivity of formazanate ligands
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Formazanate complexes as potential catalysts for lactide polymerization

The synthesis and characterization of a variety of mono- and bis(formazanate)zinc, magnesium and calcium complexes are presented in this chapter. The structure of the complexes in the solid-state and in solution was studied by X-ray crystallography and DOSY NMR spectroscopy, respectively. In contrast to formazanate zinc methyl compounds, which are monomeric even in the solid state, the corresponding alkoxide complexes are shown to be dimeric in all the cases in solid state. However, in solution state dimeric or monomeric species were found depending on the nature of the ligand and/or alkoxide present.

Cyclic voltammetry studies were performed for some representative complexes. The data show that the Zn compounds are stable in a 1-electron reduced state, which suggests that these could be used as redox-switchable catalyst systems in future studies. Preliminary studies of these complexes show activity, in all the cases, toward polymerization of rac-lactide.

6.1 Introduction

Biodegradable polymers are gaining increasing attention to reduce the environmental impact of the waste generated upon their disposal. Specially, polyesters are excellent candidates thanks to the presence of the ester bond, which can be cleaved by hydrolysis and ultimately generate CO₂ and H₂O using bacterial (Amycolatopsis or Saccharotrix) or enzymatic degradation (proteinase K). Poly(lactic acid) (PLA), poly(ε-caprolactone) (PCL) and poly(glycolide) (PGA) are promising polyesters due to their biocompatibility, biodegradability and permeability. PLA stands out from the rest because the precursor (lactic acid) used for the synthesis of the lactide monomer used for the polymerization can be obtained from any fermentable sugar. In view of corn being one of the most abundant sources of sugar in the world, the synthesis of PLA is cheap and ecofriendly. However, to minimize the use of edible food for industry purposes, there is still a need for the development of non-destructively harvested perennial starch crops. This offers an use for a class of plants that has, until now, been largely neglected: plants producing poisonous or non-edible carbohydrates, for example inedible nuts such as horse chestnuts, cycad nuts, and Moreton Bay chestnuts, inedible forms of air potato, and starchy fruits.

Even though CO₂ is released when PLA is degraded, the process itself is environmentally friendly because all the carbon in PLA comes from the CO₂ in the atmosphere by following the process in Figure 6.1 (PLA life cycle). During photosynthesis, plants convert CO₂ to sugars and after fermentation the monomer lactic acid is produced, which is used as a precursor for polymerization. Due to the high performance and durability of the polymer obtained, PLA is a promising alternative to petroleum based plastics like PET, Nylon, Cellophane, etc., with applications ranging from packaging films, coatings, drug delivery agents, artificial tissue matrices, and the biomedical field.
Despite all the previously mentioned advantages, some energy during the process is needed for the agricultural system to grow the corn, product transportation, polymer processing, etc., which generally comes from fossil resources. Overall, it is estimated that the production of PLA (polylactide, Figure 6.2), uses 25-55% less fossil energy than petroleum-based polymers. Future perspectives point towards a further decrease in 90% of the fossil energy used by the incorporation of biomass and wind power to the process (PLA Bio/WP, Figure 6.2).\textsuperscript{10}

\textbf{Figure 6.1} PLA life cycle.

\textbf{Figure 6.2} Fossil energy requirements for some petroleum based polymers and polylactide. The red part of the bars represent the fossil energy used as chemical feedstock (the fossil resource to build the polymer chain). The blue part represents the gross fossil energy use for the fuels and operations supplies used to drive the production processes. LD Polyethylene =
Poly(lactic acid) (PLA) was first synthesized already in 1845 by polycondensation of lactic acid. Almost a century later a method was developed to polymerize lactide into PLA, which was patented by Du Pont in 1954. A new synthetic route for PLA was discovered by Cargill Dow in the early 1990s by ring-opening polymerization (ROP) of lactide, the corresponding dimer of lactic acid. This breakthrough was a big step due to the possibility to obtain high molecular weight PLA using relatively mild reaction conditions (temperatures lower than 130 °C) and short reaction times. In contrast, conventional polycondensation of lactide acid requires temperatures between 180-200 °C, low pressure (5 mmHg) and significantly longer reaction times. In 2002, Cargill Dow LLC officially launched the first world-scale production facility for PLA based on ROP of lactide. This plant started with the annual capacity to produce 140,000 metric tons. In 2010, PLA had the second highest consumption volume of any bioplastic in the world. Nowadays, many companies have emerged that manufacture PLA, such as Corbion PURAC Biomaterials, Evonik Industries, and NatureWorks, Futerro among others.

Currently, for the production of PLA in industry the most commonly employed catalyst is tin(II) bis(2-ethylhexanoate), widely known as tin(II)octanoate Sn(Oct)$_2$, to which lauryl alcohol (1-dodecanol) is usually added as a real initiator for the Ring Opening Polymerization (ROP). However, the melt polymerization process used leaves tin present in the polymer in concentration levels between 140 and 281 ppm. Even though Sn(II) is not considered as a toxic heavy metal, it has been proven that Sn(Oct)$_2$ inhibits cell growth within the range of 26-125 ppm. Thus, many research groups are focusing on developing alternative catalysts for lactide polymerization via ROP. Three different mechanisms can lead to PLA via ROP depending on the catalyst involved. Due to the fact that a cationic mechanism usually leads to PLA with low molecular weights and anionic polymerization results in poor control of the molecular weight and the molecular weight distribution, the coordination-insertion mechanism has been the focus of many researchers in the last decades. One of the most popular catalyst classes for the ROP via coordination-insertion mechanism is based on metal alkoxide complexes. The formation of PLA using these catalysts is generally believed to involve the four steps shown in Figure 6.3: (1) Firstly, coordination of the lactide monomer to the Lewis-acid metal center takes place, (2) followed by nucleophilic attack of the alkoxide moiety onto the bound carbonyl group of the lactide monomer, resulting in the formation of a new M-O(lactide) bond, (3) consecutive ring-opening of the lactide monomer to generate a...
new, lactide-derived metal-alkoxide, which then acts as the nucleophile towards a new lactide monomer to grow the PLA polymer chain.

Figure 6.3 Proposed mechanism of a coordination-insertion mechanism in the ROP of lactide. Adapted from *Polym. Chem.* **2011**, *2* (3), 520.

Besides Sn(Oct)$_2$, many other catalysts have been proven to be active towards lactide polymerization. The general formula of single-site metal catalysts for ROP is $L_nMR$ where ‘$L_n$’ is the ancillary ligand, which through tuning the steric and electronic properties allows modification of the bonding properties to the metal center and therefore alters the activity and stereoselectivity of the catalyst. ‘$M$’ is the metal center and depending on the Lewis acidity and the availability of open sites in the coordination sphere it will influence the activation of the monomer upon coordination of the carbonyl group of the monomer to the metal center.$^{7,8,22–24}$

Finally, the group ‘$R$’ is the initiating group that can be also tuned to modify the rate of initiation; in this way in presence of a more nucleophilic $R$ the second step in Figure 6.3 will be faster. With these three contributions in mind ($L_n$, $M$ and $R$) there are virtually endless combinations for the design of new catalysts for ROP polymerization of lactide, to form polymers with different polymerization rate, molecular weight, molecular weight distribution, co-monomer incorporation and polymer stereochemistry. The possibility to rationally modify the three components of the catalyst to influence the polymer properties is a great advantage of homogeneous versus heterogeneous catalysts. Even though there is a vast number of studies on molecular catalysts for olefin polymerization,$^{25,26}$ less attention has been given to single-site metal catalyst for the ROP of heterocycles such as epoxides and lactones.

Careful consideration must be taken when choosing the metal involved in the catalysis because after polymerization complete removal of the metal is cumbersome. Thus, special attention has been given to metals with no or low toxicity such as Zn, Mg, Al, Ca, Fe and to a minor extent also lanthanide metals.$^{27}$ For a wide variety of $L_nM$-$R$, the highest catalytic activity is found when alkoxydes are used as initiating group ($R = OR$, Figure 6.3). Many studies make use of the presence of ≤1 equivalent of alcohol (e.g. BnOH) to react with the pre-catalyst generating in situ a more active catalyst, which contains an alkoxy group. Often
Chapter 6

this alcohol is incorporated in the media to increase the chain growth by chain transfer but this generally yields lower molecular weight polymers. 27–29 Some of the most active single-site catalysts for ROP of lactide are summarized in Figure 6.4.

Coates has contributed with several studies based on $\beta$-diketiminate complexes mainly with Zn and Mg, 30–31 with $[(BDI-1)\text{MgO}Pr]_2$ (1, Fig. 6.4) being the fastest catalyst among its analogues ((BDI-1)ZnEt, (BDI-1)Zn(NTMS), (BDI-1)ZnOAc, $[(BDI-1)\text{ZnO}Pr]_2$; 2, Fig. 6.4). Schaper reported in 2014 a series of Zn and Mg catalysts employing also $\beta$-diketimimates as supporting ligand, for which the complex (3 Fig. 6.4), was the fastest magnesium based catalyst reported in the literature to date. 29

Although, much less attention has been given to the larger group 2 metals, Wang et. al demonstrated the activity of a series of calcium and strontium phenolate complexes. 32

Recently, Williams et. al showed enhancement of reactivity by bimetallic cooperativity of a di-zinc catalyst supported by bis(imino)diphenylamido ligands. 33 (4, Fig. 6.4) 34.

(1), (2): BDI-1 = 2-((2,6-diisopropylphenyl)amido)-4-((2,6-diisopropylphenyl)-imino)-2-pentene

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An interesting class of catalysts for ROP are those for which the polymerization activity can be switched by the incorporation of a redox-active entity in the scaffold of the ligand, such as ferroceny136,37, or by redox reactions at the metal center35,38. Through these means, the polymerization can be controlled by electrochemical switching of the redox entities. The first example showing redox control in lactide polymerization was reported in 2006 by White et al. using a Ti(salen) alkoxide complex containing two ferrocenyl units in the ligand backbone.36 When lactide was added to the neutral form the catalyst was active towards lactide polymerization. However, after oxidation by the addition of two equivalents of AgOTf, a dicationic ferrocenium-containing species is formed, which shows a drastic decrease in the catalytic activity. Addition of a reducing agent restores the active form of the catalyst.

In 2011 Diaconescu et al. reported a metal-based catalyst for redox control of lactide polymerization by switching between active Ce(III) and inactive Ce(IV) complexes (5, Fig. 6.4).35 The active Ce(III) catalyst polymerizes lactide (Figure 6.5) and upon addition of FeBARF, in situ oxidation takes place leading to the formation of a Ce(IV) complex, which doesn’t show any activity at room temperature. Reduction with CoCp₂ to regenerate the Ce(III) complex restarts the polymerization.

An even more interesting approach was shown by the Diaconescu group in 2014, where they used a Zr complex with a ferrocene-base ligand to control the copolymerization between lactide and ε-caprolactone to give block copolymers. In this catalyst, the oxidized form is inactive towards lactide polymerization but active towards ε-caprolactone polymerization while the activity is reversed in the reduced form.37 A similar approach by Byers et al. shows redox switchable block copolymerization of lactide and epoxide by changing the redox-state of the metal center, without involving the ligand. In this way Fe(II) shows activity towards lactide polymerization but not for cyclohexene oxide (CHO), while the oxidized Fe(III) catalyst reverses its activity, being active only for CHO polymerization.38
Based on the above, it is of current interest to design new catalysts that are active towards lactide polymerization using metals with no or low toxicity, while including redox-active moieties in these complexes that allows redox-control of polymerization catalysis. As discussed in Chapter 1, section 1.4.1, formazans closely resemble the structure of \( \beta \)-diketimines, which have been shown to be suitable supporting ligands for lactide polymerization catalysts. In addition, previous work on zinc\(^{39} \) and boron\(^{40,41} \) complexes with formazanate ligands by our group and Gilroy et al. demonstrated their use as redox-switchable moieties, that potentially could be used for redox-control of catalytic behaviour.

Thus, in this chapter we discuss the synthesis and characterization of various formazanate complexes based on the cheap and abundant elements Zn, Mg and Ca, and report preliminary results of (catalytic) reactivity of these complexes towards lactide. Cyclic voltammetry shows quasi-reversible ligand-based redox-chemistry for these complexes, which suggests that modulating their (catalytic) reactivity might be possible by changing the ligand oxidation state.

### 6.2 Formazanate zinc methyl complexes (LZnMe)

The formazanate zinc methyl complexes were synthesized by reacting the corresponding formazan with one equivalent of dimethyl zinc (Scheme 6.1) with consequent change in color.
from deep red (1-H), terracotta (4-H) or orange (3-H, 5-H) to deep blue-violet in all cases (1-ZnMe-5-ZnMe).

**Scheme 6.1** Synthesis of LZnMe (1-ZnMe-5-ZnMe).

The $^1$H NMR spectra of LZnMe (1-ZnMe-5-ZnMe) show the expected signals for the formazanate ligand in the range of 6.75 to 8.37 ppm for the aromatic protons of the phenyl and mesityl rings. In the aliphatic region (2.05 to 2.71 ppm) the characteristic singlets of the para-CH$_3$ (p-tol) (1-ZnMe, 4-ZnMe and 5-ZnMe), and the ortho- and para-CH$_3$ of the Mes group (4-ZnMe and 5-ZnMe) are present. In addition to the formazanate signals, all compounds show a singlet corresponding to the ZnMe group. This peak is located in the range of -0.15 to -0.39 ppm and the integration ratio in the $^1$H NMR is in agreement with a 1:1 ratio between the formazanate ligand and Zn-Me moiety (Figure 6.6).
Figure 6.6 $^1$H NMR spectrum of 1-ZnMe (C$_6$D$_6$, 400 MHz) with inset showing an expansion of the aromatic region.

Single crystals suitable for X-ray crystallography of 1-ZnMe-5-ZnMe were obtained by slow diffusion of hexane into a solution of the corresponding L.ZnMe complex in toluene (Figure 6.7, metrical parameters in Table 6.1). For compounds 1-ZnMe-5-ZnMe the unit cell contains three (1-ZnMe) or two (3-ZnMe-5-ZnMe) independent molecules. The metrical parameters of these are within experimental error and only one of the independent molecules will be shown and discussed (Figure 6.7 and Table 6.1).
Figure 6.7 Molecular structures of 1-ZnMe-5-ZnMe showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

Table 6.1 Selected bond length (Å) and bond angles (°) of compounds 1-ZnMe-5-ZnMe.

<table>
<thead>
<tr>
<th>Bond Type</th>
<th>1-ZnMe</th>
<th>3-ZnMe</th>
<th>4-ZnMe</th>
<th>5-ZnMe</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-N2</td>
<td>1.299(3)</td>
<td>1.307(3)</td>
<td>1.304(2)</td>
<td>1.311(4)</td>
</tr>
<tr>
<td>N2-C7</td>
<td>1.346(2)</td>
<td>1.345(2)</td>
<td>1.348(3)</td>
<td>1.344(4)</td>
</tr>
<tr>
<td>C7-N3</td>
<td>1.337(3)</td>
<td>1.340(3)</td>
<td>1.353(3)</td>
<td>1.350(4)</td>
</tr>
<tr>
<td>N3-N4</td>
<td>1.310(3)</td>
<td>1.316(3)</td>
<td>1.302(2)</td>
<td>1.307(4)</td>
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<tr>
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<td>1.985(2)</td>
<td>1.988(2)</td>
<td>1.970(3)</td>
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<td>1.989(2)</td>
<td>1.985(2)</td>
<td>1.989(2)</td>
<td>1.969(3)</td>
</tr>
<tr>
<td>Zn1-C21</td>
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<td>1.953(3)</td>
<td>1.949(2)</td>
<td>1.941(4)</td>
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<tr>
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<td>90.52(7)</td>
<td>89.09(7)</td>
<td>89.21(7)</td>
</tr>
<tr>
<td>N1-Zn1-C21</td>
<td>129.95(9)</td>
<td>135.90(8)</td>
<td>139.28(9)</td>
<td>136.9(1)</td>
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<tr>
<td>N4-Zn1-C21</td>
<td>138.62(9)</td>
<td>133.57(9)</td>
<td>130.37(9)</td>
<td>133.9(1)</td>
</tr>
</tbody>
</table>

a: Distance between Zn and N-N-N-N plane; b: Distance between Zn and N-N-C(Me) plane; c: three similar molecules in the unit cell, shown only one for clarity; d: two similar molecules in the unit cell, shown only one for clarity.

In all the cases, complexes 1-ZnMe-5-ZnMe show full delocalization within the formazanate framework, indicated by the equivalent N-N and C-N bond lengths. When the electron donating properties of the R₃ substituent are altered, going from p-tol (1-ZnMe) to the more donating ¹Bu (3-ZnMe), little variation in the metrical values of the formazanate backbone is observed. Similarly, when the substituent(s) at the terminal nitrogens (R₁ and R₅, Figure 6.7) are modified going from Ph to Mes (1-ZnMe and 3-ZnMe vs. 4-ZnMe and 5-ZnMe), changes in the formazanate backbone are minimal, although the Zn-N bond lengths decrease slightly upon going to the more sterically demanding NMes substituents. This is likely due to the increased dihedral angle between the NMes group and the ligand backbone, which
prevents π-conjugation with the Mes ring and makes the N atom a better donor. Indeed, the N-Ph rings in \textbf{1-ZnMe-4-ZnMe} are found to be approximately coplanar with the ligand backbone (NCCN/Ph dihedral angles < 34°), a situation that maximizes conjugation. Steric interactions in \textbf{4-ZnMe} and \textbf{5-ZnMe} between the 2,6-Me groups on the N-Mes substituents and the ligand backbone cause these groups have much larger dihedral angles (NCCN/Mes dihedral angles 54-69°). This is in agreement with previous studies of β-diketiminate Zn ethyl\textsuperscript{42} and bis(formazanate)zinc complexes\textsuperscript{43–47}.

Even though \textbf{1-ZnMe} can be isolated as a crystalline material and fully characterized, it is unstable in the solution state. It establishes a Schlenk equilibrium with bis(formazanate)Zn complex \textbf{1-Zn} with the color changing from deep blue-violet to deep blue (Scheme 6.2) and appearance of the corresponding signals of \textbf{1-Zn} in the NMR spectrum.

Heteroleptic alkaline earth metal complexes show almost exclusively the form RMX in the solid state. However, they often establish an equilibrium with their respective homoleptic species MR\textsubscript{2} and MX\textsubscript{2} (Scheme 6.2).\textsuperscript{48} The schlenk equilibrium is dependent on the donor strength and polarity of the solvent, the nature of the metal and its substituents, concentration and temperature.\textsuperscript{49–51}

In order to use these compounds as single-site catalysts, it is desirable to prevent the formation of multiple species in solution due to this Schlenk equilibrium. It has been shown that the Schlenk equilibrium can be considerably decreased or avoided by making use of sterically demanding ligands.\textsuperscript{48,51–54} Many active Zn catalysts make use of bulky β-dimines (BDI)\textsuperscript{30,31,42,44,55} specially β-diketiminate (nacnac) with diisopropylphenyl as N-substituent (Dippnacnac).\textsuperscript{29,56}

Preliminary data on the solution stability of complex \textbf{1-ZnMe} shows that at 20 °C in C\textsubscript{6}D\textsubscript{6} solution after 12 hours, a mixture of ZnMe\textsubscript{2} and the bis(formazanate)zinc complex \textbf{1-Zn} is obtained (10% \textbf{1-Zn}). At 50 °C, significant conversion (ca. 20%) to the homoleptic species is already observed after 1 hour (Scheme 6.2). Since the position of the Schlenk equilibrium and the rate at which it is established is highly solvent dependent,\textsuperscript{50,51} we evaluated the stability of \textbf{1-ZnMe} by NMR spectroscopy in the polar solvent THF-d\textsubscript{8}. Upon heating this solution to 50 °C for 21 hours, only 3% conversion is observed by \textsuperscript{1}H NMR spectroscopy, showing that the (formazanate)zinc methyl complex is considerably more stable under those conditions which might be due to the formation of a four-coordinate THF adduct.
In line with preceding literature results, the steric effect on going from Ph (1-ZnMe) to the bulkier mesityl (5-ZnMe) has a direct influence in the Schlenk equilibrium, and 5-ZnMe is much more stable in solution.

**Scheme 6.2** Schlenk equilibrium for mono-formazanate zinc complexes.

6.3 Synthesis of alkoxide complexes [LMOR]_n (M = Zn, Mg)

6.3.1 Synthesis of alkoxide complexes [LZnOR]_n

Formazanate zinc alkoxide complexes were successfully synthesized by reacting the precursor LZnMe with the corresponding alcohol, with concomitant release of methane (Scheme 6.3). In all cases, the reaction is accompanied by a color change from deep-violet for the starting material (n-ZnMe) to blue-violet for the alkoxide products (n-ZnOR). However, 5-ZnMe and 5-ZnO'Pr are both orange in solution, therefore no color change is observed during the reaction.

The reaction is most conveniently carried out by slow diffusion of a toluene solution containing the corresponding formazanate zinc methyl complex (1-ZnMe, 5-ZnMe) into a top layer of pentane containing one equivalent of the corresponding alcohol, leading to the precipitation of the desired products (1-ZnOR, 5-ZnO'Pr) as crystalline material that was suitable for X-ray analysis. The 1H-NMR spectroscopic data (CD_2Cl_2) of the crystals is consistent with the formation of the products n-ZnOR by the disappearance of the diagnostic peak at -0.15 ppm from the starting material LZnMe (n-ZnMe, Figure 6.6) and the appearance of new set of peaks corresponding to the alkoxide signals. The isopropoxide group (R = 'Pr) of compound [1-ZnO'Pr] is observed as a septet at δ 3.98 ppm and a doublet at δ 0.85 ppm (CH and Me groups, respectively), while the tert-butoxide (R = 'Pr, 1-ZnO'Bu) shows a singlet at 1.01 ppm. In case of the phenoxide complex (R = Ph, 1-ZnOPh), the signals overlap with those of the formazanate ligand in the range of 6.6 – 7.1 ppm.
Scheme 6.3 Synthesis of $[\text{LZnOR}]_2$ (1-ZnOR and 5-ZnOiPr).

In solution, the Schlenk equilibrium is also present in these compounds although the generation of the homoleptic ZnL$_2$ is slower than for the zinc methyl analogue 1-ZnMe, leading to the formation of only 7% of ZnL$_2$ at room temperature over a day. Single crystal X-ray diffraction studies show 1-ZnOR and 5-ZnOiPr to be dimeric species with alkoxide-bridged distorted tetrahedral zinc centers (Figure 6.8), similar to what was observed by Coates$^{30,31,44,55}$, Schaper$^{29}$ and Wang$^{57}$ in analogous zinc and magnesium alkoxide complexes.

Figure 6.8 Molecular structures of 1-ZnOR, 5-ZnOiPr showing 50% probability ellipsoids. The hydrogen atoms in all structures and the solvate molecules in 1-ZnO'Bu (pentane) and 1-ZnOPh (toluene) are omitted for clarity.

The C-N and N-N bonds lengths of compounds 1-ZnOR-5-ZnOiPr suggest in all the cases that the formazanate backbone is fully delocalized. In all the complexes (1-ZnOR) containing an N-Ph substituent, this aromatic ring is almost coplanar with the NNCNN backbone, with a
dihedral angle between 8.39°-24.37°. For 5-ZnOPr, where Mes substituents are present on both terminal nitrogens, this dihedral angle is close to perpendicular (74.30°-79.47°). The Zn center is displaced out of the plane of the formazanate backbone in the range of 0.45-0.54 Å, similar what was observed for other zinc39 and boron41 formazanate derivatives.

In all the cases, no significant perturbation in the Zn2O2 core is observed and the dihedral angle between the four membered ring Zn2O2 and the formazanate framework is nearly perpendicular (85.63-89.96°). Due to the crystallographic inversion center in the center of the Zn2O2 core, the two formazanate ligands are parallel to each other in all the cases.

Table 6.2 Selected bond length (Å) and bond angles (°) of compounds 1-ZnOR - 5-ZnOPr.

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</tr>
<tr>
<td>Av. R5-NNCNN</td>
<td>16.48</td>
<td>8.39</td>
<td>15.57</td>
<td>74.30</td>
</tr>
<tr>
<td>(NNCNN)-(Zn2O2)</td>
<td>89.96</td>
<td>86.95</td>
<td>85.68</td>
<td>85.63</td>
</tr>
<tr>
<td>Av. cone angle O-R</td>
<td>102.68</td>
<td>103.38</td>
<td>103.87</td>
<td>104.25</td>
</tr>
</tbody>
</table>

a: Distance between Zn and N-N-C-N-N plane; b: dihedral angle between the plane containing the substituents N1 or N5 and the plane containing the backbone N1-N-C-N-N5; c: dihedral angle between the backbone N-N-C-N-N and the plane with the four member ring Zn2O2.

6.3.2 Synthesis of alkoxide complexes [LMgOR]n

In view of the higher reactivity of magnesium complexes versus the zinc analogues when exposed to a protic source such H2O or alcohols, we anticipated the synthesis of LMgOR via reaction of the corresponding bis(formazanate) complex and alcohol to be cumbersome. Thus, alternatively LMgOR was synthesized by dropwise addition of a deep red solution of formazan (1-H) in toluene to a white suspension of Mg[OCCH2Ph2]58 in toluene. Stirring at room temperature for two days led to a violet solution (Scheme 6.4). Because all the zinc alkoxide complexes discussed in the previous section showed a dimeric structure in the solid...
state, we chose a bulky substituent in the alkoxide group for the synthesis of the magnesium complex $1\text{-MgOC(CH}_3\text{Ph}_2)$ to increase the possibility to have a monomeric structure in the solution state. $^1$H-NMR spectroscopic data (C$_6$D$_6$) indicate a mixture of products, which contains the desired (formazanate)$\text{MgOCCH}_3(\text{Ph})_2$ complex as is indicated by the appearance of a new peak in the aliphatic region with integration 1:1 with respect to the CH$_3$ of the p-tol peak. In addition, free alcohol (HOCCH$_3$(Ph)$_2$) with an OH peak at 1.60 ppm and free ligand (1-H) with the characteristic NH peak at 15.3 ppm are observed. By diffusion of hexane into a concentrated solution of the reaction mixture in toluene single crystals suitable for X-ray determination were obtained of the desired product $1\text{-MgOC(CH}_3\text{Ph}_2)$.

Scheme 6.4 Synthesis of [LMgOR]$_2$ ($1\text{-MgOC(CH}_3\text{Ph}_2)$).

Just like the analogous formazanate Zn alkoxide complexes discussed in the previous section (1-ZnOR-5-ZnO-iPr), single crystal X-ray diffraction studies reveal a distorted tetrahedral magnesium center with alkoxide-bridge in the solid state (Figure 6.9).

Figure 6.9 Molecular structure of $1\text{-MgOC(CH}_3\text{Ph}_2)$ showing 50% probability ellipsoids. The hydrogen atoms are omitted for clarity.

The two independent molecules that are present in the unit cell for $1\text{-MgOC(CH}_3\text{Ph}_2)$ are overall very similar, although they differ in the orientation of the OC(CH$_3$)Ph$_2$ unit relative to the central Mg$_2$O$_2$ moiety, with either a CH$_3$ or a Ph group in the plane of the core (Table 6.3, Figure 6.10).
As expected, due to the more ionic character of the Mg metal center in compound 1-MgOC(CH$_3$Ph$_2$), the M-N distances are slightly elongated compared to the Zn analogues, 2.085(1)-2.109(1) Å vs. 1.962(2)-2.008(2) Å.

**Table 6.3** Selected bond length (Å) and bond angles (°) of the two molecules contained in the unit cell for compound 1-MgOC(CH$_3$Ph$_2$).

<table>
<thead>
<tr>
<th>Bond/Angle</th>
<th>Molecule 2 (top)</th>
<th>Molecule 1 (bottom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1-N2</td>
<td>1.309(2)</td>
<td>1.300(2)</td>
</tr>
<tr>
<td>N2-C7</td>
<td>1.347(2)</td>
<td>1.355(2)</td>
</tr>
<tr>
<td>C7-N3</td>
<td>1.341(2)</td>
<td>1.342(2)</td>
</tr>
<tr>
<td>N3-N4</td>
<td>1.312(2)</td>
<td>1.307(2)</td>
</tr>
<tr>
<td>N1-Mg</td>
<td>2.109(1)</td>
<td>2.074(1)</td>
</tr>
<tr>
<td>N4-Mg</td>
<td>2.085(1)</td>
<td>2.088(1)</td>
</tr>
<tr>
<td>Mg-O1</td>
<td>1.969(1)</td>
<td>1.970(1)</td>
</tr>
<tr>
<td>Mg-O2</td>
<td>1.978(1)</td>
<td>1.979(1)</td>
</tr>
<tr>
<td>Av. Mg -O</td>
<td>1.974</td>
<td>1.975</td>
</tr>
<tr>
<td>N- Mg -N</td>
<td>85.15(5)</td>
<td>86.95(6)</td>
</tr>
<tr>
<td>Mg -O-Mg</td>
<td>96.93(5)</td>
<td>97.23(5)</td>
</tr>
<tr>
<td>O- Mg -O</td>
<td>83.07(5)</td>
<td>82.73(5)</td>
</tr>
<tr>
<td>Mg -(NCCN)N</td>
<td>0.624</td>
<td>0.612</td>
</tr>
<tr>
<td>R1-NNCNN</td>
<td>34.56</td>
<td>44.83</td>
</tr>
<tr>
<td>R5-NNCNN</td>
<td>10.75</td>
<td>8.46</td>
</tr>
<tr>
<td>(NNCNN)-(Mg$_2$O$_2$)</td>
<td>79.72</td>
<td>89.26</td>
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<tr>
<td>Av. cone angle O-R</td>
<td>123.21</td>
<td></td>
</tr>
<tr>
<td>OPh$_2$Me-OPh$_2$Me$^d$</td>
<td></td>
<td>88.40</td>
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</tbody>
</table>

$^a$ Distance between Mg and N-N-C-N plane; $^b$: dihedral between the plane containing the substituents N1 or N4 and the plane containing the backbone N1-N-C-N-N; $^c$: dihedral angle between plane of the backbone N-N-C-N-N and the plane with the four member ring Mg$_2$O$_2$; $^d$: dihedral angle between the two phenyl groups present in alkoxy group –OCMePh$_2$.

**Figure 6.10** Molecular structure of the two independent molecules in the unit cell for 1-MgOC(CH$_3$Ph$_2$). Showing 50% probability ellipsoids. The hydrogen atoms and substituents R1, R3 and R5 of the formazan are omitted for clarity.

Mg-O for BDI-MgOPr, 1.97-1.98, well within the acceptable range and the Mg-N distances ranging from 2.074(1) to 2.109(1) Å are normal for a four-coordinate magnesium complex. 29,30,57,59,60
6.4 DOSY experiments

One factor that contributes to the activity of the catalyst is its ability to activate substrates towards nucleophilic attack, which is related to the structure of the catalyst in the solution state. Thus, dimeric structures have a coordination sphere that is more/completely saturated in comparison with its monomeric form, therefore reducing its ability to coordinate lactide. Thus, monomeric structures are required in the solution state to initiate the ring opening of lactide as shown in Figure 6.3. We mentioned in the previous section (Figures 6.8 and 6.9) that the alkoxides LMOR adopt, in all the cases, a dimeric structure in the solid state. To elucidate their structure in solution, Diffusion Ordered Spectroscopy (DOSY) experiments were carried out.

The DOSY NMR experiment differentiates molecules with different sizes by their diffusion coefficient. Large molecules have a smaller diffusion coefficient than small molecules, and from their diffusion coefficient the hydrodynamic radius can be calculated with the Stokes-Einstein equation where all particles are approximated as spheres (equation 6.1). For LZnMe (1-ZnMe, 5-ZnMe), which is a monomer in both the solution and solid state the hydrodynamic radii (r) determined using DOSY NMR are somewhat smaller than those extracted from the X-ray crystal structures (r’) (6.2 Å vs ~4.7 Å, respectively, entries 0 and 1 Table 6.4). The radius r’ is calculated as half of the diameter, which is taken as the average of the length (a) and width (b) of the X-ray crystal structures (r’ = (a+b)/4, Figure 6.11).

These differences can be explained because the Stokes-Einstein equation applies to perfectly spherical objects (a = b = c), and these complexes are better described as prolate ellipsoids (a > b = c, Figure 6.11). Thus, the Stokes-Einstein equation 6.1 is a rough estimate but nevertheless useful in estimating the aggregation state of molecules in solution.

![Figure 6.11](image-url) [LZnO\(^{1}\)Pr\(_2\) \((1-ZnO^{1}Pr)\) X-ray structure (space-filling model) showing ellipsoid for axis a (major axis) and b (minor axis).]
Equation 6.1 Stokes-Einstein equation with diffusion coefficient $D$ (m$^2$.s$^{-1}$), gas constant $R$ (J.mol$^{-1}$.K$^{-1}$), temperature $T$ (K), Avogadro number $N_A$, viscosity of the solvent $\eta$ (kg.m$^{-1}$.s$^{-1}$) and the hydrodynamic radius $r$ (m).

As expected, the (crystallographically determined) radius $r'$ of LZnMe is slightly bigger when going from Ph (1-ZnMe) to Mes (5-ZnMe) (6.2 vs. 6.6 Å, respectively, entries 0 and 6, Table 6.4). This trend is also observed in the dimeric alkoxy complexes when going from the phenyl substituted to the bulkier Mes (1-ZnOPr-1-ZnOPh: 8.9-8.8 Å entries 2-4 and 5-ZnOPr: 9.4 Å in entry 7 Table 6.4). In all cases, the approximate radii $r'$ extracted from the X-ray for LMOR is 1.42-1.43 times larger than those for the corresponding monomeric species (entries 2-4 and 7, Table 6.4).

Although compounds LZnMe (n-ZnMe) and LMOR (n-MOR) complexes are not perfect prolate ellipsoids (a > b ≈ c for prolates where a ≈ b > c for LZnMe and a > b > c for LMOR) (Figure 6.11 and Table 6.4). Nevertheless, DOSY experiments should provide useful information on the structure of these species in the solution state, comparing the hydrodynamic radii in solution ($r$) by applying Equation 6.1, and the estimated radii in solid state ($r'$) extracted from X-ray crystal structures (see above).

The DOSY spectra of the zinc alkoxy formazanate complexes (1-ZnOR-1-MgOC(CH$_3$Ph)$_2$) were compared to the zinc methyl formazanate complexes (1-ZnMe and 5-ZnMe), which exist as a monomer both in solution and in the solid state. All the diffusion coefficients obtained and described in this section were determined on the CH$_3$ resonance of the $p$-tol group. Since this resonance, which is present in all compounds studied, presents a sharp singlet, it gives the cleanest decay curve in the DOSY experiment that is least affected by shimming and/or phasing artifacts. The alkoxide complexes 1-ZnOR show in all the cases similar diffusion coefficients in dichloromethane solvent (7.2 - 7.7.10$^{-10}$ m$^2$.s$^{-1}$, entries 2-4 Table 6.4) being 1.37-1.45 times smaller than the corresponding monomer LZnMe (1-ZnMe, 10.5.10$^{-10}$ m$^2$.s$^{-1}$, entry 1 Table 6.4 and Figure 6.12). These ratios are comparable to the ones in solid state (1.42-1.43), therefore we can assume that dimeric are retained in the solution state.
When comparing complex 1-MgOC(CH$_3$Ph$_2$), the size difference between 1-MgOC(CH$_3$Ph$_2$)-1-ZnMe in X-ray is 1.45 (dimeric vs. monomeric, entries 5 and 0, respectively, table 6.4). However, in solution state it is far from this ratio, with a value of 1.16 (entries 5 and 0, respectively, both measured in C$_6$D$_6$, table 6.4). This indicates that probably it is monomeric in the solution state.

Table 6.4 Experimental results (diffusion coefficients $D$ and radii $r$) compared with estimated radii ($r'$) from X-ray crystal structures.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Complex</th>
<th>D (10$^{-10}$ m$^2$/s)</th>
<th>r (Å)</th>
<th>r' (Å)</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>$[\text{LMOR}]_n$/LZnMe Ratio r</th>
<th>$[\text{LMOR}]_n$/LZnMe Ratio r'</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1-ZnMe*</td>
<td>6.94</td>
<td>4.74</td>
<td>6.2</td>
<td>12.9</td>
<td>11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>1-ZnMe#</td>
<td>10.48</td>
<td>4.76</td>
<td>6.2</td>
<td>12.9</td>
<td>11.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>1-ZnOiPr#</td>
<td>7.32</td>
<td>6.82</td>
<td>8.9</td>
<td>21.4</td>
<td>14.1</td>
<td>1.43 (n = 2)</td>
<td>1.43 (n = 2)</td>
</tr>
<tr>
<td>3</td>
<td>1-ZnOtbu#</td>
<td>7.22</td>
<td>6.92</td>
<td>8.9</td>
<td>21.4</td>
<td>14.2</td>
<td>1.45 (n = 2)</td>
<td>1.43 (n = 2)</td>
</tr>
<tr>
<td>4</td>
<td>1-ZnOPr#</td>
<td>7.66</td>
<td>6.52</td>
<td>8.8</td>
<td>21.2</td>
<td>14.1</td>
<td>1.37 (n = 2)</td>
<td>1.42 (n = 2)</td>
</tr>
<tr>
<td>5</td>
<td>1-MgOC(CH$_3$Ph$_2$)</td>
<td>6.0</td>
<td>5.5</td>
<td>9.0</td>
<td>21.6</td>
<td>14.5</td>
<td>1.16 (n = 1)</td>
<td>1.45 (n = 2)</td>
</tr>
<tr>
<td>6</td>
<td>5-ZnMe*</td>
<td>6.5</td>
<td>5.1</td>
<td>6.6</td>
<td>14.7</td>
<td>11.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5-ZnOiPr*</td>
<td>5.7</td>
<td>5.8</td>
<td>9.4</td>
<td>21.3</td>
<td>16.2</td>
<td>1.14 (n = 1)</td>
<td>1.42 (n = 2)</td>
</tr>
</tbody>
</table>

a: major axis of the prolate spheroid; b: minor axis of the prolate spheroid (Figure 6.11). * C$_6$D$_6$ as a solvent. ** C$_6$D$_6$ as a solvent. r (Å): hydrodynamic radii in solution by applying Equation 6.1. r' (Å): estimated radii in solid state extracted from X-ray crystal structures. Blue shade: monomeric species. Red shade: dimeric species.

As expected and consistent with solid-state studies, the radius (r) of LZnMe is slightly bigger when going from an N-Ph substituted ligand (1-ZnMe) to the bulkier N-Mes analogue (5-ZnMe) (4.7 vs. 5.1 Å, respectively, in C$_6$D$_6$, entries 0 and 6, Table 6.4).

When the more sterically demanding Mes substituent is present, the differences in radii between the monomeric LznMe (5-ZnMe) and the corresponding alkoxide 5-ZnOPr are 1.14 in solution state versus the 1.42 in the solid state, where the dimeric structure of 5-ZnOPr is present (entries 6 and 7, respectively, in C$_6$D$_6$, in Table 6.4). In contrast with its analogues 1-ZnOR and similarly to 1-MgOC(CH$_3$Ph$_2$), these results suggest the presence of monomeric species in solution for both 5-ZnMe and 5-ZnOPr.
6.5 Cyclic voltammetry experiments

Studies on the ligand-based redox reactions of formazanate zinc methyl and alkoxide complexes were performed by cyclic voltammetry (CV) experiments in THF solution using [Bu4N][B(C6F5)4] as electrolyte. LZnMe (1-ZnMe) shows two quasi-reversible redox couples at -1.63 V and -2.39 V versus FeO+/ (shown as I/I' and II/II' respectively in Figure 6.13). Scanning in a reductive direction leads to the first reduction peak at -1.76 V corresponding to a one-electron process to generate the radical anion \([\text{LZnMe}]^-\) (I in Figure 6.13). A more negative potential (-2.52 V versus FeO+/) is required to introduce a second electron in the formazanate framework leading to the dianionic species \([\text{LZnMe}]^{2-}\) (II in Figure 6.13). Scanning back in an oxidative direction, \([\text{LZnMe}]^-\) (II') is generated, and consecutively the neutral LZnMe (I') is formed. A third oxidation wave is observed with a peak potential at -
1.25 V (vs Fc\(^{0+}\)). This is likely related to a decomposition product generated upon two-electron reduction (II), as it is absent when the potential is not swept past the (II/II') couple.

The electrochemistry of compound **1-ZnMe** is compared to its analogue bis(formazanate)zinc, previously reported by our group. The bis(formazanate) analogues show two quasi-reversible redox couples which correspond to the formation of the radical anion \([\text{ZnL}_2]^{-}\) and dianion \([\text{ZnL}_2]^{2-}\). In the latter bis(formazanate) complexes, the first two reduction events take place in different ligands, whereas in the present mono(formazanate) compounds the reductions are proposed to occur within the same ligand. Although rare, two-electron reduction of a monoanionic formazanate to generate a trianionic form of the ligand was recently shown to be feasible.\(^{61}\)

**Figure 6.13** Cyclic voltammogram of compound LZnMe (1-ZnMe) (1.5 mM solution of zinc complex in THF, 0.1 M [Bu\(_4\)N][PF\(_6\)] electrolyte, scan rate 100 mV.s\(^{-1}\)). Inlet: scanning only from 0.0 to -2.2 V under the same conditions and different scan rate (500 mV.s\(^{-1}\)).

Similar studies were performed for [LZnO\(_{2}\)Pr\(_2\)] (1-ZnO\(_{2}\)Pr) where three redox events are observed: the first two reductions are close to each other, at -1.51 V and -1.73 V (both vs. Fe\(^{0+}\)), and the third one at -2.66 V (vs. Fe\(^{0+}\)) (I'/II' and III/III', respectively, Figure 6.14). The presence of two independent, sequential reductions with a difference of only 0.21 V suggests that there is predominantly dimeric species in solution, thus, the first electron is introduced in one of the formazanate ligand to give \([\text{LLZn}_2(\mu-O\text{Pr})(\mu\text{O})_2])^{-}\) (I) (with L = formazanate anion, and L' = formazanate radical dianion). Subsequent reduction of the other ligand to give \([\text{LL'Zn}_2(\mu-O\text{Pr})_2])^{-}\) (II), is somewhat more difficult because the compound is already negatively charged at that stage. This is in agreement with previous redox studies on
bis(formazanate)zinc complexes (1-Zn) where the difference between the first two redox couples is 0.29 V, corresponding to the formation of the mono and subsequent diradical anions [LL’Zn]− and [L’L’Zn]2−.43 The first reduction of 1-ZnOiPr occurs at a less negative potential than in the case of 1-ZnMe (E0,i = -1.51 V and -1.63 V vs. Fe0/+, respectively), suggesting that the formazanate ligand in the three-coordinate zinc methyl complex 1-ZnMe is more electron-rich than that in the four-coordinate isopropoxide derivative.

The third reduction process for 1-ZnOiPr likely involves introduction of a second electron in one of the formazanate ligands to give [L’L’Zn2(μ-OiPr)2]3− (III) (L'' = formazanate trianion). The potential difference between the second (II, [L’L’Zn2(μ-OiPr)2]2− and the third (III, [L’L’Zn2(μ-OiPr)2]3−) reduction peaks is 0.93 V, which once again is consistent with the bis(formazanate)Zn complexes where there is a difference of 0.87 V between the potentials where [L’L’Zn]2− and [L’L’Zn]3− are formed.

In analogy to 1-ZnMe, a new irreversible peak appears at -1.19 V (vs. Fe0/+) (*, Figure 6.14) when the potential is swept past the (III/III’) couple. As can be seen in the inset in Figure 6.14 when a CV is recorded for 1-ZnOiPr scanning the potential between 0.00 and -2.00 V (vs. Fe0/+), this species are not generated and therefore the peak is not present in the cyclic voltammogram. Once more the nature of this new species is unknown but it is clear that it is formed due to the reduction that occurs at -2.66 V (vs. Fe0/+).

**Figure 6.14** Cyclic voltammogram of compound [LZnOiPr]2 (1-ZnOiPr) (1.5 mM solution of zinc complex in THF, 0.1 M [Bu4N][PF6] electrolyte, scan rate 100 mV.s⁻¹). Inset: scanning between -2.0 and 0.0 V.
Chapter 6

The voltammograms for LZnO\textsuperscript{i}Pr \textit{5-ZnO}\textsuperscript{i}Pr and the magnesium alkoxides are complex in all the cases, and they indicate that reduction is likely accompanied by subsequent chemical (decomposition) steps (Figure 6.15). We have not investigated this in detail, but note that the cyclic voltammograms for bis(formazanate) magnesium compounds (see Chapter 3) are similarly complicated, which is likely due to the ionic nature of these compounds.

Figure 6.15 Cyclic voltammogram of compound LZnO\textsuperscript{i}Pr (\textit{5-ZnO}\textsuperscript{i}Pr) (1.5 mM solution of zinc complex in THF, 0.1 M [Bu\textsubscript{4}N][PF\textsubscript{6}] electrolyte, scan rate 500 mV.s\textsuperscript{-1}).

6.6 Reactivity towards lactide

6.6.1 Conversion of lactide by LZnMe

To date, some of the best catalysts for lactide polymerization are homogeneous zinc complexes, coordinated by electron-donating ligands, such as \(\beta\)-diiminate (BDI)\textsuperscript{30}, bis-(amino)phenolates\textsuperscript{34} or pyrazolyl borates\textsuperscript{62}.

The ionic character of the complexes has a direct impact in the initiation and propagation of ROP as well as in the catalytic activity.\textsuperscript{63} Thus, in this section we compare the catalytic activity of different complexes when different metal centers are present (Ca, Mg and Zn).

Preliminary studies for the reactivity of complex \textit{5-ZnMe} (R\textsubscript{1} = R\textsubscript{5} = Mes) were performed by reacting 1.0 equivalent of the complex with 4.28 equiv. of lactide in NMR scale in C\textsubscript{6}D\textsubscript{6}. After stirring at room temperature for 1 day and 15 hours, a decrease in the two signals corresponding to the lactide (quartet at 3.82 ppm and doublet at 1.17 ppm) are accompanied...
by the increase of two broad peaks, one at 5.04 ppm with a shoulder at 5.09 ppm and the other one at 1.35 ppm with a shoulder at 1.23 ppm, which indicate formation of lactide oligomers (ca. 50% conversion).

At this stage, however, free ligand (5-H) and bis(formazanate)Zn (5-Zn) are present together with the starting material LZnMe (5-ZnMe) in a ratio 0.20 : 1.00 : 0.47, respectively, based on ^1H NMR integration. The appearance of ZnL₂ (5-Zn) is attributed to the Schlenk equilibrium (vide supra). However, the presence of LH is more surprising but could be due to the reaction of LZnMe with traces of water in the lactide. After stirring at room temperature for an additional 24 hours, only ZnL₂ is present, and lactide conversion is ongoing (oligomers: lactide = 2.55 : 1.00). Now that only the bis(formazanate)Zn is present, stirring at room temperature for another 4 days leads to > 95% conversion of the lactide.

To further corroborate that ZnL₂ is a catalyst by itself, 1.00 equiv. of pure (5-Zn) was reacted with 20.0 equiv. of lactide. Monitoring by NMR spectroscopy shows that during the reaction only ZnL₂ (5-Zn), lactide and oligomers are present. After 3 days of reaction at room temperature the conversion to oligomers was 33%.

Similarly to 5-Zn (R₁ = R₅ = Mes, R₃ = p-tol), 1-Zn (R₁ = R₅ = Ph, R₃ = p-tol) was tested as a potential catalyst for polymerization. As predicted, it shows similar behavior to its analogue 5-Zn but with an even lower activity. In this case, heating to 70 °C was needed for 8 days to reach full conversion of 8.38 equivalents of lactide. This is in line with many other studies where the activity of the polymerization/oligomerization can be drastically modified by tuning the ligand substituents.30,64,65

The ligand PhNNC(p-tol)NNPh (1-H) was used to compare the activity of bis(formazanate) complexes with different metals (1-Ca, 1-Mg and 1-Zn) towards lactide polymerization. The consumption of lactide is slower when going from the more ionic (Ca) to the more covalent (Zn) complex. After stirring for 110 min at room temperature a solution of 1 equivalent of 1-Ca and 135 equivalents of rac-lactide in C₆D₆, 71% conversion towards oligomers was observed, and full conversion was achieved overnight. The active catalyst is still present, which was proven by addition of another 135 equivalents of rac-lactide to the reaction mixture, leading to a conversion of 68% in an hour. However, for 1.0 equiv. of (1-Mg), 5 days are required to convert 34.4 equivalents of lactide. When the more covalent catalyst, 1-Zn, is used much longer reaction times are required (see above). Theoretical studies on the initiation stage of the ring-opening polymerization of meso-lactide catalyzed by various metal
alkoxides have been reported by Galabov et al. Their results reveal that the activity of the initiators follows the trend in ionic character, i.e., Li > Mg > Zn.

Our studies are also in agreement with previously reported results from Coates where a series of β-diiminate Mg and Zn alkoxy complexes where tested for polymerization of lactide. Their studies indicate that the Mg catalyst [(BDI-1)MgOPr] shows a much faster polymerization rate than the Zn analogue (500 equiv. in less than 5 min versus 200 equiv. in 19.8 min at 20 °C, respectively, compounds 1 and 2 in Figure 6.4). This also holds for other ligands such as bis(iminopyrrolide) with dimeric Mg, Zn or Al complexes, for which the activity with Mg is higher than with Zn. However it should be noted that our formazanate complexes show relatively poor catalytic activity for lactide polymerization in comparison to many systems reported in the literature.

Previous studies also suggest activity in complexes due to reaction with monomer impurities such as water, lactic acid, etc., resulting in slower rate of initiation than the propagating rate of polymerization leading to the formation of polymers with broad molecular weight distributions and higher than expected molecular weights.

Although preliminary studies indicate activity (albeit low) in all the catalysts tested, the elucidation of the active initiating species proved to be non-trivial. Mass spectroscopy revealed for complex 1-Mg an initiating group with molecular weight 17 (Figure 6.16), which we presume is due to reaction of 1-Mg with traces of water, generating a new active complex with a hydroxo group which will be involved in the ring-opening of the lactide monomer (Figure 6.3). In fact, Coates suggested that slower initiation than propagation rate when employing catalyst (BDI)ZnEt, together with a broad polydisperities and molecular weights comparing with (BDI)ZnOPr, could be explained by reaction of these complexes with monomer impurities (lactic acid, hydrolyzed lactide or water), forming in this way a new initiation group that is more active than the zinc alkyl in the catalyst precursor.

However, the calculated mass for the initiating group in complex 1-Ca is the same as for the complex 5-Zn, corresponding to 52 g/mol (Figure 6.17). The mass spectrum for the product obtained with 5-Zn suggests the presence of two initiating groups, corresponding to 52 and 124 g/mol. Attempts to elucidate the initiating group corresponding to this mass were unsuccessful and it remains unknown till date. In the absence of conclusive evidence of the initiating group, we cannot rule out that conversion of the bis(formazanate) complexes to a different (as yet unidentified) active species is required before reaction with lactide occurs.
Further studies are needed to clarify this point, and provide insight in potential ways to improve catalytic activity.

Figure 6.16 Electrospray MS of crude reaction product of lactide and 1-Mg (35:1), quenched with MeOD.d4 after reaction complete. Region m/z = 0 to 1750.

Figure 6.17 Electrospray MS of crude reaction product of lactide and 5-Mg (20:1), quenched with MeOD.d4 after reaction is complete. Region m/z = 600 to 1100.
6.6.2 Conversion of lactide by [LMOR]n (M = Zn, Mg)

Complexes n-ZnOR-1-MgOC(CH₃Ph₂) were also tested in the polymerization of rac-lactide, being active catalysts in all the cases. All the catalysts are dimeric in the solid state as revealed by X-ray crystallography. However, as shown in the previous section, by DOSY experiments this dimeric species can be retained (1-ZnOR) or not (5-ZnO’Pr, 1-MgOC(CH₃Ph₂)) in solution state (Table 6.4).

The retention of the dimeric species in solution state directly affects the activity of these complexes due to the lower nucleophilic ability and the more saturated coordination sphere than the monomeric species. Consequently, we would expect slower rate for polymerization of lactide when the dimeric species are present in solution. This is in line with the results obtained, where 5-ZnO’Pr shows the highest activity among all the Zn alkoxide catalysts (n-ZnOR) by converting 16 equivalents of rac-lactide in 1 day and 15 hours at room temperature with a 93% conversion. For Zn alkoxide complexes 1-ZnOR, 7 days and 20 hours are needed to reach >93% conversion under identical conditions. For this group of catalysts, 1-ZnO’Pr shows slightly higher activity than 1-ZnOPh, showing 1-ZnO’Bu the slowest activity of this group of catalysts (89%, 73% and 49%, respectively, 20 equivalents of lactide after 1 day at room temperature).

Even a higher activity than 5-ZnO’Pr was found when 1-MgOC(CH₃Ph₂) was examined. A conversion >99% of 20 equivalents of rac-lactide was achieved within an hour at room temperature, being the catalyst with the highest activity among all the catalyst reported in this Chapter. The fastest magnesium catalyst reported till date shows in the presence of 1.3 equivalents of BzOH, a 95% conversion of 300 equivalents of lactide in 30 seconds at room temperature. However, in the absence of the alcohol only 20-30% conversion of 100 equivalents was achieved in one minute and after prolonged reaction times the maximum conversion achieved was 60-65%. The relatively high activity of complex 1-MgOC(CH₃Ph₂) in comparison to the other alkoxide compounds tested is proposed to be due to its monomeric nature in solution and the hard Lewis acidic character of the metal center involved. Our findings are in agreement with the trends that have been reported in the literature where magnesium catalysts showed higher activities than the related zinc compounds when the same ligand framework is used for comparison.
Although these preliminary studies show activity for a range of different formazanate complexes, further characterization of the products is required to obtain more detailed insight in the efficacy of these catalysts.

6.7 Conclusions

In this chapter, several formazanate complexes were synthesized, characterized and tested towards conversion of lactide. These complexes can be gathered in three kind of catalysts: i) mono(formazanate) zinc methyl (LZnMe), ii) bis(formazanate) (ML2, M = Zn, Mg, Ca) and iii) mono(formazanate) alkoxy complexes (LMOR, M = Zn, Mg). The first group of complexes, LZnMe, manifest Schlenk equilibrium in solution and lead to the formation of the corresponding bis(formazanate) ZnL2 complexes. Steric modification on the terminal nitrogen of the formazanate allows control of the Schlenk equilibrium. Thus, the formation of ZnL2 is minimized when sterically demanding substituents such as N-mesityl are present.

The corresponding alkoxy complexes show in all the cases dimeric structures in solid state. DOSY NMR experiments also reveal dimeric structure for the zinc alkoxy [LZnOR]2, (1-ZnOR). However, monomeric species LMOR in solution were found when bulkier formazanate ligands (5-ZnO\text{Pr}) or bulkier alkoxides (1-MgOC(CH3Ph2)) are used. All the complexes show activity in the conversion of lactide, with 1-MgOC(CH3Ph2) being the most active catalyst which converts 20 equivalents of lactide in less than an hour. Higher activities were achieved by going to a larger, more Lewis acidic metal center (Ca > Mg > Zn) and by the presence of better nucleophiles as initiator groups (LMOR > ML2 > LMMe). However, more studies are needed to clarify the precise nature of the initiating groups and provide mechanistic insight.

Finally, the formazanate zinc complexes described in this chapter show reversible ligand-based reductions by cyclic voltammetry. This property of formazanates suggests that metal complexes incorporating these ligands could be applied as redox-switchable catalysts.
Chapter 6

6.8 Experimental

6.8.1 General considerations

All manipulations were carried out under nitrogen atmosphere using standard glovebox, Schlenk, and vacuum-line techniques. Toluene, hexane, and pentane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). Diethyl ether and THF (Aldrich, anhydrous, 99.8%) were dried by percolation over columns of Al₂O₃ (Fluka). Deuterated solvents were vacuum transferred from Na/K alloy (C₆D₆, toluene-d₈, Aldrich) and stored under nitrogen. Dimethylzinc (Aldrich, 2.0 M in toluene) was used as received. Mg(OC₆H₅)₂CH₃ was made according to a reported procedure. rac-lactide was purchased from Sigma-Aldrich and recrystallized three times from toluene. NMR spectra were recorded on Varian Gemini 200, VXR 300, Mercury 400 or Varian 500 spectrometers. The ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm); J is reported in Hz. Assignment of NMR resonances was aided by gradient-selected COSY, NOESY, HSQC and/or HMBC experiments using standard pulse sequences.

All electrochemical measurements were performed under an inert N₂ atmosphere in a glove box using an Autolab PGSTAT 100 (or PGSTAT 302N) computer-controlled potentiostat. Cyclic voltammetry (CV) was performed using a three-electrode configuration comprising of a Pt wire counter electrode, a Ag wire pseudoreference electrode and a Pt disk working electrode (CHI102, CH Instruments, diameter = 2 mm). The Pt working electrode was polished before experiment using alumina slurry (0.05 μm), rinsed with distilled water and subjected to brief ultrasonication to remove any adhered alumina microparticles. The electrodes were then dried in an oven at 75 °C overnight to remove any residual traces of water. The CV data was calibrated by adding ferrocene (as a THF solution) at the end of the experiments. In all cases, there is no indication that addition of ferrocene influences the electrochemical behaviour of the compounds of interest. All electrochemical measurements were performed at ambient temperatures under an inert N₂ atmosphere in THF containing 0.1 M [Bu₄N][PF₆] as the supporting electrolyte. Elemental analyses were performed at the Microanalytical Department of the University of Groningen or Kolbe Microanalytical Laboratory (Mülheim an der Ruhr, Germany).
6.8.2 Synthesis of L\textsubscript{ZnMe}

**Synthesis of [PhNNC(p-tol)NNPh]ZnMe (1-ZnMe)**

1,5-Diphenyl-3-\textit{para}-tolyl formazan (1-H) (0.715 g, 2.27 mmol) was dissolved in toluene (20 mL) and a 1.2 M solution of dimethyl zinc in toluene (2.1 mL, 2.52 mmol) was added. The solution turned from dark red to dark violet and gas evolution was observed. The solution was stirred for 30 minutes and removing the solvent in vacuum afforded the product (0.705 g, 1.79 mmol, yield: 89%). Crystals suitable for X-ray analysis were obtained from toluene cooled to -30 °C. $^1$H NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz): δ 8.37 (2H, d, $J = 7.8$ Hz, \textit{p}-tol \textit{m}-H), 7.84 (4H, d, $J = 8.0$ Hz, Ph \textit{o}-H), 7.33 (2H, d, $J = 7.8$ Hz, \textit{p}-tol \textit{o}-H), 7.21 (2H, t, $J = 7.7$ Hz, Ph \textit{m}-H), 7.05 (2H, t, $J = 7.2$ Hz, Ph \textit{p}-H), 2.28 (3H, s, \textit{p}-tol \textit{p}-CH\textsubscript{3}), -0.15 (3H, s, ZnMe). $^{13}$C NMR (C\textsubscript{6}D\textsubscript{6}, 126 MHz): δ 154.33 (Ph \textit{i}-C), 144.37 (\textit{p}-tol \textit{i}-C), 138.24 (NNCNN), 137.25 (\textit{p}-tol \textit{p}-C), 130.02 (\textit{p}-tol \textit{o}-C), 129.77 (Ph \textit{m}-C), 128.05 (Ph \textit{p}-C), 126.52 (\textit{p}-tol \textit{m}-C), 121.45 (Ph \textit{o}-C), 21.64 (\textit{p}-tol \textit{p}-CH\textsubscript{3}), -8.60 (ZnMe). Elemental analysis calculated for C\textsubscript{21}H\textsubscript{20}N\textsubscript{4}Zn: C, 64.05; H, 5.12; N, 14.23. Found: C, 64.30; H, 5.16; N, 13.90.

**Synthesis of [PhNNC(p-tol)NNMes]ZnMe (4-ZnMe)**

1-Phenyl-5-mesityl-3-\textit{para}-tolyl formazan (4-H) (676 mg, 1.90 mmol) was dissolved in toluene (20 mL) and a 1.2 M solution of dimethyl zinc in toluene (2.1 mL, 2.52 mmol) was added. The solution turned from dark red to dark violet and gas evolution was observed. The solution was stirred for 30 minutes and removing the solvent in vacuum afforded the product (541 mg, 1.24 mmol, yield: 65%). Crystals suitable for X-ray analysis were obtained from toluene cooled to -30 °C. $^1$H NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz): δ 8.29 (2H, d, $J = 7.8$ Hz, \textit{p}-tol \textit{m}-H), 7.95 (2H, d, $J = 7.8$ Hz, Ph \textit{o}-H), 7.22 (2H, d, $J = 7.8$ Hz, \textit{p}-tol \textit{o}-H), 7.20 (2H, t, $J = 7.7$ Hz, Ph \textit{m}-H), 7.03 (2H, t, $J = 7.2$ Hz, Ph \textit{p}-H), 6.75 (2H, s, Mes \textit{m}-H), 2.21 (3H, s, \textit{p}-tol \textit{p}-CH\textsubscript{3}), 2.11 (3H, s, Mes \textit{p}-CH\textsubscript{3}), 2.05 (6H, s, Mes \textit{o}-CH\textsubscript{3}), -0.28 (3H, s, ZnMe). $^{13}$C NMR (C\textsubscript{6}D\textsubscript{6}, 126 MHz): δ 154.52 (Ph \textit{i}-C), 149.39 (Mes \textit{i}-C), 144.37 (\textit{p}-tol \textit{i}-C), 130.02 (\textit{p}-tol \textit{m}-C), 129.77 (Ph \textit{m}-C), 128.05 (Ph \textit{p}-C), 126.52 (\textit{p}-tol \textit{m}-C), 121.45 (Ph \textit{o}-C), 21.64 (\textit{p}-tol \textit{p}-CH\textsubscript{3}), -8.60 (ZnMe).
Synthesis of \([\text{MesNNC}(p\text{-tol})\text{NNMes}]\text{ZnMe} \) (5-ZnMe)

1,5-Dimesityl-3-\textit{para}-tolyl formazan (5-H) (136.7 mg, 0.34 mmol) was dissolved in toluene (15 mL). To the resulting orange solution a 1.2 M dimethyl zinc solution in toluene (343 μL, 0.42 mmol) was added. The solution was stirred overnight without change in color, after which the solvent was removed in vacuum to afford the product. Slow evaporation of C6D6 afforded orange crystals of 6d (126.1 mg, 0.26 mmol, yield: 77%). 

\[ \text{^1}H \text{NMR (C}_6\text{D}_6, 500 \text{ MHz): } \delta 8.22 (2\text{H, d, } J = 7.8 \text{ Hz, } p\text{-tol \text{o-H}}, 7.13 (2\text{H, d, } J = 7.8 \text{ Hz, } p\text{-tol \text{m-H}}), 6.78 (4\text{H, s, Mes \text{m-H}}), 2.71 (12\text{H, s, Mes \text{o-CH}_3}), 2.14 (3\text{H, s, } p\text{-tol \text{p-CH}_3}), 2.13 (6\text{H, s, Mes \text{p-CH}_3}), -0.39 (3\text{H, s, ZnMe}). \]

\[ \text{^13C NMR (C}_6\text{D}_6, 126 \text{ MHz): } \delta 149.42 (\text{Mes \text{i-C}}), 146.10 (p\text{-tol \text{i-C}}, 137.31 (p\text{-tol \text{p-C}}), 137.24 (\text{NNCNN}), 136.89 (\text{Mes \text{p-C}}), 131.04 (\text{Mes \text{m-C}}), 130.55 (\text{Mes \text{o-C}}), 130.02 (p\text{-tol \text{o-C}}), 126.57 (p\text{-tol \text{m-C}}), 19.10 (\text{Mes \text{o-CH}_3}), -15.25 (\text{ZnMe}). \]

6.8.3 Synthesis of \([\text{LMOR}]_n \) (M = Zn, Mg)

Synthesis of \([\text{PhNNC}(p\text{-tol})\text{NNPh}]\text{ZnO}^\text{iPr}_2 \) (1-ZnO\text{iPr})

Zinc methyl 1,5-diphenyl-3-\textit{para}-tolyl formazanate LZnMe (1-ZnMe, 98.6 mg, 0.250 mmol) was dissolved in toluene (5 mL). The solution was layered with pentane (3 mL) containing isopropanol (19 μL, 0.248 mmol) and was left to stand overnight. The mother liquor was decanted and the crystals were washed with pentane (3 portions of 1 mL) and dried in vacuum to afford the product. (75.5 mg, 0.156 mmol, yield: 63%). Crystals suitable for X-ray analysis containing one molecule of toluene per dimer were obtained from toluene/pentane. 

\[ \text{^1}H \text{NMR (C}_6\text{D}_6, 500 \text{ MHz): } \delta 8.40 (4\text{H, d, } J = 7.8 \text{ Hz, } p\text{-tol \text{m-H}}), 8.17 (8\text{H, d, } J = 7.9 \text{ Hz, } \text{Ph \text{o-H}}), 7.28 (4\text{H, d, } J = 7.8 \text{ Hz, } p\text{-tol \text{o-H}}), 7.09 (8\text{H, t, } J = 7.6 \text{ Hz, } \text{Ph \text{m-H}}), 6.99 (4\text{H, t, } J = 7.2 \text{ Hz, } \text{Ph \text{p-H}}), 3.98 (2\text{H, m, } J = 5.7 \text{ Hz, } \text{OCH}_3(\text{CH}_3)_2), 2.24 (6\text{H, s, } p\text{-tol \text{p-CH}_3}), 0.85 (12\text{H, d, } J = 5.7 \text{ Hz, } \text{OCH}_3(\text{CH}_3)_2). \]

\[ \text{^13C NMR (C}_6\text{D}_6, 126 \text{ MHz): } \delta 153.66 (\text{Ph \text{i-C}}), 143.96 (p\text{-tol \text{i-C}}), 137.83 (\text{NNCNN}), 137.45 (p\text{-tol \text{p-C}}), 130.05 (\text{Ph \text{m-C}}), 130.00 (p\text{-tol \text{o-C}}), 128.08 (\text{Ph \text{p-C}}), 126.58 (p\text{-tol \text{m-C}}), 121.73 (\text{Ph \text{o-C}}), 67.81 (\text{OCH}_3(\text{CH}_3)_2), 27.87 (\text{OCH}_3(\text{CH}_3)_2), 21.60 (p\text{-tol \text{p-CH}_3}). \]

Elemental analysis calculated for C_{53}H_{56}N_8O_2Zn_2: C, 65.77; H, 5.83; N, 11.58. Found: C, 65.73; H, 5.86; N, 11.47.

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Synthesis of [{PhNNC(p-tol)NNPh}ZnO\textsubscript{2}]\textsubscript{2} (1-ZnO\textsubscript{Bu})

Zinc methyl 1,5-diphenyl-3-\textit{para}-tolyl formazanate LZnMe (1-ZnMe, 98.4 mg, 0.250 mmol) was dissolved in toluene (5 mL). The solution was layered with pentane (3 mL) containing \textit{tert}-butanol (23.9 \textmu L, 0.250 mmol) and was left to stand overnight. The mother liquor was decanted and the crystals were washed with pentane (3 portions of 1 mL) and dried in vacuum to afford the product. (81.2 mg, 0.166 mmol, yield: 66%). \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 500 MHz): \& 8.41 (4H, d, \textit{J} = 7.8 Hz, \textit{p}-tol \textit{m}-H), 8.26 (8H, d, \textit{J} = 7.9 Hz, Ph \textit{o}-H), 7.28 (4H, d, \textit{J} = 7.8 Hz, \textit{p}-tol \textit{o}-H), 7.11 (8H, t, \textit{J} = 7.6 Hz, Ph \textit{m}-H), 7.00 (4H, t, \textit{J} = 7.2 Hz, Ph \textit{p}-H), 2.23 (6H, s, \textit{p}-tol \textit{p}-CH\textsubscript{3}), 1.01 (18H, s, OC(CH\textsubscript{3})\textsubscript{3}). \textsuperscript{13}C NMR (C\textsubscript{6}D\textsubscript{6}, 126 MHz): \& 153.40 (Ph \textit{i}-C), 144.26 (p-tol \textit{i}-C), 137.77 (NNCNN), 137.49 (\textit{p}-tol \textit{p}-C), 130.02 (\textit{p}-tol \textit{o}-C), 129.90 (Ph \textit{m}-C), 128.14 (Ph \textit{p}-C). Crystals suitable for X-ray analysis were obtained from toluene/pentane. Elemental analysis calculated for C\textsubscript{55}H\textsubscript{60}N\textsubscript{8}O\textsubscript{2}Zn\textsubscript{2}: C, 66.33; H, 6.07; N, 11.25. Found: C, 66.51; H, 6.16; N, 11.18.

Synthesis of [{PhNNC(p-tol)NNPh}ZnOPh\textsubscript{2}]\textsubscript{2} (1-ZnOPh)

Zinc methyl 1,5-diphenyl-3-\textit{para}-tolyl formazanate LZnMe (1-ZnMe, 107.5 mg, 0.273 mmol) was dissolved in toluene (5 mL). The solution was layered with pentane (3 mL) containing phenol (25.7 mg, 0.273 mmol) and was left to stand overnight. The mother liquor was decanted and the crystals were washed with pentane (3 portions of 1 mL) and dried in vacuum to afford the product, containing an impurity (73.3 mg). Crystals suitable for X-ray analysis were obtained from toluene/pentane. \textsuperscript{1}H NMR (C\textsubscript{6}D\textsubscript{6}, 400 MHz): \& 8.39 (4H, d, \textit{J} = 7.8 Hz, \textit{p}-tol \textit{m}-H), 8.02 (8H, d, \textit{J} = 7.1 Hz, Ph \textit{o}-H), 7.30 (8H, t, \textit{J} = 8.0 Hz, \textit{p}-tol \textit{o}-H), 7.1-6.6 (26H, m), 6.45 (2H, t, 2.26, \textit{J} = 7.2 Hz, Ph \textit{p}-H), 2.26 (6H, s, \textit{p}-tol \textit{p}-CH\textsubscript{3}). Elemental analysis calculated for C\textsubscript{59}H\textsubscript{52}N\textsubscript{8}O\textsubscript{2}Zn\textsubscript{2}: C, 68.41; H, 6.07; N, 10.82. Found: C, 68.37; H, 5.06; N, 10.69.
Synthesis of \([\text{MesNNC}(\text{p-tol})\text{NNMes}]\text{ZnOiPr}\)\(_2\) (5-ZnOiPr)

Zinc methyl 1,5-dimesityl-3-para-tolyl formazanate \(\text{LZnMe}\) (5-ZnMe, 55.3 mg, 0.116 mmol) was dissolved in toluene (1.4 mL). The solution was layered with hexane (2.4 mL) containing isopropanol (8.9 μL, 0.116 mmol) and was left to stand overnight. The mother liquor was decanted and the orange crystals were washed with hexane (3 portions of 0.2 mL) and dried in vacuum (yield not determined). The crystals were suitable for X-ray analysis. \(^1\)H NMR (C\(_6\)D\(_6\)/THF-\(d_8\), 600 MHz): δ 8.08 (4H, d, \(J = 7.8\) Hz, p-tol o-H), 7.03 (4H, d, \(J = 7.8\) Hz, p-tol m-H), 6.89 (8H, s, Mes m-H), 3.75 (2H, m, \(J = 5.7\) Hz, OCH(CH\(_3\))\(_2\)), 2.26 (12H, s, Mes p-CH\(_3\)), 2.20 (24, s, Mes o-CH\(_3\)), 2.07 (6H, s, p-tol p-CH\(_3\)), 0.72 (12H, d, \(J = 5.7\) Hz, OCH(CH\(_3\))\(_2\)).

Synthesis of \([\text{PhNNC}(\text{p-tol})\text{NNPh}]\text{MgOCCH}_3(\text{Ph})_2\)\(_2\) (1-MgOC(CH\(_3\)Ph\(_2\))

A deep red solution of 1-H (211.8 mg, 0.673 mmol) in toluene was added dropwise to a white suspension of MgOCCH\(_3\)(Ph)\(_2\))\(_2\) (282.0 mg, 0.673 mmol) in toluene. After stirring at room temperature during two hours the solution turns to violet. Evaporation of the solvent under vacuum and subsequently crystallization by slow diffusion of hexane into a solution of 1-MgOC(CH\(_3\)Ph\(_2\)) afford suitable crystals for X-ray characterization (23%, 89.4 mg, 0.155 mmol). \(^1\)H NMR (C\(_6\)D\(_6\), 25 ºC, 500 MHz): δ 8.25 (d, 2H, \(J = 7.8\) Hz, p-tol o-H), 8.03 (d, 4H, \(J = 7.8\) Hz, p-tol p-H), 7.27 (d, 2H, \(J = 7.8\) Hz, p-tol m-H), 7.20 (br, 4H, Ph o-H), 7.14 (br, 6H, \(m,p\)-Ph,OCPh\(_2\)CH\(_3\)), 7.08 (t, 2H, p-Ph), 6.74 (m, 6H, p-Ph,OCPh\(_2\)CH\(_3\)), 2.26 (s, 3H, CH\(_3\), p-tol), 1.80 (s, 3H, CH\(_3\), OR). \(^{13}\)C NMR (C\(_6\)D\(_6\), 25 ºC, 126 MHz): δ 154.02 (Ph ipso-C), 149.30 (Ph ipso-C,OR), 144.54 (NCN), 138.12 (p-tol p-C), 136.52 (p-tol ipso-C), 129.67 (m/p-CH,Ph,OR), 129.39 (p-tol m-CH), 127.16 (Ph p-CH), 127.10 (Ph p-CH,OR), 126.66 (m/p-CH,Ph,OR), 126.34 (p-tol o-CH), 121.61 (Ph o-CH), 78.31 (OCPh\(_2\)CH\(_3\)), 32.52 (OCPh\(_2\)CH\(_3\)), 21.26 (p-tol CH\(_3\)). Anal. calcd. for C\(_{36}\)H\(_{30}\)MgN\(_4\)O: C 76.34, H 5.65, N 10.47; found: C 76.04, H 5.59, N 10.34.
Crystallographic data
Suitable crystals of 1,3,4,5-ZnMe, 1,5-ZnO\textsuperscript{Pr}, 1-ZnO\textsuperscript{Bu} and 1-ZnOPh were mounted on a cryo-loop in a drybox and transferred, using inert-atmosphere handling techniques, into the cold nitrogen stream of a Bruker D8 Venture diffractometer. Intensity data were corrected for Lorentz and polarisation effects, scale variation, for decay and absorption: a multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS).\textsuperscript{66} The structures were solved by direct methods using the program SHELXS.\textsuperscript{67} The hydrogen atoms were generated by geometrical considerations and constrained to idealise geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. Structure refinement was performed with the program package SHEXL.\textsuperscript{67} Crystal data and details on data collection and refinement are presented in following tables.
### 1-ZnMe
- **Chem formula**: C21 H20 N4 Zn
- **Mr**: 393.78
- **Cryst syst**: monoclinic
- **Color, habit**: dark blue, platelet
- **Size (mm)**: 0.14x0.13x0.03
- **Space group**: P 21/c
- **a (Å)**: 17.3788(4)
- **b (Å)**: 15.6932(3)
- **c (Å)**: 21.3006(5)
- **α (°)**: 90.00
- **β (°)**: 111.7590(10)
- **γ (°)**: 90.00
- **V (Å³)**: 5395.4(2)
- **ρ (calc), g cm⁻³**: 1.454
- **μ (Mo Kα), mm⁻¹**: 1.432
- **F(000)**: 2448
- **Reflections**: 67652
- **R (F) (%)**: 3.57
- **GooF**: 1.045
- **Weighting a,b**: 0.0419
- **Params refined**: 709
- **Residuals**: -0.477, 0.080

### 3-ZnMe
- **Chem formula**: C36 H44 N8 Zn2
- **Mr**: 719.53
- **Cryst syst**: monoclinic
- **Color, habit**: red, needle
- **Size (mm)**: 0.32x0.13x0.09
- **Space group**: P 21/n
- **a (Å)**: 22.9905(9)
- **b (Å)**: 6.8231(3)
- **c (Å)**: 23.2771(10)
- **α (°)**: 90.00
- **β (°)**: 109.5900(10)
- **γ (°)**: 90.00
- **V (Å³)**: 3440.0(3)
- **ρ (calc), g cm⁻³**: 1.389
- **μ (Cu Kα), mm⁻¹**: 1.727
- **F(000)**: 1504
- **Reflections**: 117763
- **R (F) (%)**: 3.20
- **GooF**: 1.062
- **Weighting a,b**: 0.0291
- **Params refined**: 7622
- **Residuals**: -0.283, 0.067

### 4-ZnMe
- **Chem formula**: C24 H26 N4 Zn
- **Mr**: 435.86
- **Cryst syst**: triclinic
- **Color, habit**: red, plate
- **Size (mm)**: 0.20x0.05x0.02
- **Space group**: P -1
- **a (Å)**: 14.9030(11)
- **b (Å)**: 16.5384(12)
- **c (Å)**: 9.0159(4)
- **α (°)**: 103.249(3)
- **β (°)**: 109.5900(10)
- **γ (°)**: 90.00
- **V (Å³)**: 2120.8(3)
- **ρ (calc), g cm⁻³**: 1.365
- **μ (Cu Kα), mm⁻¹**: 1.727
- **F(000)**: 912
- **Reflections**: 30254
- **R (F) (%)**: 3.32
- **GooF**: 1.997
- **Weighting a,b**: 0.0372
- **Params refined**: 7266
- **Residuals**: -0.318, 0.58

### 5-ZnMe
- **Chem formula**: C27 H32 N4 Zn
- **Mr**: 477.93
- **Cryst syst**: triclinic
- **Color, habit**: red, plate
- **Size (mm)**: 0.20x0.08x0.10
- **Space group**: P -1
- **a (Å)**: 9.0159(4)
- **b (Å)**: 9.00
- **c (Å)**: 9.00
- **α (°)**: 101.617(2)
- **β (°)**: 91.234(2)
- **γ (°)**: 90.00
- **V (Å³)**: 2531.8(2)
- **ρ (calc), g cm⁻³**: 1.254
- **μ (Mo Kα), mm⁻¹**: 1.432
- **F(000)**: 1008
- **Reflections**: 76580
- **R (F) (%)**: 5.11
- **GooF**: 0.990
- **Weighting a,b**: 0.0304
- **Params refined**: 10347
- **Residuals**: -0.441, 0.074

---

**Chapter 6**
<table>
<thead>
<tr>
<th></th>
<th>1-ZnO(^{i})Pr</th>
<th>1-ZnO(^{i})Bu</th>
<th>1-ZnOPh</th>
<th>5-ZnO(^{i})Pr</th>
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</thead>
<tbody>
<tr>
<td><strong>chem formula</strong></td>
<td>C23 H24 N4 O Zn</td>
<td>C27.50 H26 N4 O Zn</td>
<td>C29.50 H25.50 N4 O Zn</td>
<td>C29 H36 N4 O Zn</td>
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<tr>
<td><strong>M(_t)</strong></td>
<td>437.83</td>
<td>493.89</td>
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<td>521.99</td>
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<td><strong>cryst syst</strong></td>
<td>triclinic</td>
<td>triclinic</td>
<td>triclinic</td>
<td>monoclinic</td>
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<tr>
<td><strong>color, habit</strong></td>
<td>metallic dark violet, block</td>
<td>metallic dark violet, block</td>
<td>dark violet, needle</td>
<td>red, long plate</td>
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<tr>
<td><strong>size (mm)</strong></td>
<td>0.32x0.29x0.23</td>
<td>0.48x0.39x0.24</td>
<td>0.28x0.18x0.10</td>
<td>0.37x0.07x0.05</td>
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<tr>
<td><strong>space group</strong></td>
<td>P-1</td>
<td>P-1</td>
<td>P-1</td>
<td>P 2(_{1}/c)</td>
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<tr>
<td><strong>a (Å)</strong></td>
<td>9.0929(9)</td>
<td>9.9994(4)</td>
<td>9.1511(12)</td>
<td>13.7715(7)</td>
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<tr>
<td><strong>b (Å)</strong></td>
<td>9.6398(10)</td>
<td>10.4132(5)</td>
<td>10.8536(12)</td>
<td>22.7460(11)</td>
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<tr>
<td><strong>c (Å)</strong></td>
<td>14.3351(15)</td>
<td>13.8900(7)</td>
<td>14.2303(17)</td>
<td>9.1472(4)</td>
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<tr>
<td><strong>α (°)</strong></td>
<td>85.066(3)</td>
<td>74.192(2)</td>
<td>80.745(4)</td>
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<td><strong>β (°)</strong></td>
<td>74.530(3)</td>
<td>71.623(2)</td>
<td>73.236(4)</td>
<td>105.8325(16)</td>
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<tr>
<td><strong>γ (°)</strong></td>
<td>77.012(3)</td>
<td>63.577(2)</td>
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<tr>
<td><strong>V (Å(^3))</strong></td>
<td>1179.6</td>
<td>1214.22(10)</td>
<td>1245.7</td>
<td>2756.6(2)</td>
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<td><strong>Z</strong></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>4</td>
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<td><strong>ρ(_{calc}), g.cm(^{-3})</strong></td>
<td>1.233</td>
<td>1.351</td>
<td>1.379</td>
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<tr>
<td><strong>Radiation [Å]</strong></td>
<td>Mo K(_{α}) 0.71073</td>
<td>Mo K(_{α}) 0.71073</td>
<td>Mo K(_{α}) 0.71073</td>
<td>Mo K(_{α}) 0.71073</td>
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<td><strong>μ(Mo K(_{α})), mm(^{-1})</strong></td>
<td>1.060</td>
<td>1.038</td>
<td>1.016</td>
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<td><strong>F(000)</strong></td>
<td>456</td>
<td>514</td>
<td>537</td>
<td>1104</td>
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<td><strong>temp (K)</strong></td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
<td>100(2)</td>
</tr>
<tr>
<td><strong>θ range (°)</strong></td>
<td>2.59 - 28.29</td>
<td>2.33 - 30.00</td>
<td>2.46 - 28.71</td>
<td>2.93 - 27.15</td>
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<tr>
<td><strong>data collected</strong></td>
<td>-11:12; -12:12; -14:14; -14:14; -12:12; -14:14; -17:17; -29:29; -27:27</td>
<td>-11:12; -12:12; -14:14; -14:14; -12:12; -14:14; -17:17; -29:29; -27:27</td>
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<tr>
<td><strong>min, max transm</strong></td>
<td>0.6557, 0.7457</td>
<td>0.6356, 0.7887</td>
<td>0.7641, 0.9052</td>
<td>0.8566, 0.9560</td>
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<td><strong>rflns collected</strong></td>
<td>23833</td>
<td>44414</td>
<td>52688</td>
<td>46195</td>
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<tr>
<td><strong>indpt reflns</strong></td>
<td>5762</td>
<td>7075</td>
<td>6455</td>
<td>6095</td>
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<td><strong>observed reflns F(_{o})</strong></td>
<td>5287</td>
<td>6530</td>
<td>5326</td>
<td>4566</td>
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<tr>
<td><strong>≥ 2.0 σ (P(_{o}))</strong></td>
<td>5287</td>
<td>6530</td>
<td>5326</td>
<td>4566</td>
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<tr>
<td><strong>R(F)%</strong></td>
<td>3.04</td>
<td>3.12</td>
<td>3.82</td>
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<tr>
<td><strong>wrR(F(^2))%</strong></td>
<td>8.68</td>
<td>8.53</td>
<td>9.63</td>
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<td><strong>GooF</strong></td>
<td>1.137</td>
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<td>0.0472, 0.6735</td>
<td>0.0376, 0.8614</td>
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<td><strong>params refined</strong></td>
<td>265</td>
<td>320</td>
<td>327</td>
<td>325</td>
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<td><strong>min, max resid dens</strong></td>
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<td>-0.499, 0.082</td>
<td>-0.914, 0.067</td>
<td>-0.380, 0.067</td>
</tr>
</tbody>
</table>

Formazanate Complexes as Potential Catalysts for Lactide Polymerization
Chapter 6

6.9 References


Formazanate Complexes as Potential Catalysts for Lactide Polymerization


(66) Bruker, APEX2 (v2012.4-3), SAINT (Version 8.18C) and SADABS (Version 2012/1), Bruker AXS Inc., Madison, Wisconsin, USA, 2012.