FULL PAPER

Synthesis of Zn(II) and Al(III) complexes of diaminocyclohexane derived ligands and their exploitation for the ring opening polymerization of *rac*-lactide

Sarah M. Kirk,[a] Paul McKeown,*,[a] Mary F. Mahon,[b] Gabriele Kociok-Köhn,[b] Timothy J. Woodman[c] and Matthew D. Jones*,[b]

Abstract: Two series of ligands based on diaminocyclohexane (DACH) have been prepared and successfully complexed to Al(III) and Zn(II) metal centres. Solution and solid-state studies reveal a tendency to form mono- or bis-ligated forms depending on the steric bulk of the ligand. These complexes have been tested for their ability to ring open *rac*-lactide. Al(III) based complexes generally gave atactic PLA after a polymerization time of 1-2 days. The Zn(II) complexes, were found to be more active and furnished PLA with a slight heterotactic bias.

Introduction

There is a growing need for the production of plastics derived from renewable sources.[1] What is more, there is a strong desire that such materials are biodegradable.[2] Poly (lactic acid) (PLA) is an important example of such a material that fulfils these criteria.[3] A key challenge for the production of PLA is the control of polymer microstructure which can dramatically influence the materials physical properties. For PLA prepared from a racemic blend of monomers (L/D), atactic, heterotactic or isotactic configurations are possible.[4] Therefore, a range of metal complexes have been trialled for the ROP of *rac*-LA with emphasis on stereocontrol and activity. Successful control of stereochemistry has been achieved with a range of different metal complexes including Na(I)/K(I),[5] Mg(II),[6] Ca(II),[7] Y(III),[8] Zr(IV)/Hf(IV),[9] and In(III).[10] Early investigations into metal mediated ROP of *rac*-LA favoured the use of aluminium complexes which often impart excellent selectivity and control but can also suffer from relatively poor activity.[11] A seminal initiator for the stereoselective ROP of *rac*-LA was demonstrated by Feijen et al.[11m, n] The use of chiral *trans* diaminocyclohexane (DACH) salen Al(III) complexes afforded highly isotactic PLA (P_m = 0.88 - 0.93) albeit only after a polymerisation time of seven days. Jones et al have reported several DACH based salalen ligands with Al(III).[12] More variation in stereocontrol was seen for these complexes with both heterotacticity (P_r = 0.73) and isotacticity (P_m = 0.69) possible dependent on aryl substituents. Symmetrical DACH based salan complexes have also been prepared by Feijen et al.[11b] These complexes were found to be diastereomers in solution and demonstrated either a slight preference for isotacticity or heterotacticity depending on aryl substituents. There are also several examples of monophenolato Al(III) complexes being successfully for the ROP of cyclic esters.[13] The use of Zn(II) complexes has also been shown to be an attractive route to PLA. High activity is often observed and, under certain conditions, good stereocontrol can be achieved.[14] Coates et al have utilised β-diketiminato Zn(II) complexes which boasted high activity and heteroselectivity (P_r = 0.90 {20 °C, 20 minutes}).[14b, c] Abbina and Du have reported a series of chiral amido-oxazolinates which featured a three coordinate Zn(II) centre.[14a] At room temperature, isotactic PLA (P_m = 0.91) is produced albeit at a low rate. There are also several examples of monophenolato Zn(II) complexes that demonstrate high activity and selectivity. Darensbourg and Karroonnirun have prepared imino phenolato complexes which have a heterotactic preference (P_r = 0.83 - 0.89).[14d] Ma et al have trialled several aminophenolato Zn(II) complexes with regio- and diastereomeric characteristics.[14i, j, 14p, 15] Both heterotactic (P_r < 0.61) and isotactic (P_m < 0.92) PLA resulted from these systems. Their latest work is notable for high activity and success for the immortal ROP.[14p] More recently, Kol et al have employed [ONNN] Zn(II) complexes which also demonstrated high activity and a marked isoselectivity (P_m = 0.81).[14h] For the preparation of asymmetrical salalens, a common method is the selective protection of a diamine to allow for sequential reaction of the amine functionality.[12, 16] This methodology has been used here to prepare monophenol ligands based on DACH. One set of ligands incorporates the Boc protecting group as a structural feature. Subsequent complexes with Al(III) and Zn(II) is discussed followed by their application to the ROP of *rac*-LA.

Results and Discussion

All ligands are derived from monoprotected *trans*-diaminocyclohexane which was prepared using di-*tert*-butyl dicarbonate (Boc anhydride) (See ESI). The free primary amine was then reacted with substituted salicylaldehydes yielding imino ligands **1**-**3**H which maintain the Boc group (Figure 1). Ligands **4**-**6**H were prepared from **1**-**3**H via a series of processes including reduction/methylation and deprotection (Figure 2). **4**-**6**H feature a methylated amine and imine functionality. All ligands were fully characterised via ^{1}H/^{13}C{^{1}H} NMR spectroscopy, ESI mass spectrometry, and for **1/6**H, the solid-state structure was further elucidated via X-ray diffraction (See ESI).

[a] Doctoral Training Centre in Sustainable Chemical Technologies, University of Bath, Bath, BA2 7AY, UK.
[b] Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK. E-mail: mj205@bath.ac.uk or p.mckeown@bath.ac.uk ; Fax: +44 (0)1225 386231; Tel: +44 (0)1225 384908.
[c] Department of Pharmacy and Pharmacology, University of Bath, Claverton Down, Bath, BA2 7AY, UK

Supporting information for this article is given via a link at the end of the document. Supporting information contains all the data necessary for this paper.

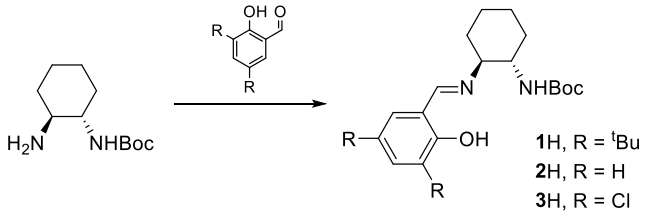

Figure 1. Preparation of ligands *trans*-**1**-**3**H. All ligands are racemic.

The products of the complexation of **1**-**3**H with Al(III) were fully characterised in solution by multi-nuclear NMR spectroscopy and in the solid state via X-ray crystallography and elemental analysis. The reaction of **1**-**3**H with Al(III) afforded two distinct coordination modes depending on the nature of the aryl substituents (Figure 3). The coordination of **1**H, with ^{t}Bu aryl substituents, yielded a four coordinate aluminium complex, Al(**1**)Me_2, as shown by X-ray crystallography. For this structure, the ligand binds in a bidentate fashion through the phenoxy and imino groups with a strong bias towards a tetrahedral geometry (τ_4 = 0.91). As for all subsequent crystal structures involving **1**-**3**H, the NH group of the amide is intact. The solid-state structure is retained in solution as evidenced by the ^{1}H/^{13}C{^{1}H} NMR spectra with the amide NH present in the ^{1}H NMR spectrum. In contrast, reaction of **2**H, with an unsubstituted aryl group, preferentially yielded a bis-ligated species irrespective of the ligand-to-metal stoichiometry employed. The solid-state structure of Al(**2**)$_2$Me reveals a five coordinate Al(III) centre with a preference for a trigonal bipyramidal geometry (τ_5 = 0.85). Within this geometry, the imino groups occupy axial positions {N(1)-Al-N(3) = 174.53(6)°} and the two phenoxy groups equatorial positions {O(1)-Al-O(2) = 126.47(12)°}. The difference in coordination for **1**H and **2**H is undoubtedly related to the relative steric contribution for each ligand set. Ligand **3**H (R = Cl) has a steric bulk that is intermediate to that of **1**H and **2**H; it was therefore possible to isolate both Al(**3**)Me_2 and Al(**3**)$_2$Me (Figure 4). For Al(**3**)Me_2, a tetrahedral geometry is observed for the solid-state structure with similar metrics to that of Al(**1**)Me_2 (τ_4 = 0.92). The NMR spectra are also consistent with the solid-state structure being maintained in solution. The trigonal bipyramidal geometry of Al(**3**)$_2$Me, however, is subject to greater distortion relative to Al(**2**)$_2$Me (τ_5 = 0.71), likely caused by the presence of the Cl substituents.

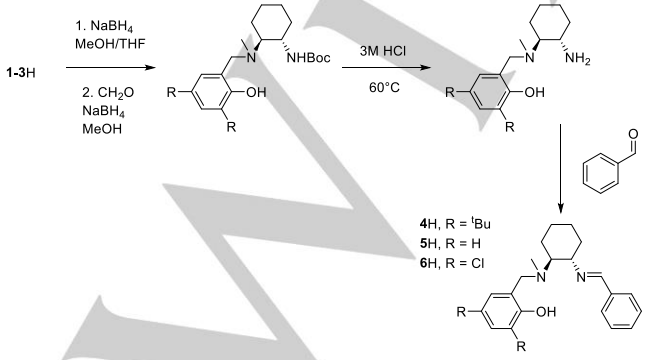

Figure 2: Preparation of ligands *trans*-**4**-**6**H. All ligands are racemic.

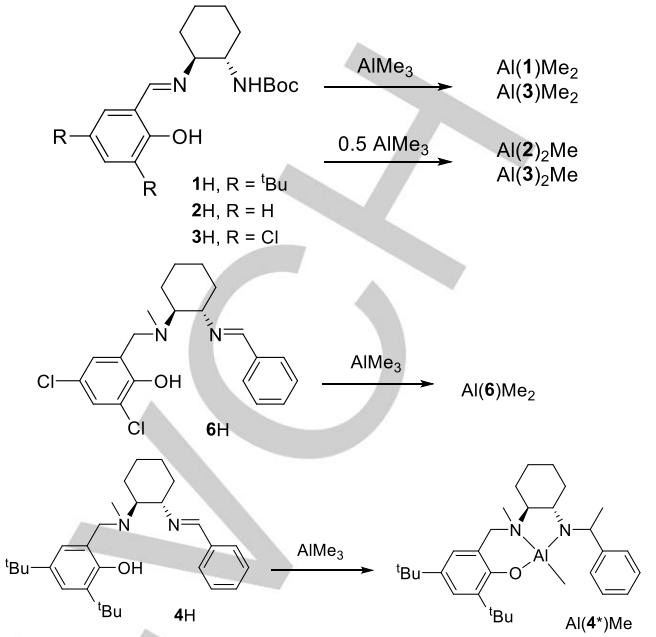

Figure 3. Complexation of **1**-**3**H and **4**/**6**H with Al(III).

This distortion is exemplified by a greater deviation of the angle at the metal involving the axial ligands from ideality {N(1)-Al-N(1#) = 168.91(11)°}. The bis-ligated complexes, Al(**2**)$_2$Me and Al(**3**)$_2$Me, have poor solubility in common NMR solvents. Further evidence of structure and purity comes from elemental analysis which are both in good agreement with the theoretical values. The corresponding methylated ligand, **6**H, successfully formed a complex with Al(III) (Figure 3). The solid state structure for Al(**6**)Me_2 revealed a four coordinate aluminium centre with the imino nitrogen not participating in bonding (Figure 5). Similar to Al(**3**)Me_2, there is a strong preference towards a tetrahedral geometry (τ_4 = 0.91) with bond lengths and angles also being similar. There is however a discernible difference in the nitrogen-to-metal centre bond which is relatively lengthened for the amino coordination {Al-N(1) = 2.035(2) Å}. Despite being low intensity due to poor solubility, the ^{1}H NMR spectra for Al(**6**)Me_2 conforms to that expected from the solid-state structure. The bulk sample also conforms to the expected formula as measured by elemental analysis. Complexation of **4**H under analogous conditions caused a methyl migration to yield Al(**4***)Me (Figure 3). To generate this compound, an aluminium-bound methyl group has inserted into the imino bond formally creating an anionic nitrogen centre. Such a migration has been observed previously for similar Al(III) systems and the rearrangement is often triggered through heating.[17] For the solid-state structure, a distorted tetrahedral geometry (τ_4 = 0.86) is observed (Figure 5). The formally anionic nitrogen centre has a shorter bond distance to the aluminium centre compared to that involving the neutral nitrogen centre {Al-N(1) = 2.0012(10) Å; Al-N(2) = 1.8204(10) Å }.

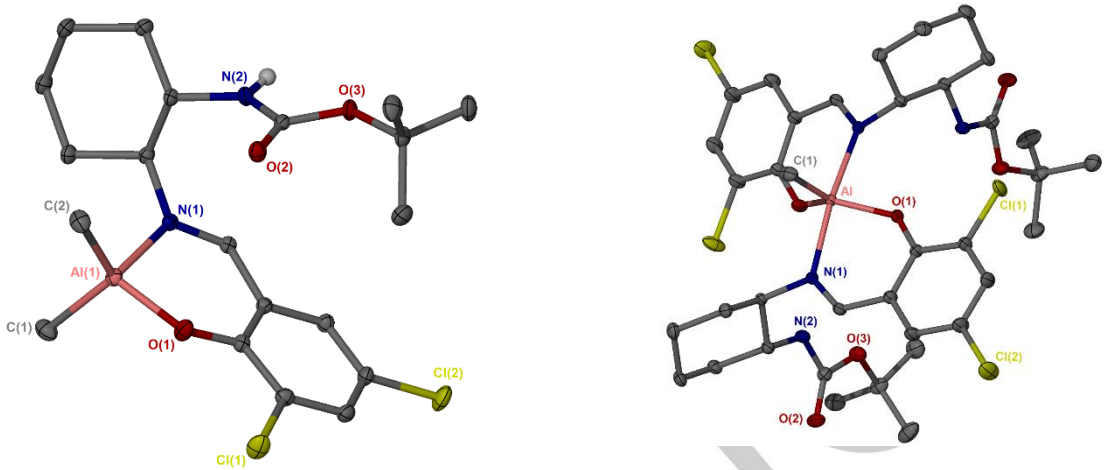

Figure 4. Solid-state structure of Al(**3**)Me_2 (left) and Al(**3**)$_2$Me (Right). Hydrogen atoms have been removed for clarity. Ellipsoids are shown at the 30 % probability level. Selected bond lengths (Å) and angles (°), Al(**3**)Me_2: Al-O(1) 1.784(1), Al-N(1) 1.980(1), Al-C(1) 1.961(2), Al-C(2) 1.952(2); O(1)-Al-C(1) 111.26(7), O(1)-Al-N(1) 94.67(5), N(1)-Al-C(1) 108.40(6). Al(**3**)$_2$Me: Al-O(1) 1.803(2), Al-N(1) 2.090(2), Al-C(1) 1.969(4); O(1)-Al-O(1) 126.47(12), O(1)-Al-C(1) 116.76(6), O(1)-Al-N(1) 88.36(7), N(1)-Al-N(1) 168.91(11).

Concomitantly, carbon- nitrogen bond distance was noted to increase, becoming more comparable to a single bond {N(2)-C(24) = 1.4595(15) Å}. The ^{1}H NMR spectrum is consistent with the solid-state structure having no imine resonance, a new doublet assignable to the migrated methyl group and one upfield resonance due to the Al-Me group. Successful complexation to Zn(II) was achieved with **2-3**H and **5**-**6**H (Figure 6). Similar to the Al(III) complexes, both monoligated and bisligated species could be selectively isolated by varying the reaction stoichiometry. Zn(**2**)$_2$ and Zn(**3**)$_3$ were prepared through addition of half an equivalent of $ZnMe_2$ and the solid state structures characterised by X-ray crystallography {for Zn(**3**)$_2$, Figure 7}. For these complexes, a four coordinate Zn(II) centre is observed with no bonding contribution from the NHBoc group. Both structures adopt a distorted tetrahedral geometry (τ_4 = 0.80 and τ_4 = 0.85 respectively). Due to poor solubility, the resultant ^{1}H NMR spectra are broad but diagnostic with the absence of resonances attributable to Zn-Me and –OH groups. For Zn(**2**)$_2$ and Zn(**3**)$_2$, elemental analysis also conforms to the chemical formulae. For **2**H, the Zn-Me species was successfully isolated. Structural characterisation of Zn(**2**)Me was achieved through ^{1}H/^{13}C{^{1}H} NMR spectroscopy which showed a Zn-Me resonance which integrates to ligand resonances on a 1:1 basis and a resonance due to the amide NH. It is assumed, based on the related Zn(II) structures of **5/6**H, that the geometry of Zn(**2**)Me is also tetrahedral with the nitrogen centre of the NHBoc group coordinated to the metal centre. The successful formation of Zn(**5**)Me and Zn(**6**)Me was consolidated via X-ray crystallography {for Zn(**6**)$_2$, Figure 7}. Unlike Al(**6**)Me_2, the imine nitrogen is observed to coordinate to the Zn(II) centre to give a distorted tetrahedral geometry (τ_4 = 0.81 and τ_4 = 0.84 respectively).

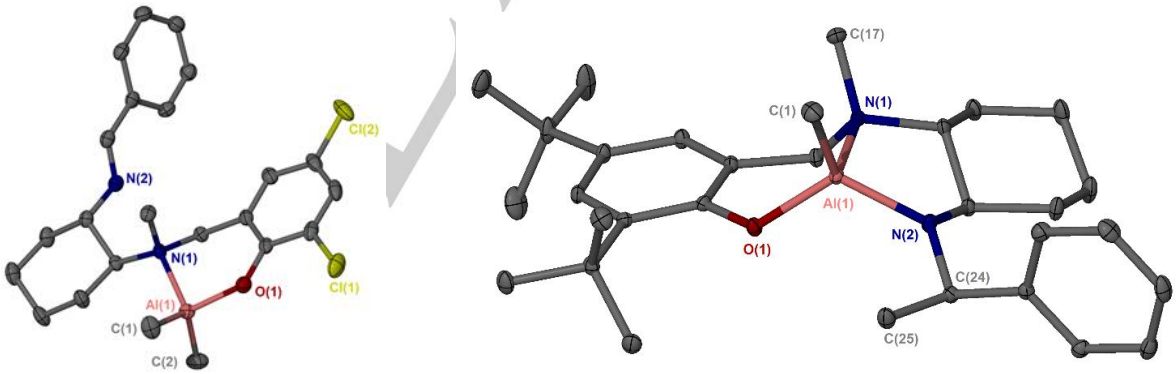

Figure 5. Solid-state structure of Al(**6**)Me_2 (left) and Al(**4***)$_2$Me (Right). Hydrogen atoms have been removed for clarity. Ellipsoids are shown at the 30 % probability level. Selected bond lengths (Å) and angles (°), Al(**6**)Me_2: Al-O(1) 1.775(1), Al-N(1) 2.035(2), Al-C(1) 1.958(2), Al-C(2) 1.955(2); O(1)-Al-C(1) 109.07(8), O(1)-Al-N(1) 95.94(6), N(1)-Al-C(1) 111.83(7). Al(**4***)Me: Al-O(1) 1.766(1), Al-N(1) 2.001(1), Al-N(2) 1.850(1), Al-C(1) 1.951(1); O(1)-Al-C(1) 110.30(5), O(1)-Al-N(1) 99.17(4), O(1)-Al-N(2) 118.21(4), N(1)-Al-N(2) 90.15(5).

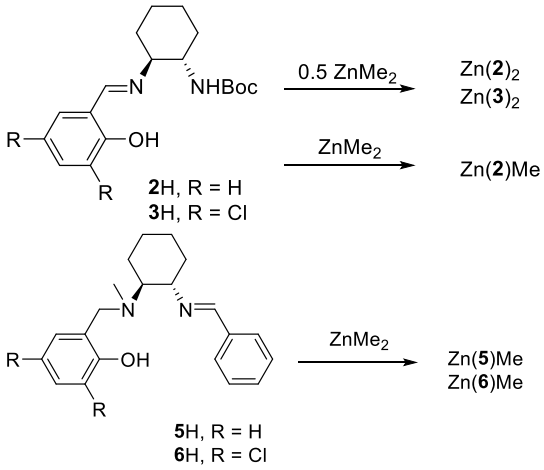

Figure 6. Complexation of **2-3**H and **5**-**6H** with Zn(II).

In solution, however, multiple species are present in the NMR spectrum. For Zn(**5**)Me, there are two series at a ratio of 3:1 and for Zn(**6**)Me, at 5:1. Both series contain similar features including a Zn-Me and imine resonance and DOSY NMR analysis of Zn(**5**)Me indicates the two species diffuse at the same rate (D = 8.9×10^{-10} m^2s^{-1}). Within the structure of Zn(**5/6**)Me, there are four points of chirality (See ESI) and it is therefore proposed that the two species present in solution are diastereomers. Unlike, Zn(**2**)Me, which features an coordinating imino functionality, Zn(**5/6**)Me have an amino group. On coordination, this presents a new stereocentre, thereby augmenting the chiral centres of the cyclohexane ring. In addition, due to coordination of the imino nitrogen, the zinc centre also possesses stereochemistry; in the solid state structure, a configuration of *SRSS* (ZnNCC) is observed and other diastereomeric configurations are anticipated (e.g. *RRSS*). It is noted that complexation was carried out at room temperature and it may be possible to adjust the ratio of diastereomeric species by changing the temperature.

All complexes were trialled for the ROP of *rac*-LA using doubly sublimed monomer (Tables 1 & 2).The conditions used are dependent on the identity of the metal with the Zn(II) complexes generally requiring shorter reaction times and lower temperatures to reach high conversion. For the majority of polymerisations, benzyl alcohol was added to allow for efficient initiation of the polymerisation, likely via a coordination insertion mechanism. Polymerisations carried out with Al(III) complexes are shown in Table 1. For the mono-ligated Boc protected complexes, Al(**1/3**)Me_2, high conversion was achieved after two days at 80°C in toluene. None of the complexes exerted stereocontrol over the polymerisation giving atactic PLA. Al(**3**)Me_2 appeared to have a higher activity compared to Al(**1**)Me_2, attaining a higher conversion in the same time frame. These observations may be related to the relative steric bulk between complexes (^{t}Bu *vs.* Cl) as well as a more Lewis acidic Al(III) centre for Al(**3**)Me_2. This complex also appeared to have greater molecular weight control as indicated by the lower dispersity (Đ = 1.08 *vs*. 1.24) however the observed molecular weight was lower than expected based on conversion. Analysis of the resultant polymer by MALDI-ToF mass spectrometry (See ESI) revealed a symmetrical distribution for the polymer derived from Al(**1**)Me_2 with a lower molecular weight compared to GPC analysis (which is relative to polystyrene) (M_n = 5,750). A degree of undesired transesterification is indicated by the presence of a second series with spacing of 72 Da. Both series have BnO- and H- end groups as predicted by the coordination-insertion mechanism. Analysis of polymer derived from Al(**3**)Me_2 gave a broader, less symmetrical MALDI-ToF spectrum. The main series has a peak separation of 72 Da indication the operation of side reactions but maintains the expected BnO-/-H end groups. At lower molecular weight, there is overlap of a third series which can be attributed to cyclic PLA. This could be caused by intramolecular “back-biting”.For the bis-ligated Boc protected complexes, Al(**2/3**)$_2$Me, high conversion could be achieved in 24 hours. Chloro substituents enabled a faster polymerisation compared to the unsubstituted aryl group despite a reduction in steric bulk for the latter. This is, again, likely related to the increased complex Lewis acidity similar to that seen for Al(**3**)Me. For both Al(**2/3**)$_2$Me, the polymer is observed to have lower molecular weight than that predicted by conversion (Table 1).

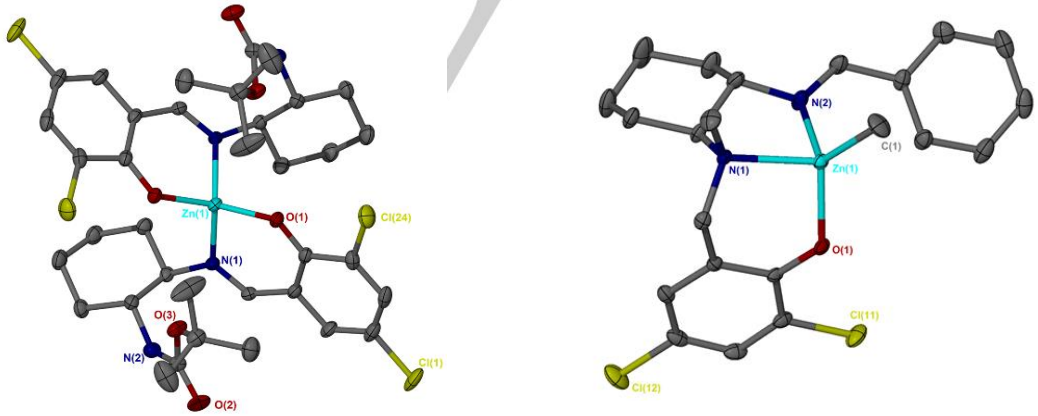

Figure 7. Solid-state structure of Zn(**3**)$_2$ (left) and Zn(**6**)Me (Right). Hydrogen atoms have been removed for clarity. Ellipsoids are shown at the 30 % probability level. Selected bond lengths (Å) and angles (°), Zn(**3**)$_2$: Zn-O(1) 1.905(2), Zn-N(1) 2.016(3); O(1)-Zn-O(1) 124.21(18), O(1)-Zn-N(1) 96.67(12), O(1)-Zn-N(1)# 12.17(12), N(1)-Zn-N(1) 116.34(18). Zn(**6**)Me: Zn-O(1) 1.951(2), Zn-N(1) 2.140(3), Zn-N(2) 2.169(3), Zn-C(1) 1.978(5); O(1)-Zn-C(1) 123.88(18), O(1)-Zn-N(1) 94.7(1), N(1)-Zn-C(1) 123.8(2) N(2)-Zn-C(1) 123.8(2) N(1)-Zn-N(2) 81.2(2).

Table 1: Polymerisations of *rac*-LA with A(III) complexes

Initiator	Conv. (%)[a]	Time (days)	P_r[b]	$M_{n\ theo}$[c]	M_n[d]	Đ[d]
Al(**1**)Me_2	75	2	0.50	10,900	12,800	1.24
Al(**3**)Me_2	97	2	0.49	14,100	7,600	1.08
Al(**2**)$_2$Me	87	1	0.45	12,650	10,800	1.20
Al(**3**)$_2$Me	94	1	0.49	13,650	9,700	1.16
Al(**6**)Me_2	83	1	0.58	12,050	19,050	1.05

Conditions: 80°C, Toluene, [LA]:[BnOH]:[Al] = 100:1:1. [a] Determined via ^{1}H NMR spectroscopy [b] P_r is the probability of heterotactic enchainment, determined via homonuclear decoupled ^{1}H NMR spectroscopy. [c] Theoretical molecular weight calculated from conversion {[LA]/[BnOH] × (Conv. × 144.13) + 108.14} (rounded to the nearest 50). [d] Determined from GPC (in THF) referenced against polystyrene standards.

Analysis of polymer derived from Al(**3**)$_2$Me by MALDI-ToF mass spectrometry revealed a major and minor series with a separation of 72 Da suggesting undesirable transesterification reactions are occurring. These series were determined to have BnO- and -H end groups as expected by the coordination insertion mechanism. A third distribution is also seen at lower molecular weight and this is found to contain series of cyclic PLA and polymer with MeO-/-H or BnO-/-H end groups. The polymerisation of *rac*-LA with Al(**6**)Me_2 was found to be faster than the related complex Al(**3**)Me_2, requiring one day to attain high conversion. The resultant polymer had a narrow dispersity (Đ = 1.05) with the molecular weight observed to be high (M_n = 19,050), again atactic PLA is produced. The Zn(II) complexes were tested under a range of conditions with temperature, co-initiator addition and solvent being varied (Table 2). Both Zn(**2/3**)$_2$ were found to be active for the bulk polymerisation of *rac*-LA at 130°C. These reactions were carried out in the absence of co-initiator and reached moderate conversions within one hour. Due to the absence of aryl substituents, Zn(**2**)$_2$ was observed to be four times more active compared to Zn(**3**)$_2$, which contains four chloro substituents. PLA of relatively high molecular weight is obtained (M_n = 90,500 – 149,000) with initiation of the polymerisation likely being caused by low concentration of impurities in the monomer feed. In the absence of a classical initiating group on the metal centre, it is suggested that polymerisation with Zn(**2/3**)$_2$ proceed via an activated monomer mechanism (See ESI). Under these conditions, PLA derived from Zn(**2**)$_2$ has a slight heterotactic bias (P_r = 0.65). Zn(**2/3**)$_2$ were also trialled in solution. In the first instance, polymerisation at 80°C in toluene afforded moderate conversion after 4 hours with Zn(**2**)$_2$ ([LA]:[BnOH]:[Zn] = 200:1:1); however the measured molecular weight was much lower than expected. Better results were achievable with Zn(**3**)$_2$ at this temperature albeit at a higher initiator loading ([LA]:[BnOH]:[Zn] = 100:1:1). For this initiator, high conversion was achieved after 1 hour and good molecular weight control is demonstrated (Đ = 1.12) A slight heterotactic preference is also exerted by this initiator (P_r = 0.64). MALDI-ToF analysis of PLA derived from Zn(**3**)$_2$ is consistent with the molecular weight observed via GPC (M_p = 11,515). The end groups are found to be BnO- /-H as

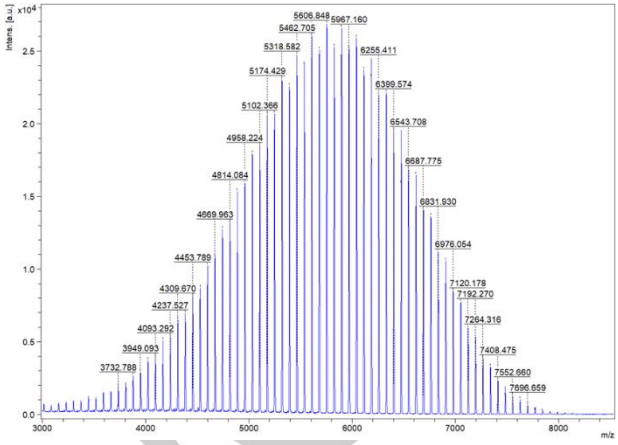

Figure 8. Representative MALDI-ToF spectra of polymer derived from Al(**1**)Me_2.

expected and there is a peak separation of 144 Da for this series. However, there is also a small series, at lower molecular weight, with a peak spacing of 72 Da indicating a degree of undesirable transesterifcation for this sample. For Zn(**2**)$_2$, more control was achieved by carrying out polymerisations at 40°C albeit with an increase in polymerisation time. Under these conditions, the effect of varying the amount of co-initiator was tested. For all polymerisations, there is a good control of the molecular weight distribution (Đ = 1.10 –1.11) and a clear decrease in chain size with increasing benzyl alcohol concentration.

Table 2. Polymerisations of *rac*-LA with Zn(II) complexes

Initiator	Time (h)	BnOH	Conv. (%)[f]	P_r[g]	$M_{n\ theo}$[h]	M_n[i]	Đ[i]
Zn(**2**)$_2$[a]	0.25	0	53	0.65	15,300	90,500	1.36
Zn(**2**)$_2$[b]	4	1	61	0.58	17,700	8,700	1.12
Zn(**2**)$_2$[c]	18	1	75	0.66	21,700	38,900	1.10
Zn(**2**)$_2$[c]	18	2	93	0.64	13,500	21,700	1.11
Zn(**2**)$_2$[c]	18	4	92	0.67	6,750	15,350	1.11
Zn(**2**)Me[d]	120	1	77	0.60	11,200	5,400	1.19
Zn(**3**)$_2$[a]	1	0	46	0.56	13,250	149,100	1.28
Zn(**3**)$_2$[d]	1	1	85	0.64	12,250	16,350	1.12
Zn(**5**)Me[e]	1	1	98	0.63	14,250	11,950	1.35
Zn(**6**)Me[e]	1	1	97	0.65	14,100	16,950	1.15

Conditions: [a] 130°C, [LA]:[Zn] = 200:1, [b] 80°C, Toluene, [LA]:[BnOH]:[Zn] = 200:1:1, [c] 40°C, Toluene, [LA]:[BnOH]:[Zn] = 200:x:1, [d] 80°C, Toluene, [LA]:[BnOH]:[Zn] = 100:1:1, [e] 20°C, Toluene, [LA]:[BnOH]:[Zn] = 100:1:1. [f] Determined via ^{1}H NMR spectroscopy. [g] P_r is the probability of heterotactic enchainment, determined via homonuclear decoupled ^{1}H NMR spectroscopy. [h] Theoretical molecular weight calculated from conversion {[LA]/[BnOH] × (Conv. × 144.13) + 108.14} (rounded to the nearest 50). [i] Determined from GPC (in THF) referenced against polystyrene standards.

A heterotactic preference is also observed under these condition (P_r = 0.64 – 0.67). Analysis of the lowest molecular weight polymer derived from Zn(**2**)$_2$ {[LA]:[BnOH]:[Zn] = 200:4:1, M_n = 15,350} by MALDI-ToF showed a symmetrical distribution with a peak separation of 144 Da suggesting minimal transesterification for this series. The molecular weight observed by MALDI-ToF (M_p = 8,056) is comparable to the theoretical molecular weight based on conversion ($M_{n\ theo}$ = 6,750). However, there is also an overlapping series at low molecular weight which has a peak separation of 72 Da, suggesting the operation of undesirable side reactions. For both series, the expected end groups of BnO- and –H are indicated. The corresponding zinc methyl species, Zn(**2**)Me, was tested in toluene at 80°C. Compared to the bis-ligated complexes, Zn(**2**)Me was observed to be much less active requiring 5 days to achieve appreciable conversion at 80°C ([LA]:[BnOH]:[Zn] = 100:1:1). There is a mild heterotactic preference for this initiator (P_r = 0.60). Despite having narrow dispersity (Đ = 1.19), the molecular weight of the polymer is lower than expected. MALDI-ToF analysis shows there are two observable distributions within this polymer sample. The lowest molecular weight distribution (M_p = 2,436) is symmetrical with a repeat unit of 144 Da suggesting a lack of side reactions for this distribution. End group analysis suggests the presence of the expected BnO- and –H moieties. The second distribution is at higher molecular weight and less intense (M_p = 4940) and two distinct series can be observed both of which have a peak separation of 72 Da. One series is observed to have HO- and –H end groups while the second is capped with either MeO-/-H or ligand **2**H. The Zn(II) complexes based upon **5**/**6**H were trialled under identical conditions to Zn(**2**)Me and these were found to be much more active. High conversion is reached within 1 hour for Zn(**5**/**6**)Me and there is a measureable heterotactic preference once more (P_r = 0.61 – 0.65). The conversion for these complexes was achieved with no clear dependence on the aryl substituents. However, Zn(**6**)Me, which has chloro substituents was observed to exert more control over molecular weight and dispersity relative to the unsubstituted complex, Zn(**5**)Me.

Conclusions

A series of monophenol diaminocyclohexyl ligands have been prepared and complexed to Al(III) and Zn(II). Depending on aryl substituents a preference for mono- or bis- ligation could be observed. The complexation of **4**H to Al(III) resulted in a methyl migration to give a dianionic ligand-complex. For Zn(**5**/**6**)Me, a mixture of diastereomers was observed in solution as a consequence of increased nitrogen coordination. These samples were generally found to be active for the ROP of *rac*-lactide. The Al(III) complexes required 24 to 48 hours to achieve high conversion and produce PLA of reasonable molecular weight. In comparison, the Zn(II) complexes were found to be more active, with the exception of Zn(**2**)Me. There was a slight preference for heterotactic PLA on application of the Zn(II) complexes.

Experimental Section

General methods

All chemicals used were purchased from Sigma Aldrich and used as received with the exception of *rac*-lactide. *rac*-LA was recrystallised from dry toluene and doubly sublimed prior to use. The preparation and characterisation of all metal complexes was carried out under inert argon atmosphere using standard Schlenk or glovebox techniques. Dry solvents used in handling metal complexes were obtained via SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 300, 400 or 500 MHz instrument and referenced to residual solvent resonances. $CDCl_3$ was dried over CaH_2 prior to use with metal complexes. C_6D_6 and d_8-toluene were degassed and stored over molecular sieves for use with metal complexes. All ligands were characterised by electron-spray ionisation-mass spectrometry (ESI-MS) in positive mode. CHN microanalysis was performed by Mr. Stephen Boyer of London Metropolitan University. All crystallographic data was collected on a SuperNova, EOS detector diffractometer using radiation CuKα (λ= 1.54184 Å) or Mo-Kα (λ= 0.71073 Å) or a Nonius kappa diffractometer using Mo-Kα (λ= 0.71073 Å) all recorded at 150(2) K. All structures were solved by direct methods and refined on all F^2 data using the SHELXL-2014 suite of programs. All hydrogen atoms were included in idealized positions and refined using the riding model. All crystallographic data were collected at 150(2)K either on a SuperNova, Dual, EosS2 diffractometer using radiation Cu-K$_\alpha$ (λ= 1.54184 Å) or Mo-K$_\alpha$ (λ= 0.71073 Å) or on a Nonius Kappa CCD diffractometer using Mo-K$_\alpha$ (λ= 0.71073 Å) radiation, see ESI for data and refinement details. All structures were solved by direct methods followed by full-matrix least squares refinement on F^2 using the WINGX-2014 suite of programs.[18] All hydrogen atoms were included in idealized positions and refined using the riding model.

Polymerisation methods

Polymerisations were carried out in a Young's ampoule under inert argon conditions. For a typical solution based polymerisation, *rac*-lactide (1.0 g, 0.69 mmol) was dissolved in dry toluene (10 ml) with the required amount of initiator. When required, a benzyl alcohol co-initiator was added. The ampoule was then placed in a preheated oil bath and stirred for the set time. After polymerisation, reaction was quenched by addition of a few drops of MeOH and solvent was removed in vacuo and a crude ^{1}H NMR recorded. The polymer was then purified by washing with methanol and dried in vacuo. For solvent free polymerisations, reaction was carried out at 130 °C. After polymerisation, the residue was dissolved in CH_2Cl_2 and a few drops of MeOH were added to quench the polymerisation. solvent was removed in vacuo and a crude ^{1}H NMR recorded. The polymer was then purified by washing with methanol and dried in vacuo.

All purified polymers were characterised by a combination of gel permeation chromatography (GPC) and homonuclear decoupled ^{1}H NMR spectroscopy. GPC was carried out at 1 ml min^{-1} at 35 °C with a THF eluent using a PLgel 5 µm MIXED-D 300 × 7.5 mm column. The system was referenced against 11 narrow molecular weight standards polystyrene standards with detection via refractive index response. Polymer tacticity was determined via ^{1}H NMR spectroscopy ($CDCl_3$) analysis of the homonuclear decoupled methine region utilizing the relationships demonstrated by Coates et al.[14b] MALDI-ToF mass spectra were determined on a Bruker Autoflex speed instrument using DCTB (trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile) as the matrix and ionized using NaTFA. Spectra were recorded in reflector-positive mode.

Ligand synthesis

1-**3**H: *tert*-butyl (2-aminocyclohexyl)carbamate (1 eq) was dissolved in methanol (25 mL) and a solution of substituted salicylaldehyde (1 eq) in methanol (25 mL) was added. The resultant precipitate was filtered and washed with methanol (3 x 10 mL) to yield the product

1H: 3,5-Di-*tert*-butyl-2-hydroxybenzaldehyde (6.30 mmol). Yellow solid (1.83 g, 4.24 mmol, 67 %).^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.08 - 1.26 (m, 2 H, CH_2) 1.31 (s, 18 H, $C(CH_3)_3$) 1.44 (s, 9 H, $C(CH_3)_3$) 1.63 - 1.84 (m, 4 H, CH_2) 1.90 (d, *J*=10.3 Hz, 1 H, CH_2) 2.09 (d, *J*=10.3 Hz, 1 H, CH_2) 3.08 (s, 1 H, CH) 3.53 - 3.65 (m, 1 H, CH) 4.39 (br. s, 1 H, NH) 7.09 (s, 1 H, Ar-H) 7.37 (d, *J*=2.5 Hz, 1 H, Ar-H) 8.38 (s, 1 H, N=CH) 13.48 (br. s, 1 H, OH).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm 24.1 (CH_2) 24.8 (CH_2) 28.1 (C(**C**H_3)$_3$) 29.4 (C(**C**H_3)$_3$) 31.5 (C(**C**H_3)$_3$) 33.5 (**C**$(CH_3)_3$) 34.1 (**C**$(CH_3)_3$) 35.0 (CH_2) 54.4 (O-**C**$(CH_3)_3$) 72.3 (CH) 79.3 (CH) 117.8 (Ar-H) 125.9 (Ar-C) 126.7 (Ar-C) 136.6 (Ar-H) 139.8 (Ar-C) 155.2 (Ar-OH) 158.0 (N=CH) 165.2 (C=O). m/z $[C_{26}H_{42}N_2O_3 + H]^+$ Calculated: 431.3274 gmol^{-1} Found: 431.3268 gmol^{-1}

2H: Salicylaldehyde (11.7 mmol). Yellow solid (2.89 g, 9.07 mmol, 77 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.29 (s, 9 H, $C(CH_3)_3$) 1.32 - 1.51 (m, 3 H, CH_2) 1.61 - 1.73 (m, 1 H, CH_2) 1.73 - 1.85 (m, 2 H, CH_2) 1.85 - 1.94 (m, 1 H, CH_2) 2.02 - 2.14 (m, 1 H, CH_2) 3.05 (br. s, 1 H, CH) 3.57 (d, *J*=1.0 Hz, 1 H, CH) 4.36 (br. s, 1 H, NH) 6.86 (td, *J*=7.5, 1.0 Hz, 1 H, Ar-H) 6.95 (d, *J*=8.3 Hz, 1 H, Ar-H) 7.23 (dd, *J*=7.7, 1.6 Hz, 1 H, Ar-H) 7.26 - 7.32 (m, 1 H, Ar-H) 8.33 (s, 1 H, N=CH) 13.28 (br. s, 1 H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm 23.9 (CH_2) 24.7 (CH_2) 28.1 (C(**C**H_3)$_3$) 31.4 (CH_2) 33.2 (CH_2) 54.2 (O-**C**$(CH_3)_3$) 72.3 (CH) 79.2 (CH) 117.0 (Ar-H) 118.4 (Ar-H) 118.7 (Ar-H) 131.3 (Ar-H) 132.2 (Ar-C) 155.1 (Ar-OH) 161.2 (N=CH) 164.0 (C=O). m/z $[C_{18}H_{26}N_2O_3 + H]^+$ Calculated: 319.2022 gmol^{-1} Found: 319.2007 gmol^{-1}.

3H: 3,5-di-chloro-salicylaldehyde (9.69 mmol). Yellow solid (2.20 g, 5.70 mmol, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.31 (s, 9 H, $C(CH_3)_3$) 1.36 - 1.51 (m, 2 H, CH_2) 1.53 - 1.72 (m, 2 H, CH_2) 1.73 - 1.87 (m, 2 H, CH_2) 1.93 (d, *J*=9.8 Hz, 1 H, CH_2), 2.06 (d, *J*=8.8 Hz, 1 H, CH_2) 3.24 (s, 1 H, CH) 3.54 (d, *J*=7.8 Hz, 1 H, CH) 4.43 (br. s, 1 H, NH) 7.13 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.39 (d, *J*=2.5 Hz, 1 H, Ar-H) 8.24 (s, 1 H, CH=N) 14.41 (br. s, 1 H, OH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm 23.7 (CH_2) 24.5 (CH_2) 28.1 (C(**C**H_3)$_3$) 31.2 (CH_2) 32.7 (CH_2) 53.8 (O-**C**$(CH_3)_3$) 70.8 (N-CH), 79.4 (N-CH) 119.1 (Ar-H) 121.8 (Ar-H) 123.1 (Ar-C) 128.9 (Ar-Cl) 132.2 (Ar-Cl) 155.0 (Ar-OH) 157.6 (N=CH) 162.4 (C=O). m/z $[C_{18}H_{24}Cl_2N_2O_3 + H]^+$ Calculated: 387.1242 gmol^{-1} Found: 387.1234 gmol^{-1}.

4-**6**H: **1**/**2**/**3**H (1 eq) was dissolved in THF (30 mL) and methanol (10 mL) and sodium borohydride (0.18 g, 4.64 mmol) was slowly added and stirred for 1 hour. The reaction was quenched with water (10 mL) and the solvent was partially removed in vacuo until some precipitate formed. Water (50 mL) was added to precipitate the rest of the product which was filtered and washed with water (3 × 10mL). The white solid was dissolved in ethanol (50 mL) and formaldehyde (38 % in H_2O, 3 in vacuo eq) was added and allowed to stir for 1 hour. The solvent was removed and the solid redissolved in THF (30 mL) and methanol (30 mL) and cooled to 0 °C. Sodium borohydride (1 eq) was slowly added and the solution stirred for 1 hour. The reaction was quenched with water (10 mL) and the solvent partially removed in vacuo. Water (50 mL) was added to precipitate the product which was filtered and washed with water (3 × 10 mL). The white solid was dissolved in methanol (30 mL) and 3 M HCl then heated to 60 °C and stirred overnight. The mixture was neutralised with 3 M NaOH and the purple oil extracted with ethyl acetate (3 × 30 mL). The organic phase was washed with brine (20 mL) and dried with $MgSO_4$. The solution was filtered and the solvent removed in vacuo. The residue was dissolved in methanol (30 mL) and an small excess of benzaldehyde (2-3 eq) was added. A precipitate formed after 1 hour, which was filtered and washed with cold methanol (3 × 10 mL) to yield the product.

4H: From **1**H (4.64 mmol). White solid (0.65 g, 1.49 mmol, 32 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.22 (s, 9 H, $C(CH_3)_3$) 1.28 (s, 9 H, $C(CH_3)_3$) 1.38 - 1.46 (m, 3 H, CH_2) 1.73 - 1.88 (m, 3 H, CH_2) 1.88 - 1.96 (m, 1 H, CH_2) 2.00 (d, *J*=9.5 Hz, 1 H, CH_2) 2.14 (s, 3 H, N-CH_3) 3.05 - 3.17 (m, 1 H, CH) 3.26 - 3.36 (m, 1 H, CH) 3.78 (d, *J*=13.3 Hz, 1 H, N-CH_2) 3.91 (d, *J*=12.6 Hz, 1 H, N-CH_2) 6.81 (d, *J*=2.01 Hz, 1 H, Ar-H) 7.15 (d, *J*=2.3 Hz, 1 H, Ar-H) 7.40 - 7.46 (m, 3 H, Ar-H) 7.85 - 7.90 (m, 2 H, Ar-H) 8.35 (s, 1 H, N=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm 24.8 (CH_2), 25.2 (CH_2), 29.3 (C(**C**H_3)$_3$), 31.7 (C(**C**H_3)$_3$), 34.0 (**C**$(CH_3)_3$), 34.6 (CH_2), 34.6 (**C**$(CH_3)_3$), 67.4 (N-CH_3), 70.8 (N-CH_2), 121.2 (Ar-C), 122.5 (Ar-H), 123.1 (Ar-H), 128.3 (Ar-H), 128.6 (Ar-H), 130.4 (Ar-H), 135.4 (Ar-C), 136.3 (Ar-C), 139.6 (Ar-C), 154.8 (Ar-OH), 160.9 (N=CH). m/z $[C_{29}H_{42}N_2O + H]^+$ Calculated: 435.3331 gmol^{-1} Found: 435.3505 gmol^{-1}.

5H: From **2**H (10.30 mmol). White solid (0.338 g, 1 mmol, 10 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.32 - 1.50 (m, 3 H, CH_2) 1.66 - 1.74 (m, 2 H, CH_2) 1.80 (d, *J*=5.5 Hz, 1 H, CH_2) 1.89 (br. s, 1 H, CH_2) 1.98 (d, *J*=12.1 Hz, 1 H, CH_2) 2.18 (s, 3 H, N-CH_3) 3.09 (td, *J*=11.3, 3.3 Hz, 1 H, CH) 3.29 - 3.38 (m, 1 H, CH) 3.88 (d, *J*=4.8 Hz, 2 H, N-CH_2) 6.68 - 6.75 (m, 2 H, Ar-H) 6.93 (d, *J*=7.3 Hz, 1 H, Ar-H) 7.10 (td, *J*=7.7, 1.6 Hz, 1 H, Ar-H) 7.42 - 7.49 (m, 3 H, Ar-H) 7.78 - 7.87 (m, 2 H, Ar-H) 8.35 (s, 1 H, N=CH). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm 23.4 (CH_2) 24.8 (CH_2) 34.3 (CH_2) 34.8 (CH_2) 58.71 (N-CH_3) 62.1 (N-CH) 66.9 (N-CH_2) 70.7 (N-CH) 116.2 (Ar-H) 118.5 (Ar-H) 122.2 (Ar-H) 128.3 (Ar-H) 128.3 (Ar-H) 128.5 (Ar-H) 129.0 (Ar-H) 129.7 (Ar-H) 130.5 (Ar-H) 136.2 (Ar-C) 158.3 (Ar-OH) 160.8 (N=CH). m/z $[C_{21}H_{25}N_2O + H]^+$ Calculated: 323.2123 gmol^{-1}. Found: 323.2114 gmol^{-1}.

6H: From **3**H (8.20 mmol). White solid (0.64 g, 1.65 mmol, 59 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 1.32 - 1.52 (m, 3 H, CH_2) 1.61 - 1.76 (m, 2 H, CH_2) 1.77 - 1.84 (m, 1 H, CH_2) 1.86 - 1.92 (m, 1 H, CH_2) 1.95 (d, *J*=13.1 Hz, 1 H, CH_2) 2.20 (s, 3 H, N-CH_3) 2.96 - 3.11 (m, 1 H, CH) 3.33 (td, *J*=10.2, 5.0 Hz, 1 H, CH) 3.80 - 3.93 (m, 2 H, N-CH_2) 6.80 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.20 (d, *J*=2.5 Hz, 1 H, Ar-H) 7.42 - 7.50 (m, 3 H, Ar-H) 7.81 - 7.90 (m, 2 H, Ar-H) 8.35 (s, 1 H, N=CH).^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ ppm 24.4 (CH_2) 24.7 (CH_2) 25.2 (CH_2) 34.3 (N-CH_3) 34.7 (CH_2) 59.0 (N-CH_2) 67.2 (N-CH) 70.4 (N-CH) 121.5 (Ar-C) 122.7 (Ar-Cl) 124.4 (Ar-Cl) 126.5 (Ar-H) 128.3 (Ar-H) 128.5 (Ar-H) 130.7 (Ar-H) 136.1 (Ar-C) 153.3 (Ar-OH) 161.1 (N=CH). m/z $[C_{21}H_{24}N_2OCl_2 + Na]^+$ Calculated: 413.1163 gmol^{-1} Found: 413.1155 gmol^{-1}.

Complex synthesis

Al(III) complexes: A solution of $AlMe_3$ (1 eq, 2 M in hexane) was added to a ligand solution (1 or 2 eq, 20 mL, toluene) dropwise and stirred for 30 min before work up.

Al(**1**)Me_2: **1**H (1 eq, 1.03 mmol). Recrystallisation from hexane, dried in vacuo to pale yellow powder (0.23 g, 0.48 mmol, 47 %). ^{1}H NMR (300 MHz, d_8-Tol) δ ppm -0.36 (s, 3 H, Al-CH_3) -0.22 (s, 3 H, Al-CH_3) 0.82 - 1.09 (m, 4 H, CH_2) 1.18 (s, 9 H, $C(CH_3)_3$) 1.34 (s, 9 H, $C(CH_3)_3$) 1.37 - 1.47 (m, 3 H, CH_2) 1.56 (s, 9 H, $C(CH_3)_3$) 1.89 (d, *J*=10.6 Hz, 1 H, CH_2) 2.98 (t, *J*=9.2 Hz, 1 H, CH) 3.32 - 3.52 (m, 1 H, CH) 3.90 (d, *J*=8.3 Hz, 1 H, NH) 7.06 (d, *J*=2.6 Hz, 1 H, Ar-H) 7.63 (d, *J*=2.6 Hz, 1 H, Ar-H) 7.88 (s, 1 H, N=CH). ^{13}C{^{1}H} NMR (75 MHz, d_8-Tol) δ ppm -8.3 (Al-CH_3) -8.0 (Al-CH_3) 25.0 (CH_2) 25.3 (CH_2) 28.1 (C(**C**H_3)$_3$) 29.6 (C(**C**H_3)$_3$) 31.6 (C(**C**H_3)$_3$) 32.1 (CH_2) 33.0 (CH_2) 34.2 (**C**$(CH_3)_3$) 35.6 (**C**$(CH_3)_3$) 53.0 (N-CH) 69.8 (N-CH) 79.0 (O-**C**$(CH_3)_3$) 118.8 (Ar-C) 129.5 (Ar-H) 131.6 (Ar-H) 138.6 (Ar-C) 140.7 (Ar-C) 154.9 (Ar-O) 162.3 (N=CH) 171.9 (C=O).$C_{28}H_{47}AlN_2O_3$ Calculated: C 69.10 % H 9.73 % N 5.76 % Found: C 68.24 % H 9.67 % N 5.85 %.

Al(**2**)$_2$Me: **2**H (2 eq, 2.64 mmol). Recrystallisation from toluene, dried in vacuo to pale yellow powder (0.37 g, 0.54 mmol, 41 %). The complex was

extremely insoluble in common deuterated organic solvents, characterisation was carried out by X-ray crystallography and elemental analysis only. $C_{37}H_{53}AlN_4O_6$ Calculated: C 65.66 % H 7.89 % N 8.28 % Found: C 65.70 % H 7.98 % N 8.16.

Al(**3**)Me_2: **3**H (1 eq, 1.29 mmol). Recrystallisation from toluene, dried in vacuo to a yellow powder (0.28 g, 0.63 mmol, 49 %).^{1}H NMR (300 MHz, d_8-Tol) δ ppm -0.43 (s, 3 H, $AlCH_3$) -0.33 (s, 3 H, $AlCH_3$) 0.70 - 1.00 (m, 4 H, CH_2) 1.17 (s, 9 H, $C(CH_3)_3$) 1.27 - 1.41 (m, 2 H, CH_2) 1.46 (d, *J*=11.3 Hz, 1 H, CH_2) 1.78 (d, *J*=12.8 Hz, 1 H, CH_2) 2.93 (t, *J*=11.3 Hz, 1 H, CH) 3.33 - 3.50 (m, 1 H, CH) 3.85 (d, *J*=8.7 Hz, 1 H, NH) 6.83 (d, *J*=2.6 Hz, 1 H, Ar-H) 7.22 (d, *J*=2.6 Hz, 1 H, Ar-H) 7.65 (s, 1 H, N=CH). $^{13}C\{^1H\}$ NMR (75 MHz, d_8-Tol) δ ppm -8.9 (Al-CH_3) -8.7 (Al-CH_3) 24.8 (CH_2) 25.1 (CH_2) 28.0 (C(**C**H_3)$_3$) 32.1 (CH_2) 33.0 (CH_2) 52.3 (N-CH) 69.0 (N-CH) 79.5 (O-**C**$(CH_3)_3$) 120.1 (Ar-H) 121.0 (Ar-H) 127.4 (Ar-C) 132.2 (Ar-Cl) 135.8 (Ar-Cl) 155.0 (Ar-O) 158.7 (N=CH) 169.6 (C=O). $C_{20}H_{29}AlCl_2N_2O_3$ Calculated: C 54.18 % H 6.59 % N 6.32 % Found: C 53.96 % H 6.65 %, N 6.23 %.

Al(**3**)$_2$Me: **3**H (2 eq, 1.03 mmol). Recrystallisation from toluene, dried in vacuo to a pale yellow powder (0.077 g, 0.09 mmol, 18 %). The complex was extremely insoluble in common deuterated organic solvents, characterisation was carried out by X-ray crystallography and elemental analysis only. $C_{37}H_{49}AlCl_4N_4O_6$ Calculated: C 54.56 % H 6.06 % N 6.88 % Found: C 54.51 % H 6.14 % N 6.80 %

Al(**4***)Me: **4**H (1 eq, 0.46 mmol). Recrystallisation from hexane, dried in vacuo to a pale yellow powder (0.11 g, 0.21 mmol, 47 %). ^{1}H NMR (300 MHz, C_6D_6) δ ppm -0.94 (s, 3 H, Al-CH_3) 0.62 - 1.02 (m, 4 H, CH_2) 1.16 - 1.26 (m, 1 H, CH_2) 1.40 - 1.43 (m, 1 H, CH_2) 1.44 (s, 9 H, $C(CH_3)_3$) 1.46 - 1.53 (m, 2 H, CH_2) 1.65 (s, 3 H, N-CH_3) 1.68 (d, *J*=6.40 Hz, 3 H, CH-C**H**$_3$) 1.72 (s, 9 H, $C(CH_3)_3$) 2.14 - 2.25 (m, 1 H, CH) 2.55 (d, *J*=12.4 Hz, 1 H, N-CH_2) 3.04 (td, *J*=9.9, 3.6 Hz, 1 H, CH) 3.89 (d, *J*=12.4 Hz, 1 H, N-CH_2) 4.22 (q, *J*=6.4 Hz, 1 H, CH_3-C**H**) 6.88 (d, *J*=2.6 Hz, 1 H, Ar-H) 7.19 - 7.26 (m, 1 H, Ar-H) 7.42 (t, *J*=7.7 Hz, 2 H, Ar-H) 7.61 (d, *J*=2.6 Hz, 1 H, Ar-H) 7.77 (d, *J*=7.2 Hz, 2 H, Ar-H). $^{13}C\{^1H\}$ NMR (75 MHz, C_6D_6) δ ppm -12.3 (Al-CH_3) 21.4 (CH_2) 22.9 (CH-**C**H_3) 25.0 (CH_2) 26.1 (CH_2) 30.4 (C(**C**H_3)$_3$) 32.5 (C(**C**H_3)$_3$) 33.5 (CH_2) 34.7 (**C**$(CH_3)_3$) 35.8 (**C**$(CH_3)_3$) 39.4 (N-CH_3) 53.2 (N-CH_2) 55.7 (**C**H-CH_3) 59.0 (CH) 72.9 (CH) 122.2 (Ar-H) 125.1 (Ar-H) 125.2 (Ar-H) 127.5 (Ar-H) 128.3 (Ar-H) 129.4 (Ar-H) 139.0 (Ar-C) 139.3 (Ar-C) 150.1 (Ar-C) 156.9 (Ar-O). Satisfactory elemental analysis data could not be obtained for this compound, most likely due to the high sensitivity of the complex to air and moisture.

Al(**6**)Me_2: **6**H (1 eq, 0.46 mmol). Recrystallisation from toluene, dried in vacuo to a white powder (0.13 g, 0.30 mmol, 65 %). ^{1}H NMR (400 MHz, d_8-Tol) δ ppm -0.37 (s, 3 H, Al-Me) -0.30 (s, 3 H, Al-Me) 1.02 - 1.18 (m, 3 H, CH_2) 1.25 - 1.30 (m, 1 H, CH_2) 1.39 - 1.48 (m, 2 H, CH_2) 1.53 (d, *J*=8.8 Hz, 2 H, CH_2) 1.74 (s, 3 H, N-Me) 2.28 (d, *J*=11.5 Hz, 1 H, CH) 2.97 - 3.08 (m, 1 H, CH) 4.01 (d, *J*=13.8 Hz, 1 H, N-CH_2) 4.60 (d, *J*=14.1 Hz, 1 H, N-CH_2) 6.35 (d, *J*=1.76 Hz, 1 H, Ar-H) 7.27 - 7.33 (m, 4 H, Ar-H) 7.68 (d, *J*=5.3 Hz, 2 H, Ar-H) 7.75 (s, 1 H, N=CH). No ^{13}C NMR data, compound only partially soluble in d_8 toluene. $C_{23}H_{29}N_2OCl_2Al$ Calculated: C 61.75 % H 6.53 % N 6.15 % Found: C 61.67 % H 6.66 % N 6.26 %

Zn(II) complexes: A solution of $ZnMe_2$ (1 eq) was added to a ligand solution (1 or 2 eq, 20 mL, toluene) dropwise at 20°C and stirred for 30 min before work up.

Zn(**2**)$_2$: **2**H (2 eq, 3.14 mmol). Recrystallisation from toluene, dried in vacuo to a white powder (0.97 g, 1.39 mmol, 89 %). ^{1}H NMR (400 MHz, d_6-DMSO) δ ppm 0.74 (d, *J*=10.8 Hz, 2 H, CH_2) 0.97 - 1.33 (m, 22 H, 2C$(CH_3)_3$, 2CH_2) 1.45 (br. s, 6 H, CH_2) 1.78 (br. s, 4 H, CH_2) 3.14 (br. s, 3 H, CH) 3.58 (br. s, 1 H, CH) 6.48 - 6.82 (m, 4 H, Ar-H) 7.07 - 7.33 (m, 4 H, Ar-H) 8.08 - 8.42 (m, 2 H, N=CH). $^{13}C\{^1H\}$ NMR (100 MHz, d_6-DMSO) δ ppm 21.1 (CH_2) 24.2 (CH_2) 27.9 (C(**C**H_3)$_3$) 28.1 (C(**C**H_3)$_3$) 52.8 (HN-CH) 71.6 (N-CH) 77.5 (O-**C**$(CH_3)_3$) 77.6 (O-**C**$(CH_3)_3$) 113.8 (Ar-H) 118.1 (Ar-H) 118.4 (Ar-H) 122.3 (Ar-H) 125.4 (Ar-H) 128.2 (Ar-H) 128.9 (Ar-H) 134.2 (Ar-H) 136.2 (Ar-C) 137.4 (Ar-C) 154.6 (Ar-O) 169.7 (N=CH) 170.0 (C=O) 170.7 (C=O). $C_{36}H_{50}N_4O_6Zn$ Calculated: C 61.75 % H 7.20 % N 8.00 % Found: C 61.56 %, H 7.30 %, N 7.94 %.

Zn(**2**)Me: **2**H (1 eq, 0.94 mmol). Recrystallisation from toluene, dried in vacuo to a pale yellow powder (0.082 g, 0.21 mmol, 22 %).

^{1}H NMR (400 MHz, d_8-Tol) δ ppm -0.07 (s, 3 H, Zn-CH_3) 0.51 (qd, *J*=12.0, 3.5 Hz, 1 H, CH_2) 0.78 - 0.93 (m, 1 H, CH_2) 0.94 - 1.09 (m, 1 H, CH_2) 1.13 (s, 9 H, $C(CH_3)_3$) 1.18 - 1.31 (m, 2H, CH_2) 1.34 (m, 3 H, CH_2) 1.61 - 1.78 (m, 1 H, CH) 3.66 (td, *J*=16.6, 8.8 Hz, 1 H, CH) 4.06 (d, *J*=8.5 Hz, 1 H, NH) 6.53 (t, *J*=6.8 Hz, 1 H, Ar-H) 6.93 (d, *J*=7.8 Hz, 1 H, Ar-H) 6.98 (s, 1 H, Ar-H) 7.02 (s, 1 H, Ar-H) 7.08 - 7.15 (m, 2 H, Ar-H) 7.19 - 7.25 (m, 1 H, Ar-H) 7.55 (s, 1 H, N=CH). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-Tol) δ ppm -13.9 (Zn-CH_3), 24.5 (CH_2) 25.2 (CH_2) 27.9 (C(**C**H_3)$_3$) 30.6 (CH_2) 32.7 (CH_2) 54.6 (HN-CH) 78.6 (N-CH) 81.8 (O-**C**$(CH_3)_3$) 113.3 (Ar-H) 118.4 (Ar-H) 124.2 (Ar-H) 134.8 (Ar-H) 135.3 (Ar-C) 158.7 (Ar-O) 167.8 (N=CH). $C_{19}H_{28}N_2O_3Zn$ Calculated: C 57.36 % H 7.09 % N 7.04 % Found: C 57.23 %, H 7.16 %, N 7.00 %

Zn(**3**)$_2$: **3**H (2 eq, 1.29 mmol). Recrystallisation from toluene, dried in vacuo to a pale yellow powder (0.17 g, 0.20 mmol, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 0.98 - 1.18 (m, 2 H, CH_2) 1.31 (s, 20 H, $C(CH_3)_3$, CH_2) 1.36 - 1.74 (m, 5 H, CH_2) 1.75 - 2.00 (m, 7 H, CH_2) 3.29 (br. s, 2 H, CH) 3.86 (br. s, 2 H, CH) 5.56 (br. s, 2 H, NH) 7.02 (d, *J*=2.8 Hz, 2 H, Ar-H0) 7.45 (d, *J*=2.8 Hz, 1 H, Ar-H) 8.20 (br. s, 2 H, N=CH). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ ppm 24.4 (CH_2) 25.2 (CH_2) 28.2 (C(**C**H_3)$_3$) 33.8 (CH_2) 55.2 (N-CH) 79.3 (O**C**$(CH_3)_3$) 79.5 (O**C**$(CH_3)_3$) 117.8 (Ar-H) 118.8 (Ar-H) 127.4 (Ar-H) 129.0 (Ar-H) 133.0 (Ar-Cl) 133.8 (Ar-Cl) 155.3 (Ar-O) 155.6 (Ar-O) 163.0 (N=CH) 169.3 (C=O). $C_{36}H_{46}Cl_4N_4O_6Zn$ Calculated: C 51.60 % H 5.53 % N 6.69 % Found: C 48.69 % H 5.46 % N 5.78 %.

Zn(**5**)Me: **5**H (1 eq, 1.40 mmol). Recrystallisation from toluene, dried in vacuo to a white powder (0.43 g, 1.06 mmol, 76 %). The ^{1}H NMR showed a mixture of diastereomers, the data below is for the major isomer. ^{1}H NMR (400 MHz, d_8-Tol) δ ppm -0.63 (m, 3 H, Zn-CH_3) 0.60 - 0.78 (m, 3 H, CH_2) 1.25 (d, *J*=11.3 Hz, 1 H, CH_2) 1.33 - 1.43 (m, 2 H, CH_2) 1.51 (d, *J*=12.6 Hz, 2 H, CH_2) 1.97 (s, 3 H, N-CH_3) 2.45 - 2.57 (m, 1 H, CH) 2.59 - 2.71 (m, 1 H, CH) 3.01 (d, *J*=12.6 Hz, 1 H, N-CH_2) 3.98 (d, *J*=12.6 Hz, 1 H, N-CH_2) 6.61 (td, *J*=7.2, 1.4 Hz, 1 H) 6.86 (dd, *J*=7.3, 1.8 Hz, 1 H) 7.15 - 7.18 (m, 1 H) 7.19 - 7.27 (m, 3 H) 7.61 (d, *J*=2.3 Hz, 1 H) 8.08 (d, *J*=7.3 Hz, 2 H). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-Tol) δ ppm -16.8 (Zn-CH_3) 21.8 (CH_2) 24.0 (CH_2) 24.5 (CH_2) 29.7 (CH_2) 38.0 (N-CH_3) 59.4 (CH_2-N) 60.4 (CH) 60.8 (CH) 113.3 (Ar-H) 121.1 (Ar-H) 122.0 (Ar-H) 128.5 (Ar-H) 129.9 (Ar-H) 130.9 (Ar-H) 132.5 (Ar-H) 134.6 (Ar-N) 164.7 (Ar-O) 168.4 (CH=N). $C_{22}H_{28}N_2OZn$ Calculated: C 65.75 % H 7.02 % N 6.97 % Found: C 65.59 % H 7.18 % N 6.85 %

Zn(**6**)Me: **6**H (1 eq, 1.59 mmol). Recrystallisation from toluene, dried in vacuo to a white powder (0.44 g, 0.92 mmol, 58 %). The ^{1}H NMR showed a mixture of diastereomers, the data below is for the major isomer.

^{1}H NMR (400 MHz, d_8-Tol) δ ppm -0.54 (s, 3 H, Zn-CH_3) 0.45 - 0.64 (m, 3 H, CH_2) 1.16 (d, *J*=12.6 Hz, 1 H, CH_2) 1.20 - 1.35 (m, 3 H, CH_2) 1.41 (d, *J*=11.0 Hz, 1 H, CH_2) 1.84 (s, 3 H, N-CH_3) 2.24 (t, *J*=11.4 Hz, 1 H, CH) 2.48 (t, *J*=10.3 Hz, 1 H, CH) 2.78 (d, *J*=12.8 Hz, 1 H, CH_2) 3.73 (d, *J*=12.8 Hz, 1 H, CH_2) 6.80 (s, 1 H, N=CH) 7.10 - 7.15 (m, 1 H, Ar-H) 7.33 (t, *J*=7.3 Hz, 2 H, Ar-H) 7.52 (s, 1 H, Ar-H) 7.57 (br. s, 1 H, Ar-H) 8.17 (d, *J*=7.5 Hz,

2 H, Ar-H). $^{13}C\{^1H\}$ NMR (100 MHz, d_8-Tol) δ ppm -17.0 (Zn-CH_3) 21.7 (CH_2) 23.8 (CH_2) 24.3 (CH_2) 29.3 (CH_2) 37.9 (N-CH_3) 58.3 (CH) 59.9 (CH) 61.2 (N-CH_2) 124.1 (Ar-H) 125.8 (Ar-H) 129.3 (Ar-H) 130.0 (Ar-H) 130.3 (Ar-H) 132.8 (Ar-Cl) 134.2 (Ar-Cl) 162.1 (Ar-O) 165.4 (N=CH). $C_{22}H_{26}N_2OCl_2Zn$ Calculated: C 56.13 % H 5.57 % N 5.95 % Found: C 56.04 % H 5.65 % N 5.89 %

Acknowledgements

We wish to thank the EPSRC (EP/G03768X/1 and EP/L027267/1) for funding the CDT in Sustainable Chemical Technologies at the University of Bath. We also acknowledge Purac for the donation of lactide. X-ray diffraction, NMR, MALDI-ToF and GPC facilities were provided through the Chemical Characterisation and Analysis Facility (CCAF) at the University of Bath.

Keywords: lactide • zinc • aluminium • salen •

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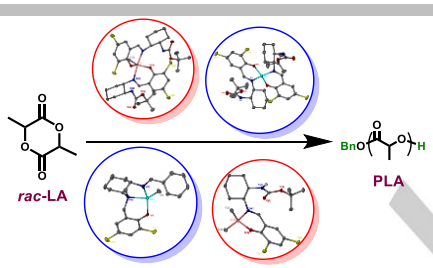
Layout 1:

FULL PAPER

Several ligands and complexes based on diaminocyclohexane are reported. Full structural characterisation has been carried out as well as assessment of these complexes for their ability to polymerise *rac*-lactide.



Lactide polymerisation

Sarah M. Kirk, Paul McKeown, Mary F. Mahon, Gabriele Kociok-Köhn, Timothy J. Woodman and Matthew D. Jones**

Synthesis of Zn(II) and Al(III) complexes of diaminocyclohexane derived ligands and their exploitation for the ring opening polymerization of rac-lactide

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