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Zinc(II) Homogeneous and Heterogeneous Species and Their Application for the Ring-Opening Polymerisation of *rac*-Lactide

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Schiff base ligands (**L1**H–**L8**H) have been prepared and complexed to Zn^{II} centres. All eight complexes have been characterised by single-crystal X-ray diffraction methods, multinuclear NMR spectroscopy and elemental analysis. It was shown that for **L1**H and **L2**H trimetallic complexes of the form $Zn_3(OAc)_4$(**L1**–**2**)$_2$ were isolated. However, for **L3**H to **L7**H monometallic complexes were formed, Zn(**L3**–**7**)$_2$. For **L8**H a trimetallic complex was also isolated with the same stoichiometry as $Zn_3(OAc)_4$(**L1**–**2**)$_2$ but a different coordination motif was detected. The Schiff base ligand **L1**H was anchored to silica and treated with $Zn(OAc)_2{\cdot}2H_2O$ to form the heterogeneous Zn^{II} system. This was characterised by $^{13}C\{^1H\}$ CP/MAS NMR spectroscopy. All homogeneous and heterogeneous catalysts were assessed for the ring-opening polymerisation of *rac*-lactide at 130 °C in the absence of solvent, using unsublimed monomer. All catalysts offered good conversions and a moderate degree of control.

Introduction

Currently, there is a compelling argument for the production of commodity chemicals from naturally occurring sustainable resources.[1] One example is the production of polylactide (PLA) as an alternative to traditional petrochemical-based polymers.[2] PLA is typically prepared by the ring-opening polymerisation (ROP) of the cyclic monomer *rac*-LA (*rac*-lactide). In recent years, tremendous effort has yielded much progress in this area. Typical examples of active metal centres are group 3 and group 4 metals, aluminium, lanthanides and alkaline earth metals.[3–13] Zinc complexes have been shown to be extremely active for the ROP of *rac*-LA[11–24] and for the copolymerisation of CO_2 and epoxides to form polycarbonates.[25]

A main aim of this study is to prepare a range of Zn^{II} Schiff base complexes and screen them for the ROP of unsublimed *rac*-LA. The majority of initiators in the literature are air- and moisture-sensitive and are not stable to small impurities in the monomer. There is an exigent need to prepare initiators that are stable to these trace impurities, thus negating the need to purify the monomer and reducing processing costs to industry.

There is continued interest in the preparation and characterisation of heterogeneous catalysts as replacements for their homogeneous counterparts in polymer production, as heterogeneous catalysts minimise the catalyst residue in the final product. Several groups have reported the use of heterogeneous catalysts for the ROP of cyclic esters. For example, Jérôme et al. have prepared heterogeneous tin initiators anchored to polystyrene and lanthanide complexes anchored to zeolites.[26,27] Pertinent to this study is the work of C. W. Jones et al.,[28] who have covalently anchored Zn^{II}-diiminate complexes to SBA-15. They found that for L-lactide narrow molecular weight PLA could be prepared in yields up to 70% after 24 h. The PLA was shown to have molecular weights in the range of 1000–5000.[28] As the ligands described in this work are capable of being facilely heterogenised using a simple protocol we decided investigate these as heterogeneous initiators.

The homogeneous initiators are prepared by reacting the ligand with $Zn(OAc)_2{\cdot}2H_2O$. In this study, depending on the ligand choice, either monometallic complexes of the form $Zn(L)_2$ were isolated, in accordance with precedent literature,[25] or rare trimetallic complexes $\{Zn_3(OAc)_4(L)_2\}$ were produced. Three unique Zn^{II} trimetallic complexes are reported and fully characterised via NMR and X-ray crystallography. To the best of our knowledge these latter complexes are the first crystallographically characterised examples of this trimetallic structure with this ligand class, although similar motifs have been observed for related li-

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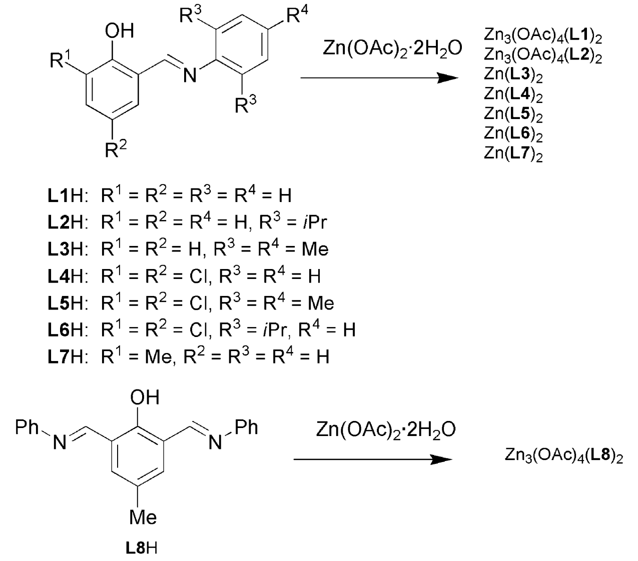
gands.[29–32] For example, Reedijk et al. prepared a related complex with 4-methyl-2-*N*-(2-pyridyl-methyl)aminophenol.[33]

Results and Discussion

Synthesis and Characterisation of Ligands and Complexes

The ligands were simply prepared by the reaction of a substituted aldehyde with the corresponding amine and were isolated as yellow solids in high yields.[34] The Zn^{II} complexes were prepared by taking $Zn(OAc)_2\cdot 2H_2O$ in methanol with the corresponding Schiff base precursors, Scheme 1.



Scheme 1. The ligands and complexes prepared in this study.

The metal complexation reactions were performed with a 1:1 stoichiometry of zinc to ligand with MeOH as the solvent. In all cases, after approximately one hour at room temperature a microcrystalline material precipitated, which was collected and recrystallised from either MeOH or CH_2Cl_2. In all cases, the 1:1 complexes were not isolated. In the case of **L1**H and **L2**H, a Zn^{II} trimetallic complex was prepared, and for **L3**H–**L7**H, monometallic species were observed. All complex structures were confirmed by single-crystal X-ray diffraction, see Figure 1 for the molecular structure of $Zn_3(OAc)_4(\mathbf{L1})_2$. Importantly all complexes could be prepared in near quantitative yields using a 3:2 or 1:2 stoichiometry of metal to ligand.

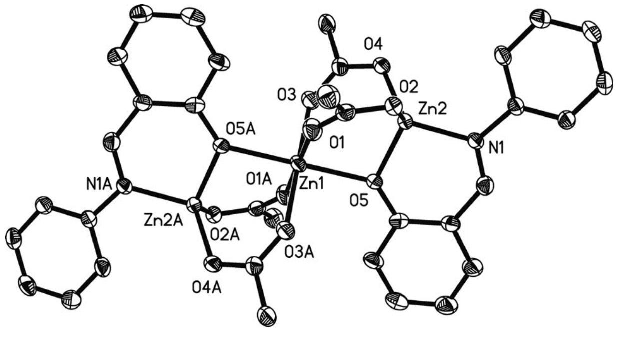


Figure 1. Molecular structure of $Zn_3(OAc)_4(\mathbf{L1})_2$. Ellipsoids are shown at the 50% probability level and the hydrogen atoms have been removed for clarity. Labels with suffix A relate to those in the asymmetric unit by the –x, *–y*, *–z* symmetry operation.

The structure consists of two Schiff base ligands, three zinc atoms and four acetate groups. The molecular structure is centrosymmetric with Zn(1) located at an inversion centre. The three zinc centres [Zn(2), Zn(1) and Zn(2A)] are bridged by four carboxylate groups and two Schiff base ligands. Zn(1) sits in a pseudooctahedral environment and is coordinated to the four acetate groups and the phenoxide groups of the ligand. This is exemplified by O(1)–Zn(1)–O(5) of 89.42(9)°. Zn(2) is in a pseudotetrahedral environment and is bound to two acetate groups, the phenoxide and the imine of the ligand. Bond lengths and angles are in agreement for zinc carboxylate structures in the literature.[33,35,36] For **L2**H an analogous complex was isolated, selected bond lengths and angles for both compounds are given in Table 1.[29] The associated ^1H and $^{13}C\{^1H\}$ solution-state NMR ([D$_6$]DMSO) spectra showed the presence of one imine H resonance at ca. 8.5 ppm and the acetate methyl at ca. 1.9 ppm in the ratio 2:12 as predicted from the solid-state structure.

Table 1. Selected bond lengths [Å] and bond angles [°] for the trimetallic complexes $Zn_3(OAc)_4(\mathbf{L1})_2$ and $Zn_3(OAc)_4(\mathbf{L2})_2$.

	$Zn_3(OAc)_4(\mathbf{L1})_2$	$Zn_3(OAc)_4(\mathbf{L2})_2$
Zn(1)–O(1)	2.104(3)	2.077(3)
Zn(1)–O(3)	2.060(2)	2.091(3)
Zn(1)–O(5)	2.150(2)	2.161(3)
Zn(2)–O(2)	1.964(3)	1.932(3)
Zn(2)–O(4)	1.938(2)	1.938(3)
Zn(2)–O(5)	1.939(2)	1.938(3)
Zn(2)–N(1)	1.984(3)	1.989(3)
O(1)–Zn(1)–O(5)	89.42(9)	90.07(12)
O(1)–Zn(1)–O(3)	92.34(10)	92.08(13)
O(5)–Zn(2)–N(1)	98.39(10)	96.93(13)
O(2)–Zn(2)–N(1)	109.10(11)	114.43(14)

For ligands **L3**H–**L7**H monometallic complexes were isolated (at ligand/Zn^{II} ratios of 2:1 and 1:1), in the case of **L6**H a methanol adduct was isolated, Figure 2. The complexes $Zn(\mathbf{L3})_2$–$Zn(\mathbf{L5})_2$ and $Zn(\mathbf{L7})_2$ were found to be pseudotetrahedral in coordination.[37–39] The metric data are similar to those for $Zn_3(OAc)_4(\mathbf{L1})_2$ and $Zn_3(OAc)_4(\mathbf{L2})_2$. For $Zn(\mathbf{L6})_2(MeOH)_2$ the zinc centre is pseudo-square pyramidal with an O(1)–Zn-(1)–O(2) angle of 173.05(5)°. As expected for $Zn(\mathbf{L6})_2(MeOH)_2$ the Zn-phenoxide and Zn–N distances are significantly longer than those seen for $Zn(\mathbf{L3})_2$–$Zn(\mathbf{L5})_2$. The metal centre is coordinated to a MeOH molecule, which in turn is hydrogen-bonded to a lattice MeOH molecule that hydrogen bonds to O(1) of the phenoxide to form a six-membered ring. Selected bond lengths and angles are given in Table 2.

Table 2. Selected bond lengths [Å] and bond angles [°] for the monometallic complexes Zn(**L3**)$_2$ to Zn(**L7**)$_2$.

	Zn(**L3**)$_2$	Zn(**L4**)$_2$	Zn(**L5**)$_2$	Zn(**L6**)$_2$(MeOH)$_2$	Zn(**L7**)$_2$
Zn(1)–O(1)	1.9109(14)	1.9210(14)	1.923(3)	2.0218(11)	1.9088(14)
Zn(1)–O(2)	1.9256(14)	[b]	[b]	1.9864(11)	1.9174(14)
Zn(1)–O(3)	[a]	[a]	[a]	2.0562(13)	[a]
Zn(1)–N(1)	2.0167(17)	2.0135(15)	2.012(3)	2.0822(14)	2.0238(16)
Zn(1)–N(2)	2.0000(16)	[b]	[b]	2.0700(13)	2.0182(16)
O(1)–Zn(1)–N(1)	95.64(6)	97.08(6)	95.33(11)	88.00(5)	96.17(6)
O(2)–Zn(1)–N(2)	96.27(6)	[b]	[b]	90.27(5)	96.11(6)
O(1)–Zn(1)–O(3)	[a]	[a]	[a]	85.87(5)	[a]

[a] Not applicable. [b] In the case of Zn(**L4**)$_2$ and Zn(**L5**)$_2$ there is only one crystallographically unique ligand.

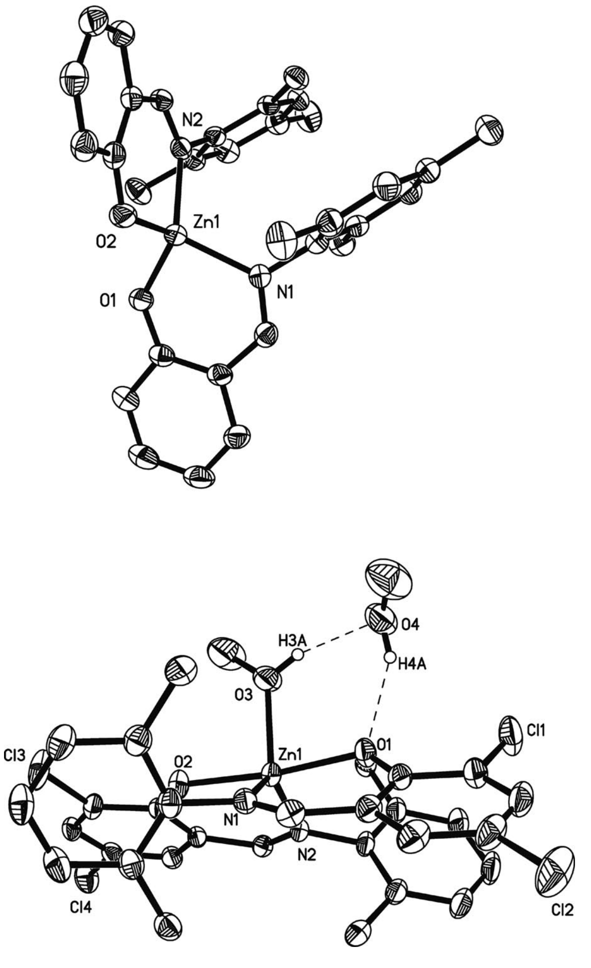


Figure 2. Molecular structure of Zn(**L3**)$_2$ (top) and Zn(**L6**)$_2$(MeOH)$_2$ (bottom) the ellipsoids are shown at the 50% probability level and the hydrogen atoms not involved in hydrogen bonding have been omitted for clarity as have the methyl groups of the isopropyl groups in Zn(**L6**)$_2$(MeOH)$_2$. The hydrogen bonding details for Zn(**L6**)$_2$(MeOH)$_2$ are (distances in Å and angles in °) O(3)–H(3A)···O(4) O(3)–H(3A) 0.81(3), H(3A)–O(4) 1.87(3), O(3)–O(4) 2.659(2), O(3)–H(3A)–O(4) 164(3). O(4)–H(4A)···O(1) O(4)–H(4A) 0.80(3), H(4A)–O(1) 2.04(3), O(4)–O(1) 2.775(2), O(4)–H(4A)–O(1) 153(3).

To further investigate the coordination chemistry, the Schiff base **L8**H was utilised. This is simply prepared from the reaction of aniline with 2-hydroxy-5-methyl-1,3-benzenedicarboxaldehyde. **L8**H was treated with Zn(OAc)$_2$·2H$_2$O to produce a trimetallic complex, Figure 3:

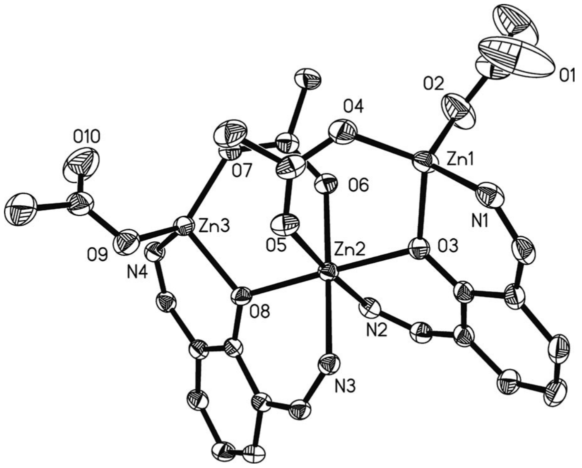
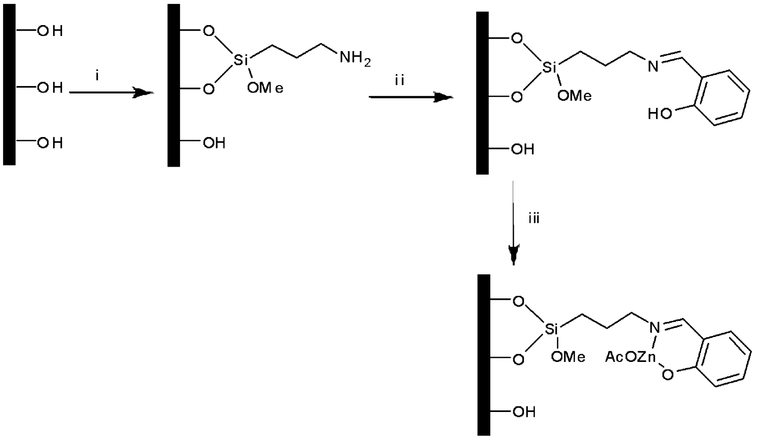


Figure 3. Molecular structure of Zn$_3$(OAc)$_4$(**L8**)$_2$ the ellipsoids are shown at the 50% probability level and the hydrogen atoms have been omitted for clarity as have the carbon atoms of the phenyl rings {attached to N(1), N(2), N(3) and N(4)} and the methyl carbon of the ligand.

In this case the ligand forces two acetate groups {O(9) and O(2)} to only coordinate to the zinc centres through one oxygen, with Zn(1)–O(2) 1.951(2) Å and Zn(3)–O(9) 1.9550(18) Å. Two acetates bridge the central zinc {Zn(2)} and outer zinc centres {Zn(1) and Zn(3)} with Zn(2)–O(5) 2.1245(16) Å and Zn(1)–O(4) 1.9419(19) Å, which are analogous to Zn$_3$(OAc)$_4$(**L1**)$_2$ and Zn$_3$(OAc)$_4$(**L2**)$_2$. The nitrogen donors of each ligand are coordinated to the central zinc and the outer zinc centres, with Zn(1)–N(1) 2.040(2) Å and Zn(2)–N(2) 2.1814(19) Å. At room temperature the ^{1}H NMR (CDCl$_3$) was very broad indicating dynamic behaviour on the NMR timescale, cooling to –40 °C sharpened the peaks and the NMR is in agreement with the solid-state structure. For example, two resonances were observed for the acetate groups in the ^{1}H and ^{13}C{^{1}H} NMR spectra for the two chemical distinct acetate moieties.

Synthesis and Characterisation of Silica-Supported Heterogeneous System

(3-Aminopropyl)trimethoxysilane (AMPS) was added to dry silica (60 Å Davisil Grade 635) to form the heterogenised amine as shown in Scheme 2, SiO$_2$-AMPS. ^{13}C{^{1}H}CP/MAS NMR showed four environments centred



Scheme 2. Preparation of the heterogeneous catalyst. i) $(MeO)_3Si(CH_2)_3NH_2$/toluene (SiO_2-AMPS); ii) salicylaldehyde/MeOH (SiO_2-AMPS-SAL); iii) $Zn(OAc)_2.2H_2O$/MeOH (SiO_2-AMPS-SAL-Zn).

at 9, 27, 44 and 49 ppm, respectively. Dipolar dephasing experiments indicated that the peak at δ = 49 ppm arises from Si–OCH_3.[40] This material was treated with salicylaldehyde, using a standard literature procedure to form SiO_2-AMPS-SAL as a bright yellow solid.[41–43]

Upon formation of SiO_2-AMPS-SAL a new resonance in the $^{13}C\{^1H\}$ CP/MAS NMR at δ = 62 ppm (CH_2–N=) was observed [with concurrent reduction in the resonance at δ = 44 ppm (CH_2NH_2)], together with new resonances for the aryl carbon atoms and the imine (CH=N) at δ = 165 ppm. This material was treated with $Zn(OAc)_2{\cdot}2H_2O$ to form SiO_2-AMPS-SAL-Zn, as a pale yellow solid. There is significant broadening in the $^{13}C\{^1H\}$ CP/MAS NMR spectrum of SiO_2-AMPS-SAL-Zn, suggesting more disorder is present, compared to the precursor materials. There is a new resonance at δ = 170 ppm, which is assigned to the carbonyl of the acetate group, the peak at δ = 23.5 ppm is asymmetric and encompasses the CH_2 of the tether and CH_3 of the acetate (Figure 4).

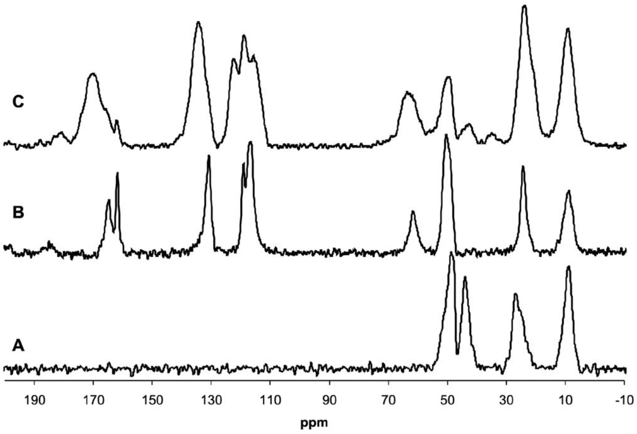


Figure 4. $^{13}C\{^1H\}$ CP/MAS solid-state NMR analysis of A) SiO_2-AMPS B) SiO_2-AMPS-SAL and C) SiO_2-AMPS-SAL-Zn.

Polymerisation of *rac*-Lactide

The Zn^{II} complexes were screened for the polymerisation of unsublimed *rac*-lactide, in melt conditions at 130 °C. The trimetallic complexes showed reasonable activity and after 30 min ca. 50% conversion was achieved, except for $Zn_3(OAc)_4(\mathbf{L8})_2$ where no polymer was produced. The PDIs were relatively high [1.83 for $Zn_3(OAc)_4(\mathbf{L1})_2$ and 1.50 for $Zn_3(OAc)_4(\mathbf{L2})_2$]. For the trimetallic complexes, analysis of the ^1H homonuclear decoupled NMR spectrum indicated that the polymers have a slight heterotactic bias with a P_r of 0.60. The monometallic complexes $Zn(\mathbf{L3}–\mathbf{L7})_2$ were active for the polymerisation and PDIs in the range 1.42–1.55 were observed. Complexes $Zn(\mathbf{L3})_2$ and $Zn(\mathbf{L7})_2$ showed similar activity to the trimetallic complexes. Complexes $Zn(\mathbf{L4})_2$ and $Zn(\mathbf{L5})_2$ where the ligand has a chloro group, gave very poor conversions after two hours. Interestingly, $Zn(\mathbf{L6})_2(MeOH)_2$ gave the highest yield of PLA (polylactide). The heterogeneous initiator was also shown to be active for the polymerisation, albeit to a much lesser extent than the homogeneous examples. However, the PDI is noticeably narrower than that for the homogeneous Zn^{II} complexes at similar conversion. This compares favourable to literature Zn^{II} complexes anchored to porous silica which produced low molecular weight PLA, as in this case

Table 3. Results for the polymerisation of *rac*-lactide for the Zn^{II} homogeneous and heterogeneous complexes.

Initiator[a]	Time [h]	Yield (%)[b]	M_n[c]	PDI[c]	P_r[d]
$Zn_3(OAc)_4(\mathbf{L1})_2$	0.5	55	21600	1.83	0.60
$Zn_3(OAc)_4(\mathbf{L1})_2$	1	69	44400	1.52	0.60
$Zn_3(OAc)_4(\mathbf{L1})_2$	2	90	51400	1.55	0.60
$Zn_3(OAc)_4(\mathbf{L2})_2$	0.5	40	23700	1.50	0.63
$Zn(\mathbf{L3})_2$	0.5	47	35100	1.50	0.50
$Zn(\mathbf{L4})_2$	2	10	8000	1.42	0.50
$Zn(\mathbf{L5})_2$	2	20	11700	1.43	0.50
$Zn(\mathbf{L6})_2(MeOH)_2$	0.5	80	41200	1.43	0.50
$Zn(\mathbf{L7})_2$	0.5	33	42500	1.55	0.50
Heterogeneous	24	40	19300	1.34	0.50

[a] For the homogeneous examples a monomer/initiator ratio of 300:1 was employed, for the heterogeneous initiator 100 mg was used. In all cases, 2 g of unsublimed lactide was used and the polymerisations were performed at 130 °C. [b] Isolated yield. [c] Determined from GPC measurements (THF at 1 mL per minute, relative to polystyrene standards.). [d] Calculated from analysis of the methine region of the ^1H homonuclear decoupled spectrum.

relatively high molecular weight PLA is produced.[28] The monometallic complexes and the heterogeneous system all produced atactic PLA, Table 3. To investigate the catalysis further polymerisations were attempted using i) pure ligands; ii) silica only and iii) utilising unsublimed *rac*-LA without a catalyst. These three control experiments failed to produce polymer after 24 h, indicating the active catalytic centre must be the Zn^{II} centre itself, and not water in the monomer, silica or dissociation of the ligand. For $Zn_3(OAc)_4(\mathbf{L1})_2$ polymerisation were investigated in more detail. The yield and M_n increase with time indicating that this complex does offer a moderate degree of control in molecular weight for the ROP of *rac*-LA.

Conclusions

A series of homogeneous and heterogeneous Zn^{II} complexes have been prepared, either trimetallic or monometallic complexes have been isolated. The complexes were shown to be active for the ROP of *rac*-lactide. A silica-supported heterogeneous catalyst was also prepared and this was shown to be moderately active for the polymerisation affording atactic PLA under melt conditions with a PDI of 1.34.

Experimental Section

General Procedures: The ligands were prepared according to standard literature procedures and the purity confirmed by $^1H/^{13}C$ NMR and HR-MS prior to use.[44,45] $Zn(OAc)_2{\cdot}2H_2O$ was purchased from Aldrich and used without further purification. ^1H and $^{13}C\{^1H\}$ NMR spectra were recorded with a Bruker 300 MHz spectrometer, variable-temperature NMR experiments were performed with a Bruker 500 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in Hertz. Elemental analysis was performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. Solid-state NMR spectra were recorded at the EPSRC national solid-state NMR service centre (Durham, UK) with a Varian VNMRS 400 MHz spectrometer (100.562 MHz for ^{13}C), using the cross-polarization pulse sequence (contact time 3.0 ms and recycle delay 1.0 s), with TPPM decoupling. A spinning rate of 6.8 kHz was employed for SiO_2-AMPS and SiO_2-AMPS-SAL; for SiO_2-AMPS-SAL-Zn a rate of 10 kHz was used to remove complications from spinning sidebands. Dipolar dephasing experiments (with a 40 μs dephasing delay) were run to distinguish between CH_2 and CH_3 centres present. Spectral referencing is with respect to TMS.

X-ray Crystallography: Crystallographic data are summarised in (Tables 4 and 5). All data were collected with a Nonius Kappa CCD area detector diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at a temperature of 150(2) K, and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs. Hydrogen atoms, were included in idealised positions and refined using the riding model, except those involved in hydrogen bonding and the imine N=CH atoms of the metal complexes, which were located in difference maps and refined freely. For $Zn(\mathbf{L5})_2$ a molecule of CH_2Cl_2 was also in the asymmetric unit and this was disordered over two positions in a 50:50 ratio. For $Zn_3(OAc)_4(\mathbf{L8})_2$ the ADPs for O(1) and O(2) are slightly less isotropic than desirable, efforts to model disorder in this region of the electron density map afforded no improvement in convergence. Multiscan absorption corrections were applied where appropriate.

CCDC-696979 [for $Zn_3(OAc)_4(\mathbf{L1})_2$], -696980 [for $Zn_3(OAc)_4(\mathbf{L2})_2$], -696981 [for $Zn(\mathbf{L3})_2$], -696982 [for $Zn(\mathbf{L4})_2$], -696983 [for $Zn(\mathbf{L5})_2$], -696984 [for $Zn(\mathbf{L6})_2(MeOH)_2$], -696985 [for $Zn(\mathbf{L7})_2$], -696986 [for $Zn_3(OAc)_4(\mathbf{L8})_2$] and -706554 [for **L5**H] contain the supplementary crystallographic data for this paper and can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of Ligands: An example of the typical synthesis for the ligands is as follows for **L5**H: 3,5-dichloro-2-hydroxybenzaldehyde (6.83 g, 35.6 mmol) was dissolved in MeOH (30 mL), to which 2,4,6-trimethylaniline (5.0 mL, 35.6 mmol) was added. After 30 min a yellow precipitate had formed which was filtered and washed with methanol (3 × 100 mL) and dried (yield 10.1 g, 92%) ^1H NMR (300 MHz, $CDCl_3$): δ = 2.18 (s, 6 H, CH_3), 2.31 (s, 3 H; CH_3), 6.95 (s, 2 H, Ar-H), 7.25 (d, J = 2.5 Hz, 1 H, Ar-H), 7.50 (d, J = 2.5 Hz, 1 H, Ar-H), 8.28 (s, 1 H, N=CH) ppm.

Synthesis and Characterisation of the Complexes: In all cases 5.1 mmol of $Zn(OAc)_2{\cdot}2H_2O$ was employed. The yields quoted are for those of the crystalline material.

$Zn_3(OAc)_4(L1)_2$: $Zn(OAc)_2{\cdot}2H_2O$ (1.10 g, 5.1 mmol) was dissolved in MeOH (20 mL) to which **L1**H (1.0 g, 5.1 mmol) was added. The solution was stirred for 1 h, during which time a yellow solid precipitated out of solution. The solution was filtered and washed with cold MeOH. The product was recrystallised from hot methanol (yield 0.8 g, 57%) ^1H NMR (300 MHz, MeOD): δ = 1.99 (s, 12 H, $O_2C\text{-}CH_3$), 6.76 (m, 2 H, Ar-H), 6.90 (m, 2 H, Ar-H), 7.25–7.47 (m, 14 H, Ar-H), 8.62 (s, 2 H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, MeOD): δ = 22.3 (CH_3 acetate), 120.6 (C), 122.8 (CH), 123.4 (CH), 128.3 (CH), 130.9 (CH), 137.3 (CH), 137.3 (CH), 138.6 (CH), 150.5 (C), 171.1 (CH=N), 181.8 (CO_2) ppm. $C_{34}H_{32}N_2O_{10}Zn_3$ (824.7): calcd. C 49.5, H 3.91, N 3.40; found C 49.5, H 3.91, N 3.40.

$Zn_3(OAc)_4(L2)_2$: An analogous procedure was followed (yield 0.75 g, 44%): ^1H NMR (300 MHz, DMSO): δ = 1.11 (m, 24 H, CH_3), 1.79 (s, 12 H, $O_2C\text{-}CH_3$), 2.99 [m, 4 H, $CH(CH_3)_2$], 6.52 (s, 2 H, Ar-H), 6.71 (s, 2 H, Ar-H), 7.12–7.40 (m, 10 H, Ar-H), 8.25 (s, 2 H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, DMSO): δ = 22.4 (CH_3), 25.3 (CH_3 acetate), 27.5 (CH), 114.1 (CH), 118.4 (C), 122.5 (CH), 123.3 (CH), 126.3 (CH), 135.3 (CH), 137.0 (CH), 141.0 (C), 146.3 (C), 169.9 (C), 173.4 (CH=N), 177.4 (CO_2) ppm. $C_{46}H_{56}N_2O_{10}Zn_3$ (993.0): calcd. C 55.6, H 5.68, N 2.82; found C 55.9, H 5.77, N 2.90.

$Zn(L3)_2$: An analogous procedure was followed (yield 0.62 g, 45%): ^1H NMR (300 MHz, DMSO): δ = 1.79 (s, 12 H, CH_3), 2.25 (s, 6 H, CH_3), 6.60 (m, 2 H, Ar-H), 6.74 (d, J = 8.5 Hz, 2 H, Ar-H), 6.88 (s, 4 H, Ar-H), 7.35 (m, 4 H, Ar-H), 8.26 (s, 2 H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, DMSO): δ = 17.4 (CH_3), 20.4 (CH_3), 114.3 (CH), 118.0 (CH), 122.5 (CH), 129.1 (CH), 130.0 (C), 135.2 (C), 135.8 (CH), 137.1 (CH), 145.5 (C), 170.7 (C), 175.3 (N=CH) ppm. $C_{32}H_{32}N_2O_2Zn_1$ (542.0): calcd. C 70.9, H 5.95, N 5.17; found C 70.5, H 5.92, N 5.19.

$Zn(L4)_2$: An analogous procedure was followed (yield 0.65 g, 43%). ^1H NMR (300 MHz, DMSO): δ = 7.19–7.43 (m, 6 H, Ar-H), 7.44–7.64 (m, 8 H, Ar-H), 8.51 (s, 2 H, HC=N) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, DMSO): δ = 115.5 (C), 120.4 (C), 122.6 (CH), 126.3 (C), 126.5 (CH), 128.9 (CH), 132.7 (CH), 133.8 (CH), 150.5 (C), 163.4 (C), 167.9 (CH=N) ppm. $C_{26}H_{16}Cl_4N_2O_2Zn_1$ (595.6): calcd. C 52.4, H 2.71, N 4.70; found C 52.4, H 2.68, N 4.68.

Table 4. Crystallographic parameters for the Zn^{II} complexes.

Complex	$Zn_3(OAc)_4(\mathbf{L1})_2$	$Zn_3(OAc)_4(\mathbf{L2})_2$	$Zn(\mathbf{L3})_2$	$Zn(\mathbf{L4})_2$
Empirical formula	$C_{34}H_{32}N_2O_{10}Zn_3$	$C_{23}H_{28}NO_5Zn_{1.5}$	$C_{16}H_{16}NOZn_{0.5}$	$C_{26}H_{16}Cl_4N_2O_2Zn$
Formula weight	824.73	496.52	270.98	595.58
Crystal system	triclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*Pcab*	*C*2/*c*
a [Å]	7.5650(3)	8.4590(2)	16.1880(2)	23.9480(6)
b [Å]	9.7100(4)	9.3100(3)	16.7170(2)	9.1820(2)
c [Å]	11.5100(5)	16.3850(6)	20.0650(2)	11.7830(3)
α [°]	93.511(2)	82.833(2)	90	90
β [°]	98.233(2)	77.882(2)	90	110.131(1)
γ [°]	100.016(2)	64.206(1)	90	90
Volume [$Å^3$]	820.79(6)	1135.10(6)	5429.89(11)	2432.68(10)
Z	1	2	16	4
D_{calc}d. [$g\,cm^{-3}$]	1.669	1.453	1.326	1.626
μ [mm^{-1}]	2.236	1.631	0.936	1.477
Reflections collected	8284	12453	72317	20007
θ Range [°]	3.52–25.12	3.59–25.10	3.65–27.47	3.62–27.49
Independent reflections (R_{int})	2885 (0.0552)	3993 (0.0515)	6189 (0.0754)	2783 (0.0433)
Goodness-of-fit	1.021	1.161	1.054	0.989
R_1, wR_2 [$I>2\sigma(I)$]	0.0359, 0.0849	0.0472, 0.1050	0.0366, 0.0876	0.0316, 0.0738
R_1, wR_2 [all data]	0.0516, 0.0934	0.0616, 0.1106	0.0722, 0.0996	0.0425, 0.0796
Max/min difference [$e\,Å^{-3}$]	0.553/–0.698	0.646/–0.464	0.398/–0.495	0.243/–0.521

Table 5. Crystallographic parameters for the Zn^{II} complexes and **LH**5.

Complex	$Zn(\mathbf{L5})_2$	$Zn(\mathbf{L6})_2{\cdot}2MeOH$	$Zn(\mathbf{L7})_2$	$Zn_3(OAc)_4(\mathbf{L8})_2$	**LH5**
Empirical formula	$C_{17}H_{16}Cl_4NOZn_{0.5}$	$C_{20}H_{24}Cl_2NO_2Zn_{0.5}$	$C_{28}H_{24}N_2O_2Zn$	$C_{25}H_{23}N_2O_5Zn_{1.5}$	$C_{32}H_{30}Cl_4N_2O_2$
Formula weight	424.79	413.99	485.86	529.51	616.38
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
Space group	*P*2/*c*	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a [Å]	11.600(2)	13.5150(1)	9.4060(1)	13.6510(1)	7.8540(2)
b [Å]	8.3470(1)	13.9170(1)	18.582(3)	21.1730(2)	8.1440(3)
c [Å]	18.4130(3)	22.0440(2)	13.5230(2)	17.0070(2)	12.3450(4)
α [°]	90	90	90	90	89.513(2)
β [°]	105.174(1)	97.040(1)	106.277(1)	103.140(2)	82.829(2)
γ [°]	90	90	90	90	68.382(1)
Volume [$Å^3$]	1720.68(5)	4114.96(6)	2268.84(6)	4786.82(8)	727.74(4)
Z	4	8	4	8	1
$D_{calcd.}$ [$g\,cm^{-3}$]	1.640	1.336	1.422	1.469	1.406
μ [mm^{-1}]	1.371	0.897	1.111	1.553	0.440
Reflections collected	27921	75865	43347	88622	11255
θ Range [°]	3.64–27.51	3.60–27.51	3.14–27.49	3.06–27.47	4.07–27.44
Independent reflections (R_{int})	3938 (0.0397)	9428 (0.0433)	5192 (0.0636)	10940 (0.0480)	3306 (0.0589)
Goodness-of-fit	1.083	0.939	1.004	0.984	1.003
R_1, wR_2 [$I>2\sigma(I)$]	0.0650, 0.1784	0.0322, 0.0768	0.0357, 0.0883	0.0360, 0.0887	0.0428, 0.0967
R_1, wR_2 [all data]	0.0736, 0.1876	0.0441, 0.0846	0.0553, 0.0992	0.0470, 0.0961	0.0730, 0.1098
Max/min difference [$e\,Å^{-3}$]	0.855/–1.620	0.336/–0.484	0.620/–0.674	1.154/–0.828	0.260/–0.290

$Zn(L5)_2$: An analogous procedure was followed (yield 0.44 g, 25%). ^1H NMR (300 MHz, DMSO): δ = 1.89 (s, 12 H, CH_3), 2.21 (s, 6 H, CH_3), 6.80 (s, 4 H, Ar-H), 7.36 (m, 4 H, Ar-H), 8.22 (s, 2 H, N=CH) 8.32 ($CHCl_3$) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, DMSO): δ = 17.9 (CH_3), 20.4 (CH_3), 114.9 (C), 119.0 (C), 126.6 (C), 128.6 (CH), 129.2 (C), 132.9 (CH), 133.4 (CH), 134.4 (C), 146.5 (C), 163.8 (C), 173.4 (CH=N) ppm. $C_{32}H_{28}Cl_4N_2O_2Zn_1$ (679.8): calcd. C 56.5, H 4.15, N 4.12; found C 56.2, H 4.08, N 4.11.

$Zn(L6)_2(MeOH)_2$: An analogous procedure was followed (yield 0.65 g, 31%). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.79 (br. s, 9 H, CH_3), 1.07 (d, *J* = 7.0 Hz, 12 H, CH_3), 1.19 (d, *J* = 7.0 Hz, 3 H, CH_3), 2.08 (s, 2 H, H_3C-O*H*), 2.94 [m, 4 H, *H*$C(CH_3)_2$], 3.46 (s, 6 H, H_3C-OH), 6.95 (d, *J* = 3.0 Hz, 2 H, Ar-H), 7.08 (m, 4 H, Ar-H), 7.18 (m, 2 H, Ar-H), 7.40 (d, *J* = 3.0 Hz, 2 H, Ar-H), 7.94 (s, 2 H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, $CDCl_3$): δ = 22.6, 23.5 [H*C*$(CH_3)_2$], 25.0, 28.3 [HC$(CH_3)_2$], 50.7 (CH_3OH), 117.3 (C), 118.1 (C), 124.0 (CH), 127.2 (CH), 128.1 (C), 132.8 (CH), 134.6 (CH), 140.9 (C), 145.9 (C), 164.8 (C), 173.4 (CH=N) ppm. $C_{40}H_{48}Cl_4N_2O_4Zn_1$ (828.0): calcd. C 58.0, H 5.79, N 3.38; found C 57.9, H 5.83, N 3.44.

$Zn(L7)_2$: An analogous procedure was followed (yield 0.55 g, 45%). ^1H NMR (300 MHz, DMSO): δ = 2.12 (s, 6 H, CH_3), 6.52–6.61 (m, 2 H, Ar-H), 7.15–7.51 (m, 14 H, Ar-H), 8.71 (s, 2 H, N=CH) ppm. $^{13}C\{^1H\}$ NMR (300 MHz, DMSO): δ = 17.0 (CH_3), 114.2 (CH), 117.7 (C), 121.4 (CH), 126.7 (CH), 129.5 (CH), 130.2 (C), 135.3 (CH), 135.7 (CH), 148.9 (C), 169.3 (C), 170.5 (CH=N) ppm. $C_{28}H_{24}N_2O_2Zn_1$ (485.9): calcd. C 69.2, H 4.98, N 5.77; found C 70.0, H 5.04, N 5.83.

$Zn_3(OAc)_4(L8)_2$: An analogous procedure was followed, except the complex was recrystallised from cold MeOH (yield 0.32 g, 17%). ^1H NMR (500 MHz, $CDCl_3$, –40 °C): δ = 1.91 (s, 6 H, O_2C-C*H*$_3$), 2.17 (s, 6 H, Ar-CH_3), 2.25 (s, 6 H, O_2C-CH_3), 6.78 (m, 6 H, Ar-H) ppm. 6.92 (m, 6 H, Ar-H), 7.10 (s, 2 H, Ar-H), 7.45 (m, 10 H, Ar-H), 7.79 (s, 2 H, N=CH), 7.85 (s, 2 H, N=CH). $^{13}C\{^1H\}$ NMR (500 MHz, $CDCl_3$, –40 °C): δ = 19.6, 22.1, 23.6 (CH_3), 121.3, 122.8, 125.1, 125.6, 127.4, 127.9, 129.6, 141.2, 142.4, 148.0, 151.6 (Ar), 163.3 (Ar-O), 166.6, 168.4 (CH=N), 179.0, 180.3 (CO_2) ppm. $C_{50}H_{46}N_4O_{10}Zn_3$ (1059.0): calcd. C 56.7, H 4.34, N 5.29; found C 56.5, H 4.36, N 5.16.

Preparation of Silica-Supported Heterogeneous Catalyst: Silica (60 Å pore diameter) was initially dried at 130 °C under a dynamic vacuum for 24 h. 3-Aminopropyltrimethoxysilane (3.60 g, 20 mmol) was added to the silica (20 g) in toluene (100 mL) and the slurry stirred at room temperature for 24 h. The solid was filtered and washed with MeOH (4 × 50 mL) and Et_2O (4 × 50 mL) and dried at 100 °C under vacuum to yield SiO_2-AMPS. Elemental analysis: found C 4.45, H 1.30, N 1.56. The solid was added to MeOH (100 mL) to which salicylaldehyde was added (2.44 g, 20 mmol) and the solution stirred for 1 h, during which time the solid became bright yellow. The solid was filtered and washed with MeOH (4 × 50 mL) and Et_2O (4 × 50 mL) to yield SiO_2-AMPS-SAL. Elemental analysis: found C 11.9, H 1.61, N 1.44. SiO_2-AMPS-SAL [3.0 g, 3 mmol (based on salicylaldehyde)] was added to MeOH (30 mL) to which $Zn(OAc)_2 \cdot 2H_2O$ (0.70 g, 3.2 mmol) was added and the solution stirred for 1 h, in which time the solid became pale yellow. After 1 h the solution was filtered and purified via Soxhlet extraction with MeOH to form SiO_2-AMPS-SAL-Zn and dried in vacuo. Elemental analysis: found C 12.2, H 2.61, N 0.99. At each stage the solids were analysed by $^{13}C\{^1H\}$ CP/MAS solid-state NMR spectroscopy.

Polymerisation Procedure: For solvent-free polymerizations the monomer/initiator ratio employed was 300:1 at a temperature of 130 °C, in all cases 2 g of *rac*-lactide were used. After the reaction time methanol (20 mL) was added to quench the reaction and the resulting solid was dissolved in dichloromethane. The solvents were removed in vacuo and the resulting solid was washed with methanol (3 × 100 mL) to remove any unreacted monomer. ^1H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_r (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^1H NMR spectra, the Equation used to calculate P_r and P_m are given by Coates et al.[16] ^1H homonuclear decoupled spectra are given in the Supporting Information. Gel Permeation Chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 µm MIXED-D 300 × 7.5 mm column at 35 °C, THF solvent (flow rate, 1.0 mL/min). The polydispersity index (PDI) was determined from M_w/M_n, where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615–568000 Da. For PLA the M_n values obtained from GPC are typically higher than expected due to the hydrodynamic volume difference between PLA and the polystyrene standards.[46]

Supporting Information (see footnote on the first page of this article): ^1H homonuclear decoupled NMR spectra.

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