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PAPER

Zinc and magnesium complexes supported by bulky multidentate amino-ether phenolate ligands: potent pre-catalysts for the *immortal* ring-opening polymerisation of cyclic esters†

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A family of heteroleptic complexes of zinc and magnesium supported by bulky multidentate amino-ether phenolate ligands has been developed; in combination with external chain transfer agents, they constitute efficient binary catalytic systems for the *immortal* ring-opening polymerisation of cyclic esters.

Introduction

Because they are suitable for a vast array of applications,[1] bio-resourced polyesters such as poly(lactid acid) (PLA) or poly(trimethylene carbonate) (PTMC) are steadily attracting increasing attention from industrial and academic scientists. These polymers are most commonly prepared by ring-opening polymerisation (ROP) of lactide (LA), a monomer obtained by fermentation of sugars, and trimethylene carbonate (TMC), a product derived from glycerol.[2] Other polyesters such as poly(hydroxyalkanoate)s (PHAs) have also emerged as potentially valuable materials,[3] and efforts are for instance now aimed at the ROP of β-butyrolactone (BBL) to yield poly(3-hydroxybutyrate) (PHB), the most common PHA, with controlled macromolecular features.[4] Although the ill-defined tin(II) octoate remains the archetypical initiator used for ROP in industry,[5] a broad range of single-site initiators for the controlled ROP of cyclic esters has been introduced.[6] Thus, in addition to the organocatalysts initially developed by Hedrick and Waymouth,[7] metal complexes based mostly on zinc,[8] aluminium[9] or lanthanides[10] promote living ROP reactions and can sometimes exert a significant degree of control over the tacticity of the resulting polymers through chain-end controlled mechanism.[4,6,8–10] More recently, initiators based on alkaline-earth metals have also shown a remarkable potential,[11] while our group[12] and those of Bochmann,[13] Mountford[10d,10j] and Hayes[14] have shown that well-defined cationic complexes with exacerbated Lewis acidity at the metal centre generate efficient and controlled initiating/catalytic systems.

The implementation of these well-defined catalytic systems at the industrial level remains one of the major challenges in this field. To start addressing this issue, we have shown (following Inoue's pioneering work on epoxides in the 1980s')[15] that some binary catalytic systems combining a chain transfer agent (typically an alcohol such as ^{i}PrOH) with a discrete metal complex or a metal salt for the *immortal* ROP (*i*ROP) of cyclic esters allowed the large-scale polymerisation of these monomers with minute amounts (as low as 10 ppm) of metal catalysts;[16] however, there is undeniably ample room for improvement in this area.

We have recently developed a family of heteroleptic complexes of Zn, Mg and Ca where the metal centres are stabilized by a bulky bis(morpholinomethyl)phenoxy ligand, and shown that effective binary *i*ROP catalysts are generated upon addition of a nucleophilic transfer agent.[11h] In the present contribution, we are extending on these initial results and present a range of heteroleptic complexes of zinc and magnesium where the metal centres are supported by various multidentate amino-ether phenolate ligands. Their versatility and catalytic efficiency in the presence of external transfer agents for the *i*ROP of LA, L-lactide (L-LA), TMC and BBL (Scheme 1) under a wide range of experimental conditions is also discussed.

Results and discussion

Syntheses and characterization

The four pro-ligands {LO^{x}}H (x = 1–4, Scheme 2) were synthesized through one-step Mannich condensations and isolated in high yields (80–95%).[17] The new {LO^{2}}H and {LO^{4}}H are colourless solids that are very soluble in ethers, chlorinated solvents and toluene, but more moderately so in aliphatic hydrocarbons. X-ray quality crystals of these pro-ligands were readily grown from concentrated pentane solutions.

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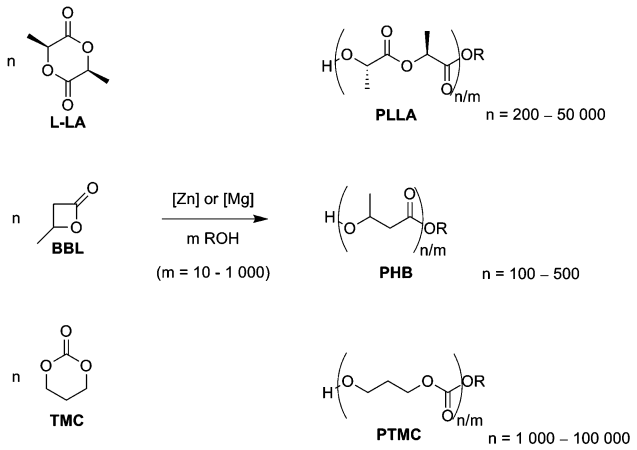
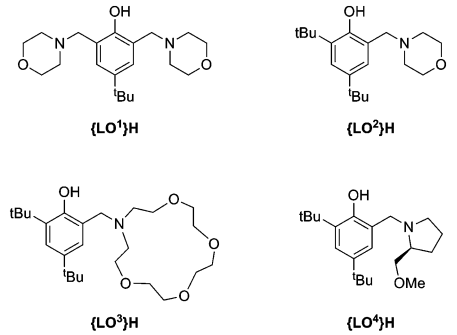
† Electronic supplementary information (ESI) available: VT NMR spectra for **2** and **5**; ^{1}H NMR spectra of compounds **6–10**; FTIR spectrum of **9**, X-ray structure of {LO^{1}}$_2$Zn$_5$(OAc)$_8$; full polymerisation data, NMR and MALDI-ToF MS data of PLLA samples. CCDC reference numbers for {**LO^{2}**}**H** (780419), {**LO^{4}**}**H** (780420), **6** (780417), **7** (780416), **8** (780418) and **9** (782555), and {LO^{1}}$_2$Zn$_5$(OAc)$_8$ (786156). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt01219j



Scheme 1



Scheme 2

Unexpectedly, the reaction of stoichiometric amounts of $\{LO^1\}H$ and $Zn[N(SiMe_3)_2]_2$ did not give the targeted heteroleptic complex $\{LO^1\}ZnN(SiMe_3)$. Instead, under a wide range of experimental conditions (polar or non-polar solvent; –45 to +60 °C), the homoleptic compound $\{LO^1\}_2Zn$ (**1**) was the only isolated product in all cases (eqn (1)). An NMR-scale reaction in toluene-d_8 ($\{LO^1\}H/Zn[N(SiMe_3)_2]_2$ = 1 : 1, 10 min, 23 °C) indicated that although $\{LO^1\}ZnN(SiMe_3)$ could be observed, **1** was already by far the main product at the first point of analysis. Such behaviour was in stark contrast with that previously observed for $Ca[N(SiMe_3)_2]_2(THF)_2$ and $ZnEt_2$, which readily afford the formation of the corresponding heteroleptic complexes $\{LO^1\}ZnEt$ (**2**) and $\{LO^1\}CaN(SiMe_3)$, respectively, upon treatment with $\{LO^1\}H$ (eqn (2) and (3)).[11h] Compound **1** could also be quantitatively prepared by the 2 : 1 reaction of $\{LO^1\}H$ and $Zn[N(SiMe_3)_2]_2$. However, it is noteworthy that the reaction of 2 equiv. of $\{LO^1\}H$ and $ZnEt_2$ yielded **2** (the expected intermediate en route to the formation of **1**) but eventually failed to yield the homoleptic product; the addition of an excess of isopropanol followed by evaporation of the volatiles was required to give **1** in moderate yield (44%).[18]

$$2\ \{LO^1\}H + Zn[N(SiMe_3)_2]_2 \rightarrow \{LO^1\}_2Zn \quad (1)$$

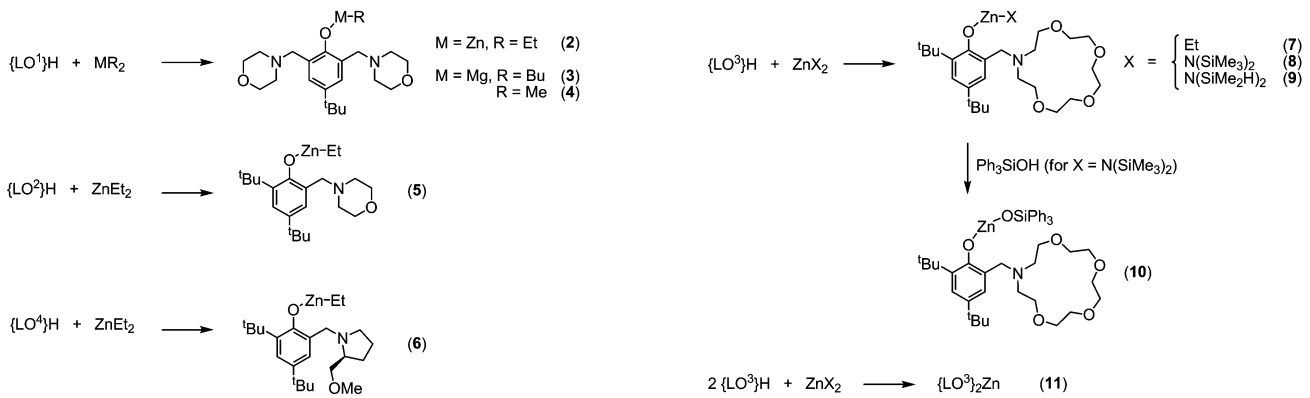
$$\{LO^1\}H + ZnEt_2 \rightarrow \{LO^1\}ZnEt \quad (2)$$

$$\{LO^1\}H + Ca[N(SiMe_3)_2]_2(THF)_2 \rightarrow \{LO^1\}CaN(SiMe_3)_2 \quad (3)$$

Attempts to synthesise the acetate derivative $\{LO^1\}ZnOAc$ by salt metathesis were unsuccessful. The only isolable product from the reaction of $\{LO^1\}K$ with $Zn(OAc)_2$ was again the homoleptic complex **1**, while using the lithium analogue $\{LO^1\}Li$ led to the formation of a hydrocarbon-soluble compound. Based on ^1H NMR data (ESI†), we tentatively describe it as the heterobimetallic complex $\{LO^1\}ZnOAc{\cdot}LiOAc$, but it could not be unambiguously characterised. Moreover, the addition of $\{LO^1\}H$ to $Zn_5(OAc)_6Et_4$ (prepared by comproportionation of $ZnEt_2$ and $Zn(OAc)_2$)[19] yielded an intractable mixture of products which could not be clearly identified by spectroscopic methods. Following recrystallisation, colourless crystals of a polymetallic species with the composition $\{LO^1\}_2Zn_5(OAc)_8$ were isolated, and its solid-state structure was determined (ESI†).

The related reactions of $\{LO^1\}H$ with Mg derivatives gave similar results, and $\{LO^1\}Mg[N(SiMe_3)_2]_2$ free of impurities could not be isolated. However, following the route established for the preparation of $\{LO^1\}MgBu$ (**3**),[11h] the methyl complex $\{LO^1\}MgMe$ (**4**) was successfully synthesised by reaction of $\{LO^1\}H$ with $MgMe_2(THF)_{1.5}$ (Scheme 3). This compound was isolated as a highly air-sensitive white solid, which is very soluble in THF but moderately so in Et_2O and toluene, and only sparingly soluble in aliphatic hydrocarbons. All attempts to obtain crystals of **4** suitable for X-ray diffraction crystallography have been unsuccessful so far.

The heteroleptic complexes $\{LO^2\}ZnEt$ (**5**) and $\{LO^4\}ZnEt$ (**6**) were prepared in high yields from the reaction of the corresponding pro-ligands with $ZnEt_2$ in toluene at –45 °C. The rationale was that the presence of a single functionalized side-arm (chiral in the



Scheme 3 Syntheses of heteroleptic complexes **4**–**11**.[22]

case of **6**) in these complexes, by opposition to two in compound **2**, would bear an influence on their *i*ROP catalytic activity (*vide infra*). Whereas the solubility properties of **5** were similar to those of **2** (*i.e.* soluble in THF, Et_2O and chlorinated solvents, but very poorly so in hydrocarbons), **6** was surprisingly soluble in pentane, and colourless X-ray quality crystals were obtained by re-crystallization from a concentrated solution in this solvent at –30 °C.

Because of its greater flexibility and chelating ability, the use of {LO^3}H was investigated in further details (Scheme 3). The alkyl derivative {LO^3}ZnEt (**7**) was prepared in 81% yield. More interestingly, the {LO^3}$^-$ framework proved able to stabilize other heteroleptic species, and {LO^3}ZnN(SiMe$_3$)$_2$ (**8**) and {LO^3}ZnN(SiMe$_2$H)$_2$ (**9**) were obtained by reaction of {LO^3}H with Zn[N(SiMe$_3$)$_2$]$_2$ and Zn[N(SiMe$_2$H)$_2$]$_2$, respectively. Both compounds are soluble in all common organic solvents, and crystals suitable for X-ray diffraction crystallography were grown from saturated solutions in heptane (**8**) or pentane (**9**). The initial assumption that **9** could be potentially stabilized against ligand re-distribution reactions thanks to internal β-Si–H agostic interactions[20–21] was not verified, as no evidence of such secondary interactions with the metal centre could be detected either in solution or in the solid-state (*vide infra*). Indeed, in the ^{1}H NMR spectrum of **9**, the resonance for the Si–*H* moiety is rather deshielded (δ = 5.10 ppm), but the $^1J_{Si-H}$ coupling constant of 180 Hz is diagnostic of non-interacting Si–H.[20] This is further confirmed by FTIR spectroscopy, where the ν_{Si-H} band at 2064 cm^{-1} is indicative of the absence of interactions with the metal. {LO^3}ZnOSiPh$_3$ (**10**) was cleanly obtained upon addition of 1 equiv. of Ph$_3$SiOH to a solution of **8** at –20 °C. The presence of the homoleptic species {LO^3}$_2$Zn (**11**) could hardly be detected at any stage of the formation or characterisation of **10**; besides, no sign of degradation or evolution was detected during the NMR monitoring of a solution of **10** in C_6D_6 over a period of several days, which further supported the remarkable ability of the {LO^3}$^-$ platform to stabilize heteroleptic species. Finally, the homoleptic complex **11** was independently synthesised in quantitative fashion by reaction of {LO^3}H (2 equiv.) and Zn[N(SiMe$_3$)$_2$]$_2$.

Like previously with **2** and **3**,[11h] the room temperature ^{1}H NMR spectra in C_6D_6 of compounds **4** and **5** exhibited very broad signals for the morpholinomethyl substituents and low temperature NMR in toluene-d_8 was necessary to freeze the fluxionality. On the other hand, the ^{1}H NMR spectra recorded at room temperature in C_6D_6 of **6** and, more surprisingly, **7–10**, were remarkably well resolved, indicating a certain level of rigidity even in solution. Unambiguous assignments could be achieved without need to perform low temperature NMR experiments (ESI†).

Crystallographic studies

The solid-state structures of the pro-ligands {LO^2}H and {LO^4}H were determined by X-ray diffraction methods (Fig. 1 and 2). Both compounds crystallized as large colourless blocks from cold pentane solutions. Each unit cell of the enantiomerically pure {LO^4}H contained two independent molecules of the (*S*) enantiomer.

Colourless crystals of **1** were obtained from a solution in C_6D_6. Although their quality was insufficient (R_1 = 11.82%) to allow a satisfactory determination of the structure and thus

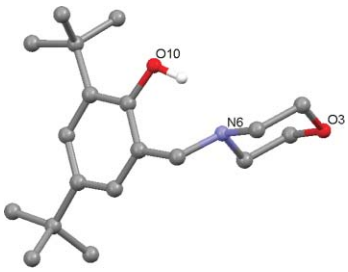


Fig. 1 Solid-state structure of {LO^2}H with atom labelling scheme. Hydrogen atoms (except the phenolic H) are omitted for clarity.

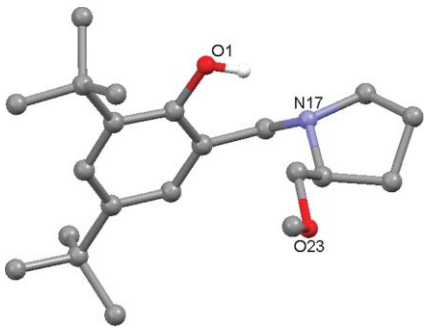


Fig. 2 Solid-state structure of {LO^4}H with atom labelling scheme. Only one of two independent molecules in the unit cell is displayed. Hydrogen atoms (except the phenolic H) are omitted for clarity.

prevented accurate discussion of the bonding parameters in **1**, the environment around the metal centre could be established (Fig. 3). The Zn atom lies in a tetrahedral environment and is coordinated by the two surrounding O-phenolate atoms and two nitrogen atoms from morpholine side-arms carried by different ligands. Thus, in each {LO^1}$^-$ fragment, one morpholine tether is involved in the stabilization of the metal by coordination of the N atom only, while the second one does not interact with it. All four morpholine groups retain their chair conformation in the solid-state.

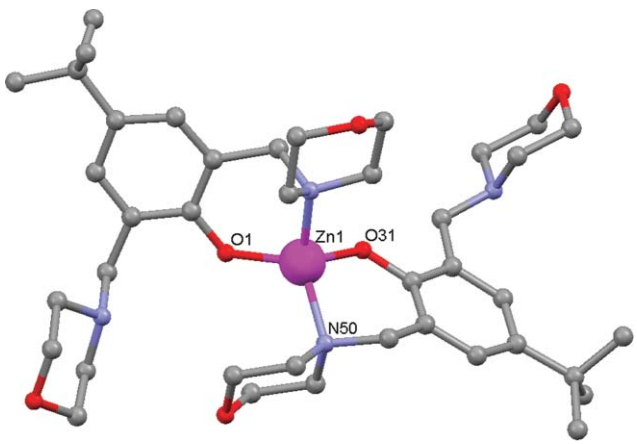


Fig. 3 Solid-state structure of {LO^1}$_2$Zn (**1**) with atom labelling scheme. Hydrogen atoms are omitted for clarity.

In complex **6**, the ligand is κ^3-*O*,*O*,*N* coordinated to the metal centre. The geometry is completed by the ethyl substituent and adopts a distorted tetrahedral arrangement (Fig. 4). All bond lengths to the Zn atom are unexceptional, and fall in the typical

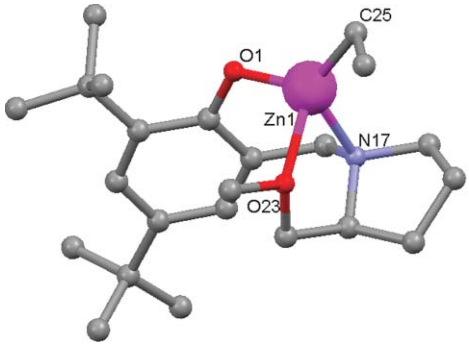


Fig. 4 Solid-state structure of {LO4}ZnEt (**6**) with atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Zn1–O1 = 1.926(1), Zn1–O23 = 2.214(1), Zn1–N17 = 2.129(1), Zn1–C25 = 1.973(15).

range expected for such bonds.[8f-g,11h] The distance to the σ-bonded oxygen atom (1.926 Å) is substantially shorter than that the π-donating one (2.214 Å). It is noteworthy that the metal is relatively accessible owing to the limited bulkiness of the various ligands: while one half of the coordination sphere is adequately filled by the tridentate $\{LO^4\}^-$, the other half is only occupied by the small ethyl group.

Compounds **7, 8** and **9** all crystallized as colourless blocks and their solid-state structures were also elucidated (Fig. 5, 6 and 7); **7** contains two independent but similar molecules per asymmetric unit. In all cases, the metal is 4-coordinated and lies in a slightly distorted tetrahedral environment: the bulky $\{LO^3\}^-$ ancillary ligand coordinates in a κ^3-*N*,*O*,*O* fashion to the central metal atom, and the coordination sphere is fully completed by the amide/ethyl group. The large crown-ether tether in **7–9** confers more steric shielding to the metal centre than observed with the pyrolidinyl fragment in the case of **6**. The distances between Zn and the coordinated N and O atoms in compounds **7–9** are similar to those identified for related complexes.[8f-g] Interestingly, there is no indication in the solid-state of secondary β–Si···H agostic interaction with the metal centre in **9**, as the Si1–N1–Zn1, Si2–N1–Zn1 and Si1–N1–Si2 angles of 120.28(8), 114.03(8) and 125.64(9)° respectively are very similar to those found (for instance) in **8**. This is in agreement with the NMR and FTIR spectroscopic data (*vide supra*), but nonetheless contrasts starkly with the observations we

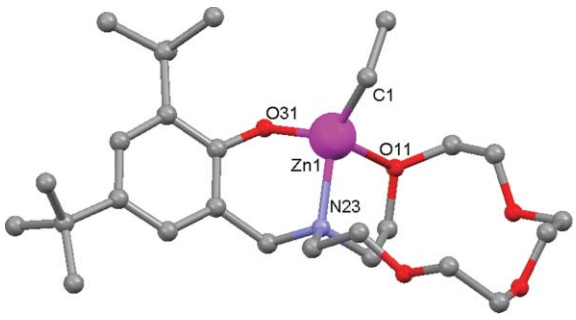


Fig. 5 Solid-state structure of $\{LO^3\}$ZnEt (**7**) with atom labelling scheme. Only one of the two independent molecules in the unit cell is displayed. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: Zn1–O31 = 1.956(1), Zn1–C1 = 1.987(2), Zn1–N23 = 2.152(2), Zn1–O11 = 2.184(1).

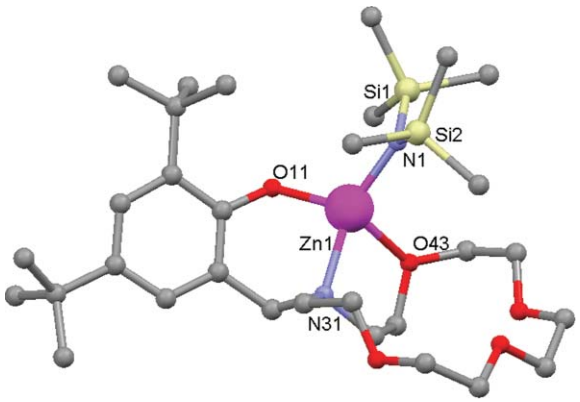


Fig. 6 Solid-state structure of $\{LO^3\}ZnN(SiMe_3)_2$ (**8**) with atom labelling scheme. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and bond angles [°]: Zn1–N1 = 1.921(1), Zn1–O11 = 1.939(1), Zn1–N31 = 2.121(1), Zn1–O43 = 2.213(1); Si1–N1–Zn1 = 114.47(7), Si2–N1–Zn1 = 119.17(7), Si1–N1–Si2 = 125.71(7).

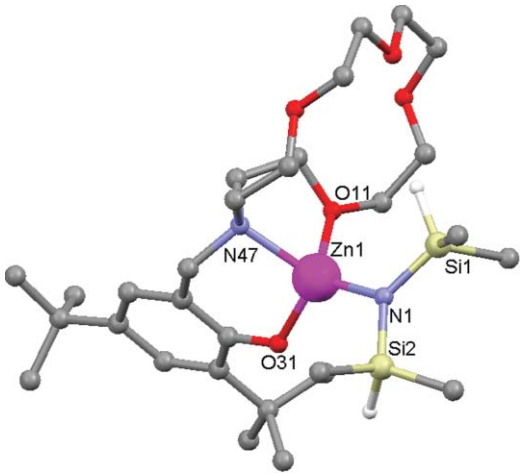


Fig. 7 Solid-state structure of $\{LO^3\}ZnN(SiMe_2H)_2$ (**9**) with atom labelling scheme. Hydrogen atoms are omitted (except those on Si atoms) for clarity. Selected bond lengths [Å] and bond angles [°]: Zn1–N1 = 1.911(1), Zn1–O31 = 1.9117(11), Zn1–N47 = 2.100(1), Zn1–O11 = 2.117(1); Si1–N1–Zn1 = 120.28(8), Si2–N1–Zn1 = 114.03(8), Si1–N1–Si2 = 125.64(9).

recently made during the study of the analogous large alkaline-earth derivatives (Ca, Sr and Ba).[21]

Polymerisation studies

As part of our ongoing studies aiming at developing efficient catalytic systems (in terms of monomer consumed *and* polymer chains formed) for the *immortal* ROP of cyclic esters,[11h,12,16] the ability of compounds **4–10** to promote the *i*ROP of (L-)LA, BBL and TMC in the presence of external chain transfer agents was assessed.

Upon addition of an excess of ^{i}PrOH, all complexes provided efficient binary catalytic systems for the controlled *i*ROP of L-LA (Table 1), without detectable epimerisation of the chiral centres. Under our standard experimental conditions (toluene, 60 °C, $[L\text{-}LA]_0 = 2.0$ M, $[L\text{-}LA]_0/[Met]_0/[^iPrOH]_0 = 1000:1:10$), Zn complexes **5–9** displayed good to excellent activities (entries 5, 8, 10, 12 and 15) and were able to quantitatively convert

Table 1 Selected data for the ROP of L-LA and *rac*-LA using **2–10**/^{i}PrOH binary catalytic systems[a]

Entry	Initiator	LA	$[LA]_0$:$[Met]_0$:$[^{i}PrOH]_0$	$[LA]_0$/mol L^{-1}	Time/min	Yield[b] (%)	TOF[c]/h^{-1}	$M_{n,calc}$[d]/g mol^{-1}	$M_{n,SEC}$[e]/g mol^{-1}	M_w/M_n[e]	P_r[f]
1	**2**[h]	L-	1 000:1:10	2.0	60	97	970	14 030	15 100	1.10	0
2	**2**[h]	L-	5 000:1:25	4.0	60	71	3550	20 510	20 600	1.09	
3	**2**[h]	L-	5 000:1:25	4.0	90	94	3130	27 130	26 200	1.16	
4	**4**	L-	1000:1:10	2.0	15	98	3920	14 170	12 900	1.12	
5	**5**	L-	1000:1:10	2.0	60	98	980	14 170	15 100	1.09	0
6	**5**	L-	5000:1:25	4.0	60	45	2250	13 020	13 200	1.09	
7	**5**	L-	5000:1:25	4.0	90	92	3070	26 560	26 300	1.12	
8	**6**	L-	1000:1:10	2.0	60	97	970	14 030	15 300	1.09	0
9	**6**	L-	5000:1:25	4.0	90	98	3270	28 280	26 100	1.14	
10	**7**	L-	1000:1:10	2.0	60	96	960	13 880	15 500	1.07	
11	**8**	L-	200:1:-	0.5	15	49	392	14 170	67 400	1.39	
12	**8**	L-	1000:1:10	2.0	10	94	5640	13 600	16 600	1.07	0
13	**8**	L-	5000:1:25	4.0	60	95	4750	27 420	24 700	1.18	
14	**8**	L-	5000:1:250	4.0	60	96	4800	2820	2900	1.16	
15	**9**	L-	1000:1:10	2.0	10	96	5760	13 880	13 800	1.08	
16	**10**	L-	1000:1:10	2.0	60	52	520	7 550	8700	1.07	0
17	**2**[h]	*rac*-	1000:1:10	2.0	60	99	990	14 320	12 200	1.20	0.50
18[g]	**2**[h]	*rac*-	1000:1:10	2.0	60	68	680	9850	9600	1.12	0.55
19	**5**	*rac*-	1000:1:10	2.0	60	99	990	14 320	15 200	1.21	0.46
20[g]	**5**	*rac*-	1000:1:10	2.0	60	92	920	13 310	9100	1.32	0.60
21	**6**	*rac*-	1000:1:10	2.0	60	99	990	14 320	13 700	1.23	0.61
22[g]	**6**	*rac*-	1000:1:10	2.0	60	95	950	13 740	11 100	1.20	0.61
23	**8**	*rac*-	1000:1:10	2.0	15	97	3880	14 030	13 000	1.08	0.51
24[g]	**8**	*rac*-	1000:1:10	2.0	15	88	3520	12 730	9900	1.09	0.63

[a] Polymerisations in toluene at 60 °C. [b] Isolated yield of PLLA. [c] Non-optimized turnover frequency (mol(LA)·mol(Met)$^{-1}$·h^{-1}). [d] Calculated from $[LA]_0/[^{i}PrOH]_0 \times$ monomer conversion $\times M_{LA} + M_{iPrOH}$, with M_{LA} = 144 g mol^{-1} and M_{iPrOH} = 60 g mol^{-1}. [e] Determined by size exclusion chromatography *vs.* polystyrene standards and corrected by a factor of 0.58.[30] [f] Probability of a racemic linkage between two repetitive units as determined by ^{1}H NMR.[24] [g] Reactions carried out in THF. [h] Taken from reference 11h.

the monomer in 60 min; they compared at least equally with initiator **2** (entries 1–3) which we have already reported.[11h,22] Compound **2**, which possesses two morpholine groups, is as active as its congener **5**, which only has one morpholinomethyl tether (compare entries 1–3 and 5–7): this presumably reflects that no significant stabilizing effect arises from the presence of the second heterocyclic substituent.[23] The amido derivative **8** yielded the most outstanding catalyst, typically requiring less than 10 min to polymerize 1000 equiv. of monomer (TOF = 5640 h^{-1}, entry 12) or 60 min to fully convert 5000 equiv. of L-LA in the presence of 25–250 equiv. of ^{i}PrOH (entries 13–14, TOF = 4800 h^{-1}). There was essentially no difference in the *i*ROP catalytic behaviour of compounds **8** and **9** (entries 12 and 15), highlighting that the identity of the initial amido group bears little influence on the outcome of the *immortal* ROP of L-LA: indeed, both lead to the immediate *in situ* formation of "{LO^3}ZnO^{i}Pr", the putative initial active species, upon treatment with excess ^{i}PrOH (ESI†).[16f] In agreement with our earlier observations with **3**,[11h] the Mg-based system **4**/^{i}PrOH also proved very active (entry 4, TOF = 3900 h^{-1}), but owing to the sensitivity of this highly electrophilic species, the conversion of higher monomer loadings (*ca.* 2500–5000 equiv.) could not be accomplished in a reproducible fashion.[23] All systems exhibited good control over the polymerisation parameters with rapid and efficient transfer between the growing polymer chains and the dormant (macro)alcohols, as evidenced by the narrow molecular weight distributions of the resulting polymers (in the range 1.1–1.2) and the agreement between theoretical and observed molecular weights.[16f,23]

The best compromise, **8**/^{i}PrOH, was subjected to closer scrutiny. Characteristically for amido derivatives,[8g] the addition of external transfer agent was required to produce a suitable initiator and/or catalyst, as otherwise the polymerisation was fast but poorly controlled (entry 11, TOF = 392 h^{-1}, M_w/M_n = 1.39, $M_{n,SEC} \gg M_{n,theo}$). In fact, full conversion of 1000 equiv. of monomer ($[L\text{-}LA]_0/[Met]_0/[^{i}PrOH]_0$ = 1000 : 1 : 10; $[L\text{-}LA]_0$ = 2.0 M) in toluene at 60 °C was essentially reached within 8 min, and the molecular weight increased linearly with conversion (ESI†). A semi-logarithmic plot of monomer conversion *vs.* reaction time gave $k_{app,60}$ = 0.651 min^{-1}; this value compares favourably with those found for the *i*ROP of L-LA in styrene promoted by {BDI^{iPr}}ZnN($SiMe_3$)$_2$ (BDI^{iPr} = CH(MeCN$C_6H_3{}^{i}Pr_2$)$_2$; $k_{app,50}$ = 0.094 min^{-1}, $k_{app,100}$ = 0.483 min^{-1}).[16e] The polymerisation of 5000 equiv. of L-LA was then conducted in the presence of **8** and varying amounts of ^{i}PrOH (25–250 equiv.): over the whole range, the control was good (M_w/M_n = 1.11–1.18), and the values of the experimental molecular weights matched closely their calculated ones (Fig. 8).

The *immortal* nature of these ROP catalytic systems was confirmed by detailed examination of the polymer end-groups. Thus, analysis by MALDI-ToF mass spectroscopy of low molecular weight samples produced by **8**/^{i}PrOH (Fig. 9) indicated the existence of a single family of polymer chains capped by –CH(CH_3)OH and ^{i}PrOC(O)– *termini*. This was further substantiated by NMR spectroscopy (ESI†). Moreover, the absence of undesirable transesterification reactions in the *i*ROP of L-LA (m.w. = 144 g mol^{-1}) catalyzed by these systems is supported by MALDI-ToF MS analyses, as consecutive peaks are separated by increments of 144 Da (Fig. 9).

This is in agreement with the very low values found for the molecular weight distributions of these polymers (*vide supra*).

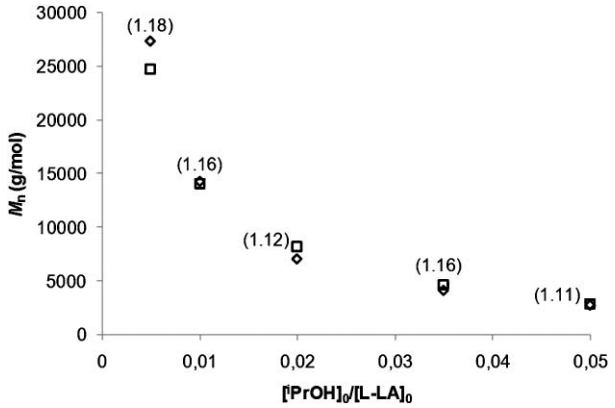


Fig. 8 Plot of M_n *vs.* alcohol-to-metal ratio for the polymerisation of L-LA (complete conversion) in toluene at 60 °C with **8**/^{i}PrOH at $[L\text{-}LA]_0$ = 2.0 M and $[L\text{-}LA]_0/[\mathbf{8}]_0$ = 5 000:1. (□) Experimental M_n determined by SEC (M_w/M_n in brackets); (◇) Calculated M_n.

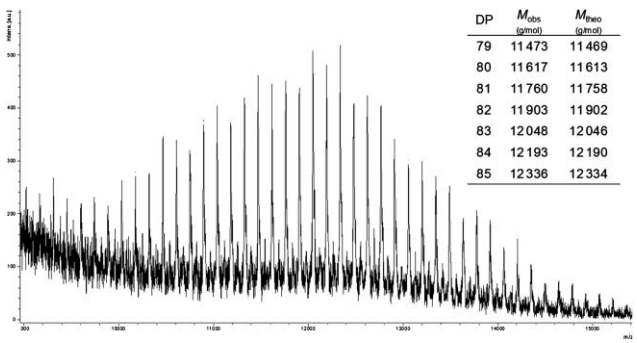


Fig. 9 MALDI-ToF MS spectrum (main population: Na^+; minor population: K^+) of a PLLA sample obtained with $[L\text{-}LA]_0/[\mathbf{8}]_0/[^i PrOH]_0$ = 5000 : 1 : 50, 99% conversion); theoretical molecular weights calculated according to DP × M_{LA}+M_{iPrOH}+M_{Na}, where DP is the degree of polymerisation, M_{LA} = 144.13, M_{iPrOH} = 60.10 and M_{Na} = 23.09 g mol^{-1}.

Compounds **2**, **5**, **6** and **8** were also tested for the *i*ROP of *racemic* lactide (Table 1, entries 13–23). Although they displayed equally good activities, the resulting polymers disappointingly were only slimly heterotactic-enriched, with P_r values typically[8g] in the range 0.5–0.6.[24] The reactions run in THF were slower than those performed in toluene, most probably as a result of competitive coordination of the solvent onto the metal centre, but resulted in slightly higher probability of racemic enchainment of two repetitive units.

The effectiveness of the binary catalyst **8**/^{i}PrOH to promote the *i*ROP of other monomers illustrated the versatility of this family of catalysts. The bulk polymerisation of *rac*-BBL with $[BBL]_0/[\mathbf{8}]_0/[^i PrOH]_0$ = 500 : 1 : 10 gave atactic PHB with 63% conversion after 3 h (non-optimized reaction time) and a corresponding TOF of 105 h^{-1}. The agreement between theoretical ($M_{n,theo}$ = 2700 g mol^{-1}) and experimental ($M_{n,SEC}$ = 2900 g mol^{-1}) molecular weight was satisfactory, and the molecular weight distribution was relatively narrow (M_n/M_n = 1.26). Besides, the polymerisation of TMC in toluene catalyzed by **8**/^{i}PrOH ($[TMC]_0/[\mathbf{8}]_0/[^i PrOH]_0$ = 1000 : 1 : 10, $[TMC]_0$ = 2.0 M, 60 °C) proceeded even more rapidly than that of *rac*- or L-LA: indeed, full conversion was obtained within as little as 5 min (TOF = 11 280 h^{-1}), and the controlled nature of the mechanism was supported by molecular weight features ($M_{n,theo}$ = 15 700 g mol^{-1}, $M_{n,SEC}$ = 13 800 g mol^{-1}, M_n/M_n = 1.49) characteristic of this type of polymerisation.[16b,c] Finally, this family of catalytic precursors can also operate under very specific experimental conditions: in combination with a bi-functional alcohol such as 4-hydroxy-2,2,6,6-tetramethylpiperidinyloxy (TEMPO-OH) or 1-hydroxy-2-phenyl-2-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)-ethane (10–50 equiv.), **2** or **8** afford (in toluene or styrene) complete conversion of the monomer (L-LA or TMC, 1000–5000 equiv.) to give end-capped PLLAs or PTMCs which constitute suitable initiators for the nitroxy-mediated polymerisation of styrene (ESI†).[16e]

Conclusions

We have extended the use of multidentate amino-ether phenolate ligands for the preparation of heteroleptic complexes of zinc and magnesium. The specific ability of the bulky, yet flexible, phenolate-aza-crown-ether ligand framework $\{LO^3\}^-$ to support the formation of various heteroleptic species (where the metal bears an alkyl, amido or alkoxy nucleophilic group) has been illustrated. These complexes constitute remarkable pre-catalysts for the rapid *immortal* ring-opening polymerisation of cyclic esters, and produce some of the most active ROP catalysts known to date. The ease of synthesis and the versatility of these precursors represent their most attractive features, as they can promote the ROP of a wide array of monomers under various experimental conditions. We are currently investigating the use of these and other related complexes as co-catalysts for the large-scale production of bio-resourced polymers, while also trying to improve their degree of control over the stereochemistry of these reactions.

Experimental

General procedures

All manipulations were performed under inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; O_2 < 1 ppm, H_2O < 5 ppm) for catalyst loading. Compounds $Zn[N(SiMe_3)_2]_2$,[25] $Zn[N(SiMe_2H)_2]_2$,[26] $\{Mg[N(SiMe_3)_2]_2\}_2$,[27] $MgMe_2(THF)_{1.5}$,[28] $\{LO^1\}H$,[29] $\{LO^1\}ZnEt$ (**2**)[11h] and $\{LO^1\}MgBu$ (**3**)[11h] were prepared as described in the literature. $ZnEt_2$ (1.0 M in hexanes) and $MgBu_2$ (1.0 M in heptane) were received from Aldrich and transferred to sealed ampoules for storage. 4-*tert*-butyl-phenol (Alfa Aesar, 99%), formaldehyde (Acros, 37 wt-% solution in water) and morpholine (Acros, 99%) were used directly as received. $HN(SiMe_3)_2$ (Aldrich), $HN(SiMe_2H)_2$ (Aldrich), Ph_3SiOH (Acros), 1-aza-15-crown-5 (IBC), 2,4-di-*tert*-butylphenol (Acros) and (*R*)-2-(methoxymethyl)pyrrolidine (Apollo) were used as purchased. ^{i}PrOH (HPLC grade, VWR) was dried and distilled over magnesium turnings and then stored over activated 3 Å molecular sieves. Toluene was pre-dried over sodium, and distilled under Argon from melted sodium prior to use. THF was first pre-dried over sodium hydroxide and distilled under argon over CaH_2, and then freshly distilled a second time under argon from sodium mirror/benzophenone prior to use. Dioxane was distilled from sodium mirror/benzophenone. All deuterated solvents (Eurisotop) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several

freeze-thaw cycles. Technical grade L-lactide (L-LA) was provided by Total Petrochemicals; *rac*-lactide (*rac*-LA, 99%) was received from Acros. Purification of either of these isomers of lactide (LA) was typically ensured according to a three-step procedure by re-crystallisation from a hot, concentrated ^{i}PrOH solution (80 °C), followed by two subsequent re-crystallisations in hot toluene (105 °C). After purification, LA was stored at a temperature of –30 °C in the glove-box. Racemic β-butyrolactone (*rac*-BBL; TCI Europe, 97%) was purified by vacuum distillation from calcium hydride and kept over activated 3 Å molecular sieves. Trimethylene carbonate (TMC, Boehringer Ingelheim) was purified by stirring a concentrated solution of the monomer in THF over CaH_2 for a minimum of 48 h, followed by filtration and re-crystallization at –24 °C.

NMR spectra were recorded on Bruker AC-300, AM-400 and AM-500 spectrometers. All chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated *vs.* $SiMe_4$. Assignment of the signals was carried out using 1D (^{1}H, ^{13}C{^{1}H}) and 2D (COSY, HMBC, HMQC) NMR experiments.

FTIR spectra were recorded at room temperature as nujol mulls in KBr plates on a IR Affinity-1 Shimadzu apparatus.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyser instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements.

Size Exclusion Chromatography (SEC) measurements were performed on a Polymer Laboratories PL-GPC 50 instrument equipped with a PLgel 5 Å MIXED-C column and a refractive index detector. The GPC column was eluted with THF at room temperature at 1 mL min^{-1} and was calibrated using 11 monodisperse polystyrene standards in the range 580 to 380000 g mol^{-1}. According to literature recommendations, the molecular weights of all PLAs were corrected by a factor of 0.58,[30] while the values for PTMCs were adjusted by a factor of 0.88.[16c] The molecular weight of PHBs are directly given *vs.* polystyrene equivalents.

The microstructures of PLA samples were determined by examination of the methine region in the homodecoupled ^{1}H NMR spectrum of the polymers recorded at room temperature in $CDCl_3$ on a Bruker AM-500 spectrometer with concentrations in the range 1.0 to 2.0 mg mL^{-1}.

MALDI-TOF MS spectra were obtained with a Bruker Daltonic MicroFlex LT, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20kV. Samples were prepared as follow: 1 μL of a 2 : 1 mixture of a saturated solution of α-cyano-4-hydroxycinnamic acid (Bruker Care) in HPLC quality acetonitrile and a 0.1% solution of trifluoroacetic acid in ultrapure water was deposited on the sample plate. After evaporation, 1 μL of a 5 to 10 mg mL^{-1} solution of the polymers in HPLC quality THF were deposited. Bruker Care Peptide Calibration Standard and Protein Calibration Standard I were used for external calibration.

Synthesis of {LO^2}H

Formaldehyde (6.4 g of a 37 wt-% solution in water, 78.8 mmol) was added to a mixture of 2,4-di-*tert*-butyl-phenol (12.2 g, 59.1 mmol) and morpholine (6.2 mL, 70.9 mmol) in dioxane (90 mL). The mixture was refluxed overnight (120 °C). Volatiles were then pumped off, and the resulting sticky solid was extracted with toluene. The solution was washed twice with brine, dried over $MgSO_4$, and toluene was evaporated to give {LO^2}H (17.0 g, 94%) as a white powder. Colourless X-ray quality crystals were grown overnight from a concentrated pentane solution stored at +4 °C. Found C 75.2, H 10.2, N 5.1%. $C_{19}H_{31}NO_2$ requires C 74.7, H 10.2, N 4.6%.

^{1}H NMR ($CDCl_3$, 200.13 MHz, 25 °C): δ_H 10.7 (1 H, br s, ArO-*H*), 7.26 (1 H, d, $^4J_{HH}$ = 1.7 Hz, arom-*H*), 6.88 (1 H, d, $^4J_{HH}$ = 1.7 Hz, arom-*H*), 3.79 (4 H, m, O–C*H*$_2$), 3.72 (2 H, s, Ar–C*H*$_2$–N), 2.60 (4 H, br s, N–C*H*$_2$–CH$_2$), 1.45 (9 H, s, C(C*H*$_3$)$_3$), 1.32 (9 H, s, C(C*H*$_3$)$_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 50.33 MHz, 25 °C): δ_C 153.9, 140.7, 123.6, 123.1, 120.0 (aromatic), 66.8 (O–*C*H$_2$), 62.6 (Ar–*C*H$_2$–N), 52.7 (N–*C*H$_2$–CH$_2$), 34.8 (*C*(CH$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 31.6 (C(*C*H$_3$)$_3$), 29.5 (C(*C*H$_3$)$_3$).

Synthesis of {LO^3}H

In an improvement of a literature procedure,[17b] formaldehyde (2.21 g of a 37 wt-% solution in water, 27.2 mmol) was added to a mixture of 2,4-di-*tert*-butyl-phenol (4.71 g, 22.9 mmol) and 1-aza-15-crown-5 (4.78 g, 21.8 mmol) in dioxane (140 mL). The mixture was refluxed overnight (120 °C). The volatile fraction was removed under vacuum, and the resulting oil was dissolved in Et_2O and extracted twice with acidified water (pH < 2). The combined aqueous layers were then treated with Na_2CO_3 to pH > 10, and extracted twice with Et_2O. The combined organic layers were dried over $MgSO_4$ and evaporated to give {LO^3}H (8.46 g, 88%) as a pale yellow oil. Its characterization matched that already reported for this ligand.[17b]

Synthesis of {LO^4}H

Formaldehyde (2.20 g of a 37 wt-% solution in water, 27.1 mmol) was added to a mixture of 2,4-di-*tert*-butyl-phenol (4.37 g, 21.2 mmol) and (*R*)-2-(methoxymethyl)pyrrolidine (2.44 g, 21.2 mmol) in dioxane (60 mL). The mixture was refluxed overnight (120 °C). Volatiles were then pumped off to give an orange oil which was dissolved in toluene. After several washings with water, the organic layer was dried over $MgSO_4$ and evaporated to give a pale orange oil. Analytically pure {LO^4}H (6.68 g 94%) could be isolated by re-crystallization from a cold (+4 °C), concentrated pentane solution. Found C 75.6, H 10.6, N 4.2%. $C_{21}H_{35}NO_2$ requires C 75.6, H 10.6, N 4.2%.

^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ_H 11.06 (1 H, br s, ArO-*H*), 7.48 (1 H, d, $^4J_{HH}$ = 2.4 Hz, arom-*H*), 6.94 (1 H, d, $^4J_{HH}$ = 2.4 Hz, arom-*H*), 4.19 (1 H, d, $^2J_{HH}$ = 14.1 Hz, Ar–C*H*$_2$–N), 3.18 (1 H, d, $^2J_{HH}$ = 14.1 Hz, Ar–C*H*$_2$–N), 3.14 (1 H, m, OC*H*$_2$), 3.09 (1 H, m, O–C*H*$_2$), 3.05 (3 H, s, O–C*H*$_3$), 2.83 (1 H, m, N–C*H*$_2$–CH$_2$), 2.46 (1 H, m, N–C*H*), 1.93 (1 H, m, N–C*H*$_2$–CH$_2$), 1.71 (9 H, s, C(C*H*$_3$)$_3$), 1.57 (1 H, m, N–CH–C*H*$_2$–CH$_2$), 1.42 (2 H, m, N–CH–C*H*$_2$–CH$_2$ + N–CH$_2$–C*H*$_2$), 1.37 (9 H, s, C(C*H*$_3$)$_3$), 1.27 (1 H, m, N–CH$_2$–C*H*$_2$).

^{13}C{^{1}H} NMR (C_6D_6, 100.62 MHz, 25 °C): δ_C 154.7, 140.1, 135.4, 122.7, 122.5, 122.4 (aromatic), 74.9 (O–*C*H$_2$), 63.3 (N–*C*H), 59.3 (Ar–*C*H$_2$–N), 58.4 (O–*C*H$_3$), 54.0 (N–*C*H$_2$–CH$_2$), 35.0 (*C*(CH$_3$)$_3$), 34.0 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H3)3), 29.7 (C(*C*H3)3), 28.1 (N–CH–*C*H$_2$–CH$_2$), 22.8 (N–CH$_2$–*C*H$_2$).

Synthesis of {LO¹}₂Zn (1)

Route A. A solution of {LO¹}H (1.58 g, 4.53 mmol) in toluene (50 mL) was added to a solution of $ZnEt_2$ (2.26 mL of a 1.0 M solution in hexanes, 2.26 mmol) in toluene (100 mL). Dry isopropanol (1.73 mL, 22.6 mmol) was then added with a syringe and the resulting mixture was stirred at 60 °C for 3 h. Removal of the volatiles and repeated washings with pentane and small amounts of toluene yielded **1** (0.75 g, 44%) as a white powder.

Route B. A solution of {LO¹}H (0.34 g, 0.97 mmol) in THF (10 mL) was added to a solution of $Zn[N(SiMe_3)_2]_2$ (0.19 g, 0.49 mmol) in THF (5 mL). The resulting colourless solution was stirred at 60 °C for 3 h. Volatiles were then removed under vacuum to give a white solid which was washed with pentane (2 × 15 mL). Following drying *in vacuo*, **1** (0.37 g, 99%) was isolated as a white powder. Found C 63.1, H 8.3, N 7.3%. $C_{40}H_{62}N_4O_6Zn$ requires C 63.2, H 8.2, N 7.4%.

^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ_H 7.28 (4 H, br s, arom-*H*), 3.60 (24 H, br s, O–C*H*$_2$ + Ar–C*H*$_2$–N), 2.38 (16 H, br s, N–C*H*$_2$–CH$_2$), 1.45 (18 H, s, C(C*H*$_3$)$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 100.62 MHz, 25 °C): δ_C 162.4, 136.1, 127.4 (overlapped with benzene signal), 122.0 (aromatic), 65.9 (O–*C*H$_2$), 61.7 (Ar–*C*H$_2$–N), 54.6 (N–*C*H$_2$–CH$_2$), 33.6 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$).

Synthesis of {LO¹}MgMe (4)

A solution of {LO¹}H (0.91 g, 2.6 mmol) in toluene (10 mL) was added dropwise at 0 °C over a period of 20 min to a solution of $Me_2Mg(THF)_{1,5}$ (0.42 g, 2.6 mmol) in toluene (15 mL). The resulting mixture was stirred at 0 °C for 60 min, and then at room temperature overnight. A white precipitate formed and was isolated by filtration. The solid was dried under vacuum to give **4** (0.50 g, 50%) as a white powder. Found C 66.1, H 8.4, N 6.9%. $C_{21}H_{34}N_2O_3Mg$ requires C 65.2, H 8.9, N 7.2%.

^{1}H NMR (CD_2Cl_2, 500.13 MHz, 25 °C): δ_H 7.21 (2 H, br s, arom-*H*), 4.2–3.3 (12 H, br m, O–C*H*$_2$ + Ar–C*H*$_2$–N), 2.38 (8 H, br s, N–C*H*$_2$–CH$_2$), 1.34 (9 H, s, C(C*H*$_3$)$_3$), –1.65 (3 H, s, Mg–C*H*$_3$) ppm.

^{13}C{^{1}H} NMR (CD_2Cl_2, 125.76 MHz, 25 °C): δ_C 155.7, 140.5, 128.5, 124.17 (aromatic), 66.1 (O–*C*H$_2$), 60.9 (Ar–*C*H$_2$–N), 54.22 (N–*C*H$_2$–CH$_2$), 33.7 (*C*(CH$_3$)$_3$), 31.3, (C(*C*H$_3$)$_3$), –15.9 (Mg–*C*H$_3$).

Synthesis of {LO²}ZnEt (5)

A solution of {LO²}H (3.09 g, 10.1 mmol) in toluene (30 mL) was added at –45 °C over a period of 20 min to a solution of $ZnEt_2$ (10.6 mL of a 1.0 M solution in hexanes, 10.6 mmol) in toluene (50 mL). The resulting mixture was stirred at –45 °C for 60 min, and then at room temperature for a further 60 min. The solvent was then removed under vacuum, and the resulting powder was washed three times with pentane and dried to constant weight to give analytically pure **5** (3.40 g, 84%) as a white powder. Found C 63.1, H 8.7, N 3.5%. $C_{21}H_{35}NO_2Zn$ requires C 63.2, H 8.8, N 3.5%.

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.58 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 6.88 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 3.6 (2 H, m, O–C*H*$_2$), 3.30 (2 H, br s, Ar–C*H*$_2$), 2.60 (4 H, br, N–C*H*$_2$–CH$_2$), 1.71 (2 H, m, O–C*H*$_2$), 1.66 (9 H, s, C(C*H*$_3$)$_3$), 1.39 (3 H, m, Zn–CH$_2$–C*H*$_3$), 1.37 (9 H, s, C(C*H*$_3$)$_3$), 0.54 (2 H, br s, Zn–C*H*$_2$–CH$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): δ_C 159.7, 139.5, 139.0, 129.3, 125.5, 123.9 (aromatic), 65.0 (O–*C*H$_2$), 64.8 (Ar–*C*H$_2$–N), 54.7 (N–*C*H$_2$–CH$_2$), 35.7 (*C*(CH$_3$)$_3$), 34.1 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 31.3 (C(*C*H$_3$)$_3$), 12.9 (Zn–CH$_2$–*C*H$_3$), 3.4 (Zn–*C*H$_2$–CH$_3$).

Synthesis of {LO⁴}ZnEt (6)

A solution of {LO⁴}H (1.00 g, 3.2 mmol) in toluene (20 mL) was added dropwise at –45 °C to a solution of $ZnEt_2$ (3.4 mL of a 1.0 M solution in hexanes, 3.4 mmol) in toluene (40 mL). The resulting mixture was stirred at –45 °C for 60 min, and then at room temperature for a further 60 min. The solvent was removed under vacuum, and the resulting waxy solid was dissolved in a minimal amount of pentane. The solution was decanted, and recrystallization at –30 °C afforded **6** (0.90 g, 71%) as colourless crystals suitable for crystallographic studies. Found C 64.7, H 9.0, N 3.2%. $C_{23}H_{39}NO_2Zn$ requires C 64.7, H 9.2, N 3.3%.

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.60 (1 H, m, arom-*H*), 6.86 (1 H, m, arom-*H*), 3.87 (1 H, d, $^2J_{HH}$ = 11.8 Hz, Ar–C*H*$_2$–N), 2.87 (1 H, d, $^2J_{HH}$ = 11.8 Hz, Ar–C*H*$_2$–N), 2.82 (1 H, m, N–C*H*$_2$–CH$_2$), 2.76 (3 H, s, O–C*H*$_3$), 2.69 (1 H, m, O–C*H*$_2$), 2.37 (1 H, m, O–C*H*$_2$), 2.13 (1 H, m, N–C*H*), 1.86 (9 H, s, C(C*H*$_3$)$_3$), 1.84 (1 H, m, N–C*H*$_2$–CH$_2$), 1.62 (3 H, m, Zn–CH$_2$–C*H*$_3$), 1.52 (1 H, m, N–CH$_2$–C*H*$_2$), 1.47 (9 H, C s, (C*H*$_3$)$_3$), 1.29 (2 H, m, N–CH–C*H*$_2$–CH$_2$), 1.18 (1 H, m, N–CH$_2$–C*H*$_2$), 0.65 (1 H, m, Zn–C*H*$_2$–CH$_3$), 0.52 (1 H, m, Zn–C*H*$_2$–CH$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): δ_C 164.3, 137.8, 134.8, 124.6, 124.0, 122.3 (aromatic), 72.3 (*C*H–O), 63.7 (N–*C*H), 61.0 (Ar–*C*H$_2$–N), 59.2 (O–*C*H$_3$), 56.9 (N–*C*H$_2$–CH$_2$), 35.6 (*C*(CH$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$), 27.8 (N–CH–*C*H$_2$–CH$_2$), 21.5 (N–CH$_2$–*C*H$_2$), 13.1 (Zn–CH$_2$–*C*H$_3$), 3.0 (Zn–*C*H$_2$–CH$_3$).

Synthesis of {LO³}ZnEt (7)

A solution of {LO³}H (3.00 g, 6.86 mmol) in toluene (30 mL) was added dropwise at –45 °C to a solution of $ZnEt_2$ (7.6 mL of a 1.0 M solution in hexanes, 7.6 mmol) in toluene (100 mL). The resulting mixture was stirred at –45 °C for 90 min, and then at room temperature for a further 45 min. The solvent was then removed under vacuum, and the resulting solid was washed with heptane (3 × 10 mL). It was dried *in vacuo*, affording **7** (2.95 g, 81%) as a white powder. Single-crystals suitable for X-ray studies were grown by re-crystallization in heptane. Found C 61.1, H 8.8, N 2.8%. $C_{27}H_{47}NO_5Zn$ requires C 61.1, H 8.9, N 2.6%.

^{1}H NMR (CD_2Cl_2, 500.13 MHz, 25 °C): δ_H 7.23 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 6.84 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 3.9–3.7 (10 H, br m, O–C*H*$_2$), 3.69 (2 H, br s, Ar–C*H*$_2$–N), 3.65–3.55 (6 H, br m, O–C*H*$_2$), 3.18 (2 H, m, N–C*H*$_2$–CH$_2$), 2.90 (2 H, m, N–C*H*$_2$–CH$_2$), 1.46 (9 H, s, C(C*H*$_3$)$_3$), 1.31 (9 H, s, C(C*H*$_3$)$_3$), 1.29 (3 H, t, $^3J_{HH}$ = 8.1 Hz, Zn–CH$_2$–C*H*$_3$), 0.23 (2 H, q, $^3J_{HH}$ = 8.1 Hz, Zn–C*H*$_2$–CH$_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 125.76 MHz, 25 °C): δ_C 163.6 137.5, 134.7, 125.7, 123.8, 122.1 (aromatic), 70.6, 70.1, 69.7, 69.2 (O–*C*H$_2$), 62.2 (Ar–*C*H$_2$–N), 56.3 (N–*C*H$_2$–CH$_2$), 35.0 (*C*(CH$_3$)$_3$),

33.7 ($C(CH_3)_3$), 31.6 (C(CH_3)$_3$), 29.3 (C(CH_3)$_3$), 12.5 (Zn–CH_2–CH_3), −0.6 (Zn–CH_2–CH_3).

Synthesis of {LO^3}ZnN(SiMe$_3$)$_2$ (8)

A solution of {LO^3}H (1.29 g, 2.95 mmol) in toluene (50 mL) was added at −45 °C over a period of 30 min to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (1.26 g 3.24 mmol) in toluene (80 mL). The resulting mixture was stirred at −45 °C for 2 h and the solvent was removed under vacuum. The resulting powder was washed with heptane (3 × 10 mL) and dried *in vacuo*, to give **7** (1.53 g, 78%) as a white powder. Single-crystals were obtained by re-crystallization from a cold heptane solution. Found C 55.9, H 8.9, N 4.2%. $C_{31}H_{60}N_2O_5Si_2Zn$ requires C 56.2, H 9.1, N 4.2%.

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.61 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 6.82 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 3.6–3.5 (6 H, br m, O–CH_2 and Ar–CH_2–N), 3.36 (2 H, m, O–CH_2), 3.28 (2 H, m, O–CH_2), 3.20 (2 H, m, O–CH_2), 3.11 (2 H, m, O–CH_2), 3.05 (4 H, m, O–CH_2), 3.00 (2 H, m, N–CH_2–CH_2), 2.75 (2 H, m, N–CH_2–CH_2), 1.83 (9 H, s, C(CH_3)$_3$), 1.46 (9 H, s, C(CH_3)$_3$), 0.49 (18 H, s, N(Si(CH_3)$_3$)$_2$).

^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): δ_C 164.1, 137.8, 134.9, 125.3, 124.2, 120.4 (aromatic), 70.2, 70.0, 69.9, 68.4 (O–*C*H$_2$), 63.7 (Ar–*C*H$_2$–N), 54.8 (N–*C*H$_2$–CH$_2$), 35.5 (*C*(CH$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 32.1 (C(*C*H$_3$)$_3$), 29.9 (C(*C*H$_3$)$_3$), 6.5 (N(Si(*C*H$_3$)$_3$)$_2$).

^{29}Si{^{1}H} NMR (C_6D_6, 79.49 MHz, 25 °C): δ_{Si} −3.4

Synthesis of {LO^3}ZnN(SiMe$_2$H)$_2$ (9)

A solution of {LO^3}H (0.27 g, 0.62 mmol) in pentane (20 mL) was added at −80 °C over a period of 15 min to a solution of Zn[N(SiHMe$_2$)$_2$]$_2$ (0.21 g 0.62 mmol) in pentane (20 mL). The resulting mixture was stirred at −80 °C for 30 min, and volatiles were then removed under vacumm at −20 °C. The resulting powder was stripped twice with pentane (10 mL) and dried *in vacuo*, to give pure **9** (0.28 g, 71%) as a white powder. Single-crystals were obtained by re-crystallization from a cold saturated pentane solution. Found C 52.9, H 8.1, N 3.5%. $C_{29}H_{56}N_2O_5Si_2Zn$ requires C 54.9, H 8.9, N 4.4%.[31]

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.60 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 6.80 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 5.10 (2 H, m, $^3J_{HH}$ = 3.0 Hz, $^1J_{SiH}$ = 180 Hz, Si–*H*), 3.62 (2 H, m, O–CH_2) 3.55–3.35 (8 H, br m, O–CH_2 and N–CH_2–Ar), 3.27 (2 H, m, O–CH_2), 3.14 (2 H, m, O–CH_2), 3.05 (4 H, m, O–CH_2), 2.78 (4 H, br s, N–CH_2–CH$_2$), 1.83 (9 H, s, C(CH_3)$_3$), 1.44 (9 H, s, C(CH_3)$_3$), 0.56 (12 H, d, $^3J_{HH}$ = 3.0 Hz, N(SiH(CH_3)$_2$)$_2$).

^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): δ_C 164.2, 137.8, 135.0, 125.5, 124.2, 120.7 (aromatic), 70.5, 69.9, 69.7, 69.1 (O–*C*H$_2$), 64.8 (Ar–*C*H$_2$–N), 55.6 (N–*C*H$_2$–CH$_2$), 35.4 (*C*(CH$_3$)$_3$), 33.8 (*C*(CH$_3$)$_3$), 32.0 (C(*C*H$_3$)$_3$), 29.7 (C(*C*H$_3$)$_3$), 3.8 (Si–*C*H$_3$).

^{29}Si{^{1}H} NMR (C_6D_6, 79.49 MHz, 25 °C): δ_{Si} −14.4

IR (Nujol in KBr plates):$\bar{\nu}$ = 2064 (s), 1456 (s), 1413 (sh), 1377 (s), 1362 (m), 1347 (w), 1304 (m), 1287 (sh), 1263 (sh), 1240 (s), 1203 (w), 1158 (w), 1119 (s), 1092 (m), 1032 (m), 1002 (sh), 980 (w), 930 (m), 888 (s), 841 (m), 831 (sh), 808 (w), 797 (w), 784 (w), 741 (w), 721 (w), 677(w), 643 (w), 621 (w) cm^{-1}.

Synthesis of {LO^3}ZnOSiPh$_3$ (10)

A solution of Ph_3SiOH (0.10 g, 0.37 mmol) in toluene (20 mL) was added at −20 °C over a period of 15 min to a solution of {LO^3}ZnN(SiMe$_3$)$_2$ (0.25 g, 0.37 mmol) in toluene (20 mL). The resulting mixture was stirred at −20 °C for 10 min, and the solvent was pumped off. The resulting powder was purified by stripping with pentane (3 × 5 mL) and dried *in vacuo*, to afford pure **10** (0.26 g, 89%) as a colourless powder. Found C 66.3, H 7.3, N 1.7%. $C_{43}H_{57}NO_6SiZn$ requires C 66.4, H 7.4, N 1.8%.

^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): δ_H 8.08 (6 H, m, arom-*H*), 7.63 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 7.32 (6 H, m, arom-*H*), 7.26 (3 H, m, arom-*H*), 6.80 (1 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 3.62 (2 H, m, O–CH_2) 3.52 (4 H, br m, O–CH_2), 3.32 (4 H, m, O–CH_2 + Ar–CH_2–N), 3.23 (2 H, m, O–CH_2), 3.14 (4 H, s, O–CH_2), 2.90 (2 H, m, O–CH_2), 2.50 (4 H, m, N–CH_2–CH$_2$), 1.81 (9 H, s, C(CH_3)$_3$), 1.43 (9 H, s, C(CH_3)$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 100.62 MHz, 25 °C): δ_C 164.4, 141.9, 139.0, 136.0, 135.8, 129.0, 128 (overlaped with benzene) 126.3, 124.9, 121.1 (aromatic), 71.3, 69.9, 69.5, 69.1 (O–*C*H$_2$), 64.2 (Ar–*C*H$_2$–N), 56.1 (N–*C*H$_2$–CH$_2$), 35.9 (*C*(CH$_3$)$_3$), 34.2 (*C*(CH$_3$)$_3$), 32.3 (C(*C*H$_3$)$_3$), 30.2 (C(*C*H$_3$)$_3$).

Synthesis of {LO^3}$_2$Zn (11)

A solution of {LO^3}H (2.20 g, 5.02 mmol) in toluene (50 mL) was added at room temperature to a solution of Zn[N(SiMe$_3$)$_2$]$_2$ (0.92 g, 2.39 mmol) in toluene (40 mL). The resulting mixture was stirred at 40 °C for 3 h and volatiles were removed under vacuum. Pentane was added to the resulting oil until a white solid precipitated. The solid was isolated by filtration and washed with pentane to afford **11** (2.20 g, 98%) as a colourless powder which was dried *in vacuo*. Found C 64.2, H 8.8, N 2.9%. $C_{50}H_{84}N_2O_{10}Zn$ requires C 64.0, H 9.0, N 3.0%.

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.57 (2 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 6.94 (2 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 4.3–3.0 (44 H, br m, macrocyclic-*H*), 1.69 (18 H, s, C(CH_3)$_3$), 1.45 (18 H, s, C(CH_3)$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 100.03 MHz, 25 °C): δ_C 163.9, 137.9, 134.8, 125.9, 124.0, 119.8 (aromatic), 71.1, 70.8, 70.5 (br), 67.0, 65.4, 61.2, 54.3, 49.8, 35.3 (*C*(CH$_3$)$_3$), 33.8 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 30.0 (C(*C*H$_3$)$_3$).

NMR characterization of {LO^3}$_2$Mg (12)

Compound **12** was generated in an NMR-scale reaction in CD_2Cl_2 by reaction of {Mg[N(SiMe$_3$)$_2$]$_2$}$_2$ with 4 equiv. of {LO^3}H.

^{1}H NMR (CD_2Cl_2, 400.13 MHz, 25 °C): δ_H 7.11 (2 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 6.79 (2 H, d, $^4J_{HH}$ = 2.6 Hz, arom-*H*), 3.97 (8 H, s, O–CH_2), 3.91 (4 H, m, O–CH_2), 3.83 (8 H, m, O–CH_2), 3.64 (4 H, m, O–CH_2), 3.56 (12 H, m, O–CH_2 + Ar–CH_2–N), 3.43 (4 H, m, N–CH_2–CH$_2$), 2.62 (4 H, m, N–CH_2–CH$_2$), 1.44 (18 H, s, C(CH_3)$_3$), 1.24 (18 H, s, C(CH_3)$_3$).

^{13}C{^{1}H} NMR (CD_2Cl_2, 100.62 MHz, 25 °C): δ_C 164.9, 135.7, 132.3, 124.3, 123.7, 123.1 (aromatic), 67.7, 67.4, 67.3, 66.8 (O–*C*H$_2$), 60.0 (Ar–*C*H$_2$–N), 55.4 (N–*C*H$_2$–CH$_2$), 34.9 (*C*(CH$_3$)$_3$), 33.5 (*C*(CH$_3$)$_3$), 31.7 (C(*C*H$_3$)$_3$), 29.4 (C(*C*H$_3$)$_3$).

Table 2 Summary of crystal and refinement data for compounds {**LO²**}**H**, {**LO⁴**}**H**, **6**, **7**, **8** and **9**

	{**LO²**}**H**	{**LO⁴**}**H**	**6**	**7**	**8**	**9**
Empirical formula	$C_{19}H_{31}NO_2$	$C_{42}H_{70}N_2O_4$	$C_{23}H_{39}NO_2Zn$	$C_{54}H_{94}N_2O_{10}Zn_2$	$C_{31}H_{60}N_2O_5Si_2Zn$	$C_{29}H_{56}N_2O_5Si_2Zn$
Formula weight	305.45	667.0	426.92	1062.05	662.36	634.31
Crystal system	Orthorhombic	Trigonal	Orthorhombic	Triclinic	Triclinic	Monoclinic
Space group	*Pcab*	*P*32	$P2_12_12_1$	*P*-1	*P*-1	$P2_1/n$
a/Å	8.864(2)	10.7292(3)	8.4855(2)	9.9972(5)	10.7067(4)	13.9506(17)
b/Å	10.150(2)	10.7292	14.4219(4)	16.8148(9)	10.7067(4)	13.9506(17)
c/Å	40.261(9)	29.5051(9)	19.4610(5)	17.4778(10)	13.9560(6)	23.4443(16)
α (°)	90	90	90	74.056(3)	76.371(2)	90
β (°)	90	90	90	86.334(3)	72.957(2)	95.431(4)
γ (°)	90	120	90	85.641(3)	83.477(2)	90
Volume/Å^3	3622.1(13)	2941.45(12)	2381.58(11)	2814.0(3)	1821.97(12)	3492.8(5)
Z	8	3	4	2	2	4
Density, g cm^{-3}	1.12	1.13	1.191	1.253	1.207	1.206
μ/mm^{-1}	0.071	.071	1.047	0.907	0.777	0.807
F(000)	1344	1104	920	1144	716	1368
Crystal size/mm	0.42 × 0.3 × 0.15	0.58 × 0.52 × 0.47	0.56 × 0.35 × 0.32	0.55 × 0.49 × 0.31	0.51 × 0.47 × 0.4	0.17 × 0.1 × 0.07
θ range, deg	3.04 to 27.48	3.02 to 27.48	3.01 to 27.5	2.99 to 27.47	2.93 to 27.46	2.93 to 27.48
Limiting indices	$-11 \le h \le 10$	$-12 \le h \le 13$	$-11 \le h \le 9$	$-12 \le h \le 10$	$-13 \le h \le 12$	$-18 < h < 18$
	$-12 \le k \le 13$	$-13 \le k \le 10$	$-18 \le k \le 18$	$-21 \le k \le 21$	$-16 \le k \le 16$	$-12 < k < 13$
	$-24 \le l \le 52$	$-38 \le l \le 38$	$-25 \le l \le 25$	$-22 \le l \le 22$	$-18 \le l \le 17$	$-25 < l < 30$
R_{int}	0.0815	0.0585	0.0303	0.0509	0.0404	0.0459
Reflec. collected	16205	37354	31311	42261	23988	31084
Reflec. Unique [$I > 2\sigma(I)$]	4140	4476	5426	12674	8218	7992
Data/restraints/param.	4140/0/178	4476/1/449	5426/0/252	12674/0/627	8218/0/382	7992/0/368
Goodness-of-fit on F^2	1.083	1.198	1.162	0.892	1.056	1.028
R_1 [$I > 2\sigma(I)$] (all data)	0.0682 (0.098)	0.0367 (0.0412)	0.0218 (0.0257)	0.0372 (0.0565)	0.0303 (0.0387)	0.0323 (0.0451)
wR_2 [$I > 2\sigma(I)$] (all data)	0.1359 (0.1481)	0.0879 (0.0903)	0.052 (0.0536)	0.0925(0.1039)	0.0735 (0.0772)	0.0756 (0.0816)
Largest diff. e Å^{-3}	0.259 and –0.203	0.193 and –0.2	0.273 and –0.429	0.493 and –0.338	0.384 and –0.373	0.379 and –0.227

Typical polymerisation procedure

All manipulations were performed under inert atmosphere. In the glove-box, the metal-based precursor (typically 10 to 30 mg) and the purified monomer (*ca*. 3 to 5 g) were placed at once in a large Schlenk flask. The vessel was sealed and removed from the glove-box. All subsequent operations were carried out using standard Schlenk techniques. Where needed, the required amount of dry, degassed solvent selected from toluene, styrene or THF was added with a syringe to the Schlenk flask containing the precursor and monomer. The metallic complex was then activated by addition of pure ^{i}PrOH. The alcohol was added rapidly, the Schlenk vessel was immerged in an oil bath pre-set at the desired temperature and the polymerisation time was measured from this point. The reaction was terminated by addition of acidified MeOH (HCl, 1%) and the polymer was precipitated in methanol. It was purified by re-precipitation, using dichloromethane or THF as solvent and methanol as a non-solvent. The polymer was then dried to constant weight under dynamic vacuum.

Crystal structure determinations

Suitable crystals for X-ray diffraction analyses of compounds {**LO²**}**H**, {**LO⁴**}**H**, **6**, **7**, **8** and **9** were obtained by re-crystallization of the purified products. Diffraction data were collected at 100 K ({**LO²**}**H**, {**LO⁴**}**H**, **7**), 120 K (**6**) or 150 K (**8**, **9**) using a Bruker APEX CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). A combination of ω and Φ scans was carried out to obtain at least a unique data set. The crystal structures were solved by direct methods, remaining atoms were located from difference Fourier synthesis followed by full-matrix least-squares refinement based on F^2 (programs SIR97 and SHELXL-97).[32] Many hydrogen atoms could be found from the Fourier difference analysis. Carbon- and oxygen-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities were of no chemical significance. Crystal data and details of data collection and structure refinement for the different compounds are given in Table 2 and as cif files in the ESI†.

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of cyclic esters together with mechanistic investigations will be the subject of a separate report.
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