Versatile catalytic systems based on complexes of zinc, magnesium and calcium supported by a bulky bis(morpholinomethyl)phenoxy ligand for the large-scale immortal ring-opening polymerisation of cyclic esters†

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Received 28th August 2009, Accepted 9th September 2009
First published as an Advance Article on the web 28th September 2009
DOI: 10.1039/b917799j

A new heteroleptic ethyl-zinc complex stabilized by a chelating bis(morpholinomethyl)phenoxy ligand has been synthesised and shown to be a highly potent initiator for the immortal ring-opening polymerisation (ROP) of lactide and β-butyrolactone, being able to convert up to 50 000 equiv. of monomer in the presence of up to 1000 equiv. of an alcohol as transfer agent. Two related heteroleptic complexes of magnesium and calcium have also been prepared. These complexes are stable in solution, even in the presence of large amounts of alcohol, and constitute effective catalysts for the immortal ROP of lactide under mild conditions.

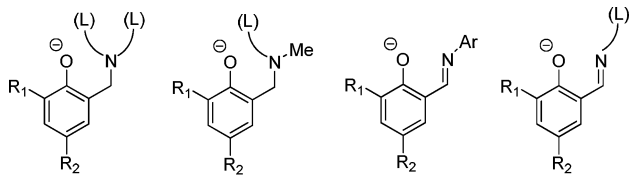
Introduction

Growing concern towards environmental issues, depletion of the fossil fuel feedstocks and unstable crude oil prices have prompted industrial and academic research groups to investigate the use of bio-friendly polymers as an alternative to the already existing synthetic commodity materials.[1] Over the past decade, the ring-opening polymerisation (ROP) of lactide (LA), a bio-renewable resource produced by fermentation from sugar-roots and corn, has attracted the most attention.[1a] For instance, Natureworks LLC inaugurated in 2002 a plant capable of producing annually up to 140 000 tons of isotactic polylactide (PLLA).[2] Industrially, tin(II) 2-ethyl-hexanoate is commonly used for the ROP of LA (and other cyclic monomers) but drawbacks include a slow, poorly controlled mechanism and serious concern revolving around the use of the heavy tin element.[1a,3] These issues were partly circumvented by the introduction of well-defined metallic initiators (based mostly on non-toxic zinc,[4] aluminium[5] or group 3 metals[6]) for the controlled, living ROP of LA according to a coordination/insertion mechanism.[7,8] Poly(3-hydroxybutyrate) (PHB), a naturally-occurring highly crystalline thermoplastic produced by several algae and bacteria under its isotactic form, constitutes another worthy target for the synthetic chemist, and breakthroughs have recently been achieved with discrete metal complexes capable of promoting the ROP of β-butyrolactone (BBL) to yield original atactic and syndiotactic PHBs.[9]

Whereas a plethora of well-defined aluminium-, zinc- and lanthanide-based initiators supported by ancillary ligands are now available for the controlled ROP of cyclic esters,[4–8] examples of similar initiators based on magnesium[7,10] and calcium,[11–12] two innocuous metals, are far less common. This is especially true of Ca, most likely because of the difficulties encountered in understanding and taming the reactivity of this very large metal (ionic radius = 1.14 Å). Only very recently have discrete complexes of calcium emerged as suitable catalysts for the transformation of small organic molecules[13] or the polymerisation of styrene[14] or cyclic esters.[11,12a] Characteristics of the complexes of the highly oxophilic alkaline-earth (Ae) elements include: (i) a high reactivity towards alcohols, which usually leads to the formation of non-reactive polynuclear species and (ii) a propensity (which increases with the ionic radius of the metal) of heteroleptic species to be involved in detrimental "Schlenk-type" equilibria:

$$2\,[L]Ae\text{-}Nu \rightleftharpoons [L]_2Ae + \{AeNu_2\}_n \quad (1)$$

The judicious selection of the ancillary ligand is crucial in order to obtain stable heteroleptic calcium species. Prime examples of robust complexes include those stabilised by encumbered trispyrazolylborate,[11a–b,15] β-diketiminate[13a,16] or aminotroponiminate[13b,17] ligands. Surprisingly enough, mono-anionic phenolate ligands containing nitrogen donors (phenoxy-amines **I–II**, or phenoxy-imines **III–IV**) that have been extensively applied to the synthesis of complexes of many transition or main-group metals[7,18] (including Mg) have scarcely been used with calcium.[11d–e,19]



Although useful for mechanistic purposes, the living nature of the large majority of these initiating systems has so far impeded their use in industry since they are known to convert only small quantities of monomer (100–2000 equiv.),[4–9] and each active centre can only generate a single polymer chain. Instead, in a truly catalytic system, each active species should yield hundreds

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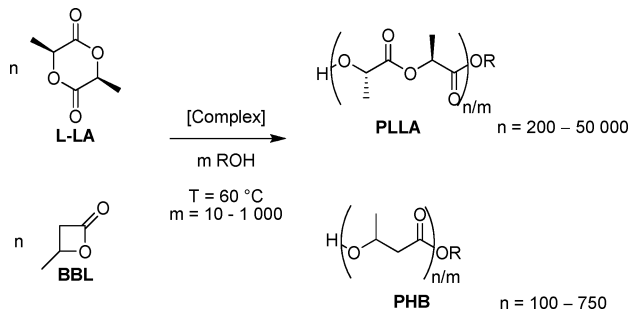
† Electronic supplementary information (ESI) available: Full polymerisation data, NMR and MALDI-TOF MS data of PLLA samples prepared with **1–3**/^{i}PrOH. CCDC reference numbers **2** (734084) and **3** (733134). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b917799j

of polymer chains from several dozen thousands of equiv. of monomer. Chain transfer with an external protic agent during the course of a so-called "immortal" ROP represents the best route towards this goal,[20] and we have already employed binary systems combining alcohols and metallic precursors for the immortal ROP of LA[20h] and trimethylene carbonate.[21] In this study, we present a new, versatile ethyl-zinc complex supported by a mono-anionic bis(morpholinomethyl)phenoxy ligand ($[LO^1]^-$) which, in presence of up to 1000 equiv. of transfer agent, is suitable for the large-scale (monomer-to-metal ratios up to 50 000), controlled, immortal ROP of LA and BBL under very mild conditions (Scheme 1). The syntheses and the ROP catalytic activities of related complexes of magnesium and calcium are also reported: both are stable in solution in the presence of a large excess of alcohol (1–100 equiv.) and promote the rapid large-scale immortal ROP of L-LA (100–5000 equiv.).

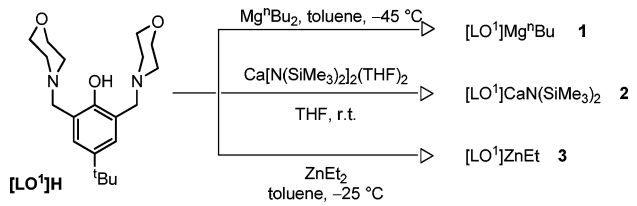


Scheme 1

Results and discussion

Synthetic and crystallographic studies

The new complex $[LO^1]Mg^nBu$ (**1**; $[LO^1]$ = 4-*tert*-butyl-2,6-bis(morpholinomethyl)phenoxy)) was obtained upon reaction of $[LO^1]H$[22] and Mg^nBu_2 in toluene at −45 °C (Scheme 2). Analytically pure **1** was isolated as a fine white powder in 84% yield after work-up, and was fully characterised by 1D and 2D NMR spectroscopy and elemental analysis. It is very soluble in ethers (Et_2O, THF) and chlorinated solvents (CH_2Cl_2, $CHCl_3$), but only sparingly so in aromatic hydrocarbons (toluene, benzene) and mostly insoluble in light petroleum ether.



Scheme 2

The reaction of $[LO^1]H$ and $Ca[N(SiMe_3)_2]_2(THF)_2$ in THF at room temperature yielded the THF-free heteroleptic $[LO^1]CaN(SiMe_3)_2$ (**2**) in almost quantitative yield. Complex **2** was isolated as a white, extremely air-sensitive solid. It was fully soluble in ethers, and moderately so in toluene, benzene and hot hexane. Full characterisation by NMR spectroscopy indicated that no THF molecule was retained, and the composition of **2** was further confirmed by elemental analysis. Its ^1H NMR spectrum recorded in C_6D_6 at room temperature displayed broad signals for the hydrogen atoms of all methylene moieties, most likely as a result of the dynamic behaviour of the morpholinomethyl side-arms. Indeed, one can legitimately assume that in solution, a rapid exchange between coordinated and free morpholino groups (*vide infra*) occurs onto the metal centre, which is possibly further complicated by fast chair–chair interconversion of the free morpholino group. ^1H NMR monitoring of a solution of **2** in $C_6D_5CD_3$ cooled from 20 °C to −80 °C did not provide significant insight into this behaviour. Similar fluxionality was also observed for **1**, although in this case it proved possible to freeze exchanges on the NMR time-scale in $C_6D_5CD_3$ at −70 °C. Remarkably, **2** was perfectly stable in solution at room temperature for days, as no sign of decomposition nor evidence for a Schlenk-type equilibrium involving $[LO^1]_2Ca$ and $Ca[N(SiMe_3)_2]_2$ could be detected during the monitoring by ^1H NMR of a solution of **2** in C_6D_6 over a period of a week. Moreover, the NMR-scale reaction of **2** and 10 equiv. of ^{i}PrOH in C_6D_6 at 60 °C (*i.e.*, typical conditions we later used for the immortal ROP of L-LA, *vide infra*) indicated the clean formation of $\{[LO^1]CaO^iPr\}_n$[23] with concomitant release of free $HN(SiMe_3)_2$, without noticeable formation of $[LO^1]_2Ca$, $Ca[N(SiMe_3)_2]_2$ or $\{Ca(O^iPr)_2\}_n$ and free ligand $[LO^1]H$. Such stability contrasts starkly with the behaviour reported for $[BDI^{iPr}]CaN(SiMe_3)_2$ (BDI^{iPr} = $CH(MeCNC_6H_3{}^iPr_2)_2$), which essentially decomposed upon addition of ^{i}PrOH.[11b] Thus, these experiments confirmed the unique ability of the mono-anionic ligand $[LO^1]^-$ to preserve the integrity of the coordination environment around the metal centre in heteroleptic complexes of the highly oxophilic Ae elements, even in the presence of a large excess of alcohol.

Only one well-defined, structurally characterized heteroleptic calcium complex supported by a multidentate phenolate ligand was known prior to this work.[11e,24] X-Ray quality crystals of **2** were successfully grown by slow diffusion of hexane vapours in a THF solution (see Experimental and ESI†). **2** is a centrosymmetric dimer in the solid-state (Fig. 1): the two Ca atoms are bridged by the *O*-atoms of the phenolate moieties, resulting in a planar Ca_2O_2 core. Each metal is pentacoordinated and lies at the centre

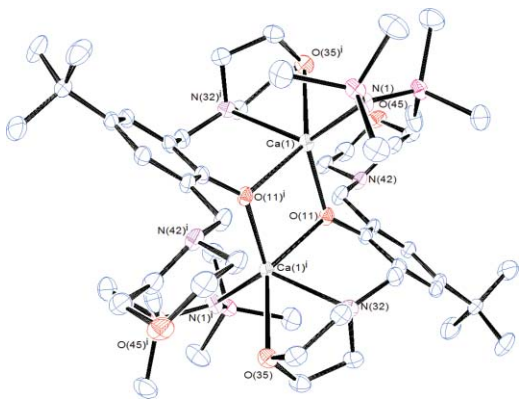


Fig. 1 ORTEP representation of $\{2\}_2$. Ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted and only one part of the disordered ^{t}Bu groups is shown for the sake of clarity. Selected distances (Å) and angles (°): Ca1–Ca1^i = 3.5757(7), Ca1–O11 = 2.2657(12), Ca1–O11^i = 2.3453(11), Ca1–O35 = 2.6123(12), Ca1–N32 = 2.5517(14), Ca1–N1^i = 2.3060(14), O35–N32 = 2.504(2), N32–Ca1–O35 = 58.01(4).

of a distorted trigonal bipyramid ($\tau = 0.84$).[25] The environment about each metal centre is completed by the *N*- and *O*-atoms of a single morpholino group in its boat conformation (the remaining morpholino substituent on each ligand retains the chair conformation exhibited in free [LO^1]H,[26] and plays no part in the stabilisation of the metal centre, at least in the solid state) and the bulky –N(SiMe$_3$)$_2$ group. The Ca1–O11 and Ca1–N32 bond lengths of respectively 2.2657(12) and 2.5517(14) Å in dimeric **2** are significantly longer than the corresponding distances (respectively 2.1914(16) and 2.474(2) Å) exhibited in the monomeric [LO]CaN(SiMe$_3$)$_2$(THF) (where [LO] = 2,4-di-*tert*-butyl-6-{[2-(dimethylamino)ethylimino]methyl}phenolate) described by Darensbourg;[11e] on the other hand, the Ca1–N1^i bond length of 2.3060(14) Å in **2** is shorter than its equivalent in this latter compound (2.3512(19) Å).

The parent zinc compound [LO^1]ZnEt (**3**) was also readily prepared in high yield (90%) by reaction of [LO^1]H and ZnEt$_2$ in toluene at −25 °C (Scheme 2). This complex was isolated as a fine colourless powder; its solubility in ethers and chlorinated solvents is good, but it is only moderately soluble in aromatic hydrocarbons and insoluble in light petroleum ether or hot hexane. The identity of **3** was determined by variable temperature NMR spectroscopy (^{1}H, ^{13}C{^{1}H}, COSY, HMBC and HMQC) and was corroborated by elemental analyses. X-Ray quality crystals of {**3**}$_2$·C$_6$D$_6$ were isolated from a concentrated solution of **3** in C$_6$D$_6$ (see Experimental and ESI†), and its structure was elucidated (Fig. 2). The zinc atoms in dimeric {**3**}$_2$ are bridged by the oxygen atoms of the phenoxy moieties. The distorted tetrahedral environment about each metal centre is completed by a single nitrogen atom from one of the morpholino side-arms (all of which are in chair conformation) and a disordered ethyl group. The bond distances and angles for this compound are unexceptional and fall in the range of values reported for related compounds.[7,19,27]

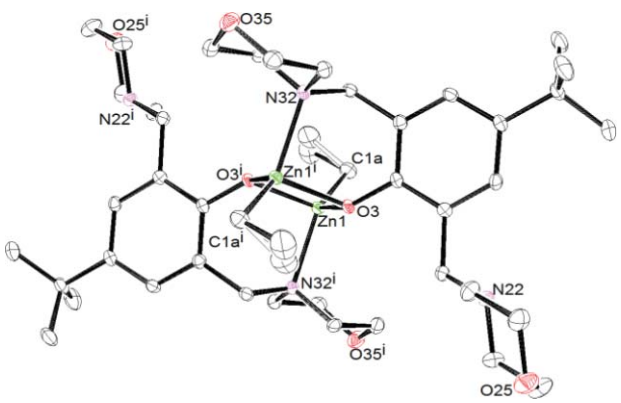
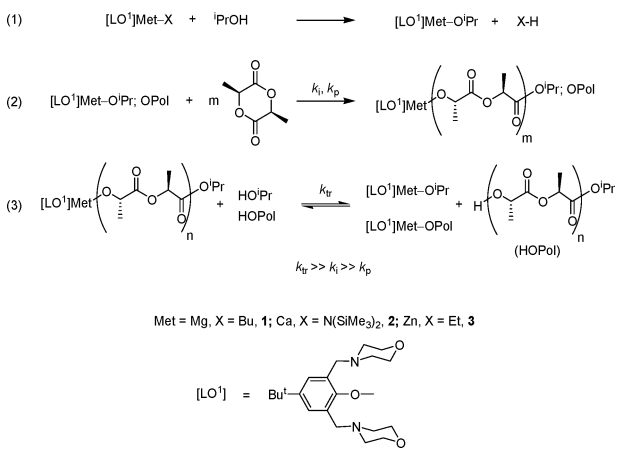


Fig. 2 ORTEP diagram of {**3**}$_2$·C$_6$D$_6$. Hydrogen atoms and the solvent molecule are omitted for clarity. Ellipsoids are drawn at the 50% probability level. Selected bond distances (Å): Zn1–O3 = 2.0394(9), Zn1–C1a = 1.9828(15), Zn1–N32^i = 2.1397(12), Zn1–Zn1^i = 3.0329(3). Symmetry operations: '*x*, *y*, *z*', '−*x*, −*y*, −*z*'.

Polymerisation studies

Following indications that Mg and Ca compounds **1** and **2** were stable in solution even in the presence of alcohol, these complexes were used in combination with ^{i}PrOH as a transfer agent for the immortal ROP of L-LA. This concept, first developed by Inoue in the 1980s (Scheme 3),[20] has never been successfully applied to Ae complexes with high alcohol and monomer loadings prior to this work. The ROP of 200 equiv. of L-LA in toluene at 60 °C was efficiently promoted by **1**, albeit in a moderately controlled fashion (Table 1, entry 1). By contrast, upon addition of 10 equiv. of ^{i}PrOH *vs.* Mg, the ROP of 1000 equiv. of monomer was extremely fast and essentially reached completion within 6 min (entries 2–3). Most interestingly, **1** proved able to polymerise up to 5000 equiv. of L-LA in the presence of up to 100 equiv. of ^{i}PrOH as a transfer agent (entries 4–5). In all cases, the polydispersity index (M_w/M_n) remained very narrow (in the range 1.10–1.20) and the agreement between the theoretical and experimental (as determined by size exclusion chromatography, SEC) molecular weights was excellent. These data suggested that the polymerisation proceeded in a well-controlled fashion, and confirmed in turn that the rate constant for the transfer between growing PLLA chains and resting alcohols (k_{tr}) was far greater than that for the chain propagation (k_p) (Scheme 3). To our knowledge, **1** is the first example of a magnesium-based complex capable of promoting the immortal ROP of L-LA on such a large scale (catalyst loading *ca.* 200 ppm) while maintaining an extremely high catalytic activity (turnover frequencies (TOF) ranged from 3000 to 19 000 h^{-1}). Remarkably, the calcium complex **2** proved even more active than its Mg-based analogue. Indeed, upon addition of 10 equiv. of ^{i}PrOH, **2** nearly quantitatively polymerised 500 equiv. of L-LA in a well-controlled fashion (M_w/M_n = 1.27) within one minute (entry 7); the corresponding TOF of 28 200 h^{-1} exceeded by far any other value reported in the literature,[7d,11a–b] and **2**/^{i}PrOH therefore represents one of the most active metal-based catalytic systems known to date for the ROP of L-LA.[28] Moreover, **2** was also able to fully convert up to 1000 equiv. of monomer in the presence of 10–50 equiv. of alcohol (entries 8–9) while maintaining a good control of the polymerisation parameters. As anticipated, the activity of the catalytic system dropped noticeably at higher monomer loading (entry 10; L-LA/**2**/^{i}PrOH = 2500/1/25, TOF = 700 h^{-1}), illustrating the higher sensitivity of **2** with respect to its Mg congener **1** (Table 1, entries 4 and 10). These results were in line with prior reports that calcium complexes were more active, but also more sensitive, than their magnesium derivatives.[11a–b,19]



Scheme 3 Immortal ROP of L-LA catalysed by **1–3**/^{i}PrOH.

Table 1 Selected data for the ROP of L-LA using $ZnEt_2$ or complexes **1–4**/^{i}PrOH binary catalytic systems[a]

Entry	Initiator	$[L\text{-LA}]_0/[Met]_0/[^i PrOH]_0$	$[L\text{-LA}]_0$/mol L^{-1}	t/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]
1	**1**	200/1/—	2.0	10	92	1100	26 700	14 000	1.63
2	**1**	1000/1/10	2.0	2	63	18 900	9100	8400	1.11
3	**1**	1000/1/10	2.0	6	96	9600	13 900	13 100	1.14
4	**1**	2500/1/25	4.0	30	94	4700	13 600	11 900	1.17
5	**1**	5000/1/100	4.0	90	91	3030	6600	5500	1.18
6	**2**	500/1/—	2.0	1	8	2400	5800	8300	1.43
7	**2**	500/1/10	2.0	1	94	28 200	6800	6500	1.27
8	**2**	1000/1/25	2.0	15	95	3800	5500	6000	1.23
9	**2**	1000/1/50	2.0	15	94	3760	2800	2600	1.19
10	**2**	2500/1/25	4.0	180	84	700	12 200	12 700	1.23
11	**3**	1000/1/—	2.0	60	18	180	26 000	10 300	2.24
12	**3**	1000/1/10	2.0	60	97	970	14 000	15 100	1.10
13	**3**	5000/1/25	4.0	60	71	3550	20 500	20 600	1.09
14	**3**	5000/1/25	4.0	90	94	3130	27 100	26 200	1.16
15	$ZnEt_2$	20 000/1/250	6.0	80	11	1650	1300	1600	1.09
16	**4**	20 000/1/250	6.0	80	65	9770	7500	6700	1.10
17	**3**	20 000/1/250	6.0	80	74	11 130	8600	8900	1.16
18	**3**	20 000/1/250	6.0	180	98	6530	11 300	11 600	1.26
19	**3**	20 000/1/500	6.0	180	97	6470	5600	5400	1.32
20	**3**	20 000/1/1000	6.0	180	99	6600	2900	2400	1.33
21	**3**	50 000/1/500	6.0	16 × 60	100	3125	14 500	13 500	1.60

[a] Polymerisations performed in toluene at 60 °C. [b] Isolated yield of PLLA. [c] Non-optimized turnover frequency (mol(L-LA) mol(Met)$^{-1}$ h^{-1}) calculated over the whole reaction time. [d] Calculated from $[L\text{-LA}]_0/[^i PrOH]_0$ × monomer conversion × $M_{L\text{-LA}}$ + $M_{^i PrOH}$, with $M_{L\text{-LA}}$ = 144 g mol^{-1} and $M_{^i PrOH}$ = 60 g mol^{-1}. [e] Determined by size exclusion chromatography *vs.* polystyrene standards and corrected by a Mark–Houwink factor of 0.58.[32]

Various PLLA samples prepared with either **1**/^{i}PrOH or **2**/^{i}PrOH were characterised by NMR spectroscopy and MALDI-TOF MS to ascertain the nature of the initiating group. The ^{1}H NMR spectrum of low molecular weight PLLAs displayed the expected resonances for –OH and $–OCH(CH_3)_2$ *termini*, whereas the presence of $(Me_3Si)_2N–$, ^{n}Bu– or [LO^1]– moieties could not be detected (ESI†). This was further corroborated by the MALDI-TOF MS spectra,[29] which allowed us to establish beyond doubt the nature of the *termini* and confirmed that the ROP of L-LA catalysed by **1**/^{i}PrOH and **2**/^{i}PrOH proceeded *via* a coordination/insertion mechanism as depicted in Scheme 3. Finally, these catalysts operated without epimerisation of the monomer, as they only yielded purely isotactic PLLAs.[4a,30]

Within a same family, zinc complexes are intrinsically less active, but also far more robust, than their Ae-based equivalents.[7,11,19] In an attempt to increase the monomer loading *vs.* the metal, that is to increase the catalytic productivity, the ability of **3** to promote the ROP of cyclic esters was assessed. Expectedly, complex **3** itself only partly promotes the ROP of L-LA (1000 equiv.) in toluene under mild conditions (Table 1, entry 11). The size exclusion chromatography data (especially the polydispersity value of 2.24) reflect a mediocre control over the polymerisation, most likely as a result of slow initiation by the poorly nucleophilic ethyl group.[4a] By contrast, upon addition of 10 equiv. of ^{i}PrOH *vs.* **3** (entry 12), complete conversion of the monomer was observed within 60 min; efficient chain-transfer between dormant alcohol (macro)molecules and growing polymer chains on the metal centre was demonstrated by the very narrow polydispersity index (M_w/M_n) and excellent agreement between calculated and observed molecular weights for the resulting PLLA, thus establishing the immortal behaviour of the **3**/^{i}PrOH binary system (Scheme 3). Full conversion of 20 000 equiv. of L-LA with **3**/^{i}PrOH was achieved in as little as 3 h in the presence of 100–1000 equiv. of alcohol (entries 17–20; Fig. 3), with corresponding

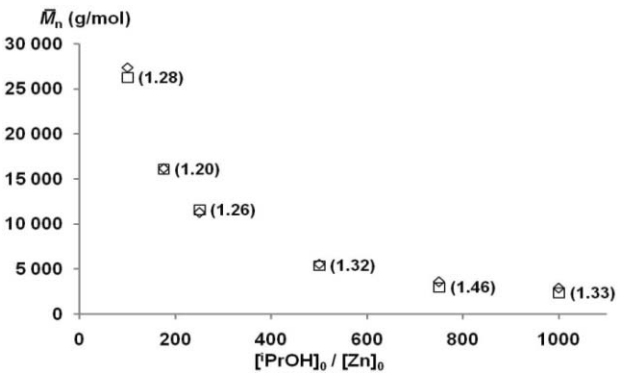


Fig. 3 Plot of M_n *vs.* alcohol-to-metal ratio for the polymerisation of L-LA with **3**/^{i}PrOH at $[L\text{-LA}]_0/\mathbf{3}$ = 20 000/1. (□) Experimental M_n determined by SEC, with M_w/M_n given in brackets. (◇) Calculated M_n.

turnover frequencies in the range 3 000–11 000 h^{-1}. Remarkably, up to 50 000 equiv. of L-LA could be quantitatively polymerised in a controlled fashion with $[\mathbf{3}]_0/[^i PrOH]_0$ = 1/500 (*i.e.*, zinc loading of 20 ppm) within a non-optimized time period of 16 h (entry 21). The binary system **3**/^{i}PrOH therefore represents an extraordinarily productive system for the controlled ROP of L-LA with real industrial potential, and to our knowledge no comparably effective catalyst has been reported to this date. By comparison, Sn(2-ethylhexanoate)$_2$, the initiator commonly used in industry, not only requires higher metal loading (typically 200–500 ppm) and much harsher polymerisation conditions (bulk monomer, T = 140–180 °C),[1a,3] but it is also at least an order of magnitude less active (TOF = 460–1260 h^{-1}).[31] In comparative experiments run to limited conversions, complex **3** (entry 17, TOF = 11 130 h^{-1}) was also found to be markedly more active than other related zinc-based systems such as the simple $ZnEt_2$ (entry 15, TOF = 1650 h^{-1}) or the well-established [BDI^{iPr}]Zn-N(SiMe$_3$)$_2$

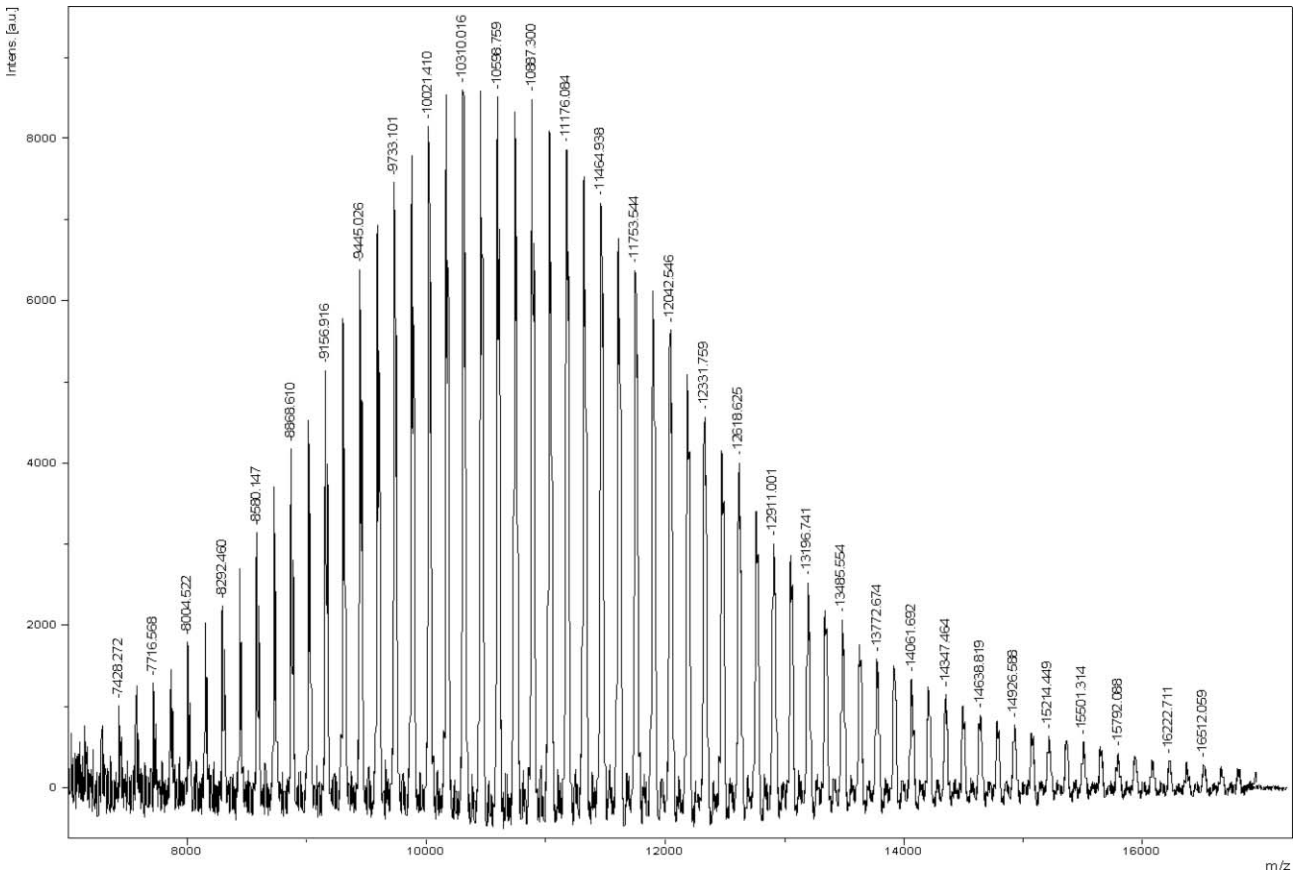


Fig. 4 MALDI-TOF MS (main population: Na^+; minor population: K^+) of a medium molecular weight PLLA ($M_{n,SEC}$ = 12 000 g mol^{-1}) prepared with L-LA/**3**/^{i}PrOH = 1000/1/10 (93% conversion).

(**4**, [BDI^{iPr}] = CH(MeCNC$_6$H$_3$^{i}Pr$_2$)$_2$;[4a] entry 16, TOF = 9770 h^{-1}). The data given in Table 1 confirm the unique ability of the sterically demanding ligand [LO^1]$^-$ to stabilize highly electro- and oxophilic species in the presence of large excesses of monomer and/or alcohol. The stability of the {[LO^1]ZnO^{i}Pr}$_n$ species[23] generated *in situ* under our typical polymerisation conditions was also confirmed by NMR monitoring of **3** and a 10-fold excess of ^{i}PrOH in $C_6D_5CD_3$ or C_6D_6 at 60 °C, where no sign of decomposition (in particular, no release of [LO^1]H) was observed even after 60 min. Moreover, the nature of the hydroxy- and isopropoxy-*termini* in various PLLAs formed with the **3**/^{i}PrOH system was unambiguously established both by NMR spectroscopy (Fig. S4, ESI†) and MALDI-TOF MS (Fig. 4 and Fig. S5, ESI†). No epimerisation of the optically active centres occurred in the course of the ROP of L-LA, as evidenced by examination of the methine region of the homonuclear decoupled ^{1}H NMR spectra of these samples.[4a,30] The large-scale ROP of *rac*-LA is equally catalysed by **3**/^{i}PrOH both in THF and toluene, although the resulting PLAs are in these cases essentially atactic (Table S1, ESI†).

These preliminary catalytic studies were also briefly extended to the ROP of other cyclic monomers. The versatility of **3** was illustrated by its capacity to polymerise *rac*-BBL in the presence of ^{i}PrOH in a highly controlled fashion. Thus, the bulk polymerisation of *rac*-BBL carried out with [BBL]$_0$/[**3**]$_0$/[^{i}PrOH]$_0$ = 500/1/10 at 60 °C reached 95% conversion within 3 h (TOF = 158 h^{-1}, $M_{n,calcd}$ = 4140 g mol^{-1}, $M_{n,SEC}$ = 4300 g mol^{-1}, M_w/M_n = 1.07).

In conclusion, the original bulky, mono-anionic [LO^1]$^-$ ligand has enabled us to prepare the first stable Zn, Mg and Ca heteroleptic complexes capable of promoting the large-scale immortal ROP of L-LA. These readily accessible complexes based on inexpensive, innocuous metals display impressive activities and excellent control. Since the pro-ligand [LO^1]H is easily synthesised on a scale of several dozen grams, this family of complexes is certainly attractive from an industrial perspective. Optimization of the catalytic activity in the presence of various alcohols and by tuning the nature of the ligand backbone is currently under way. The ability of complexes **1–3** to promote the immortal ROP of a broad range of cyclic esters and cyclic carbonates is also been explored; both will be the object of separate reports.

Experimental

General procedures

All manipulations were performed under inert atmosphere using a Schlenk line and standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; O_2 < 1 ppm, H_2O < 5 ppm) for catalyst loading. [LO^1]H,[22] [BDI^{iPr}]H wherein BDI^{iPr} is (2,6-^{i}Pr$_2$-C$_6$H$_3$)N=C(Me)-CH=C(Me)-N(2,6-^{i}Pr$_2$-C$_6$H$_3$)] and complex **4** were prepared as described in the literature.[4a] $ZnEt_2$ (1.0 M in

hexanes) was 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 from the provider. ^{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 systematically distilled under Argon from melted sodium prior to use. THF was first pre-dried over sodium hydroxyde 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, Saclay, France) 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 all times at a temperature of −30 °C under the inert atmosphere of the glovebox. Racemic β-butyrolactone (*rac*-BBL; TCI Europe, 97%) was purified by vacuum distillation from calcium hydride and kept over activated 3 Å molecular sieves.

NMR spectra were recorded on Bruker AC-200, AC-300 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. Coupling constants are given in Hertz.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyser instrument at the London Metropolitan University 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 5 monodisperse polystyrene standards in the range of 580 to 380 000 g mol^{-1}. According to literature recommendations,[32] the molecular weights of all poly(lactide)s were corrected by a Mark-Houwink factor of 0.58. The molecular weight of poly(3-hydroxybutyrate)s were directly given *vs.* poly(styrene)s equivalents.

The microstructure of poly(lactide) samples was 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 20 kV. 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 total 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^1]Mg^{n}Bu (1)

Mg^nBu_2 (3.0 mL of a 1.0 M solution in heptane, 3.00 mmol) was slowly added to a solution of [LO^1]H (0.94 g, 2.70 mmol) in 20 mL of toluene −45 °C. The resulting mixture was stirred at −45 °C for 60 min, and then at room temperature for a further 2 h to give a colourless solution. The volatiles were pumped off to give **1** as a white solid which was washed with pentane (3 × 20 mL) and dried to constant weight (0.97 g, 84%). Found C 67.3, H 9.9, N 6.2%. $C_{24}H_{40}N_2O_3Mg$ requires C 67.2, H 9.4, N 5.7%.

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.27 (2 H, br s, arom. *H*), 4.1–3.1 (12 H, br m, O-C*H*$_2$ + Ar-C*H*$_2$-N), 2.45 (8 H, br s, N-C*H*$_2$-CH$_2$), 1.68 (2 H, m, $^3J_{HH}$ = 7.5 Hz, Mg-CH$_2$-C*H*$_2$-CH$_2$-CH$_3$), 1.39 (2 H, m, $^3J_{HH}$ = 7.5 Hz, Mg-CH$_2$-CH$_2$-C*H*$_2$-CH$_3$), 1.38 (9 H, s, C(C*H*$_3$)$_3$), 1.03 (3 H, t, $^3J_{HH}$ = 7.5 Hz, Mg-CH$_2$-CH$_2$-CH$_2$-C*H*$_3$), −0.15 (2 H, t, $^3J_{HH}$ = 7.5 Hz, Mg-C*H*$_2$-CH$_2$-CH$_2$-CH$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): δ_C 156.3, 140.9, 128.3 (aromatic), 66.2 (O-*C*H$_2$), 61.2 (Ar-*C*H$_2$-N), 54.5 (N-*C*H$_2$-CH$_2$), 34.0 (*C*(CH$_3$)$_3$), 32.6 (Mg-CH$_2$-*C*H$_2$-CH$_2$-CH$_3$), 31.9 (Mg-CH$_2$-CH$_2$-*C*H$_2$-CH$_3$), 31.8 (C(*C*H$_3$)$_3$), 14.6 (Mg-CH$_2$-CH$_2$-CH$_2$-*C*H$_3$), 9.4 (Mg-*C*H$_2$-CH$_2$-CH$_2$-CH$_3$).

Synthesis of [LO^1]CaN(SiMe$_3$)$_2$ (2)

A solution of [LO^1]H (1.32 g, 3.79 mmol) in THF (20 mL) was added at room temperature over a period of time of 45 min to THF solution of Ca[N(SiMe$_3$)$_2$]$_2$(THF)$_2$ (1.71 g, 3.39 mmol) in THF. The resulting pale yellow solution was stirred overnight at room temperature, and the solvent was evaporated under vacuum to give crude **2** as a white powder in nearly quantitative yield. Repeated extraction with hot hexane followed by evaporation of the solvent and drying *in vacuo* afforded the analytically pure **2** (1.37 g, 74%). Single crystals of {**2**}$_2$ were grown by slow diffusion of hexane in a THF solution at room temperature, and its solid-state structure was elucidated by X-ray diffraction crystallography. Found C 56.9, H 8.95, N 7.5%. $C_{26}H_{49}N_3O_3Si_2Ca$ requires C 57.0, H 9.0, N 7.7%.

^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): δ_H 7.17 (2 H, s, arom. *H*), 3.69 (12 H, br, O-C*H*$_2$ + Ar-C*H*$_2$-N), 2.62 (8 H, br s, N-C*H*$_2$-CH$_2$), 1.34 (9 H, s, C(C*H*$_3$)$_3$), −0.01 (18 H, s, Si(C*H*$_3$)$_3$).

^{13}C{^{1}H} NMR (C_6D_6, 50.33 MHz, 25 °C): δ_C 159.0, 139.5, 129.9, 124.2 (aromatic), 64.6 (O-*C*H$_2$), 60.5 (Ar-*C*H$_2$-N), 54.1 (N-*C*H$_2$-CH$_2$), 33.8 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 5.8 (Si(*C*H$_3$)$_3$).

Synthesis of [LO^1]ZnEt (3)

A solution of [LO^1]H (3.5 g, 10.0 mmol) in 75 mL of toluene was added at −25 °C over a period of 20 min to a solution $ZnEt_2$ (10.2 mL of a 1.0 M solution in hexanes, 10.2 mmol) in toluene (125 mL). The resulting mixture was stirred at −25 °C for 60 min, and then at room temperature for a further 2 h to give a white suspension. The precipitate was isolated by filtration and dried *in vacuo* to give analytically pure **3** as a white powder (4.0 g, 90%). Colourless single-crystals of {**3**}$_2$·C_6H_6 were grown at room temperature from a concentrated benzene solution, and its solid-state structure was determined by X-ray crystallography. Found

C 59.8, H 8.2, N 6.05%. $C_{22}H_{36}N_2O_3Zn$ requires C 59.8, H 8.2, N 6.3%.

^{1}H NMR (CD_2Cl_2, 300.08 MHz, 25 °C): δ_H 7.15 (2 H, s, arom. *H*), 4.0–3.6 (12 H, br m, O-CH_2 + Ar-CH_2-N), 2.7–2.3 (8 H, br m, N-CH_2-CH_2), 1.32 (9 H, s, C(CH_3)$_3$), 0.93 (3 H, t, $^3J_{HH} = 7.5$ Hz, Zn-CH_2-CH_3), –0.02 (2 H, q, $^3J_{HH} = 7.5$ Hz, Zn-CH_2-CH_3) ppm.

^{13}C{^{1}H} NMR (CD_2Cl_2, 125.76 MHz, 25 °C): δ_C 158.4, 140.2, 127.4 (br) (all aromatic), 67.0–64.8 (O-*C*H_2 and Ar-*C*H_2-N), 54.6 (N-*C*H_2-CH_2), 33.7 (*C*(CH_3)$_3$), 31.4 (C(*C*H_3)$_3$), 12.0 (Zn-CH_2-*C*H_3), 1.6 (Zn-*C*H_2-CH_3) ppm.

Typical polymerisation procedure

All manipulations were performed under inert atmosphere. In the glove box, the metal-based initiator and the purified monomer 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 on a Schlenk line, using standard Schlenk techniques. Where needed, the required amount of dry, degassed solvent selected from toluene or THF was added with a syringe to the Schlenk flask containing the initiator and monomer. The metallic complex was then activated by addition of ^{i}PrOH. The alcohol was added rapidly, the Schlenk vessel was immersed 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 of less than 10^{-2} mbar.

Crystal structure determinations for 2 and 3

Suitable crystals for X-ray diffraction analysis of **2** and **3** were obtained by recrystallization of the purified products. Diffraction data were collected at 100 K using a Bruker APEX CCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ 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).[33] 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.†

Table 2 Summary of crystal and refinement data for complexes **2** and **3**

	2	**3**
Empirical formula	$C_{52}H_{98}Ca_2N_6O_6Si_4$	$C_{44}H_{72}N_4O_6Zn_2\cdot C_6D_6$
Formula weight	1095.88	961.9
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.5186(6)	11.4570(5)
b/Å	13.0169(8)	12.3401(5)
c/Å	14.3156(8)	13.3216(5)
α/°	114.588(2)	112.077(2)
β/°	104.771(2)	107.626(2)
γ/°	104.561(3)	116.642(2)
V/Å^3	1574.57(16)	1282.80(12)
Z	1	1
D/g cm^{-3}	1.156	1.245
μ/mm^{-1}	0.304	0.984
F(000)	596	514
Crystal size/mm	0.48 × 0.35 × 0.12	0.26 × 0.12 × 0.09
θ range/°	2.95–27.44	3.21–27.47
Limiting indices	$-13 \le h \le 13$, $-16 \le k \le 16$, $-18 \le l \le 18$	$-14 \le h \le 14$, $-15 \le k \le 15$, $-17 \le l \le 17$
R_{int}	0.0359	0.0335
Reflections collected	20 185	20 048
Reflections unique [$I > 2\sigma(I)$]	7101	5800
Data/restraints/parameters	7101/0/356	5800/0/292
Goodness-of-fit on F^2	1.094	1.035
R_1 [$I > 2\sigma(I)$] (all data)	0.0424 (0.0482)	0.0267 (0.0305)
wR_2 [$I > 2\sigma(I)$] (all data)	0.0968 (0.1002)	0.0642 (0.0664)
Largest difference/e Å^{-3}	0.437 and –0.324	0.397 and –0.292

Acknowledgements

The authors thank Total Petrochemicals for support (research grant to V. P.); financial assistance was also provided by the Institut Universitaire de France (J.-F. C.) and the CNRS and is gratefully acknowledged.

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