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Highly Selective and Immortal Magnesium Calixarene Complexes for Ring Opening Polymerization of *rac*-Lactide

Mark J. Walton,[a] Simon J. Lancaster,[a] and Carl Redshaw*[b]

Lithiation of 1,3-dipropoxy-*p*-*tert*-butyl-calix[4]areneH$_2$ (LH$_2$) followed by reaction with *n*-BuMgBr in THF resulted in the formation of the heterobimetallic complex [Li(THF)Mg(*n*-Bu)L] (**1**). By contrast, treatment of tripropoxy-*p*-*tert*-butylcalix[4]areneH (L′H) with *n*-Bu$_2$Mg afforded a mononuclear complex [L′Mg(*n*-Bu)] (**2**). Single-crystal X-ray diffraction studies revealed that in both structures the calix[4]arene adopts a cone conformation, with a lithium cation residing in the cavity for **1**. Both compounds **1** and **2** were active for the ring opening polymerization (ROP) of *rac*-lactide. Compound **2** not only displayed exceptional activity (100 equivalents, 3 minutes (92%, BnOH, room temperature), but also high selectivity (P$_r$ = 0.85), exhibiting immortal character in THF. Surprisingly compound **2** also showed isotactic bias (P$_r$ = 0.30 – 0.36) and immortal character when toluene was employed as solvent; 2D J-resolved ^{1}H NMR spectroscopy was employed for the assignment of the stereo-selectivity.

Introduction

Polymers with an inherent biodegradability, of which poly(lactic acid) (PLA) and poly(caprolactone) (PCL) are two of the most common, have gained significant interest due to their use in biomedical devices.[1-3] The production of PLA utilizing metal based catalysts for ring opening polymerization is considered to be the most convenient preparative route, primarily due to the ability to control molecular weight with low polydispersity.[3] Since Coates and co-workers published their seminal work on zinc and magnesium β-diiminate complexes, a large number of magnesium catalysts have appeared in the literature.[4-5] The drive toward establishing a highly active, selective and immortal catalyst for ROP of *rac*-lactide has seen a multitude of ligand systems employed, examples of which include iminophenolates,[6-7] β-diiminates,[5, 8] salan,[9] and heteroscorpionates.[10-11] The use of calix[4]arene-based ligand sets however in this area remains scant,[12] and indeed, in the case of magnesium, there are few reported complexes.[13] We note that recently there has been a resurgence of magnesium based catalysts, for example Chisholm *et al.* utilised β-diiminate magnesium compounds for the ROP of *rac*-lactide (Chart 1, **I**).[8] The catalyst exhibited exceptionally high activity as well as hetero-tactic bias when tetrahydrofuran (THF) was added to the polymerization system; however the addition of excess alcohol resulted in solvolysis and ligand loss and as a result the system was unsuitable for 'immortal' polymerization.[8] Wang *et al.* explored the use of pyridyl functionalized alkoxy zinc and magnesium complexes which exhibited immortal polymerization of *L*-lactide and ε-caprolactone (Chart 1, **II**).[14] The magnesium catalyst employed was able to polymerize ε-caprolactone even in the presence of 500 equivalents of benzyl alcohol as chain transfer agent giving the expected molecular weight. The pyridyl alkoxy magnesium catalyst also demonstrated immortal character for the ROP of *L*-lactide using triethanolamine as chain transfer/activation agent.[14]

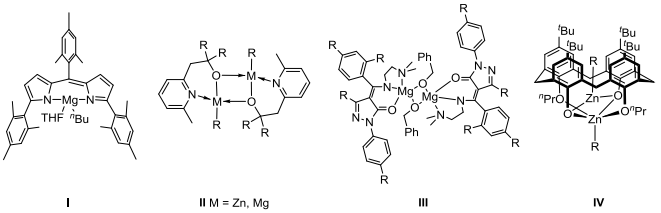

Chart 1. Previously reported magnesium and zinc compounds for the ROP of lactide.

Chuang *et al*. have utilized tridentate pyrazolonate magnesium catalysts (Chart 1, **III**),[15] and although they gave lower activities for the ROP of *rac*-lactide versus the catalysts reported by the groups of Chisholm and Coates,[5, 8] they exhibited immortal and stereo-selective behaviour (P$_r$ = 0.87). Generally ligands that are monoanionic are chosen for reaction with magnesium precursors as they will inevitably lead to a metal that still contains a viable nucleophilic group for ROP, which may be the reason calix[4]arenes have rarely been utilized. Vigalok *et al* have had success with zinc alkyl based calix[4]arenes and although the dialkoxycalix[4]arene ligand is dianionic when

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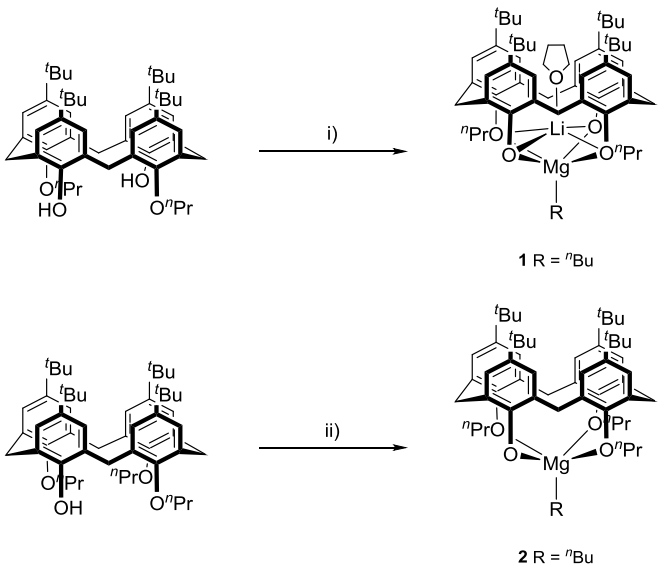


Scheme 1. Synthesis of magnesium compounds 1 and 2. i) 1) 2 *n*-BuLi, THF, 0 °C, 1 h, 2) *n*-BuMgBr, THF, 0 °C, 1 h. ii) *n*-Bu_2Mg, THF, 3 h, 0 °C.

deprotonated its use leads to a dimetallic complex that still contains a nucleophilic group (Chart 1, **IV**).[16] Herein, the exploration of calix[4]arene-based magnesium catalysts is reported. We have utilized 2D J-resolved ^{1}H NMR spectroscopy as an alternative to homo-nuclear decoupled NMR for the assignment of stereoselectivity.

Results and Discussion

Synthesis and structural studies

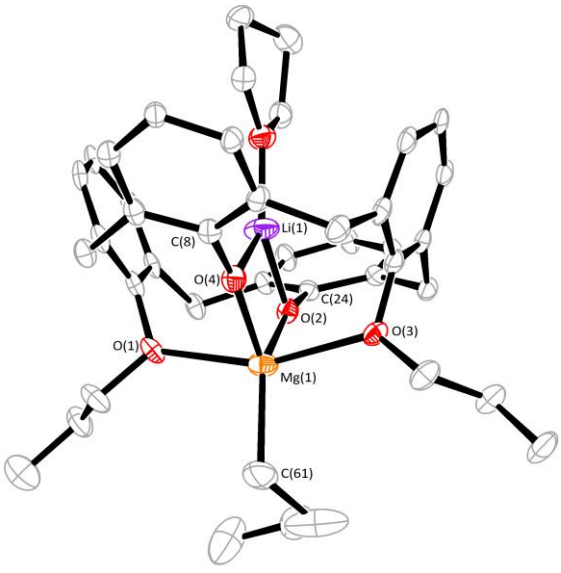


Figure 1. ORTEP representation of compound **1**. Hydrogen atoms, tert-butyl groups and minor disordered components have been removed for clarity. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Li(1)—O(5) 1.867(5), Li(1)—O(2) 1.903(5), Li(1)—O(4) 1.904(5), Mg(1)—O(1) 2.373(2), Mg(1)—O(2) 1.9261(19), Mg(1)—O(3) 2.302(2), Mg(1)—O(4) 1.9356(19). Mg(1)—C(61) 2.146(3). C(61)—Mg(1)—Li(1) 176.77(16), O(5)—Li(1)—Mg(1) 179.2(3), O(2)—Mg(1)—C(61) 137.75(13), O(4)—Mg(1)—C(61), 131.36(13).

Table 1. Selected structural data for **1** and **V**.[13]

Bond length (Å)/Angle (°)	**1**	**V**
Mg(1)—O(1)/(3)	2.373(2)/2.302(2)	2.232(4)
Mg(1)—O(2)/O(4)	1.9261(19)/1.9356(19)	1.849(4)
Mg(1)—L	2.146(3)	2.033(4)
C(24)—O(2)—Mg(1)	166.04(16)	147.2(4)
C(8)—O(4)—Mg(1)	162.96(16)	147.2(4)

Compound ***1***: The reaction of the lithiated 1,3-dipropoxy-*p-tert*-butyl-calix[4]areneH_2 (LLi_2) with 2 equivalents *n*-butyl magnesium bromide led to formation of compound **1** [Li(THF)Mg(*n*-Bu)L] in 32% by crystallisation from a THF/light light petroleum solution at room temperature. Single crystal X-ray crystallography (see figure 1) revealed, rather than formation of a di-magnesium alkyl complex, only one of the lithiated oxygen reacted with the Grignard reagent, thus forming a hetero-bimetallic complex. The lithium cation was found to reside inside the calix[4]arene cavity, similarly to our previous observations of other metallocalix[4]arene systems,[17-20] the magnesium centre bearing an *n*-butyl group is bound to the four oxygens of the lower rim; the Mg – O bonds to the alkoxy groups [O(1)/O(3)] at ~ 2.34 Å are, as expected, somewhat longer than those to the phenolic groups [O(2)/O(4)] at ~ 1.93 Å. The magnesium and lithium metal centres are 2.670(5) Å apart, with the magnesium metal centre adopting distorted trigonal bipyramidal geometry. The THF oxygen, lithium, magnesium and carbon of the *n*-butyl group are all essentially linear as represented by the angles between O(5)—Li(1)—Mg(1) and C(61)—Mg(1)—Li(1), 176.77(16) and 179.2(3), respectively. There is also a slight difference in angle around the magnesium between the non-propoxy oxygen atoms O(2)/O(4) and C(61) in the equatorial plane, the angle between O(2) and C(61) is slightly larger than that of O(4) and C(61), 137.75(13)° *vs*. 131.36(13)°.

Similar structures based on alkali and alkali earth metals have previously been reported by Floriani and co-workers;[13] in particular the treatment of 1,3-dicyclopentoxy-*p-tert*-butyl-calix[4]areneH_2 with magnesium anthracene led to the formation of [(*p*-^{t}Bu-calix[4]-$(OCyp)_2$-$(O)_2$)Mg(thf)] (**V**). The structure of **V** is similar to compound **1**; compound **1** contains both a lithium and THF molecule within the cavity whereas **V** contains only a THF molecule. The presence of the lithium centre within the cavity of **1** forces the calixarene further into an elliptical conformation as shown by the bond angles between C(24)—O(2)—Mg(1)/C(8)—O(4)—Mg(1). Each of the Mg—O bonds are extended in compound **1** *vs.* **V** (see table 1). Compound **1** has also been characterised by ^{1}H and ^{13}C NMR, mass spectroscopy, elemental analysis and IR.

Compound ***2****:* The tripropoxy-*p-tert*-butylcalix[4]areneH (L′H) was synthesized according to the method of Zhong *et al*,[21] and was then treated with one equivalent of di-*n*-butyl magnesium in THF. Single crystals of the product **2**.pentane, [L′Mg(*n*-Bu)] with a disordered alkyl molecule, suitable for X-ray diffraction, were grown from a saturated light petroleum solution. We note that although the electron density from single crystal X-ray diffraction

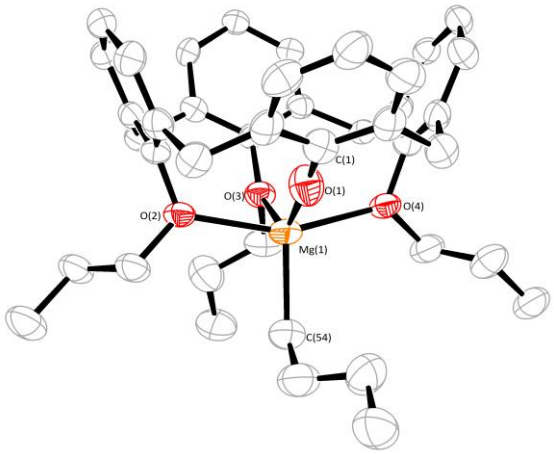


Figure 2. ORTEP representation of compound **2**·(pentane)**.** Hydrogen atoms, tert-butyl groups and a pentane molecule located in the calixarene cavity have been removed for clarity. Displacement ellipsoids are drawn at the 50 % probability level. Selected bond lengths (Å) and angles (°): Mg(1)—O(1) 1.860(4), Mg(1)—O(2) 2.247(3), Mg(1)—O(3) 2.145(3), Mg(1)—O(4) 2.255(3), Mg(1)—C(54) 2.152(5), O(1)—C(1) 1.309(5), O(1)—Mg(1)—O(3) 128.07(15), O(1)—Mg(1)—C(54) 127.0(2), O(3)—Mg(1)—C(54) 104.89(17), O(2)—Mg(1)—C(54) 101.62(18), O(4)—Mg(1)—C(54) 100.88(18), C(1)—O(1)—Mg(1) 175.8(3), O(2)—Mg(1)—O(4) 156.69(12).

studies indicate a disordered pentane molecule; it is probable that a number of different alkane molecules, from the petroleum fraction used, occupy the calixarene cavity. The solid structure of the compound contains disordered solvent within the cavity, and a magnesium *n*-butyl fragment is again bound to the lower rim of the calix[4]arene. The magnesium centre adopts a disordered trigonal bipyramidal geometry, the axial O(2)—Mg—O(4) bond angle is 156.69(12)°. The bond length for the phenolic oxygen and magnesium, O(1)—Mg(1), 1.860(4) Å is significantly shorter than the OR bond lengths, 2.145(3) – 2.255(3) Å as expected. The equatorial RO-Mg bond, O(3)—Mg(1), is the shortest of the three, 2.145(3) *vs.* 2.255(3) and 2.247(3). The C(1)—O(1)—Mg(1) bond angle is almost linear, 175.8(3)°; in contrast the Calix-OR-Mg angles are 121.1(2) – 121.6(2)° for the axial and 133.8(2)° for the equatorial positions. Compound **2** has also been characterised by ^{1}H and ^{13}C NMR, mass spectroscopy, elemental analysis and IR.

Discussion

Given that magnesium compounds have been shown to have exceptional activity for the ring opening polymerization of *rac*-lactide, higher than their zinc counterparts,[5, 8, 14] we initially attempted the synthesis of a di(alkyl magnesium)calix[4]arene, similar to the zinc species of Vigalok *et al*,[16] by reaction of two equivalents of di-*n*-butyl magnesium and 1,3-dipropoxy-*p*-*tert*-butyl-calix[4]areneH_2 in tetrahydrofuran. However, this led to the immediate formation of a white precipitate which we were unable to characterise do to its insolubility in common solvents. We suspected that one equivalent of the magnesium alkyl precursor was reacting with two of the phenolic groups rather than forming a bimetallic calix[4]arene as previously encountered in zinc chemistry.[16] To overcome this, we first lithiated the 1,3-dipropoxy-*p*-*tert*-butyl-calix[4]areneH_2 by reaction with *n*-butyllithium in THF, thereby removing any phenolic protons, and subsequently reacting the lithiated calix[4]arene with two equivalents of *n*-BuMgBr. This resulted in the formation of compound **1**, where only one equivalent of the Grignard reagent had reacted with the lithiated calix[4]arene. The reaction proceeded without formation of a precipitate, while it is probable there is formation of a so called 'turbo-Grignard reagent' with any excess Grignard reagent,[22] the fate of the presumably formed lithium bromide is currently unknown. Reaction of the lithiated calix[4]arene with an excess of *n*-BuMgBr led to the same product. To synthesize a mono-metallic magnesium species, we employed a tripropoxy-*p*-*tert*-butylcalix[4]areneH ligand, which upon reaction with *n*-Bu_2Mg in THF formed compound **2** in 50% isolated yield after crystallisation from a concentrated light petroleum solution.

Table 2. ROP of *rac*-lactide using magnesium compounds **1** and **2**

Run	Cat	Solvent	M : ROH	Time (min)	Conv[a] (%)	P_r[a,b]	$M_{n,GPC\ x10}^{-3}$	$M_{n,Cal\ x\ 10}^{-3c}$	PDI
1	**1**	toluene	100 : 1 (MeOH)	60	9.4	-	-	-	-
2	**1**	THF	100 : 1 (MeOH)	60	35	-	2.33	5.08	1.09
3	**1**	CH_2Cl_2	100 : 1 (MeOH)	60	55	-	15.4	7.96	1.22
4	**1**	CH_2Cl_2	100 : 0	480	trace	-	-	-	-
5	**1**	CH_2Cl_2	100 : 1 (^{i}PrOH)	60	6.3	-	-	-	-
6	**1**	CH_2Cl_2	100 : 1 (^{t}BuOH)	60	12	-	-	-	-
7	**1**	CH_2Cl_2	100 : 1 (BnOH)	60	8.8	-	-	-	-
8	**1**	CH_2Cl_2	100 : 2 (MeOH)	90	80	0.41	4.46	5.78	1.15
9	**1**	CH_2Cl_2	100 : 4 (MeOH)	120	94	0.42	1.79	3.40	1.19
10	**2**	CH_2Cl_2	100 : 1 (MeOH)	120	55	0.49	15.5	7.96	1.12
11	**2**	THF	100 : 1 (MeOH)	120	65	0.73	12.4	9.40	1.44
12	**2**	Toluene	100 : 1 (MeOH)	120	61	0.30	11.7	8.82	1.98
13	**2**	THF	100 : 0	30	28	-	-	-	-
14	**2**	THF	100 : 1 (^{i}PrOH)	30	97	0.79	13.6	14.0	1.46
15	**2**	THF	100 : 1 (^{t}BuOH)	30	95	0.79	15.6	13.8	1.40
16	**2**	THF	100 : 1 (BnOH)	3	92	0.85	14.8	13.4	1.25
17	**2**	THF	100 : 2 (BnOH)	5	95	0.78	8.92	6.90	1.34
18	**2**	THF	100 : 4 (BnOH)	5	93	0.80	3.61	3.38	1.32
19	**2**	Toluene	100 : 1 (BnOH)	5	94	0.35	10.5	13.5	1.54
20	**2**	Toluene	100 : 2 (BnOH)	5	99	0.35	6.17	7.20	1.54
21	**2**	Toluene	100 : 4 (BnOH)	5	99	0.36	3.57	2.82	1.50

Conditions: Polymerization carried out using 60 µmol catalyst at 20 °C, $[La]_0$ = 0.6 M, 10 mL solvent, ROH taken from a ROH/toluene solution. [a] Determined by NMR spectroscopy, [b] Probability of forming a *r* dyad, [c] Calculated from ($[LA]_0/[OH]_0$) x conv.(%) x 144.13 + ROH. M_n GPC corrected by 0.58 from polystyrene standards.

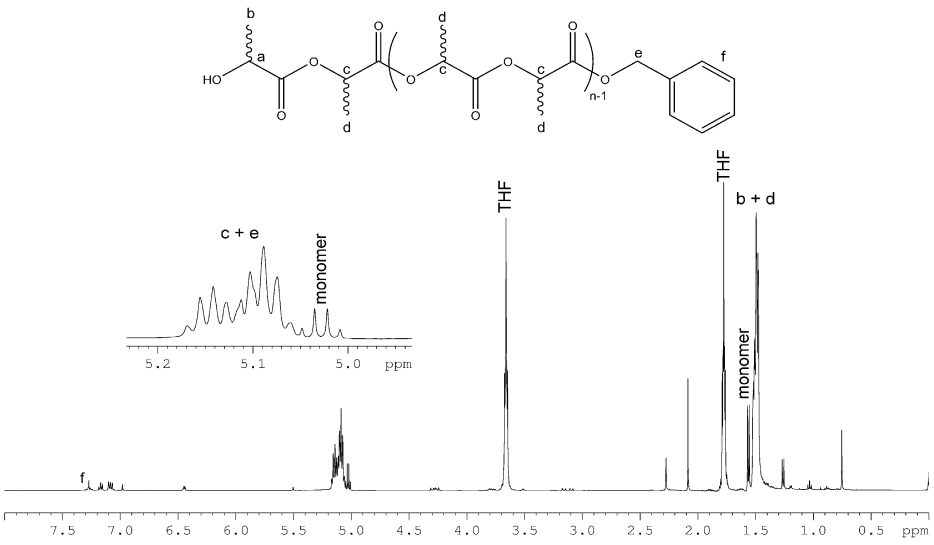
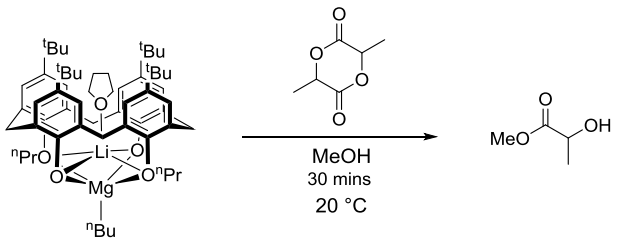


Figure 3. ^{1}H NMR spectrum from quenched PLA-100 (table 2, run 16).

Polymerization Results using magnesium catalysts

Initially, we attempted the polymerization of *rac*-lactide using benzyl alcohol (BnOH) as an activator for compound **1** (100 : 1 : 1) in THF (10 mL), however quenching this reaction with excess methanol led to the formation of Methyl-(RS)-lactate rather than any polymerization products (See scheme 2 and S1). Clearly polymerization has not occurred and a species capable of ring-opening *rac*-lactide is generated on quenching. Sobota and co-workers have recently reported a magnesium catalyst for the chemo-selective ring opening of *rac*-lactide similar to our failed quenching method.[23] For subsequent screening we used a drop of dilute hydrochloric acid (0.1 M) to quench the polymerization. We found that using one equivalent of MeOH in combination with compound **1** was more active for ROP of *rac*-lactide in dichloromethane (CH_2Cl_2) rather than THF or toluene (table 2, runs 1-3, 55 % *vs.* 35 % and 9.4 %, 100 equivalents *rac*-lactide, 60 min). The molecular weight of the polymer obtained in CH_2Cl_2 was almost double the expected values. The degradation of a magnesium butyl compound in CH_2Cl_2 was also observed by Chisholm *et al*;[8] the magnesium butyl group has reacted with the dichloromethane to form a magnesium chloride moiety incapable of ROP, leading to a higher than expected monomer:catalyst ratio. Compound **1** had low activity when isopropanol, *tert*-butanol or benzyl alcohol were used instead of methanol, and was inactive without the addition of any alcohol.



Scheme 2. Reaction of Compound **1** with *rac*-lactide in excess MeOH

In contrast to **1**, compound **2** showed increased activities in THF and toluene, rather than CH_2Cl_2 (table 2, runs 10 – 12). The molecular weight was higher than expected in all three solvents, much more so in CH_2Cl_2 than in THF or toluene indicating a degradation of the catalyst. Addition of *i*-PrOH, *t*-BuOH or BnOH rather than MeOH led to increased activities, especially in the case of BnOH which gave 92% conversion of 100 equivalents of *rac*-lactide over 3 min (table 2, run 16). Compound **2** was also more active without the addition of MeOH in THF, indicating the MeOH can deactivate the catalytic system. The molecular weight of the polymers obtained in THF using *i*-PrOH, *t*-BuOH and BnOH were close to the expected values, and additional benzyl alcohol also acts as a chain transfer agent controlling the resultant chain length giving the catalytic system 'immortal' character (table 2, runs 16 – 18) The use of toluene as solvent with BnOH also gives a highly active catalytic system with complete conversion of *rac*-lactide over 5 minutes (table 2, runs 20 – 22) with good chain length control and 'immortal' character.

To assign the stereoselectivity of the polymer produced we used 2D J-resolved ^{1}H NMR spectroscopy rather than the more common homonuclear decoupled spectroscopy. 2D J-res spectroscopy separates the 1D spectrum of PLA (see figure 4) so that the coupling constants appear on the y axis.[24] A projection on to the x axis essentially removes all coupling from the entire spectrum. The stereoselectivity of the polymer can be easily assigned by reference to the literature.[25] This has the advantage over the traditional homonuclear decoupled spectroscopy used to assign stereoselectivity that no manual information has to be entered, allowing an automated experiment. The resulting spectrum from 2D J-res spectroscopy for the assignment of PLA is shown in figure 4. Compounds **1** and **2**.pentane give essentially atactic PLA when dichloromethane is used as solvent (table 2, runs 8-10, P_r = 0.41 – 0.49). Compound **2** shows a high selectivity for heterotactic PLA in THF (table 2, run 14 – 18, P_r = 0.78 – 0.85), and rather surprisingly isotactic PLA in toluene (table 2, run 12 and 19-21, P_r = 0.30 – 0.36). The effect of THF on the selectivity has previously been discussed by Chisholm *et al,*[8] and there are many other examples.[6, 11, 15, 26] We do not as yet have

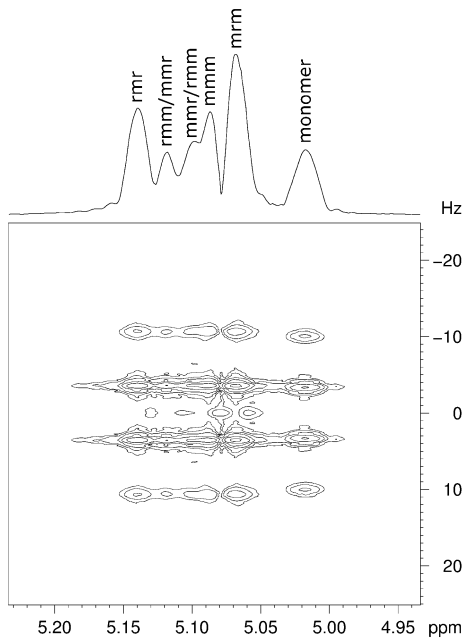


Figure 4. 2D J-resolved ^{1}H NMR of the methine region (table 2, run 16)

an explanation for the reverse selectivity involving toluene. Although a number of magnesium catalysts have been explored for the immortal and highly active polymerization of *L*-lactide,[14, 27-29] **2** is the only catalyst that has exhibits both highly active immortal and stereoselective ring opening polymerization of *rac*-lactide of which we are aware.

Conclusion

We have synthesized two magnesium based calix[4]arene compounds using either 1,3-dipropoxy-*p*-*tert*-butyl-calix[4]areneH$_2$ (LH$_2$) or tripropoxy-*p*-*tert*-butylcalix[4]areneH (L′H). Use of *n*-BuLi/1,3-dipropoxy-*p*-*tert*-butyl-calix[4]areneH$_2$ resulted in the isolation of a hetero-bi-metallic Li/Mg calix[4]arene [Li(THF)Mg(*n*-Bu)L] (**1**), in which the lithium is situated in the calixarene cavity and thus prevented from reaction with *n*-butylmagnesium bromide. By contrast, the reaction between tripropoxy-*p*-*tert*-butylcalix[4]areneH and di-*n*-butylmagnesium in THF resulted in the formation of the compound [L′Mg(*n*-Bu)] (**2.**pentane). Compounds **1** and **2** were characterized by single crystal X-ray diffraction, IR and NMR spectroscopy, elemental analysis and mass spectroscopy. Both compounds were active for the ring opening polymerization of *rac*-lactide. Hetero-bimetallic compound **1** can convert (94%) 100 equivalents of *rac*-lactide in dichloromethane/methanol in 2 hours. Compound **2** is a highly active and selective ROP catalyst, 100 equivalents of *rac*-lactide can be converted to PLA (P_r = 0.85, 92%) in 3 minutes, and also reveals 'immortal' polymerization of *rac*-lactide when THF or toluene are activated with BnOH (table 2, runs 16 – 21). We have also utilized a new method for determination of stereoselectivity of PLA produced; two-dimensional J-resolved spectroscopy allows quick and easy assignment. Compound **2** gives either isotactic or heterotactic bias PLA depending on the solvent employed (THF: table 2, runs 16 – 18, P_r = 0.79 – 0.85; toluene: run 12 and 19 – 21, P_r = 0.30 – 0.36).

Experimental Section

General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services at London Metropolitan University. NMR spectra were recorded on Bruker Ascend 500/300 MHz spectrometers at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent. IR spectra (Nujol mulls) were recorded on Perkin-Elmer 577 and 457 grating spectrophotometers. LH$_2$ and L′H were synthesized by the reported procedures.[21, 30] *rac*-Lactide was purchased from Sigma Aldrich and used without further purification. GPC analysis was performed on a Polymer Laboratories, PL-GPC 50 using THF at 0.5 mL′min flow rate and 30 °C, corrected by the Mark-Houwink factor (0.58).

Synthesis of Compound **1**

LH$_2$ (4.0 g, 5.46 mmol) was dissolved in THF (50 mL). The solution was cooled to 0 °C and *n*-BuLi (10.93 mmol, 1.6 M in hexanes, 6.83 mL) was added dropwise. The orange solution was allowed to warm to room temperature and stirred for 1 h. The Grignard reagent n-BuMgBr (10.93 mmol), freshly prepared from reaction between n-BuBr and magnesium turnings in THF, was added to the lithiated solution at 0 °C. The solution was allowed to warm to room temperature and stirred for 1 h. The THF solution was extracted and then concentrated to approximately 10 mL, and light petroleum (40 mL) was added. After standing at room temperature overnight, yellow needles of the product formed (1.54 g, 32% yield). MS (ASAP) 875.6 [M-CH$_3$]$^+$, 841.5 [M-Pr-Li+H]. IR (ATR): 2956s, 2904m, 2872m, 1627w, 1600w, 1479s, 1389m, 1362m, 1308m, 1249w, 1191m, 1123m, 1094m, 1043w, 999w, 870m, 830w, 797w, 531m. Found: C, 78.29; H 9.44. $C_{58}H_{83}LiMgO_5$ requires C, 78.23; H, 9.28 %. ^{1}H NMR (C_6D_6): δ 7.27 (s, 4H, Ar*H*), 7.10 (s, 4H, Ar*H*), 4.53 (d, 4H, *J* = 12.7 Hz, endo-C*H*$_2$), 4.16 (br t, 4H, OC*H*$_2$), 3.31 (d, 4H, *J* = 12.7 Hz, exo-C*H*$_2$), 2.38 (m, 2H, MgCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.95 (sex, 2H, *J* = 7.22 Hz, MgCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.80 (sex, 4H, J = 7.84 Hz, OCH$_2$C*H*$_2$CH$_3$), 1.43 (s, 18H, *t*-Bu), 1.32 (t, 3H, *J* = 7.31 Hz, MgCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.05 (s, 18H, *t*-Bu) 0.63 (t, 6H, *J* = 7.31 Hz, OCH$_2$CH$_2$C*H*$_3$), 0.47 (m, 2H, MgC*H*$_2$CH$_2$CH$_2$CH$_3$). ^{13}C NMR (C_6D_6): δ 152.2, 146.7, 137.6, 134.9, 130.5, 128.6, 125.8, 125.2, 78.8, 35.4, 34.2, 34.1, 33.8, 32.5, 32.4, 31.4, 30.8, 25.2, 23.0, 14.8, 14.0, 9.8, 7.0.

Synthesis of Compound **2**

L′H (2.0 g, 2.58 mmol) was dissolved in THF (30 mL), cooled to 0 °C and *n*-Bu$_2$Mg (1.0 M in heptane, 2.58 mmol, 2.58 mL) was added dropwise. After complete addition the solution was allowed to warm to room temperature and then stirred for 3 h. The volatiles were removed in vacuo and the product extracted using light petroleum (30 mL). The light petroleum solution was concentrated to approximately 15 mL and upon standing overnight colourless needles formed. Yield (1.1 g, 50%). MS (E.I.) 774 [M-Mg*n*-Bu]$^+$. IR (ATR): 2956s, 2871s, 1480s, 1390w, 1361m, 1299w, 1261w, 1200m, 1121m, 1105m, 1042m, 1008m, 985m, 870m, 799m, 635w, 532m. Found: C, 79.72; H 9.44. $C_{56}H_{80}MgO_4$ requires C, 79.93; H, 9.58 %. ^{1}H NMR (C_6D_6): δ 7.40 (s, 2H, Ar*H*), 7.39 (s, 2H, Ar*H*), 6.99 (s, 4H, Ar*H*), 4.58 (d, 2H, *J* = 12.3 Hz, endo-C*H*$_2$), 4.52 (d, 2H, *J* = 12.1 Hz, endo-C*H*$_2$), 4.33 (m, 4H, OC*H*$_2$), 3.59 (br t, 4H, OC*H*$_2$), 3.46 (d, 4H, *J* = 12.3 Hz, exo-CH$_2$), 3.38 (d, 4H, *J* = 12.1 Hz, exo-CH$_2$), 2.28 (m, 2H, MgCH$_2$C*H*$_2$CH$_2$CH$_3$), 2.07-1.80 (m, 8H), 1.62 (s, 9H, *t*-Bu), 1.40 (s, 9H, *t*-Bu), 1.31 (t, 3H, *J* = 7.3 Hz, MgCH$_2$CH$_2$CH$_2$C*H*$_3$), 0.79 (s, 18H, t-Bu) 0.56 (m, 9H, OCH$_2$CH$_2$C*H*$_3$), 0.28 (m, 2H, MgC*H*$_2$CH$_2$CH$_2$CH$_3$). ^{13}C NMR (C_6D_6): δ 160.2, 151.2, 148.8, 148.7, 148.5, 146.3, 135.2, 133.7, 133.8, 130.9, 127.5, 125.4, 123.4, 122.9, 79.6, 78.2, 40.5, 34.8, 33.4, 33.0, 32.6, 32.2, 31.6, 30.4, 29.6, 21.6, 21.5, 13.5, 13.1, 8.2, 7.9, 7.5.

Table 3. Crystallographic data for complexes **1** and **2**.(pentane)		
Compound	**1**	**2**.(pentane)
Formula	$C_{58}H_{83}LiMgO_5$	$C_{57}H_{82}MgO_4$, C_5H_{12}
Formula weight	891.49	927.68
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/c$
Unit cell dimensions		
a (Å)	26.5541(19)	16.4117(7)
b (Å)	22.8307(16)	13.4182(7)
c (Å)	21.4201(15)	25.8860(18)
α (°)	90	90
β (°)	124.770(2)	93.318(7)
γ (°)	90	90
V (Å^3)	10667.2(13)	5690.9(6)
Z	8	4
Temperature (K)	100(2)	100(2)
D_{calcd} (Mg/m^{-3})	1.110	1.083
Absorption coefficient, μ (mm^{-1})	0.079	0.075
Crystal size (mm^3)	0.01 × 0.07 × 0.17	0.02 × 0.10 × 0.11
$2\theta_{max}$ (°)	27.5	27.5
Reflections measured	64853	26366
Unique reflections, R_{int}	12206	9632
Reflections with $F^2 > 2\sigma(F^2)$	7056	5353
Transmission factors (max., min.)	1.000, 0.635	1.000, 0.299
Number of parameters	625	621
R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.074	0.090
R_1, wR_2 (all data)	0.192	0.275
Largest difference peak and hole (e Å^{-3})	0.728, −0.354	0.922, −0.339

Polymerization Procedure

Solutions of *rac*-lactide and catalyst were prepared separately using the required solvent. The required amount of alcohol, from a standard alcohol solution in toluene, was added to the catalyst. The *rac*-lactide solution was added to the catalyst solution and stirred for the allotted time at room temperature under nitrogen. 0.5 – 1.0 mL aliquots were taken out of the stirred solution where required and quenched with 1 drop of 0.1 M HCl. The aliquots were then dried and analysed by ^{1}H NMR spectroscopy and GPC.

Crystallography

Crystals were mounted in oil on a glass fibre and fixed in the cold nitrogen stream on a Rigaku Saturn724+ diffractometer equipped with MoKα radiation (λ = 0.71073 Å) at 100(2) K. The structures were solved by direct methods and refined by full-matrix least squares on F^2. All hydrogen atoms were placed in calculated positions. Refinement was performed using the SHELX-2013 program.[31] CCDC-984215 (**1**) and CCDC-984216 (**2**.pentane) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Keywords: Ring-opening polymerization • Heterobimetallic complexes • Magnesium • Lactides • Calixarenes

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