

Binolate complexes of lithium, zinc, aluminium, and titanium; preparations, structures, and studies of lactide polymerization

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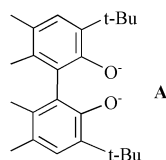
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The reaction of racemic 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol (biphenolate-H₂) with 4 mol equiv. of ⁿBuLi yields [(μ₃,μ₃-biphenolate)₂Li₄(ⁿBuLi)₄] (**1**) in high yield. **1** further reacts with 4 mol equiv. of 2,4-dimethyl-3-pentanol in the presence of tetrahydrofuran (THF) or cyclohexene oxide (CyHO) to give the lithium aggregate [(μ,μ-biphenolate)Li₂(μ₃-OCH(ⁱPr)₂)₂Li₂(L)₂] (**2-THF**, L = THF; **2-CyHO**, L = CyHO). Treatment of biphenolate-H₂ with 3 mol equiv. of ZnEt₂, followed by addition of 2 mol equiv. of 2,4-dimethyl-3-pentanol provides the zinc complex [(μ,μ-biphenolate)Zn(μ-OCH(ⁱPr)₂)₂Zn₂Et₂] (**3**). Aluminium alkoxide incorporating biphenolate ligand can also be obtained *via* a similar synthetic route. The compound [(μ-biphenolate)AlMe(μ-OCH(ⁱPr)₂)AlMe₂] (**4**) is prepared from the reaction of biphenolate-H₂ with 2 mol equiv. of AlMe₃ in the presence of 1 mol equiv. of 2,4-dimethyl-3-pentanol. The titanium (4+) binolate complex [(biphenolate)Ti₂Cl₆] (**5**) is synthesized from the reaction of biphenolate-H₂ and 2 mol equiv. of TiCl₄. In addition, **2-THF**, **3**, and **4** have been examined for *rac*-lactide polymerization, and the comparative studies of polymerization are also presented.

Introduction

It is possible for a racemic catalyst to be employed in the ring-opening polymerization of a racemic-monomer to produce isotactic polymers (50 : 50 of *R* : *S*). This is ably demonstrated by the work of Tsuruta who showed that certain zinc aggregates would polymerize *rac*-propylene oxide to give isotactic polypropylene oxide, PPO. The resulting polymer consists of 50% S-PPO and 50% R-PPO.¹ Following the work of Spassky² with chiral salen-aluminium complexes in stereoselective polymerizations from *rac*-lactide, there was a preliminary report that the racemic salen-aluminium complex produced a stereocomplex polymer of 50 : 50 poly-L-lactide and poly-D-lactide.³ This was refuted by Coates who, upon close inspection of the stereoirregularities of the polymer, concluded that the polymer consisted of isotactic blocks (L-PLA)_n(D-PLA)_m where *n* and *m* were on the order of 10 or 11.⁴ This observation can be interpreted on the basis of facile chain transfer between the two enantiomeric aluminium sites. The goal of making a stereocomplex polymer containing 50% L-PLA and 50% D-PLA, which has a significantly higher *T*_m, remains to be achieved from a racemic catalyst and the racemic form of lactide.

We describe here the preparation of binolate derivatives of lithium, zinc, aluminium and titanium employing the bulky racemic binolate, 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-bi-2,2'-phenolate (**A**) shown below. This binolate ligand has proved to be important in ring-closing metathesis reactions in both its racemic and resolved forms as evident from the work of Schrock.⁵ In principal racemic complexes incorporating this bulky binolate ligand could show the required stereoselectivity to yield catalysts capable of converting *rac*-LA to its stereocomplex isotactic PLA.



Results and discussion

Syntheses

The unusual “*n*-butyllithium trap” lithium aggregate, [(μ₃,μ₃-biphenolate)₂Li₄(ⁿBuLi)₄] (**1**), is synthesized in 89% yield from

the reaction of 4 mol equiv. of ⁿBuLi with a solution of racemic 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol (biphenolate-H₂) at 0 °C, followed by recrystallization from hexane. The octa-lithium species **1** is the first example in which four ⁿBuLi entities form an aggregate in the presence of two lithium biphenolates. The *n*-butyl group of lithium aggregate **1** can be easily converted to an alkoxy group. However, there is a dramatic change in its skeleton. The reaction of complex **1** with 4 mol equiv. of 2,4-dimethyl-3-pentanol at ambient temperature in the presence of THF yields [(μ,μ-biphenolate)Li₂(μ₃-OCH(ⁱPr)₂)₂Li₂(THF)₂] (**2-THF**) in 81% yield. Attempts to obtain a related complex without THF coordinated were unsuccessful. The lithium aggregate **2-THF** further reacts with an excess of cyclohexene oxide (CyHO) at ambient temperature to afford [(μ,μ-biphenolate)Li₂(μ₃-OCH(ⁱPr)₂)₂Li₂(CyHO)₂] (**2-CyHO**), indicating the THF molecule coordinated to lithium is substitutionally labile (see Scheme 1) and furthermore that CyHO is inert to both ring-opening polymerization or allylic proton abstraction by the LiOR group.

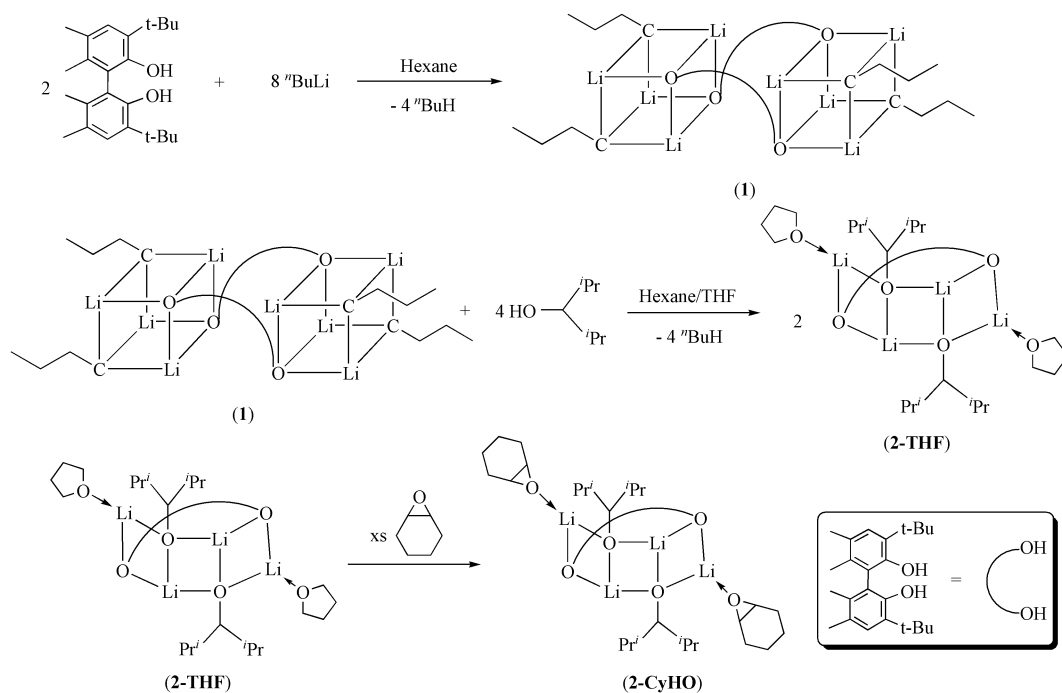
Treatment of biphenolate-H₂ with 3 mol equiv. of ZnEt₂ in hexane at 0 °C, followed by addition of 2 mol equiv. of 2,4-dimethyl-3-pentanol and recrystallization from hexane solution gives the zinc complex [(μ,μ-biphenolate)Zn(μ-OCH(ⁱPr)₂)₂Zn₂Et₂] (**3**) in 63% yield. In addition, an aluminium alkoxide supported by the biphenolate ligand also can be obtained by a similar synthetic route. The compound [(μ-biphenolate)AlMe(μ-OCH(ⁱPr)₂)AlMe₂] (**4**) is prepared in 65% yield from the reaction of biphenolate-H₂ with 2 mol equiv. of AlMe₃ in the presence of 1 mol equiv. of 2,4-dimethyl-3-pentanol.

The binolate titanium(IV) complex [(biphenolate)Ti₂Cl₆] (**5**) is synthesized from the reaction of biphenolate-H₂ and 2 mol equiv. of TiCl₄ in hexane, followed by crystallization from toluene as shown in Scheme 2. In reactions with biphenolate-H₂ and TiCl₄ in the ratio of 1 : 1, **5** was again formed, suggesting that **5** is a thermodynamically stable product. In reactions employing biphenolate-H₂ and Ti(OPr)₄, the compound (biphenolate)₂Ti was similarly found to be formed in preference to (biphenolate)Ti(OPr)₂.

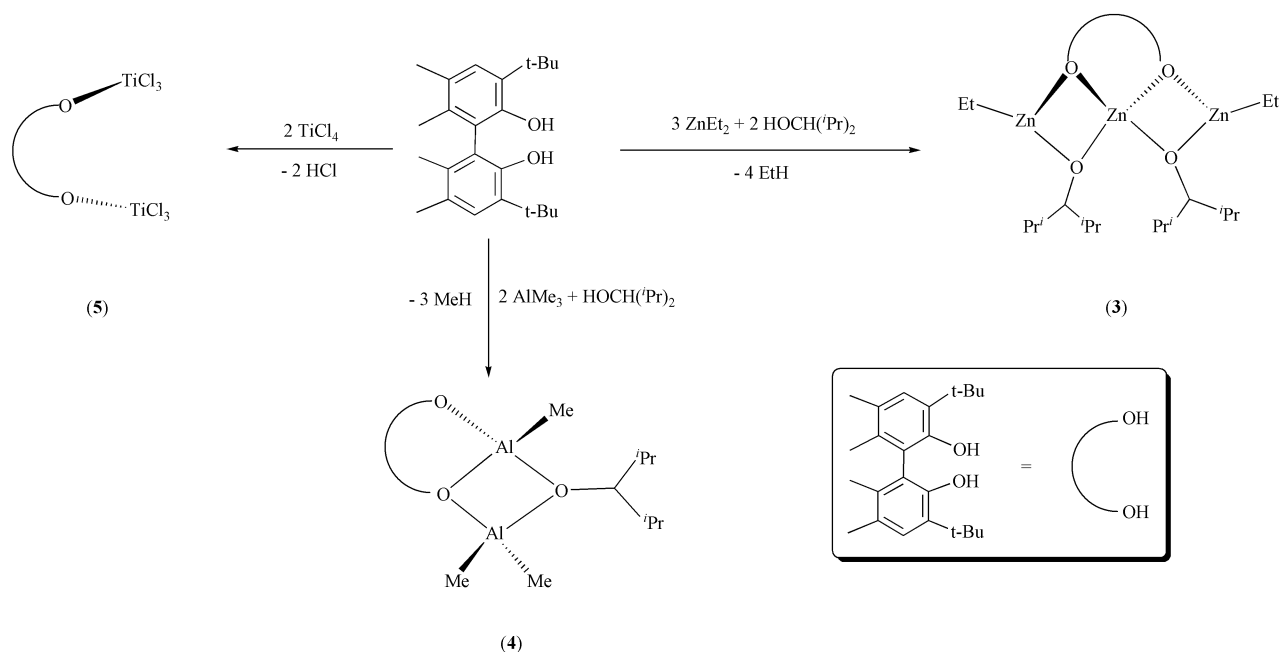
Compounds **1–5** have been characterized by spectroscopic studies as well as by X-ray structure determinations.

Solid-state and molecular structure

A summary of crystallographic data is given in Table 2.



Scheme 1



Scheme 2

Although a crystal structure of a “BuLi trap” lithium aggregate has been recently reported by Lin and Ko,⁶ the structure of the *n*-butyllithium containing aggregate is very different in the biphenolate system. The X-ray structure determination of **1**, which contains a ⁿBuLi : lithium biphenolate ratio of 4 : 2, reveals a C₂ symmetric aggregate containing two distorted cubic Li₄O₂C₂ cores united through the oxygen atoms of the biphenolate ligand as shown in Fig. 1. Each Li₄O₂C₂ core is composed of two ⁿBuLi molecules and two half biphenolate units. All oxygen atoms of the biphenolate ligands are triply bridged to three lithium atoms, and each *n*-butyllithium group is coordinated to three lithium atoms with almost equivalent average distances of Li–C(25) at 2.234(3) and Li–C(29) at 2.235(3) Å. These are within the range previously reported for “BuLi trap” complexes.^{6,7}

The molecular structures of **2-THF** and **2-CyHO** are shown in Figs. 2 and 3, respectively. The tetra-lithium

complex **2-THF** reveals an opened-cube structure, which consists of two different kinds of three-coordinated lithium atoms. Li(1) and Li(2) are bonded to one oxygen atom of the biphenolate ligand and two diisopropylmethoxide groups; Li(3) and Li(4) are coordinated to one biphenolate oxygen, one diisopropylmethoxide group, and one THF. Both of the biphenolate oxygen atoms are doubly bridged, and two diisopropylmethoxide oxygen atoms are triply bridged. The crystal structure of **2-THF** could provide us with information about active sites of ring-opening polymerization of lactide catalyzed by **2-THF**. The entering lactide could coordinate to the Li atom that is bound by the THF in **2-THF**. Then, following the attack of the alkoxy group on the carbonyl carbon of lactide, ring-opening occurs and the new alkoxy group of the growing polymer chain occupies the μ₃-OR site. X-Ray crystal analysis of **2-CyHO** reveals that it has C₂ symmetry and its molecular structure is similar to **2-THF**,

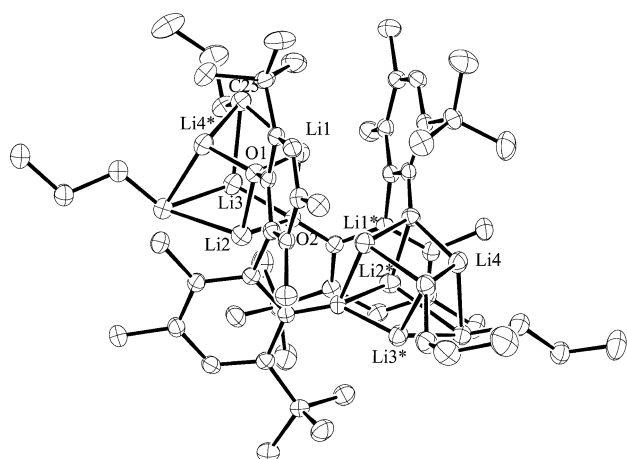


Fig. 1 ORTEP²⁰ drawing of $[(\mu_3, \mu_3\text{-biphenolate})_2\text{Li}_4(\text{“BuLi”})_4]$ (**1**) showing the atom numbering scheme. Atoms are drawn as ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Li(1)–O(2) 1.975(3), Li(1)–O(1*) 1.992(3), Li(1)–C(25) 2.344(3), Li(2)–O(2) 1.985(3), Li(2)–O(1*) 1.967(3), Li(2)–C(29) 2.344(3), Li(3)–O(2) 1.884(3), Li(3)–C(25) 2.172(3), Li(3)–C(29) 2.186(3), Li(4)–O(1) 1.888(3), Li(4*)–C(25) 2.188(3), Li(4*)–C(29) 2.175(3). The starred atoms are generated by the two-fold rotation operation: $-x, y, -z + 1/2$.

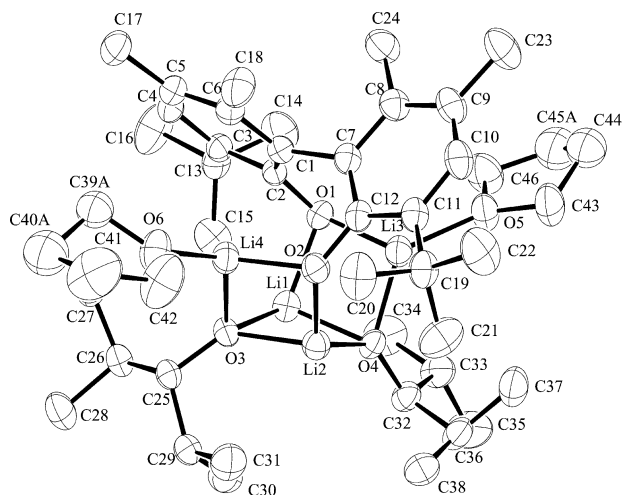


Fig. 2 ORTEP drawing of $[(\mu, \mu\text{-biphenolate})\text{Li}_2(\mu_3\text{-OCH}(\text{Pr})_2)\text{Li}_2(\text{THF})_2]$ (**2-THF**) showing the atom numbering scheme. Atoms are drawn as ellipsoids at the 50% probability level. Only the major component of each disordered THF ligand is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Li(1)–O(1) 1.914(4), Li(1)–O(3) 1.901(4), Li(1)–O(4) 1.939(3), Li(2)–O(2) 1.874(4), Li(2)–O(3) 1.929(3), Li(2)–O(4) 1.891(4), Li(3)–O(1) 1.870(3), Li(3)–O(4) 1.904(4), Li(3)–O(5) 1.938(4), Li(4)–O(2) 1.889(3), Li(4)–O(3) 1.901(4), Li(4)–O(6) 1.963(4).

wherein the tetrahydrofuran is replaced by the cyclohexene oxide.

To our knowledge, **2-CyHO** represents the first crystal structure of a complex where cyclohexene oxide coordinates to lithium and, indeed, is a rare example of a structurally characterized compound having a coordinated epoxide ligand.⁸

An ORTEP drawing of the molecular structure of compound **3** is shown in Fig. 4. The tri-zinc complex **3** consists of two three-coordinated zinc ions, Zn(2) and Zn(2*), and one four-coordinated zinc(2+) ion, Zn(1). The molecules possess a C_2 axis of symmetry passing through the Zn(1) atom. All oxygen atoms are doubly bridging. The angles involving the bonds coordinated to Zn(1) are all distorted from the idealized tetrahedral angle with the largest O(2)–Zn(1)–O(2*) angle of 160.35(7)° and the smallest O(1)–Zn(1)–O(2) angle of 81.55(4)°. The three-coordinated Zn(2+) ions exhibit a distorted trigonal planar geometry: for the ZnO₂C core, the sum of the angles at

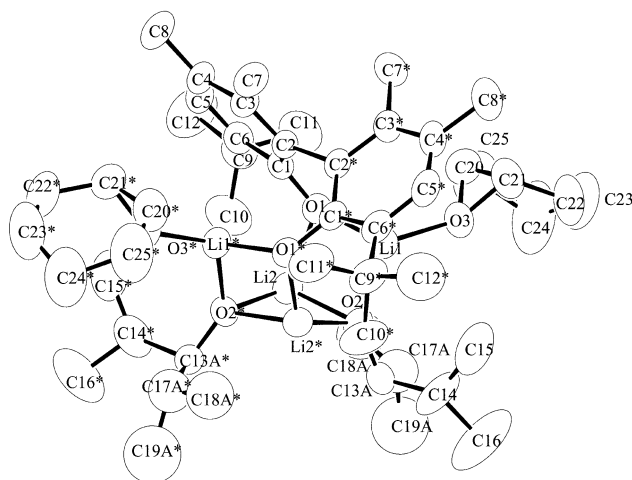


Fig. 3 ORTEP drawing of $[(\mu, \mu\text{-biphenolate})\text{Li}_2(\mu_3\text{-OCH}(\text{Pr})_2)\text{Li}_2(\text{CyHO})_2]$ (**2-CyHO**) showing the atom numbering scheme. Atoms are drawn at the 30% probability level. Only one set of atoms of the disordered isopropyl group is shown. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): O(1)–Li(1) 1.869(7), O(1)–Li(2) 1.886(8), O(2)–Li(1) 1.879(8), O(2)–Li(2*) 1.905(8), O(2)–Li(2) 1.950(7), O(3)–Li(1) 1.955(8). The starred atom is generated by the two-fold rotation operation: $-x + 1, \bar{y}, z$.

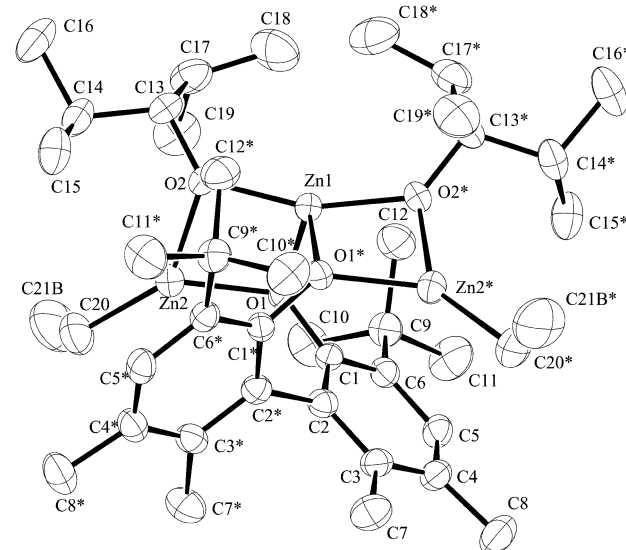


Fig. 4 ORTEP drawing of $[(\mu, \mu\text{-biphenolate})\text{Zn}(\mu\text{-OCH}(\text{Pr})_2)_2\text{Zn}_2\text{Et}_2]$ (**3**) showing the atom numbering scheme (non-hydrogen atoms) with atoms drawn as ellipsoids at the 50% probability level. Selected bond lengths (Å) and angles (°): Zn(1)–O(1) 2.035(1), Zn(1)–O(2) 1.912(1), Zn(2)–O(1) 1.965(1), Zn(2)–O(2) 1.976(1), Zn(2)–C(20) 1.947(2); O(1)–Zn(1)–O(2) 81.55(4), O(1)–Zn(1)–O(1*) 97.22(6), O(1)–Zn(1)–O(2*) 111.88(5), O(2)–Zn(1)–O(2*) 160.35(7), O(1)–Zn(2)–O(2) 81.73(4), O(1)–Zn(2)–C(20) 137.00(8), O(2)–Zn(2)–C(20) 140.35(7). The starred atoms are generated by the two-fold rotation operation: $-x, y, -z + 1/2$.

zinc is 359.1°. The bond distances, Zn(1)–O(1) = 2.035(1), Zn(1)–O(2) = 1.912(1), Zn(2)–O(1) = 1.965(1), Zn(2)–O(2) = 1.976(1), and Zn(2)–C(20) = 1.947(2) Å are within the normal range reported in the literature for zinc complexes.⁹

An ORTEP drawing of the molecular structure of compound **4** is shown in Fig. 5. Each asymmetric unit contains two independent molecules. In each, there is an Al₂O₂ core involving one biphenolate oxygen and one diisopropylmethoxide oxygen. The geometries around both aluminium atoms are distorted tetrahedral with the averaged bond distance of Al(1)–O(1) (phenoxy) at 1.837(2), Al(1)–O(2) (phenoxy) at 1.731, Al(1)–O(3) (alkoxy) at 1.837(2), Al(1)–C(32) at 1.928(3), Al(2)–O(1) (phenoxy) at 1.866(2), Al(2)–O(3) (alkoxy) at 1.868(2), Al(2)–C(33) at 1.956, and Al(2)–C(34) at 1.944(3) Å, which are all

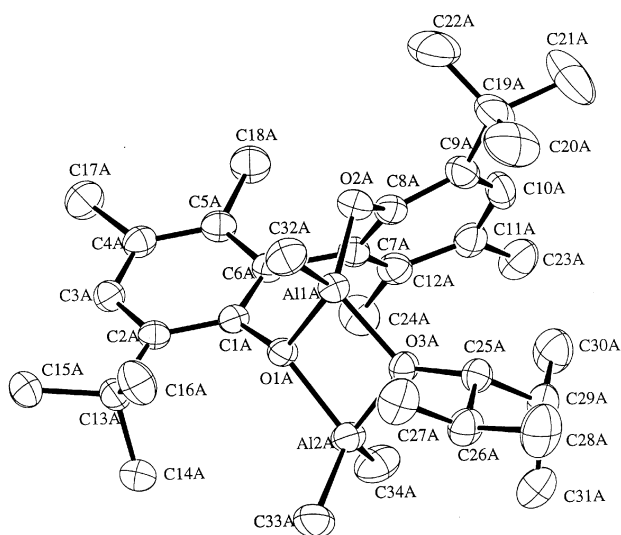


Fig. 5 ORTEP drawing of $[(\mu\text{-biphenolate})\text{AlMe}(\mu\text{-OCH}(\text{Pr})_2)\text{-AlMe}_2]$ (**4**) showing the atom numbering scheme with atoms represented by ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): Al(1A)–O(1A) 1.835(2), Al(1A)–O(2A) 1.731(2), Al(1A)–O(3A) 1.838(2), Al(1A)–C(32A) 1.929(3), Al(2A)–O(1A) 1.866(2), Al(2A)–O(3A) 1.871(2), Al(2A)–C(33A) 1.958(3), Al(2A)–C(34A) 1.946(3).

comparable with the bond distances observed for four-coordinated aluminium derivatives of steric bulky biphenolates.¹⁰ As expected, the averaged bond distance of Al(1)–O(2) (terminal phenoxy) is notably shorter than Al(1)–O(1) (bridging phenoxy).

The molecular structure of complex **5** with selected bond lengths and angles is shown in Fig. 6. In the solid state, the dititanium complex **5** has C_2 symmetry and each TiCl_2 moiety is bound to just one oxygen of the biphenolate ligand. The coordination around the Ti metal center is pseudo-tetrahedral with bond distances Ti–O and the average bond distance of Ti–Cl equal to 1.731(1) and 2.183(5) Å, respectively.¹¹

Solution NMR data and other characterization data are given in the Experimental section.

Ring-opening polymerization of *rac*-lactide

Metal alkoxides, where M = Mg, Y, Li, Sn, Zn and Al, have been reported to be effective initiators for lactide polymerization giving polymers with both high yield and high molecular weight.^{6,12} Therefore, the catalytic activities of the metal diisopropylmethoxide group containing complexes **2-THF**, **3**, and **4** toward ring-opening polymerization (ROP) of *rac*-lactide have been examined (Scheme 3). In general, 200 equivalents of *rac*-lactide were polymerized by an initiator (0.06 mmol) in CH_2Cl_2 or toluene solvent. The polymerization reaction conditions for the different initiators are summarized in Table 1.

It was found that ROP of lactide employing **2-THF** as an initiator goes to completion within 1 h at ambient temperature (entry 1) and the reaction rate decreases with decreasing temperature (entry 2). However, there is not much difference in the polydispersity indices (PDI) of PLA obtained at 0 and 25 °C (1.70 vs. 1.72). In contrast to the lithium aggregate **2-THF**, a slower reaction rate is observed employing zinc complex **3** as an initiator. Lactide polymerization proceeds to 96% conversion within 40 h at room temperature (entry 3). However, polymerization is completed when the temperature is raised to 80 °C (entry 4). The end groups H and $\text{OCH}(\text{Pr})_2$ were identified by NMR and mass spectrometry.

As expected,¹³ the aluminium complex **4** is less active than either of the lithium or zinc complexes toward polymerization of lactide, and a higher temperature is necessary to effect polymerization. The conversion yield of 40% is achieved after

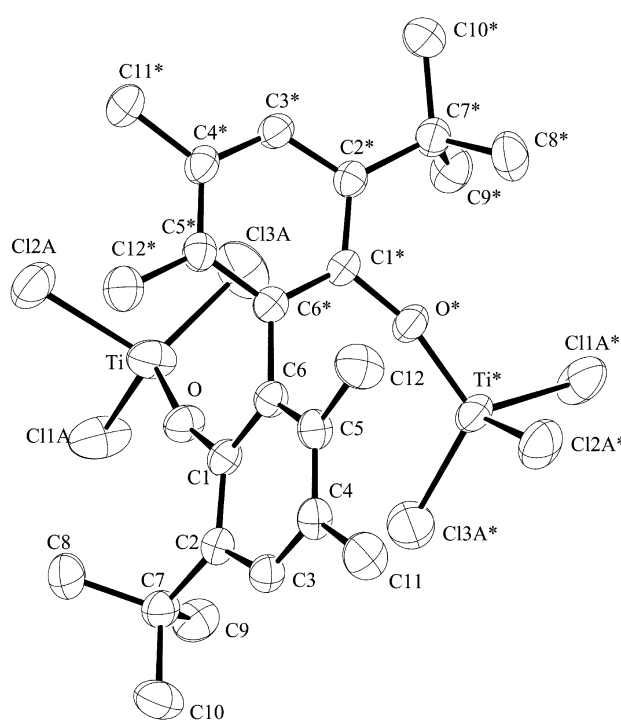
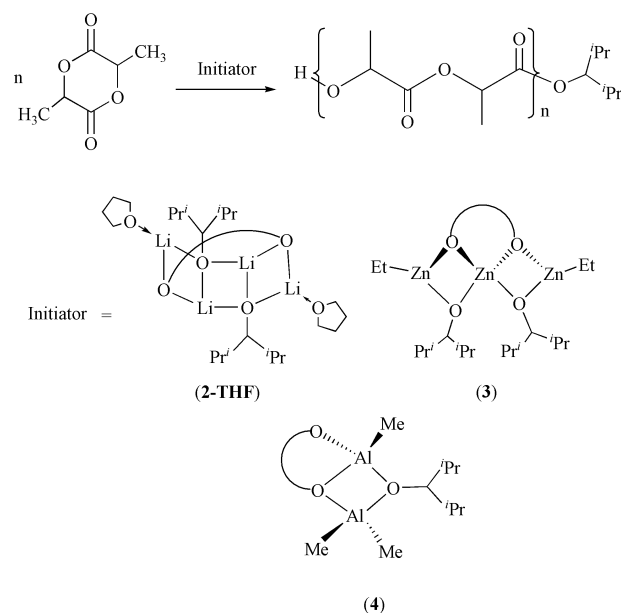


Fig. 6 ORTEP drawing of $[(\text{biphenolate})\text{Ti}_2\text{Cl}_4]$ (**5**) showing the atom numbering scheme with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Only one set of disordered Cl atoms is shown. Selected bond lengths (Å) and angles (°): Ti–O 1.731(1), Ti–Cl(1A) 2.184(10), Ti–Cl(2A) 2.295(2), Ti–Cl(3A) 2.107(2); O–Ti–Cl(1A) 111.3(3), O–Ti–Cl(2A) 104.68(6), O–Ti–Cl(3A) 117.06(6), Cl(3A)–Ti–Cl(1A) 109.7(3), Cl(3A)–Ti–Cl(2A) 109.21(7), Cl(1A)–Ti–Cl(2A) 103.9(3).



Scheme 3

40 h at 80 °C. When the reaction is carried out in refluxing toluene for 20 h, the conversion increases to 82% and a higher molecular weight polymer is obtained (entries 5–6).

While none of the binolate complexes reported here favor formation of the stereoplex of isotactic PLA, it is worth noting that the poly(lactide) produced from **3** and *rac*-lactide is enriched in the heterotactic tetrads *isi* and *sis*.¹⁴ In contrast, we observe the growth of atactic PLA polymers with stereosequences associated with all eight tetrads when using **2-THF** or **4** as catalyst precursors. This is indicative of extensive transesterification accompanying polymerization by the lithium or aluminium complexes.¹⁵

Table 1 Comparative studies of ring-opening polymerization of *rac*-lactide catalyzed by complex **2-THF**, **3**, and **4**^a

Entry	Catalyst	Temperature/°C	Time/h	Conversion ^b (%)	<i>M</i> _n ^c (GPC)	PDI ^c (GPC)	Microstructure ^d
1	2-THF	25	1	99	16000	1.72	Atactic
2	2-THF	0	4	99	13700	1.70	Atactic
3	3	25	40	96	10600	1.41	Heterotactic enriched
4	3	80	4	99	14800	2.23	Atactic
5	4	80	40	40	10800	1.41	Atactic
6	4	110	20	82	17900	1.53	Atactic

^a [LA]₀/[Catalyst]₀ = 200 in CH₂Cl₂ (entries 1–3) or toluene (entries 4–6). ^b As determined *via* integration of the methine resonances of LA and poly-LA (CDCl₃, 400 MHz). ^c Obtained from GPC analysis and calibrated by polystyrene standard. ^d Characterized from the methine region of the homonuclear decoupled ¹H NMR spectrum.

Concluding remarks

Though the series of binolate metal complexes where the metal atoms were Li, Zn and Al were supported by additional diisopropylmethoxide ligands and initiated ring-opening polymerization of lactides, none showed the desired property of being able to convert *rac*-LA to the stereoplex of isotactic PLA(L + D). The metal alkyl traps (LiBu, ZnEt and AlMe) supported by these C₂-symmetric binolate groups may still prove of synthetic utility in various organic transformations. Further studies along these lines are clearly worthwhile.

Experimental

General

All reactions, unless otherwise mentioned, were carried out under a dry nitrogen atmosphere. Flamed-out glassware and standard vacuum line, Schlenk, and N₂-atmosphere dry box techniques were employed. Solvents were dried by refluxing them for at least 24 h over sodium/benzophenone (toluene, hexane, Et₂O and tetrahydrofuran) or calcium hydride (CH₂Cl₂), and they were freshly distilled prior to use. *n*-BuLi (2.5 M in hexane), ZnEt₂ (1.0 M in hexane), AlMe₃ (2.0 M in hexane), TiCl₄ (1.0 M in CH₂Cl₂), Ti(O^{*i*}Pr)₄ and racemic 5,5',6,6'-tetramethyl-3,3'-di-*tert*-butyl-1,1'-biphenyl-2,2'-diol (biphenolate-H₂) were purchased and used without further purification. Deuterated solvents and 2,4-dimethyl-3-pentanol were dried over 4 Å molecular sieves. *rac*-Lactide was recrystallized from toluene twice prior to use. Elemental analyses were performed by Atlantic Microlab Inc. ¹H and ¹³C NMR experiments were carried out with Bruker DPX-400, and Bruker DPX-250 spectrometers, operating at proton Larmor frequencies of 400, and 250 MHz, respectively. Their peak frequencies were referenced against the respective solvent, proto impurities, benzene-*d*₆ at 7.15 ppm and chloroform-*d* at 7.24 ppm. GPC analysis was performed on a Waters Breeze system equipped with a Waters 410 Differential Refractometer RI detector using THF (HPLC grade) as an eluent, with a 100 μl loop and a concentration of polymer of 0.5% w/w. Molecular weight and polydispersity indices (PDIs) were calculated using polystyrene standards. When necessary, the catalyst residue was removed from the solution by filtration or centrifugation.

Synthesis

[(μ₃,μ₃-Biphenolate)₂Li₄(^{*n*}BuLi)₄] (1). To a solution of 1.42 g (4.0 mmol) of biphenolate-H₂ in 20 ml of hexane, precooled to 0 °C, was slowly added 7.04 ml (17.6 mmol) of a 2.5 M solution of ^{*n*}BuLi in hexane. ^{*n*}Butane gas was allowed to escape *via* a bubbler. The reaction mixture was stirred for 1 h at room temperature. The volatile components were removed under reduced pressure to give pale yellow solids. The resulting solids were recrystallized from 25 ml of hot hexane. Yield: 1.76 g (89 %). Colorless crystals suitable for X-ray analysis were obtained from saturated hexane at 8 °C for 2 weeks. Anal. calc. for C₆₄H₁₀₀O₄Li₈: C, 77.72; H, 10.19. Found: C, 76.13; H, 9.49%. ¹H

NMR (C₆D₆, ppm): δ 7.12 (s, 4H, Ph); 2.29 (s, 12H, Ar-CH₃); 1.69 (m, 8H, CH₂CH₂); 1.66 (s, 12H, Ar-CH₃); 1.50 (m, 8H, CH₂CH₂); 1.16 (s, 36H, C(CH₃)₃); 1.10 (t, 12H, CH₂CH₂); -0.89 (m, 8H, LiCH₂). ¹³C NMR (C₆D₆, ppm): δ 163.56, 136.65, 134.64, 130.74, 129.71, 125.36 (Ph); 34.06 (C(CH₃)₃); 33.03 (CH₂CH₂), 32.71 (CH₂CH₂); 31.41 (C(CH₃)₃); 20.84 (Ar-CH₃); 16.79 (Ar-CH₃); 14.43 (CH₂CH₂); 10.43 (LiCH₂).

[(μ,μ-Biphenolate)Li₂(μ₃-OCH(^{*i*}Pr))₂Li₂(THF)₂] (2-THF). 2,4-Dimethyl-3-pentanol (0.56 ml, 4.0 mmol) was added slowly to a hexane (10 ml) solution of [(μ₃,μ₃-biphenolate)₂Li₄(^{*n*}BuLi)₄] (**1**) (0.99 g, 1.0 mmol). The mixture was stirred at room temperature for 2 h and then 5 ml of THF was added. The final solution was stirred for another 1 h and then dried *in vacuo*. The residue was extracted with 10 ml of hot hexane and the extract was then concentrated to *ca.* 5 ml and cooled to -18 °C to furnish a white crystalline solid. Yield: 1.22 g (81%). Crystals suitable for X-ray structure determination were obtained from a saturated hexane solution at room temperature. Anal. calc. for C₄₆H₈₀O₆Li₄: C, 73.19; H, 10.41. Found: C, 71.60; H, 10.32%. ¹H NMR (C₆D₆, ppm): δ 7.17 (s, 2H, Ph); 3.40 (m, 8H, OCH₂CH₂); 3.07 (dd, 2H, OCH(^{*i*}Pr)₂); 2.21 (s, 6H, Ar-CH₃); 1.74 (s, 18H, C(CH₃)₃); 1.72 (s, 6H, Ar-CH₃); 1.70 (m, 2H, OCH(CH(CH₃)₂)₂); 1.55 (m, 2H, OCH(CH(CH₃)₂)₂); 1.31 (m, 8H, OCH₂CH₂); 1.05, 0.96, 0.93, 0.89 (d, 24H, OCH(CH(CH₃)₂)₂). ¹³C NMR (C₆D₆, ppm): δ 164.59, 135.55, 134.54, 131.22, 127.74, 120.04 (Ph); 84.18 (OCH(^{*i*}Pr)₂); 68.43 (OCH₂CH₂); 35.51 (C(CH₃)₃); 34.00 (OCH(CH(CH₃)₂)₂); 33.32 (OCH(CH(CH₃)₂)₂); 31.87 (C(CH₃)₃); 25.72 (OCH₂CH₂); 20.85 (Ar-CH₃); 16.91 (Ar-CH₃); 21.88, 21.38, 20.42, 18.36 (OCH(CH(CH₃)₂)₂).

[(μ,μ-Biphenolate)Li₂(μ₃-OCH(^{*i*}Pr))₂Li₂(CyHO)₂] (2-CyHO). Cyclohexene oxide (5 ml) was added to [(μ,μ-biphenolate)Li₂(μ₃-OCH(^{*i*}Pr))₂Li₂(THF)₂] (**2-THF**) (1.50 g, 2.0 mmol). The mixture was stirred at room temperature for 1 h and then dried *in vacuo*. The residue was extracted with 10 ml of warm hexane and the extract was then concentrated to *ca.* 5 ml and cooled to -18 °C to furnish white crystalline solids. Yield: 1.25 g (78%). Crystals suitable for X-ray structure determination were obtained from a saturated hexane solution at room temperature. ¹H NMR (C₆D₆, ppm): δ 7.21 (s, 2H, Ph); 3.09 (br, 2H, OCH(^{*i*}Pr)₂); 2.88 (br, 4H, OCHCH₂CH₂); 2.25 (s, 6H, Ar-CH₃); 1.78 (s, 6H, Ar-CH₃); 1.72 (s, 18H, C(CH₃)₃); 1.60–1.74 (m, 8H, OCH(CH(CH₃)₂)₂ + OCHCH₂CH₂); 1.35, 1.19 (m, 8H, OCHCH₂CH₂); 0.84–1.01 (d, 30H, OCH(CH(CH₃)₂)₂ + OCHCH₂CH₂).

[(μ,μ-Biphenolate)Zn(μ-OCH(^{*i*}Pr))₂ZnEt₂] (3). To an ice-cold solution (0 °C) of biphenolate-H₂ (0.71 g, 2.0 mmol) in hexane (10 ml) was slowly added a ZnEt₂ (6.6 ml, 1.0 M in hexane, 6.6 mmol) solution. The mixture was stirred for 1 h and then 2,4-dimethyl-3-pentanol (0.56 ml, 4.0 mmol) was added at 0 °C. The final solution was stirred at room temperature for another 1 h then the solvent was removed *in vacuo*. The residue was extracted with hot hexane (10 ml) and the extract was then

Table 2 Selected crystallographic data for 1–5

	1	2-THF	2-CyHO	3	4	5
Empirical formula	C ₃₂ H ₅₀ Li ₄ O ₂	C ₄₆ H ₇₈ Li ₄ O ₆	C ₅₀ H ₈₂ Li ₄ O ₆	C ₄₂ H ₇₂ O ₄ Zn ₃	C ₃₄ H ₅₆ O ₃ Al ₂	C ₂₄ H ₃₂ O ₂ Cl ₆ Ti ₂
FW	494.48	754.84	806.92	837.11	566.75	661.00
Crystal system	Monoclinic	Triclinic	Orthorhombic	Monoclinic	Triclinic	Monoclinic
Space group	C2/c	P1	P2 ₁ 2 ₁ 2	C2/c	P1	C2/c
<i>a</i> /Å	20.0434(2)	10.8871(1)	17.6377(3)	12.1517(1)	13.2489(1)	16.0474(1)
<i>b</i> /Å	16.0320(2)	12.3753(2)	11.5509(2)	17.2776(2)	14.5356(2)	11.9321(1)
<i>c</i> /Å	20.3345(2)	19.6433(3)	12.6251(2)	21.8457(2)	19.8429(3)	17.6166(2)
<i>a</i> °	—	75.397(1)	—	—	101.212(2)	—
<i>β</i> °	107.116(1)	77.010(1)	—	104.283(1)	103.271(1)	113.018(1)
<i>γ</i> °	—	67.596(1)	—	—	105.798(1)	—
Volume/Å ³	6244.81(12)	2343.14(6)	2572.13(7)	4444.78(8)	3441.50(7)	3104.64(5)
<i>Z</i>	8	2	2	4	4	4
Calculated density/g cm ⁻³	1.052	1.070	1.042	1.251	1.094	1.414
Temperature/K	150(2)	150(2)	270(2)	200(2)	200(2)	250(2)
Independent reflections	7168	8253	2568	5107	12146	3565
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0499	0.0589	0.0783	0.0278	0.0537	0.0390
<i>wR</i> 2 [<i>I</i> > 2σ(<i>I</i>)] ^b	0.1247	0.1446	0.2213	0.0694	0.1281	0.1060

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, \quad ^b wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

concentrated to ca. 6 ml. Colorless crystals were obtained on cooling to -18°C overnight. Yield: 1.05 g (63%). ¹H NMR (C₆D₆, ppm): δ 7.21 (s, 2H, Ph); 3.15 (dd, 2H, OCH(Pr)₂); 2.20 (s, 6H, Ar-CH₃); 1.81 (s, 6H, Ar-CH₃); 1.75 (m, 2H, OCH(CH(CH₃)₂)₂); 1.65 (s, 18H, C(CH₃)₃); 1.52 (m, 2H, OCH(CH(CH₃)₂)₂); 1.26 (t, 6H, ZnCH₂CH₃); 1.04, 0.91, 0.89, 0.68 (d, 24H, OCH(CH(CH₃)₂)₂); 0.36 (m, 4H, ZnCH₂CH₃). ¹³C NMR (C₆D₆, ppm): δ 156.10, 136.75, 135.31, 130.32, 128.32, 127.55 (Ph); 85.40 (OCH(Pr)₂); 35.51 (C(CH₃)₃); 34.32 (OCH(CH(CH₃)₂)₂); 32.14 (OCH(CH(CH₃)₂)₂); 31.49 (C(CH₃)₃); 20.78 (Ar-CH₃); 17.24 (Ar-CH₃); 21.88, 21.33, 19.68, 15.78 (OCH(CH(CH₃)₂)₂); 12.51 (ZnCH₂CH₃); 0.22 (ZnCH₂CH₃).

[(μ-Biphenolate)AlMe(μ-OCH(Pr)₂)AlMe₂] (4). To an ice-cold solution (0 °C) of biphenolate-H₂ (0.71 g, 2.0 mmol) in hexane (10 ml) was slowly added AlMe₃ (2.2 ml, 2.0 M in hexane, 4.4 mmol). The mixture was stirred for 1 h and then 2,4-dimethyl-3-pentanol (0.28 ml, 2.0 mmol) was added. The resulting solution was stirred at room temperature for another 1 h and prior to removing the volatile components *in vacuo*. The residue was extracted with hexane (10 ml) and the extract was concentrated to ca. 5 ml. Colorless crystals were obtained on cooling to 8 °C overnight. Yield: 0.74 g (65%). Anal. calc. for C₃₄H₅₆O₃Al₂: C, 72.05; H, 9.96. Found: C, 71.00; H, 9.56%. ¹H NMR (C₆D₆, ppm): δ 7.20, 7.17 (s, 2H, Ph); 3.44 (dd, 1H, OCH(Pr)₂); 2.20, 1.99 (s, 6H, Ar-CH₃); 1.85, 1.55 (s, 6H, Ar-CH₃); 1.87 (m, 1H, OCH(CH(CH₃)₂)₂); 1.82 (m, 1H, OCH(CH(CH₃)₂)₂); 1.67, 1.50 (s, 18H, C(CH₃)₃); 0.83, 0.79, 0.78, 0.61 (d, 12H, OCH(CH(CH₃)₂)₂); -0.17, -0.33, -0.77 (s, 9H, AlCH₃). ¹³C NMR (C₆D₆, ppm): δ 155.25, 148.42, 138.83, 138.47, 136.99, 136.76, 135.25, 134.23, 130.15, 129.45, 129.26, 128.07 (Ph); 88.81 (OCH(Pr)₂); 36.69, 36.36 (C(CH₃)₃); 35.01 (OCH(CH(CH₃)₂)₂); 33.42 (OCH(CH(CH₃)₂)₂); 32.71, 32.66 (C(CH₃)₃); 21.95, 21.92 (Ar-CH₃); 18.76, 18.68 (Ar-CH₃); 23.50, 21.51, 20.90, 18.03 (OCH(CH(CH₃)₂)₂); -2.47, -6.69, -10.28 (AlCH₃).

[(Biphenolate)Ti₂Cl₆] (5). To a solution of biphenolate-H₂ (0.71 g, 2.0 mmol) in hexane (15 ml) was slowly added TiCl₄ (4.4 ml, 1.0 M in CH₂Cl₂, 4.4 mmol). The reaction color changed from colorless to red immediately. The mixture was stirred for 4 h during which time red crystalline solids were precipitated. These solids were then dried *in vacuo*. The residue was extracted with toluene (15 ml) and the extract was then concentrated to ca. 10 ml. Red-brown crystals were obtained on cooling to -18°C overnight. Yield: 0.95 g (81%). Anal. calc. for C₂₄H₃₂O₂Cl₆Ti₂: C, 43.61; H, 4.88. Found: C, 43.74; H, 4.89%. ¹H NMR (C₆D₆, ppm): δ 7.08 (s, 2H, Ph); 2.05 (s, 6H, Ar-CH₃); 1.78 (s, 6H, Ar-CH₃); 1.49 (s, 18H, C(CH₃)₃).

¹³C NMR (C₆D₆, ppm): δ 171.90, 137.07, 136.70, 135.63, 132.50, 129.03 (Ph); 35.39 (C(CH₃)₃); 31.00 (C(CH₃)₃); 21.31 (Ar-CH₃); 17.37 (Ar-CH₃).

Polymerization of lactide catalyzed by 2-THF, 3 and 4

The following is a representative procedure employing 3 and *rac*-lactide: In a dry box, [(μ,μ-biphenolate)Zn(μ-OCH(Pr)₂)₂-Zn₂Et₂] (3) (0.050 g, 0.06 mmol) and *rac*-lactide (1.73 g, 12 mmol) were placed in a flask and then 10 ml of CH₂Cl₂ was added. The reaction mixture was stirred at room temperature for 40 h. Conversion yield (96%) of PLA-200 (the number 200 indicates the designed [LA]₀/[3]₀) was analyzed by ¹H NMR spectroscopic studies. The mixture was then quenched by the addition of MeOH (1 ml) (In the case of lithium aggregate 2-THF, 1 ml of water was used). Volatile materials were removed *in vacuo* to give PLA. The PLA was characterized by NMR and GPC. ¹H NMR and ESI-MS identified the end groups as H and OCH(Pr)₂.

X-Ray crystallography

The data collections of all crystals were done on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystems Cryostream cooler. The data collection strategy was set up to measure a quadrant of reciprocal space for 1, 3 and 5, a hemisphere for 2-THF and 4, and an octant for 2-CyHO. A combination of phi and omega scans with a frame width of 1° was used. Data integration was done with DENZO¹⁶ and scaling and merging of the data were done with Scalepack.¹⁶ The structures were solved by the direct methods procedure in SHELXS-86.¹⁷ Full-matrix least-squares refinements based on *F*² were performed in SHELXL-93.¹⁸ Neutral atom scattering factors were used and include terms for anomalous dispersion.¹⁹ A summary of crystal data is given in Table 2.

CCDC reference numbers 185856–185861.

See <http://www.rsc.org/suppdata/dt/b2/b211582b/> for crystallographic data in CIF or other electronic format.

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