Inorganic Chemistry
Article
pubs.acs.org/IC

Stereoselective Synthesis of Biphenolate/Binaphtolate Titanate and Zirconate Alkoxide Species: Structural Characterization and Use in the Controlled ROP of Lactide

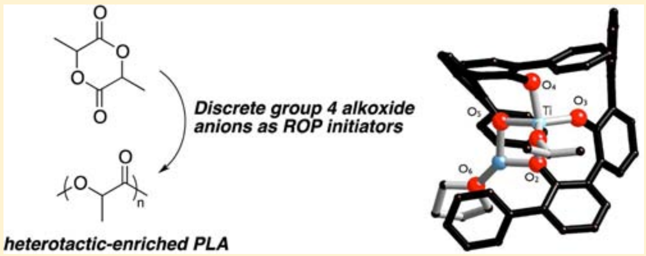
Laurine Azor,[†] Corinne Bailly,[§] Lydia Brelot,[§] Marc Henry,[‡] Pierre Mobian,[‡] and Samuel Dagorne*,[†]

[†]Laboratoire DECOMET, Institut de Chimie de Strasbourg (CNRS-Université de Strasbourg), 1 rue Blaise Pascal, 67000 Strasbourg, France

[‡]Laboratoire de Chimie moléculaire de l'Etat Solide, Université de Strasbourg, 1 rue Blaise Pascal, 67000 Strasbourg, France

[§]Service de Radiocristallographie, Institut de Chimie de Strasbourg (CNRS-Université de Strasbourg), 1 rue Blaise Pascal, 67000 Strasbourg, France

Supporting Information



ABSTRACT: Well-defined biphenol/binaphtolate group 4 alkoxide salt species $[(\text{Ph-Biphen-O})_2\text{M}(\text{O}^i\text{Pr})]\text{Li(THF)}$ (**2a**, M = Ti; **4a**, M = Zr) and $[(\text{Ph-binapht-O})_2\text{M}(\text{O}^i\text{Pr})]\text{Li(THF)}$ (**2b**, M = Ti; **4b**, M = Zr) were found to be readily accessible in good yields via alcohol elimination routes and/or substitution reactions from the corresponding pro-ligands Ph-Biphen-OH (**1a**) and *rac*-Ph-Binapht-OH (**1b**). As established via X-ray crystallographic analysis, the molecular structures of the Ti derivatives **2a** and **2b** consist of Li^+ salts of anionic $\text{Ti}{-}\text{O}^i\text{Pr}$ moieties in which the Ti center adopts a distorted tbp geometry and is effectively chelated by two biphenolate/binaphtolate units. Remarkably, the solution and solid state data for salt species **2a,b** agree with the sole presence of one diastereomer (with a (Δ, *aS*, *aS*)/(Λ, *aR*, *aR*) configuration), thus indicating that formation of the Ti and Zr alkoxide complexes **2a,b**/**4a,b** proceeds stereoselectively. In contrast, the neutral biphenolate/binaphtolate Zr complexes $(\text{Ph-biphen-O})_2\text{Zr(THF)}_2$ (**3a**) and $(\text{Ph-binapht-O})_2\text{Zr(THF)}_2$ (**3b**) were both isolated and X-ray characterized as stereomers in a heterochiral configuration (Δ, *aR*, *aS*)/(Λ, *aS*, *aR*). The Ti and Zr alkoxide anionic chelates were found to initiate the ROP of *rac*-lactide in a controlled manner for production of narrowly disperse and ester-end group PLA, as deduced from SEC, kinetic, and MALDI-TOF data. The $\text{Zr}{-}\text{O}^i\text{Pr}$ derivatives **4a,b** exhibit superior performance to their Ti counterparts (whether regarding activity, polymerization control, or stereoselectivity) to produce narrowly disperse and heterotactically enriched PLA ($P_r = 0.67$, PDI < 1.15). The significantly decreased Lewis acidity of the Zr metal center in anions **4a,b** (versus neutral analogues) due to the anionic charge and a likely substantial electronic π donation of the four $\text{Zr}{-}O_{ArO}$ oxygens to the Zr metal center may rationalize the moderate polymerization activity. Control experiments suggest that the nature of the countercation has little influence on lactide ROP activity and stereocontrol.

INTRODUCTION

Biodegradable polyesters, such as poly(lactic acid) (PLA), have been the subject of numerous studies in recent years due to their important biomedical and pharmaceutical applications as well being as a viable alternative to petrochemical-based plastics.[1] The ring-opening polymerization (ROP) of lactide, a dimer of lactic acid, promoted by discrete metal-based initiators may allow access to well-defined, narrowly disperse (and possibly stereoregular) polyesters through precise chain length control.[2] The most useful lactide metal-based catalysts include neutral alkoxide complexes of oxophilic and Lewis-acid metals such as magnesium, zinc, aluminum, yttrium, tin(II), and, to a lesser extent, group 4 metals.[3,4] In such systems, the ROP reactions typically proceed via a coordination−insertion mechanism involving an initial monomer coordination/activation onto the Lewis-acidic metal center and subsequent nucleophilic attack by the M−OR moiety to yield the metal-bonded ring-opened product.[2] Both the Lewis acidity of the metal center and the nucleophilicity of the M−*OR* group thus play an important in ROP activity.

Formally charged metal alkoxide initiators are of potential interest in cyclic esters ROP as they may provide access to either highly Lewis-acidic initiators (cationic derivatives) or anionic alkoxide complexes bearing a highly nucleophilic $\text{M}{-}\text{OR}^-$ moiety. In this area, several recent studies have highlighted the suitability of well-defined metal alkoxide cations for efficient and controlled ROP of cyclic esters.[5] On the other hand, albeit much less studied thus far, discrete anionic alkoxide metal complexes may feature an improved ROP activity because the increased nucleophilicity of the $\text{M}{-}O\text{R}^-$ alkoxide may favor both polymerization initiation and subsequent chain-

Received: June 25, 2012
Published: September 25, 2012

growth steps.[6] In addition, in such anionic systems, the counteranion (such as Li^+, for instance) may well act as a Lewis acid able to activate the incoming monomer toward nucleophilic attack by the M−*OR*⁻ alkoxide. On that matter and consistent with the above reasoning, discrete aluminum alkoxide anions were recently found to polymerize *rac*-lactide at room temperature, which is rare for Al-based initiators.[6d]

Over the past few years, several group 4-based systems have been reported to polymerize *rac*-lactide in a controlled and stereoselective manner to afford well-defined and stereoregular PLA.[4] Group 4 alkoxide species are indeed promising candidates as ROP initiators as they have been shown to be robust entities on several occasions: for instance, they may retain *rac*-lactide ROP activity and stereoselectivity in the presence of protic impurities.[4a,7] Nevertheless, when compared to their alkali, rare earth, and Mg and Zn analogues, group 4 analogues are typically less active in the ROP of *rac*-lactide and related cyclic esters, prompting us toward development of well-defined group 4 alkoxide anionic ROP initiators for possible improvements of polymerization activity.

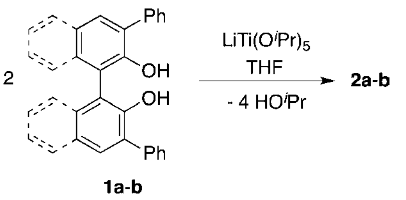
To the above purpose, we became interested in the synthesis of group 4 metal anions of the type $(X_2)_2M(OR)(L)^-$ (M = Ti, Zr; X_2^{2-} = bidentate dianionic ligand, L labile). Sterically demanding and readily available biphenolate/binaphtolate were picked as X_2^{2-}-type ligands for coordination to group 4 metal centers to ensure access to discrete and mononuclear metal complexes with a controlled architecture/metal environment and thus likely to behave as single-site catalysts.[8] Also, as will be seen, group 4 alkoxide species of the type proposed here feature coordination properties of structural interest.

Here we first report on the synthesis and structural characterization of biphenolate/binaphtolate group 4 alkoxide salt species (as Li^+ salts) and their subsequent use for controlled ROP of *rac*-lactide.

Synthesis and Structural Characterization of the Biphenolate/Binaphtolate Ti Complexes 2a and 2b. Well-defined biphenol/binaphtolate Ti alkoxide salt species **2a**,**b** were found to be readily accessible via an alcohol elimination involving reaction of an appropriate Ti alkoxide anion (as a Li^+ salt) and the corresponding pro-ligands Ph-Biphen-OH (**1a**) and *rac*-Ph-Binapht-OH (**1b**). Thus, reaction of the salt $LiTi(O^iPr)_5$, prepared and isolated in nearly quantitative yield via addition of LiO^iPr to $Ti(O^iPr)_4$,[9] with 2 equiv of pro-ligands **1a** and **1b** (THF, room temperature, overnight) afforded the respective Ti−O^iPr salts $[(\text{Ph-Biphen-O})_2Ti(O^iPr)]Li(THF)$ (**2a**) and $[(\text{Ph-binapht-O})_2Ti(O^iPr)]Li(THF)$ (**2b**) in good yield (Scheme 1). Both species were isolated as air- and moisture-sensitive yellow solids and are stable in dry CH_2Cl_2 and aromatic solvent solutions for weeks at room temperature under an inert atmosphere.

The solid state molecular structures of both **2a** and **2b** were determined by X-ray crystallography analysis, confirming the proposed formulations (see Tables S1 and S2, Supporting Information, for a summary of crystal data). The salt species **2a** cocrystallizes in an achiral space group ($P2_1/n$) with one molecule of dichloromethane. As illustrated in Figure 1, the molecular structure of salt **2a** consists of a $(\text{Ph-Biphen-O})_2TiO^iPr^-$ titanate associated with a three-coordinate and THF-bound lithium cation, resulting in an overall C_1-symmetric structure for **2a**. In the anionic moiety, the pentacoordinate Ti metal center adopts a distorted trigonal bipyramidal (tbp) geometry with two O_{PhO} oxygen atoms (O(3) and O(5)) and the O_{OiPr} oxygen occupying the equatorial positions. The two O_{PhO} oxygen atoms O(2) and O(4), located in axial positions, complete the Ti coordination sphere. Such a distorted geometry at Ti may be reasonably ascribed to the presence of the lithium cation effectively η^2-*O,O*-chelated by the O(2) and O(5) oxygen atoms, which results in significantly smaller O(4)−Ti−O(2) and O(2)−Ti−O(5) bond angles (160.74(6)° and 75.97(6)°) than those for an ideal tbp geometry. The metrical description of the bonds to the metallic center are comparable to the literature,[4j,k,10] with Ti−O_{OPh} bonds ranging from 1.835(1) to 2.018(1) Å and a much shorter Ti−O(5) alkoxide bond (1.759(1) Å). The presence of a three-coordinate (rather than a four-coordinate) and THF-bound Li^+ center is likely related to steric hindrance around Li^+: as clearly evidenced by Figure 1, the "Li^+−THF" entity may be seen as directly sandwiched by two phenyl groups of the Ph-Biphen-O⁻ ligands. Overall, in this structure, the two Ph-Biphen-O⁻ chelating ligands are wrapped around the metal center, which may lead to a chiral complex with either a Δ or a Λ configuration. A second source of chirality arising from the axial chirality of the Ph-Biphen-O⁻ ligands upon coordination to Ti is observed since a synclinal arrangement of two consecutive phenolate rings (within a given Ph-Biphen-O⁻ ligand) is observed (with C(28)−C(29)−C(40)−C(47) and C(4)−C(5)−C(17)−C(16) torsion angles of 47.0(3)° and 56.7(3)°). Thus, each Ph-Biphen-O⁻ ligand may a priori exhibit either a *aR* or a *aS* configuration. Yet, in the present case, the unit cell for **2a** contains two enantiomers adopting, respectively, (Δ, *aS*, *aS*) or (Λ, *aR*, *aR*) stereochemistry, thus indicating that, within a given complex, both Ph-Biphen-O⁻ chelating ligands

Scheme 1



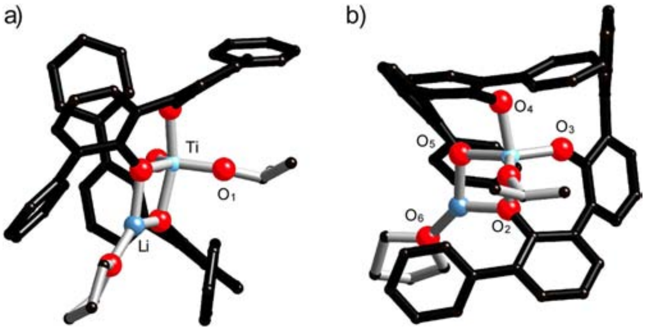


Figure 1. Solid state structure of the Ti biphenolate alkoxide complex **2a** (Δ, *aS*, *aS* enantiomer, two views) with partial atom labeling. Biphenolate ligands are colored in black (with the exception of the oxygen atoms that are colored in red). Selected bond lengths (Angstroms): Ti−O(1) = 1.759(1), Ti−O(2) = 2.018(1), Ti−O(3) = 1.835(1), Ti−O(4) = 1.897(1), Ti−O(5) = 1.956(1), Li−O(5) = 1.904(5), Li−O(2) = 1.836(4), Li−O(6) = 1.842(4). Selected bond angles (degrees): O(4)−Ti−O(2) = 160.74(6), O(2)−Ti−O(3) = 88.59(6), O(4)−Ti−O(1) = 99.16(6), O(1)−Ti−O(2) = 95.59(6), O(5)−Ti−O(2) = 75.96, O(3)−Ti−O(2) = 88.59(6).

exhibit the same configuration (see Figure 1 for the (Δ, *aS*, *aS*) configuration).

As illustrated in Figure 2, the molecular structure of the binapholate Ti analogue **2b** exhibits overall structural features that closely relate to those for complex **2a** discussed above. One should however note that the angles between the naphtolate units within a binaphtolate (61(1)°) ligand are significantly larger than the corresponding biphenolate angles observed in **2a** (vide supra) due to more severe steric repulsions within the binaphtolate units.

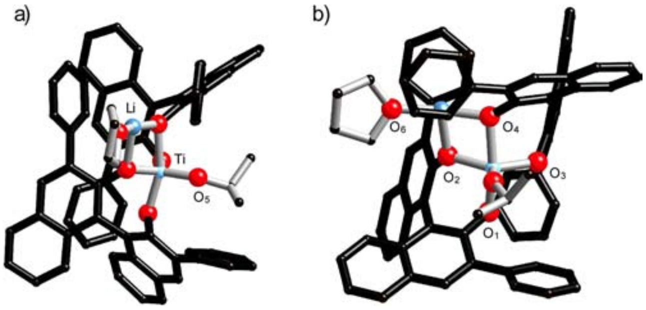


Figure 2. Solid state structure of the Ti binaphtolate alkoxide complex **2b** (Δ, *aS*, *aS* enantiomer, two views) with partial atom labeling. Binaphtolate ligand is colored in black (with the exception of the oxygen atoms that are colored in red). Selected bond lengths (Angstroms): Ti–O(1) = 1.884(1), Ti–O(2) = 1.941(1), Ti–O(3) = 1.841(1), Ti–O(4) = 2.044(1), Ti–O(5) = 1.762(1), Li–O(4) = 1.918(4), Li–O(2) = 1.937(4), Li–O(6) = 1.925(5). Selected bond angles (degrees): O(4)–Ti–O(2) = 76.59(6), O(2)–Ti–O(3) = 132.94(7), O(4)–Ti–O(1) = 162.12(6), O(1)–Ti–O(2) = 89.27(6), O(5)–Ti–O(2) = 114.75(7), O(3)–Ti–O(2) = 132.94(7).

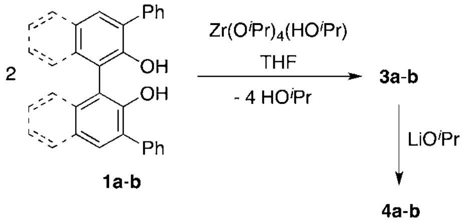
Regarding the solution structures of species **2a** and **2b**, ^{1}H and ^{13}C NMR data are consistent with the proposed formulations, i.e., effective chelation of two biphenolate/binaphtolate units onto Ti, presence of a Ti–$O^{i}Pr$ group, and a metal-coordinated THF molecule. Yet, room-temperature NMR spectra for both **2a** and **2b** feature rather broad resonances, reflecting a fluxional behavior that likely arises from conformational changes within the (Ph-Biphen-O/Ph-Binapht-O)Ti chelates under the studied conditions. In agreement with the latter, low-temperature NMR data for **2a** and **2b** (193 and 233 K, see Experimental Section) are consistent with slow conformation changes (on the NMR time scale) and the presence of one C_1-symmetric diastereomer under these conditions in each case. In particular, the ^{1}H NMR spectrum of the biphenolate Ti salt **2a** (233 K, CD_2Cl_2) contains two *Me*–^{i}Pr doublet resonances (δ 0.21 and 0.33) along with a *CH*–^{i}Pr multiplet (δ 3.60), in agreement with the presence of a Ti–$O^{i}Pr$ moiety. Also, the ^{13}C NMR spectrum for **2a** (193 K, CD_2Cl_2) clearly exhibits four distinct C_{ipso}–O signals, which is in line with a C_1-symmetric structure for **2a**. In addition, DOSY (diffusion ordered spectroscopy) measurements for **2a** and **2b**, allowing an estimation of their hydrodynamic radii in solution (CD_2Cl_2, room temperature), were carried out. From the corresponding diffusion coefficients, hydrodynamic radii of 6.0(6) and 6.4(6) Å were estimated for **2a** and **2b**, respectively. These values are to be compared with the mean radii evaluated from their solid state structures using a standard set of van der Waals radii (7.2(7) Å for **2a**; 7.9(8) Å for **2b**).[11] The DOSY-estimated hydrodynamic radii and calculated mean radii thus match reasonably well taking into account experimental and calculations margins of error. Overall, the NMR and DOSY data are consistent with the solid state structures of **2a** and **2b** being retained in solution.

Partial charges distribution analysis on the Ti species **2a** and **2b** (based on their X-ray-determined molecular structures) were performed and are consistent with the Ti(IV) center in the $(Ph\text{-}Biphen\text{-}O)_2TiO^{i}Pr^{-}$ and $(Ph\text{-}Binapht\text{-}O)_2TiO^{i}Pr^{-}$ anions retaining substantial electrophilic character. Thus, the lithium ions and Ti(IV) centers were found to be positively charged for both complexes (qLi = 0.745 and qTi = 2.685 for complexes **2a** and qLi = 0.727 and qTi = 2.697 for **2b**). The partial charges of the Ti–O^{i}Pr oxygens are comparable for species **2a** and **2b** (−0.529 and −0.598, respectively) and agree with a nucleophilic Ti–$O^{i}Pr$ moiety (for further details, see the Supporting Information).

Hence, formation of the Ti salt species **2a** and **2b** from $LiTi(O^{i}Pr)_5$ and 2 equiv of the corresponding Ph-Biphen-OH/*rac*-Ph-Binapht-OH pro-ligand appears to proceed in a highly diastereoselective manner with the sole obtainment of Ti alkoxide complexes **2a** and **2b** in a (Δ, *aS*, *aS*)/(Λ, *aR*, *aR*) configuration. On that matter, while the steric requirements imposed by ligands **1a** and **1b** for formation of the $(Ph\text{-}Biphen\text{-}O)_2Ti$ and $(Ph\text{-}binapht\text{-}O)_2Ti$ chelates are certainly important for diastereoselectivity, other factors may also be at play since the Ti neutral analogue $(Ph\text{-}Biphen\text{-}O)_2Ti(HO^{i}Pr)_2$ (synthesized via reaction of $TiO^{i}Pr_4$ with 2 equiv of **1a**) was isolated and structurally characterized in the solid state as a single diastereomer with a heterochiral configuration of the biphenolate ligands (Λ, *aS*, *aR*/Λ, *aR*, *aS*),[8] thus different from that observed for the Ti salts **2a** and **2b**.

Synthesis and Structural Characterization of the Biphenolate/Binaphtolate Zr Complexes 3a, 3b, 4a, and 4b. Access to the $(Ph\text{-}Biphen\text{-}O)_2Zr(O^{i}Pr)^{-}$ and $(Ph\text{-}binapht\text{-}O)_2Zr(O^{i}Pr)^{-}$ Zr alkoxide anions was revealed to be less straightforward than that to the Ti derivatives **2a** and **2b**. Initial attempts to prepare the $Zr(O^{i}Pr)_5^{-}$ anionic precursor (as a Li^{+}, K^{+}, or Na^{+} salt) via a deprotonation reaction of commercially available $Zr(O^{i}Pr)_4(HO^{i}Pr)$ with either LiH, ^{n}BuLi, NaH, or KH (THF, room temperature or −78 °C) were consistently unsuccessful, with the observation of an untractable mixture of products in all cases. Rather, a two-step synthesis of species $[(Ph\text{-}Biphen\text{-}O)_2Zr(O^{i}Pr)]Li(THF)$ (**4a**) and $[(Ph\text{-}binapht\text{-}O)_2Zr(O^{i}Pr)]Li(THF)$ (**4b**) could be achieved via initial preparation of the neutral species $(Ph\text{-}Biphen\text{-}O)_2Zr(THF)_2$ (**3a**) and $(Ph\text{-}binapht\text{-}O)_2Zr(THF)_2$ (**3b**), which were subsequently reacted with $LiO^{i}Pr$ to afford Zr salt species **4a** and **4b**. Thus, $Zr(O^{i}Pr)_4(HO^{i}Pr)$ was found to react with 2 equiv of pro-ligands **1a** and **1b** (THF, room temperature, overnight) to quantitatively afford the corresponding neutral bis-chelate Zr species **3a** and **3b**, as deduced from NMR data (Scheme 2). The Zr–THF adducts **3a** and **3b** were isolated in good yields as analytically pure yellow powders, and

Scheme 2



the molecular structures of these adducts were unambiguously established by X-ray crystallographic studies, as depicted in Figures 3 and 4 (see Tables S3 and S4, Supporting Information, for a summary of crystal data).

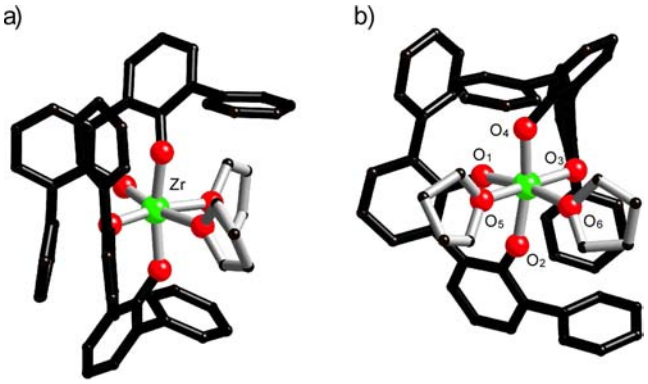


Figure 3. Solid state structure of the biphenolate $Zr(THF)_2$ adduct **3a** (Λ, *aS*, *aR* enantiomer, two views). Biphenolate ligand is colored in black (with the exception of the oxygen atoms that are colored in red). Selected bond lengths (Angstroms): Zr−O(1) = 1.991(2), Zr−O(2) = 2.031(2), Zr−O(3) = 1.999(2), Zr−O(4) = 2.025(2), Zr−O(5) = 2.272(2), Zr−O(6) = 2.245(2). Selected bond angles (degrees): O(4)−Zr−O(2) = 164.66(8), O(4)−Zr−O(3) = 89.67(7), O(4)−Zr−O(1) = 95.18(7), O(3)−Zr−O(6) = 87.19(7), O(6)−Zr−O(2) = 86.39(7), O(5)−Zr−O(1) = 91.94(9).

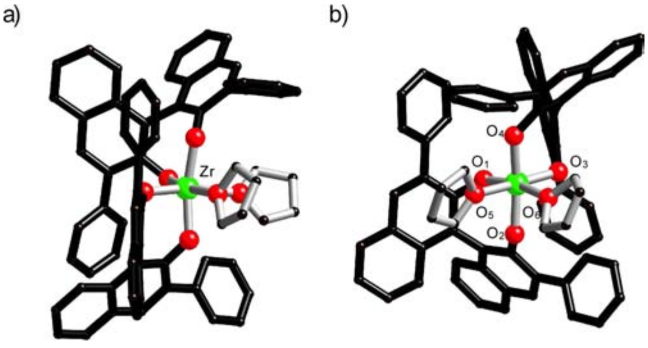


Figure 4. Solid state structure of the binaphtolate $Zr(THF)_2$ adduct **3b** (Λ, *aS*, *aR* enantiomer, two views). Binaphtolate ligand is colored in black (with the exception of the oxygen atoms that are colored in red). Selected bond lengths (Angstroms): Zr−O(1) = 1.982(3), Zr−O(2) = 2.045(3), Zr−O(3) = 2.019(3), Zr−O(4) = 2.038(3), Zr−O(5) = 2.311(3), Zr−O(6) = 2.262(3). Selected bond angles (degrees): O(4)−Zr−O(2) = 166.4(1), O(4)−Zr−O(3) = 90.1(1), O(4)− Zr−O(1) = 98.6(1), O(3)−Zr−O(6) = 90.4(1), O(6)−Zr−O(2) = 82.7(1), O(5)−Zr−O(1) = 91.2(1).

In the solid state, both **3a** and **3b** are monomeric and built around an octahedral zirconium(IV) center coordinated by two chelating bidentate ligands, with the two remaining cis positions being occupied by THF molecules. With regard to bonding and structural parameters, the molecular structures of **3a** and **3b** are rather similar to one another. While the $Zr-O_{PhO}$ bond distances average 2.01(8) Å and lie within the expected range for Zr−phenoxide bonds,[12] the average $Zr-O_{THF}$ bond distances (2.258(3) and 2.286(4) Å for **3a** and **3b**, respectively) are logically longer.[4a,13] Concerning the stereochemical situation for these two complexes and unlike the Ti alkoxide anionic analogues **2a** and **2b**, both compounds **3a** and **3b** adopt a heterochiral configuration (Λ, *aS*, *aR* and Δ, *aR*, *aS*), such as that observed for the Ti analogue *cis*-$Ti(Ph\text{-}Biphen)_2(HO^iPr)_2$ complex earlier reported.[8] Thus, going from Ti(IV) to the larger Zr(IV) metal center does not affect configurational preferences with the Ph-Biphen-OH ligand system. As for the structure in solution of species **3a** and **3b**, room-temperature NMR data agree with effective chelation of two biphenolate/binaphtolate units onto Zr, the presence of two Zr-coordinated THF molecules, and effective C_2-symmetric structures under the studied conditions. As observed for the related (Ph-Biphen-O/Ph-Binapht-O)Ti anionic chelates **2a** and **2b**, NMR resonances for **3a** and **3b** are rather broad, which is likely due to fast conformational changes (on the NMR time scale) within the (Ph-Biphen-O/Ph-Binapht-O)Zr chelates at room temperature. Notably, apart from their use in the present contribution, readily accessible species **3a** and **3b**, which are discrete Zr bis-THF adducts with a metal center confined in a fairly well-controlled architecture, may be suitable for Lewis-acid activation of various organic substrates and possibly of interest in Lewis-acid-type catalysis.[14]

Addition of 1 equiv of LiO^iPr to the zirconium bis-THF adducts **3a** and **3b** yielded the quantitative formation of the corresponding $Zr-O^iPr$ salt species $[(Ph\text{-}Biphen\text{-}O)_2Zr(O^iPr)]Li(THF)$ (**4a**) and $[(Ph\text{-}binapht\text{-}O)_2Zr(O^iPr)]Li(THF)$ (**4b**) (Scheme 2), whose molecular structures are proposed on the basis of NMR spectroscopy, elemental analysis, and analogy with the X-ray-determined Ti analogues **2a** and **2b**. While compounds **4a** and **4b** were isolated as analytically pure yellow solids (soluble aromatic and/or polar solvents), all crystallization attempts for obtainment of X-ray-quality crystals of either **4a** or **4b** failed. Nevertheless, NMR data for **4a** and **4b** closely relate those of the Ti analogues **2a** and **2b** and are consistent with (i) effective chelation of two biphenolate/binaphtolate units onto Zr, (ii) presence of a Zr−O^iPr group, and (iii) a metal-coordinated THF molecule. On the basis of available data, it thus appears very likely that the Ti and Zr compounds **2a,b** and **4a,b** are isostructural.

Ring-Opening Polymerization of *rac*-Lactide Initiated by the Group 4 Salt Species 2a, 2b, 4a, and 4b. The biphenolate/binaphtolate Ti complexes **2a** and **2b** were first tested and found to readily initiate the ROP of *rac*-lactide in a controlled manner. While inactive at room temperature, the biphenolate $Ti-O^iPr$ complex **2a** polymerizes *rac*-lactide at 80 °C in toluene to produce atactic PLA (100 equiv of *rac*-lactide, 24 h, 93% conversion to PLA, Table 1). The binaphtolate Ti analogue **2b** also mediates the ROP of *rac*-lactide but with a lower activity than **2a** (entry 4, Table 1). All polydispersities (PDI) are reasonably narrow ($1.14 < PDI < 1.39$) with SEC data featuring in all cases monomodal peaks (Figures S3 and S4, Supporting Information). This together with a linear correlation between the molecular weight number of the polymer chain and the monomer-to-polymer conversion (Figure 6) along with a first order dependence on monomer concentration (Figure 5) support a well-controlled polymerization process. In the case of initiator **2b**, the resulting PLA was also analyzed by MALDI-TOF spectrometry (Figures S1 and S2, Supporting Information); these data unambiguously establish the presence of an O^iPr moiety at the ester end of the formed PLA and also show that transesterification reactions occur as the ROP proceeds. These most likely account for the observed $M_{n(corr)}$ to be lower than the expected ones (Table 1). Altogether, these data agree with a fairly well-controlled polymerization of *rac*-lactide by initiators **2a** and **2b**. The

Table 1. Ring-Opening Polymerization of *rac*-Lactide Initiated by the Ti and Zr Complexes **2a**, **2b**, **4a**, and **4b**[a]

entry	initiator	t (h)	conv. (%)[b]	M_n (corr.)[c]	M_n (theo.)[d]	PDI[e]	P_r[f]
1	**2a**	8	48	4212	6918	1.14	
2	**2a**	15	70	5452	10 089	1.17	
3	**2a**	24	93	6508	13 404	1.30	0.48
4	**2b**	39	74	6600	10 666	1.39	0.50
5	**4a**	10	95	7580	13 500	1.12	0.65
6	**4b**	12	80	6060	11 500	1.18	0.67
7	**4a′**	10	90	12 220	12 975	1.13	0.65

[a] Conditions: 100 equiv of *rac*-lactide versus initiator, $[\text{monomer}]_0 = 1$ M, toluene, 80 °C. [b] Monomer conversion. [c] Determined by GPC analysis in THF with PS standards calibration; a correcting factor of 0.58 was applied to the M_n (equiv PS): M_n (corr.) = 0.58 × M_n (equiv PS). [d] M_n (theo.) = conv. × 100 × $M_{rac\text{-lactide}}$. [e] Determined by GPC. [f] Determined by homodecoupled ^{1}H NMR spectroscopy (methine region).

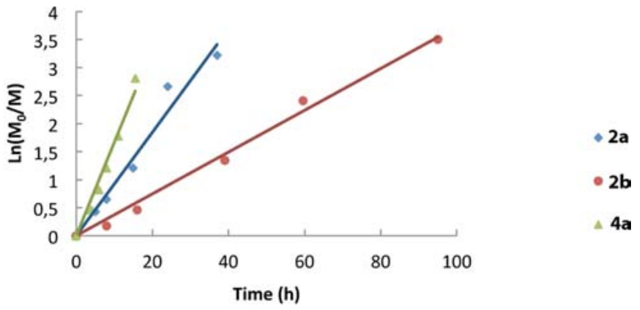


Figure 5. Plot of $\ln([M]_0/[M])$ as a function of *rac*-lactide conversion (M = monomer). Conditions: 100 equiv of *rac*-lactide vs metal initiator, $[M]_0 = 1$ M, toluene, 80 °C.

catalytic activity for species **2a** is comparable to that of other Ti-based ROP initiators reported thus far.[4]

As typically observed when going from Ti- to Zr-based ROP initiators, the biphenolate and binaphtolate Zr−O^{i}Pr were found to exhibit superior performances in *rac*-lactide ROP than their Ti counterparts, whether regarding activity, polymerization control, or stereoselectivity (Table 1). For instance, the biphenolate Zr−O^{i}Pr complex **4a** nearly quantitatively polymerizes 100 equiv of *rac*-lactide within 10 h at 80 °C in toluene to afford narrowly disperse and heterotactic-enriched PLA (95% conversion to PLA, P_r = 0.65; entry 5, Table 1). Similar results are observed for the binaphtolate derivative **4b**. In the case of **4a**, all kinetic and polymerization data support a well-controlled ROP process; these include (i) a first-order dependence in *rac*-lactide as ROP proceeds (Figure 5), (ii) a linear correlation Mn vs monomer conversion (Figure 6), and (iii) monomodal symmetric SEC traces (Figures S5 and S6, Supporting Information).

Overall, while reasonable, the *rac*-lactide ROP activity of Zr complexes **4a** and **4b** is undoubtedly lower than that of the most efficient Zr-based systems developed so far.[4] Several reasons may rationalize these observations, one being the significantly decreased Lewis acidity of the Zr metal center due to the anionic charge and a likely substantial electronic π donation of the four Zr−O_{ArO} oxygens to the Zr metal center. Also, it seems probable that steric factors play a role in the moderate activity of species **4a** and **4b**, i.e., confinement of the Zr metal center within a well-defined yet sterically demanding pocket (as may be deduced by analogy with the XRD-characterized Ti analogues **2a** and **2b**) may disfavor monomer approach and coordination/activation by the metal center.

Control experiments were carried out to probe whether or not species **2a**,**b** and **4a**,**b** are the actual ROP initiators. Indeed, under polymerization conditions (toluene, 80 °C), dissociation of the Ti and Zr "ate" complexes **2a**,**b** and **4a**,**b** into LiO^{i}Pr and neutral compounds of the type (Ph-Biphen-O)$_2$M and (Ph-binapht-O)$_2$M (M = Ti, Zr) may be conjectured, with the latter two components actually mediating the ROP process. This possibility was ruled out based on the following: (i) under identical conditions to those used for species **2a**,**b** and **4a**,**b**, LiO^{i}Pr was found to react with *rac*-lactide (100 equiv) only to afford ill-defined oligomers, as deduced from SEC data (M_n = 900 g·mol^{-1}, PDI = 1.73; Figure S7, Supporting Information); (ii) the PLA arising from the ROP of L-lactide initiated by LiO^{i}Pr (toluene, 80 °C) is partially epimerized, while no epimerization was observed with a L-lactide ROP initiated by the Ti complex **2b** (Figures S8 and S9, Supporting Information); (iii) the biphenolate/binaphtolate Zr compounds **3a**,**b** are inactive in *rac*-lactide (toluene, 80 °C, 20 h). Overall, these data suggest that the biphenolate/binaphtolate Ti and Zr alkoxide retain their integrity under polymerization conditions.

While the group 4 metal center is undoubtly involved in the *rac*-lactide ROP process, the role of Li$^+$, susceptible to act as a hard Lewis base, required further studies. In fact, part of our interest in heterometallic compounds such as **2a**,**b** and **4a**,**b** lies in the possibility that the Li$^+$ and group 4 metal centers may cooperate in polymerization catalysis. To gain more insight into the role of Li$^+$ in these lactide ROP reactions, the ammonium salt compound [(Ph-biphen-O)$_2$Zr(O^{i}Pr)][NBu$_4$] (**4a′**), closely related to **4a** yet incorporating the noncoordinative and non-Lewis-acidic ammonium cation NBu$_4^+$ (instead of Li$^+$), was prepared and subsequently tested in *rac*-lactide ROP (for comparison with **4a**). Compound **4a′**, readily accessible upon reacting species **3a** with 1 equiv of [O^{i}Pr][NBu$_4$]

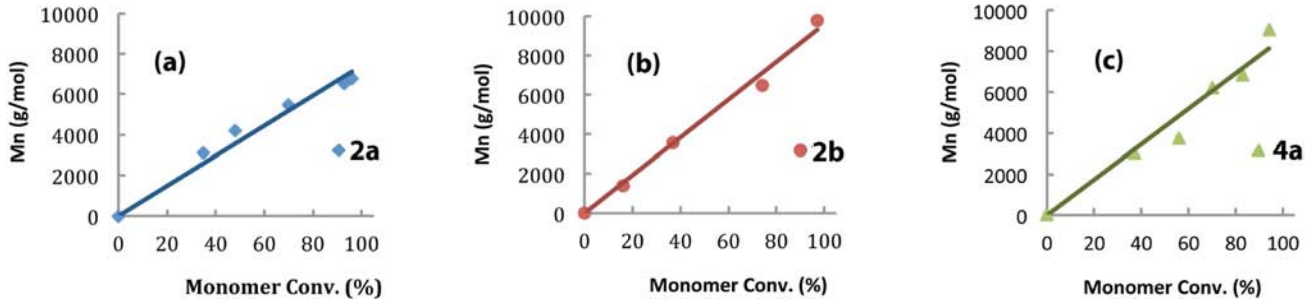
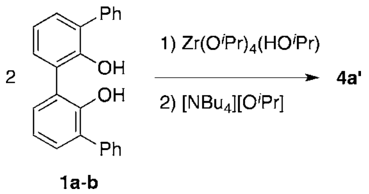


Figure 6. Plot of M_n as a function of *rac*-lactide conversion. Conditions: 100 equiv of *rac*-lactide vs metal initiator, $[M]_0 = 1$ M, toluene, 80 °C.

(Scheme 3), was isolated as a colorless solid, and its NMR data (CD_2Cl_2, room temperature) agree with well-separated (Ph-biphen-O)$_2$Zr(O^{i}Pr)$^-$ and NBu_4^+ ions in solution. Room-temperature NMR data for the (Ph-biphen-O)$_2$Zr(O^{i}Pr)$^-$ zirconate are nearly identical to those of species **4a**. Most importantly, compound **4a′** was found to ring-open polymerize *rac*-lactide with an activity, polymerization control, and stereoselectivity similar to those collected for the lithium salt analogue **4a**, as deduced from SEC and NMR data (entry 7, Table 1; Figure S10, Supporting Information). Thus, the Lewis acid Li$^+$ has no significant influence on the lactide ROP activity and stereoselectivity in species **4a**.

Scheme 3



Altogether, the above studies strongly hint at lactide ROP processes (initiated by species **2a,b** and **4a,b**) being primarily mediated by the group 4 metalate species, i.e., the Ti and Zr alkoxide "ate" complexes, and thus likely proceeding via a classical coordination/insertion mechanism.

■ CONCLUSION

Well-defined biphenolate and binaphtolate Ti and Zr alkoxide anions (Ph-Biphen-O)$_2$MO^{i}Pr$^-$ and (Ph-Binapht-O)$_2$MO^{i}Pr$^-$ (M = Ti, Zr) may be readily accessible as associated Li$^+$ salts species via alcohol elimination and/or addition reactions with simple precursors. These anionic species were all found to polymerize *rac*-lactide in a controlled manner yet with a moderate activity, with the Zr initiators **4a** and **4b** exhibiting superior catalytic performance. While the more nucleophilic M−*OR*$^-$ moiety is certainly beneficial to ROP activity, the decreased Lewis acidity at the metal center (along with, presumably, steric factors) may account for the observed ROP activity. Various control experiments agree with species **2a,b** and **4a,b** retaining their molecular integrity under polymerization conditions. The similar ROP performance of species **4a** vs **4a'**, i.e., the Li$^+$ vs NBu_4^+ salt analogue, strongly suggests that Li$^+$ has no significant influence on the lactide ROP activity and stereoselectivity in these systems.

Remarkably, formation of group 4 anionic chelates **2a,b** and **4a,b** was found to proceed stereoselectively: Ti derivatives **2a** and **2b** were isolated and XRD characterized in a (Δ, *aS*, *aS*)/(Λ, *aR*, *aR*) configuration. Thus, while the chiral binaphtol **1b** used in the present work is racemic, use of an enantiomerically pure **1b** should lead to exclusive generation of a (Δ, *aS*, *aS*)- or (Λ, *aR*, *aR*)-configurated **2b** enantiomer. Albeit unexplored thus far, access to well-defined chiral enantiopure species of the type (binapht-O)$_2$MX$^-$ (M = group 4) may be of interest for the mediation of asymmetric organic transformations.

■ EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under N_2 using standard Schlenk techniques or in a MBraun Unilab glovebox. THF, dichloromethane, and pentane were first dried through a solvent purification system (MBraun SPS) and stored for at least a couple of days over activated molecular sieves (4 Å) in a glovebox prior to use. CD_2Cl_2 and C_6D_6 were purchased from Eurisotope (CEA, Saclay, France), degassed under N_2 flow, and stored over activated molecular sieves (4 Å) in a glovebox prior to use. *r* was purchased from Sigma-Aldrich and sublimed prior to use. All other chemicals were used as received. Biphenol (Ph-Biphen-OH, **1a**) and binaphtol (Ph-Napht-OH, **1b**) ligands as well as the salt compound LiTi(O^{i}Pr)$_5$ were synthesized according to well-established literature procedures.[9] NMR spectra were recorded on Bruker AC 300, 400, or 500 MHz NMR spectrometer in Teflon-valved J-Young NMR tubes at ambient temperature, unless otherwise indicated. ^{1}H and ^{13}C chemical shifts are reported versus SiMe$_4$ and determined by reference to the residual ^{1}H and ^{13}C solvent peaks. Elemental analyses were performed by the "Service de microanalyses", Université de Strasbourg. MALDI-TOF analyses were carried out by the "Service de spectrométrie de masse de l'Université de Strasbourg" on a Bruker AutiflexII TOF/TOF (Bruker Daltonics, Bremen, Germany) using dithranol (1.8.9 trihydroxyanthracene) as a matrix. GPC analysis were performed on a system equipped with a Shimadzu RID10A refractometer detector using HPLC-grade THF as an eluant (with molecular weights and polydispersity indices (PDIs) calculated using polystyrene standards). In the case of molecular weight numbers (M_n), these were corrected with a correcting factor of 0.58.[15] Partial charges calculation was made using the PACHA software. Interested readers should refer to the original papers for more details.[16]

Apart from regular 1D and variable-temperature ^{1}H and ^{13}C NMR data, additional DEPT and COSY NMR experiments were also carried out for all compounds and allowed assignment of most resonances.

[(Ph-Biphen-O)$_2$Ti(O^{i}Pr)]Li(THF) (2a). A precooled THF colorless solution (−35 °C, 5 mL) of LiTi(O^{i}Pr)$_5$ (150 mg, 0.444 mmol) was quickly added to a precooled THF yellow solution (−35 °C, 10 mL) of ligand **1a** (300.5 mg, 0.888 mmol). Upon addition of the metal precursor to the ligand, the resulting mixture immediately turned red; it was allowed to warm to room temperature and stirred overnight. The solution was then evapored in vacuo to yield a yellow foam, which precipitated as a yellow solid upon addition of pentane. Recrystallization of the latter crude product from a 10/1 pentane/THF mixture afforded the salt compound **2a** as an analytically pure yellow solid (284 mg, 71% yield). Anal. Calcd for $C_{55}H_{47}LiO_6Ti$ (858.77): C, 75.92; H, 5.52. Found: C, 76.23; H, 5.26. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.30 (br, 3H, Me-^{i}Pr), 0.39 (br, 3H, Me-^{i}Pr), 1.40 (s, 4H, THF), 3.64 (q, ^3J = 6.1 Hz, 1H, CH-^{i}Pr), 6.75−7.75 (br, 32H, Ar). ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ 0.21 (d, ^3J = 6.1 Hz, 3H, Me-^{i}Pr), 0.33 (d, ^3J = 6.1 Hz, 3H, Me-^{i}Pr), 1.30 (s, 4H, THF), 2.46 (s, 4H, THF), 3.60 (hept, ^3J = 6.1 Hz, 1H, CH-^{i}Pr), 6.75−7.55 (m, 26H, Ar), 7.66 (t, ^3J = 7.0 Hz, 4H, Ar), 7.79 (d, ^3J = 7.5 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 193 K): δ 24.2 (Me-^{i}Pr), 24.3 (Me-^{i}Pr), 25.2 (THF), 67.7 (THF), 82.3 (CH-^{i}Pr), 120.6 (Ar), 120.8 (Ar), 121.0 (Ar), 122.1 (Ar), 126.5 (Ar), 126.7 (Ar), 127.1 (Ar), 127.4 (Ar), 127.8 (br, Ar), 128.1 (br, Ar), 128.4 (Ar), 128.5 (Ar), 128.7 (Ar), 129.2 (Ar), 129.5 (br, Ar), 129.6 (br, Ar), 129.7 (br, Ar), 129.8 (br, Ar), 130.0 (br, Ar), 130.4 (Ar), 130.5 (Ar), 130.7 (Ar), 130.9 (Ar), 131.1 (Ar), 131.3 (Ar), 132.2 (Ar), 132.6 (Ar), 137.8 (Ar), 139.0 (Ar), 139.8 (Ar), 157.9 (C$_{ipso}$−O), 159.1 (C$_{ipso}$−O), 159.4 (C$_{ipso}$−O), 159.7 (C$_{ipso}$−O).

[(Ph-binapht-O)$_2$Ti(O^{i}Pr)]Li(THF) (2b). Salt species **2b** was prepared following an identical procedure to that used for synthesis of its analogue **3a** using LiTi(O^{i}Pr)$_5$ (161 mg, 0.37 mmol) and the binaphtol ligand **1b** (324 mg, 0.74 mmol) as starting reagents. Compound **2b** was isolated as a yellow solid after recrystallization from a concentrated 10/1 pentane/THF solvent mixture (266 mg, 73% yield). Anal. Calcd for $C_{71}H_{55}LiO_6Ti$ (1059.00): C, 80.52; H, 5.23. Found: C, 80.91; H, 5.27. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.45 (br, 6H, CH_3), 1.31 (br, 4H, THF), 3.01 (br, 4H, THF), 3.81 (br, 1H, CH-^{i}Pr), 6.00−8.08 (m, 40H, Ar). ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ 0.04 (d, ^3J = 5.50 Hz, 3H, Me-^{i}Pr), 0.31 (d, ^3J = 6.0 Hz, 3H, Me-^{i}Pr), 1.47 (s, 4H, THF), 3.01 (s, 4H, THF), 3.54 (hept, ^3J = 6.5 Hz, 1H, CH-^{i}Pr), 6.52 (t, ^3J = 6.5 Hz, 2H, Ar), 6.72 (d, ^3J = 9.0 Hz, 1H, Ar), 6.79 (t, ^3J = 9.0 Hz, 2H, Ar), 6.94 (d, ^3J = 8.5 Hz, 1H, Ar), 7.05−7.39 (m, 21H, Ar), 7.60 (br s, 1H, Ar), 7.71−7.88 (m, 11H, Ar), 8.04 (br s, 1H, Ar). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 193 K): δ 24.1 (Me-^{i}Pr), 24.5 (Me-^{i}Pr), 25.2 (THF), 67.8 (THF), 81.6 (CH-^{i}Pr), 117.1 (CH-Ar), 118.4 (CH-Ar), 119.4 (CH-Ar), 119.7 (CH-Ar), 122.6 (br, CH-Ar), 122.7 (br, CH-Ar), 123.3 (CH-Ar), 123.8 (CH-Ar), 125.4 (CH-Ar), 125.6 (CH-Ar), 125.7, (CH-Ar), 125.8 (CH-Ar), 126.5 (CH-Ar), 126.6 (CH-Ar), 126.8 (CH-Ar), 127.0 (CH-Ar), 127.1 (CH-Ar), 127.5 (CH-Ar), 127.7 (CH-Ar), 127.8 (CH-Ar), 127.9 (CH-Ar), 128.0 (Ar), 128.2 (CH-Ar), 128.3 (CH-Ar), 128.6 (CH-Ar), 128.9 (Ar), 129.1 (Ar), 129.5 (CH-Ar), 129.8 (CH-Ar), 129.9 (Ar), 130.0 (CH-Ar), 130.1(Ar), 130.4 (CH-Ar), 130.5 (CH-Ar), 132.7 (Ar), 133.2 (Ar), 133.5 (Ar), 133.7 (Ar), 133.9 (Ar), 138.3 (Ar), 138.7 (Ar), 138.9 (Ar), 139.7 (Ar), 157.2 (C_{ipso}−O), 157.8 (C_{ipso}−O), 158.3 (C_{ipso}−O), 158.4 (C_{ipso}−O).

(Ph-Biphen-O)$_2$Zr(THF)$_2$ (3a). A precooled THF colorless solution (−35 °C, 5 mL) of Zr(O^{i}Pr)$_4$(HO^{i}Pr) (57.4 mg, 0.148 mmol) was quickly added to a precooled THF yellow solution (−35 °C, 10 mL) of 2 equiv of ligand **1a** (100.0 mg, 0.295 mmol). Upon addition of the metal precursor to the ligand, the resulting mixture immediately turned red; it was allowed to warm to room temperature and stirred overnight. The solution was then evaporated in vacuo to yield a yellow foam, which precipitated as a yellow solid upon addition of pentane. Recrystallization of the latter crude product from a 10/1 pentane/THF mixture afforded the Zr bis-THF adduct **3a** as an analytically pure yellow solid (101.1 mg, 75% yield). Anal. Calcd for $C_{56}H_{48}O_6Zr$ (908.20): C, 74.06; H, 5.33. Found: C, 73.89; H, 5.14. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.20 (br, 8H, THF), 2.93 (br, 4H, THF), 3.16 (br, 4H, THF), 6.58−7.54 (m, 32H, Ar). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2, 298 K): δ 25.1 (THF), 72.9 (THF), 119.0 (CH-Ar), 120.6 (CH-Ar), 126.2 (CH-Ar), 126.5 (br, CH-Ar), 128.0 (CH-Ar), 129.9 (br, CH-Ar), 130.4 (br, CH-Ar), 131.4 (C_{quat}), 132.1 (C_{quat}), 133.0 (br, Ar), 133.1 (br, Ar), 139.8 (C_{quat}), 142.4 (C_{quat}), 155.8 (C_{ipso}−O), 157.9 (C_{ipso}−O).

(Ph-Binapht-O)$_2$Zr(THF)$_2$ (3b). Species **3b** was prepared following an identical procedure to that used for synthesis of its analogue **2a** using Zr(O^{i}Pr)$_4$(HO^{i}Pr) (64.8 mg, 0.167 mmol) and 2 equiv of the binaphtol ligand **1b** (146.5 mg, 0.74 mmol) as starting reagents. Compound **2b** was isolated as a yellow solid after recrystallization from a concentrated 10/1 pentane/THF solvent mixture (118.0 mg, 64% yield). Anal. Calcd for $C_{72}H_{56}O_6Zr$ (1108.44): C, 72.02; H, 5.09. Found: C, 71.78; H, 4.96. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 1.20 (br, 8H, THF), 2.93 (br, 4H, THF), 3.16 (br, 4H, THF), 6.58−7.54 (m, 32H, Ar). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2): δ 25.1 (THF), 72.9 (THF), 119.0 (CH-Ar), 120.6 (CH-Ar), 126.2 (CH-Ar), 126.5 (br, CH-Ar), 128.0 (CH-Ar), 129.9 (br, CH-Ar), 130.4 (br, CH-Ar), 131.4 (C_{quat}), 132.1 (C_{quat}), 133.0 (br, Ar), 133.1 (br, Ar), 139.8 (C_{quat}), 142.4 (C_{quat}), 155.8 (C_{ipso}−O), 157.9 (C_{ipso}−O).

[(Ph-Biphen-O)$_2$Zr(O^{i}Pr)]Li(THF) (4a). A THF solution of LiO^{i}Pr (2 M in THF, 80.9 μL, 0.162 mmol) was quickly added via a syringe to a precooled THF solution (−35 °C, 5 mL) of the Zr bis-THF adduct **3a** (146.7 mg, 0.162 mmol). The resulting mixture remained yellow and was allowed to warm to room temperature and stirred overnight. The yellow solution was then evaporated in vacuo to yield a yellow foam, which precipitated as a yellow solid upon addition of pentane. Recrystallization of a concentrated solution of crude **4a** (10/1 pentane/THF solvent mixture) the salt compound **4a** as an analytically pure yellow solid (90.0 mg, 62% yield). Anal. Calcd for $C_{55}H_{47}LiO_6Zr$ (902.12): C, 73.23; H, 5.25. Found: C, 73.54; H, 5.33. ^{1}H NMR (500 MHz, CD_2Cl_2, 233 K): δ 0.01 (d, 3H, ^3J = 6.0 Hz, Me-^{i}Pr), 0.18 (d, 3H, ^3J = 6.0 Hz, *Me*-^{i}Pr), 0.89 (br, 2H, THF), 0.99 (m, 2H, THF), 2.89 (hept, 1H, ^3J = 6.1 Hz, *CH*-^{i}Pr), 2.95 (br, 2H, THF), 3.09 (br, 2H, THF), 6.70−7.51 (m, 32H, Ar). ^{13}C{^{1}H} NMR (600 MHz, CD_2Cl_2, 218 K) δ 24.7 (*Me*-^{i}Pr), 24.9 (*Me*-^{i}Pr), 25.1 (THF), 71.4 (*CH*-^{i}Pr), 72.5 (THF), 119.4 (br, C_{Ar}), 120.1 (C_{Ar}), 120,8 (C_{Ar}), 125.9 (C_{Ar}), 126.9 (large, C_{Ar}), 127.9 (C_{Ar}), 128.1 (C_{Ar}), 128.4 (C_{Ar}), 128.6 (C_{Ar}), 129.7 (C_{Ar}), 129.9 (large, C_{Ar}), 130.0 (large, C_{Ar}), 130.1 (large, C_{Ar}), 130.3 (C_{Ar}), 130.6 (br, C_{Ar}), 131.2 (br, C_{Ar}), 131.3 (br, C_{Ar}), 131.4 (br, C_{Ar}), 131.7 (C_{Ar}), 132.1 (br, C_{Ar}), 132.2 (br, C_{Ar}), 132.6 (C_{Ar}), 132.8 (C_{Ar}), 133.1(C_{Ar}), 133.7 (C_{Ar}), 134.3 (C_{Ar}), 135.3 (C_{Ar}), 139.7 (C_{Ar}), 140.7 (C_{Ar}), 141.4 (C_{Ar}), 142.0 (C_{Ar}), 156.8 (C_{ipso}−O), 157.8 (C_{ipso}−O), 158.3 (C_{ipso}−O), 158.9 (C_{ipso}−O).

[O^{i}Pr][NBu$_4$]. The salt [O^{i}Pr][NBu$_4$] was synthesized via a salt metathesis pathway involving reaction of LiO^{i}Pr (1.00 g, 15.15 mmol) with 1 equiv of anhydrous [NBu$_4$]Cl (4.20 g, 15.15 mmol) at room temperature in CH_2Cl_2 (15 mL). After dissolution of the two reagents in CH_2Cl_2, the resulting mixture was left under stirring at room temperature for 18 h. The resulting colorless suspension was filtered through a glass frit and dried in vacuo to quantitatively afford [O^{i}Pr][NBu$_4$] on the basis of ^{1}H NMR analysis. The resulting colorless solid was used as is. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.96 (t, ^3J = 7.2 Hz, 12H, NBu), 1.32 (m, 8H, NBu), 1.48 (m, 8H, NBu), 1.68 (d, ^3J = 7.2 Hz, 6H, Me-^{i}Pr), 3.30 (m, 8H, NBu), 4.61 (q, ^3J = 7.2 Hz, 1H, CH-^{i}Pr).

[(Ph-biphen-O)$_2$Zr(O^{i}Pr)][NBu$_4$] (4a′). A precooled THF solution (−35 °C, 2 mL) of [O^{i}Pr][NBu$_4$] (33.0 mg, 0.110 mmol) was quickly added via a syringe to a precooled THF solution (−35 °C, 5 mL) of the Zr bis-THF adduct **3a** (100.0 mg, 0.110 mmol). The resulting mixture remained pale yellow and was allowed to warm to room temperature and stirred overnight. The yellow solution was then evaporated in vacuo to yield an off-white foam, which precipitated as a colorless solid upon addition of pentane. NMR data of the latter solid were consistent with formation of dissociated [(Ph-Binapht-O)$_2$Zr-(O^{i}Pr)]$^-$ and NBu$_4$$^+$ ions. Prolonged time in vacuo of the latter Zr−THF adduct yielded crude **4a′**. Recrystallization of a concentrated solution of crude **4a′** (10/1 pentane/THF solvent mixture) afforded the salt compound **4a′** (77.0 mg, 58% yield). ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 0.62 (br, 6H, Me-^{i}Pr), 0.94 (t, ^3J = 7.2 Hz, 12H, NBu), 1.29 (m, 8H, NBu), 1.45 (m, 8H, NBu), 2.89 (m, 8H, NBu), 3.67 (br, 1H, CH-^{i}Pr), 6.40−8.05 (br, 32H, Ar). ^{13}C{^{1}H} NMR (400 MHz, CD_2Cl_2, 298 K): δ 23.5 (br, Me-^{i}Pr), 79.4 (br, CH-^{i}Pr), 119.0 (CH-Ar), 120.6 (CH-Ar), 126.2 (CH-Ar), 126.5 (br, CH-Ar), 128.0 (CH-Ar), 129.9 (br, CH-Ar), 130.4 (br, CH-Ar), 131.4 (C_{quat}), 132.1 (C_{quat}), 133.0 (br, Ar), 133.1 (br, Ar), 139.8 (C_{quat}), 142.4 (C_{quat}), 155.8 (C_{ipso}−O), 157.9 (C_{ipso}−O).

[(Ph-Binapht-O)$_2$Zr(O^{i}Pr)]Li(THF) (4b). A THF solution of LiO^{i}Pr (2 M in THF, 59.0 μL, 0.110 mmol) was quickly added via a syringe to a precooled THF solution (−35 °C, 5 mL) of the Zr bis−THF adduct **3b** (118.0 mg, 0.110 mmol). The resulting mixture remained yellow and was allowed to warm to room temperature, stirred overnight, and subsequently evapored in vacuo to yield a yellow foam, which precipitated as a yellow solid upon addition of pentane. Recrystallization of a concentrated solution of crude **4b** (10/1 pentane/THF solvent mixture) afforded the salt compound **4b** as an analytically pure yellow solid (42 mg, 35% yield). Anal. Calcd for $C_{71}H_{55}LiO_6Zr$ (1102.36): C, 77.36; H, 5.03. Found: C, 77.18; H, 4.95. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.45 (br, 6H, *Me*-^{i}Pr), 1.31 (br, 4H, THF), 3.01 (br, 4H, THF), 3.81 (br, 1H, *CH*-^{i}Pr), 6.00−8.08 (m, 40H, Ar). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 298 K): δ 23.8 (THF), 69.9 (THF), 117.6 (C_{Ar}−H), 121.1 (C_{Ar}−H), 127.3 (C_{Ar}−H), 128.1 (large, C_{Ar}−H), 128.5 (C_{Ar}−H), 129.2 (large, C_{Ar}−H), 130.7 (large, C_{Ar}−H), 132.8 (C_{quat}), 133.5 (C_{quat}), 134.0 (br, C_{Ar}), 134.5 (br, C_{Ar}), 139.8 (C_{quat}), 142.9 (C_{quat}), 156.1 (C_{ipso}−O), 158.5 (C_{ipso}−O).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Cif files for compounds **2a**, **2b**, **3a**, and **3b**; selected MALDI-TOF spectrometric data for produced PLA; selected NMR data; SEC data; summary of crystal data for **2a**, **2b**, **3a**, and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: dagorne@unistra.fr.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors thank the CNRS and the University of Strabourg for financial support. Prof. R. Welter (University of Strasbourg) is gratefully acknowledged for X-ray analysis of compound **2a**. We also wish to acknowledge the reviewers for their insightful comments.

■ REFERENCES

(1) (a) Lindblad, M. S.; Liu, Y.; Albertsson, A.-C.; Ranucci, E.; Karlsson, S. *Adv. Polym. Sci.* **2002**, *157*, 139. (b) Vert, M. *Biomacromolecules* **2005**, *6*, 538. (c) Nair, L. S.; Laurencin, C. T. *Prog. Polym. Sci.* **2007**, *32*, 762.

(2) Selected reviews: (a) O'Keefe, B. J.; Hillmeyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215. (b) Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D. *Chem. Rev.* **2004**, *104*, 6147. (c) Wu, J.; Yu, T.-L.; Chen, C.-T.; Lin, C.-C. *Coord. Chem. Rev.* **2006**, *205*, 602. (d) Dove, A. P. *Chem. Commun.* **2008**, 6446. (e) Platel, R. H.; Hodgson, L. M.; Williams, C. K. *Polym. Rev.* **2008**, *48*, 11. (f) Thomas, C. M. *Chem. Soc. Rev.* **2010**, *39*, 165. (g) Arbaoui, A.; Redshaw, C. *Polym. Chem.* **2010**, *1*, 801. (h) Buffet, J.-C.; Okuda, J. *Polym. Chem.* **2011**, *2*, 2758.

(3) For recent representative examples, see: (a) Poirier, V.; Roisnel, T.; Sinbandhit, S.; Bochmann, M.; Carpentier, J.-F.; Sarazin, Y. *Chem.—Eur. J.* **2012**, *18*, 2998. (b) Sung, C.-Y.; Li, C.-Y.; Su, J.-K.; Chen, T.-Y.; Lin, C.-H.; Ko, B.-T. *Dalton Trans.* **2012**, *41*, 953. (c) dos Santos Vieira, I.; Herres-Pawlis, S. *Eur. J. Inorg. Chem.* **2012**, 765. (d) Cao, T.-P. A.; Buchard, A.; Le Goff, X. F.; Auffrant, A.; Williams, C. K. *Inorg. Chem.* **2012**, *51*, 2157. (e) Poirier, V.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y. *Dalton Trans.* **2011**, *40*, 523. (g) Sanchez-Barba, L. F.; Garces, A.; Fernandez-Baeza, J.; Otero, A.; Alonso-Moreno, C.; Lara-Sanchez, A.; Rodriguez, A. M. *Organometallics* **2011**, *30*, 2775. (h) Zhang, Z.; Cui, D. *Chem.—Eur. J.* **2011**, *17*, 11520. (i) Bouyahyi, M.; Ajellal, N.; Kirillov, E.; Thomas, C. M.; Carpentier, J.-F. *Chem.—Eur. J.* **2011**, *17*, 1872. (j) Platel, R. H.; White, A. J. P.; Williams, C. K. *Inorg. Chem.* **2011**, *50*, 7718. (k) Dyer, H. E.; Huijser, S.; Susperregui, N.; Bonnet, F.; Schwarz, A. D.; Duchateau, R.; Maron, L.; Mountford, P. *Organometallics* **2010**, *29*, 3602. (l) Clark, L.; Cushion, M. G.; Dyer, H. E.; Schwarz, A. D.; Duchateau, R.; Mountford, P. *Chem. Commun.* **2010**, *46*, 273. (m) Wang, L.; Ma, H. *Macromolecules* **2010**, *43*, 6535. (n) Buffet, J.-C.; Kapelski, A.; Okuda, J. *Macromolecules* **2010**, *43*, 10201. (o) Shen, M.; Huang, W.; Zhang, W.; Hao, X.; Sun, W.-H.; Redshaw, C. *Dalton Trans.* **2010**, *39*, 9912. (p) Arbaoui, A.; Redshaw, C.; Elsegood, M. R. J.; Wright, V. R.; Yoshizawa, A.; Yamato, T. *Chem. Asian J.* **2010**, *5*, 621. (q) Nomura, N.; Akita, A.; Ishii, R.; Mizuno, M. *J. Am. Chem. Soc.* **2010**, *132*, 1750.

(4) For recent and representative group 4-based lactide ROP initiators, see: (a) Romain, C.; Heinrich, B.; Bellemin-Laponnaz, S.; Dagorne, S. *Chem. Commun.* **2012**, *48*, 2213. (b) Sauer, A.; Buffet, J.-C.; Spaniol, T. P.; Nagae, H.; Mashima, K.; Okuda, J. *Inorg. Chem.* **2012**, *51*, 5764. (c) Stopper, A.; Okuda, J.; Kol, M. *Macromolecules* **2012**, *45*, 698. (d) Buffet, J.-C.; Martin, A. N.; Kol, M.; Okuda, J. *Polym. Chem* **2011**, *2*, 2378. (e) Hancock, S. L.; Mahon, M. F.; Kociok-Kohn, G.; Jones, M. D. *Eur. J. Inorg. Chem.* **2011**, 4596. (f) Whitelaw, E. L.; Davidson, M. G.; Jones, M. D. *Chem. Commun.* **2011**, *47*, 10004. (g) Buffet, J.-C.; Okuda, J. *Chem. Commun.* **2011**, *47*, 4796. (h) Schwarz, A. D.; Herbert, K. R.; Paniagua, C.; Mountford, P. *Organometallics* **2010**, *29*, 4171. (i) Sergeeva, E.; Kopilov, J.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2010**, *49*, 3977. (j) Romain, C.; Brelot, L.; Bellemin-Laponnaz, S.; Dagorne, S. *Organometallics* **2010**, *29*, 1191. (k) Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Coates, G. W.; Kol, M. *Chem. Commun.* **2009**, *44*, 6804. (l) Schwarz, A. D.; Thompson, A. L.; Mountford, P. *Inorg. Chem.* **2009**, *48*, 10442.

(5) For recent use of well-defined cationic initiators in cyclic esters ROP, see: (a) Romain, C.; Rosa, V.; Fliedel, C.; Bier, F.; Hild, F.; Welter, R.; Dagorne, S.; Avilés, T. *Dalton Trans.* **2012**, *41*, 3377. (b) Sun, H.; Ritch, J. S.; Hayes, P. G. *Dalton Trans.* **2012**, *41*, 3701. (c) Piedra-Arroni, E.; Brignou, P.; Amgoune, A.; Guillaume, S. M.; Carpentier, J.-F.; Bourissou, D. *Chem. Commun.* **2011**, *47*, 9828. (d) Sarazin, Y.; Liu, B.; Roisnel, T.; Maron, L.; Carpentier, J.-F. *J. Am. Chem. Soc.* **2011**, *133*, 9069. (e) Cushion, M. G.; Mountford, P. *Chem. Commun.* **2011**, *47*, 2276. (f) Ireland, B. J.; Wheaton, C. A.; Hayes, P. G. *Organometallics* **2010**, *29*, 1079. (g) Wheaton, C. A.; Hayes, P. G. *Chem. Commun.* **2010**, *46*, 8404. (h) Sarazin, Y.; Poirier, V.; Roisnel, T.; Carpentier, J.-F. *Eur. J. Inorg. Chem.* **2010**, 3423. (i) Haddad, M.; Laghzaoui, M.; Welter, R.; Dagorne, S. *Organometallics* **2009**, *28*, 4584. (j) Issenhuth, J.-T.; Pluvinage, J.; Welter, R.; Bellemin-Laponnaz, S.; Dagorne, S. *Eur. J. Inorg. Chem.* **2009**, 4701.

(6) (a) McGuinness, D. S.; Marshall, E. L.; Gibson, V. C.; Steed, J. W. *J. Polymer Sci., Part A: Polym. Chem.* **2003**, *41*, 3798. (b) Chisholm, M. H.; Lin, C.-C.; Galluci, J. C.; Ko, B.-T. *Dalton Trans.* **2003**, 406. (c) Sarazin, Y.; Howard, R. H.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Dalton Trans.* **2006**, 340. (c) Dyer, H. E.; Huijser, S.; Schwarz, A. D.; Wang, C.; Duchateau, R.; Mountford, P. *Dalton Trans.* **2008**, 32. (d) Hild, F.; Haquette, P.; Brelot, L.; Dagorne, S. *Dalton Trans.* **2010**, *39*, 533. (e) Sutar, A. K.; Lin, C.-C. *Inorg. Chem.* **2010**, *49*, 665.

(7) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293.

(8) Diebold, C.; Mobian, P.; Huguenard, C.; Allouche, L.; Henry, M. *Dalton Trans.* **2009**, 10178.

(9) (a) Hampden-Smith, M. J.; Williams, D. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4076. (b) Boyle, T. J.; Bradley, D. C.; Hampden-Smith, M. J.; Patel, A.; Ziller, J. W. *Inorg. Chem.* **1995**, *34*, 5893. (c) Kadyrov, R.; Heller, D.; Selke, R. *Tetrahedron: Asymmetry* **1998**, *9*, 329. (d) Simonsen, K. B.; Gothelf, K. V.; Jørgensen, K. A. *J. Org. Chem.* **1998**, *63*, 7536.

(10) (a) Tshuva, E. Y.; Goldberg, I.; Kol, M.; Goldschmidt, Z. *Inorg. Chem. Commun.* **2000**, *3*, 611. (b) Mulford, D. R.; Fanwick, P. E.; Rothwell, I. P. *Polyhedron* **2000**, *19*, 35. (c) Hancock, S. L.; Mahon, M. F.; Jones, M. D. *Dalton Trans.* **2011**, *40*, 2033.

(11) Calculations were performed from virtual complexes where THF molecules were removed from the structures. For **2a**: Average between a maximum value $R_{\max} = 17.19$ Å corresponding to the longest distance from the molecule's barycenter and a minimum value $R_{\min} = (3V/4\pi)^{1/3} = 5.44$ Å derived from the molecular volume $V = 674.70$ Å^3. For **2b**: Average between a maximum value $R_{\max} = 19.93$ Å corresponding to the longest distance from the molecule's barycenter and a minimum value $R_{\min} = (3V/4\pi)^{1/3} = 5.87$ Å derived from the molecular volume $V = 845.76$ Å^3, estimated according to Gavezotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220. Van der Waals radii used: H = 1.2 Å, C = 1.7 Å, O = 1.52 Å. See: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441–451 ; Ti = 1.45 Å (assumed).

(12) (a) Shannon, R. D. *Acta Crystallogr., Sect. A* **1976**, *32*, 751. (b) Knight, P. D.; Munslow, I.; O'Shaughnessy, P. N.; Scott, P. *Chem. Commun.* **2004**, 894. (c) Natrajan, L. S.; Wilson, C.; Okuda, J.; Arnold, P. L. *Eur. J. Inorg. Chem.* **2004**, 3724. (d) Cohen, A.; Kopilov, J.; Goldberg, I.; Kol, M. *Organometallics* **2009**, *28*, 1391. (e) Tshuva, E. Y.; Goldberg, I.; Kol, M. *J. Am. Chem. Soc.* **2000**, *122*, 10706. (f) Cohen, A.; Yeori, A.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2007**, *46*, 8114.

(13) Brauer, D. J.; Krüger, C. *Inorg. Chem.* **1975**, *14*, 3053.

(14) For organic transformations catalyzed by discrete Zr complexes bearing two Lewis-acidic sites, see, for instance: Bondar, G. V.; Aldea, R.; Levy, C. J.; Jaquith, J. B.; Collins, S. *Organometallics* **2000**, *19*, 947.

(15) (a) Kowalski, A.; Duda, A.; Penczek, S. *Macromolecules* **1998**, *31*, 2114. (b) Save, M.; Schappacher, M.; Soum, A. *Macromol. Chem. Phys.* **2002**, *203*, 889.

(16) Partial charges calculation was estimated using the PACHA software. For more information, see: (a) Henry, M. *Chem. Phys. Chem* **2002**, *3*, 561. (b) Henry, M. In *Advances in Quantum Chemical Bonding Structures*; Putz, M. V., Ed.; Transworld Research Network: Kerala, India, 2008; p 153.