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Titanium and Zirconium Complexes of Dianionic and Trianionic Amine–Phenolate-Type Ligands in Catalysis of Lactide Polymerization

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The synthesis of alkoxotitanium(IV) and -zirconium(IV) complexes of seven chelating tetradentate di- or trianionic amine–phenolate ligands belonging to three families and their application in L-lactide polymerization are described. The isopropoxotitanium complexes were synthesized by a direct reaction between the ligand precursors and titanium tetraisopropoxide, whereas the zirconium complexes were synthesized by various routes. For titanium, complexes of all seven ligands could be synthesized. For zirconium, the hexacoordinate complexes derived from all dianionic ligands were synthesized; however, the only pentacoordinate complex that could be produced was the one derived from the bulky trianionic ligand. X-ray structures of zirconium complexes of the three families indicated a substantial π donation from the alkoxo ligand to the metal. All complexes were found to be active lactide polymerization catalysts, and their activity was found to depend strongly on the metal, the coordination number around the metal, and the phenolate substituents but not on the ligand backbone.

Introduction

The ring-opening polymerization (ROP) of lactones to produce polyester-based materials is attracting considerable interest lately.[1] Relative to the traditional polycondensation of α-hydroxy esters, the ROP provides better control of molecular weight and molecular weight distribution (PDI), enabling the production of block copolymers, and the direction of polymer stereochemistry by a proper catalyst design. Poly(lactide) (PLA) is of special value because its feedstock, lactide, is obtained from annually renewable resources such as corn, beets, and dairy products. Because PLA is biodegradable and its degradation products are nontoxic, it has found biomedical applications such as adsorbable stitches, resorbable medical implants, and matrixes for controlled release of pharmaceuticals.[2] More recently, applications of PLA as a substitute for the traditional thermoplastics derived from fossil fuels, e.g., in packaging films, are being developed.[3] The most useful catalysts for lactide polymerization are alkoxide complexes of main-group elements magnesium,[4] zinc,[5] aluminum,[6–9] and yttrium[10] and the lanthanides,[11] tin(II),[12] group IV metals,[13] and iron.[14] The

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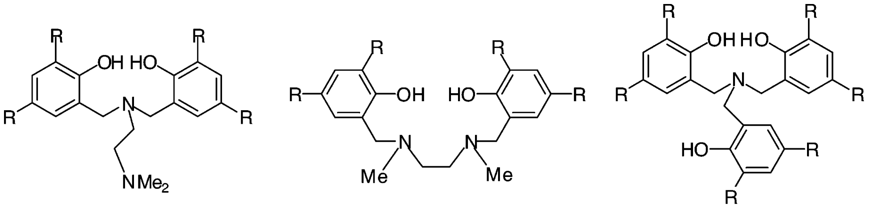

Lig^1H_2, R = t-Bu
Lig^2H_2, R = Cl

Lig^3H_2, R = t-Bu
Lig^4H_2, R = Cl

Lig^5H_3, R = Me
Lig^6H_3, R = Cl
Lig^7H_3, R = t-Bu

Figure 1. Ligand precursors employed in this study: (left) amine−bis(phenolate) ligand precursors bearing a dimethylamino side-arm donor; (middle) diamine−bis(phenolate) ligand precursors; (right) amine−tris(phenolate) ligand precursors.

catalysts are required to lead to controlled polymerization, namely, a process involving minimal chain transfer. Combined with a fast initiation, such processes may be defined as "living" polymerizations that may lead to polymers of predetermined molecular weights (achieved by a specific monomer/catalyst ratio) and narrow PDIs (PDI $= M_w/M_n$ approaching 1.0).

Recently, we introduced several families of tetradentate di- and trianionic amine−phenolate ligands to group IV transition-metal chemistry.[15] These ligands exhibited a variety of well-defined wrapping modes around group IV transition metals, and some of their dialkyl complexes exhibited unique activity modes in α-olefin polymerization following activation. The rich coordination chemistry of chelating amine−phenolate ligands that lead to well-defined group IV complexes and the ability to tune metal geometry as well as electronic and steric parameters by ligand structure and substitution pattern have prompted us to try to develop new group IV catalysts for lactide polymerization and address the parameters that control their activity. Titanium complexes of several amine−tris(phenolate) ligands studied by Verkade and co-workers,[16] as well as several other titanium complexes, were previously shown to be active catalysts for this transformation; however, the corresponding zirconium complexes were almost unexplored. In this work, we describe the synthesis, structure, and activity of alkoxotitanium and -zirconium complexes of three families of ligands: amine−bis(phenolate) ligands, diamine−bis(phenolate) ligands, and amine−tris(phenolate) ligands (Figure 1).[17]

Results and Discussion

Synthesis and Structure. The dianionic ligand precursors were synthesized by a one-step Mannich reaction between formaldehyde and the corresponding diamine and phenol, and the trianionic ligand precursors were synthesized by an analogous procedure employing hexamethylenetetramine, formaldehyde, and the corresponding phenol as previously reported.[15k,18] The most suitable catalysts for lactide polymerization are metal alkoxide complexes because they easily initiate the polymerization process and are relatively inert to hydrolysis. Therefore, our synthetic targets were titanium and zirconium isopropoxide complexes of these ligands. The titanium isopropoxide complexes could be obtained by a direct reaction between $Ti(O\text{-}i\text{-}Pr)_4$ and the ligand precursors as outlined in Scheme 1. To attain reliable activity values of the resulting polymerization catalysts, it is crucial to purify the titanium complexes from traces of $Ti(O\text{-}i\text{-}Pr)_4$, which is an active catalyst on its own. The low solubility of the complexes bearing the chloro substituents on the phenolate rings [$Lig^2Ti(O\text{-}i\text{-}Pr)_2$, $Lig^4Ti(O\text{-}i\text{-}Pr)_2$, and $Lig^6Ti(O\text{-}i\text{-}Pr)$] enabled their purification by washing off of the impurities with pentane. The other complexes were obtained free of $Ti(O\text{-}i\text{-}Pr)_4$ by employing a slight excess of the ligand precursors.

Scheme 1. Synthesis of Titanium Isopropoxide Complexes of Ligands Lig^1−Lig^7

$$Lig^{1\text{-}7}H_n + Ti(Oi\text{-}Pr)_4 \xrightarrow[\text{ether}]{\text{2 h, RT}} Lig^{1\text{-}7}Ti(Oi\text{-}Pr)_{4-n} + n\ i\text{-PrOH}$$

$n = 2,3$

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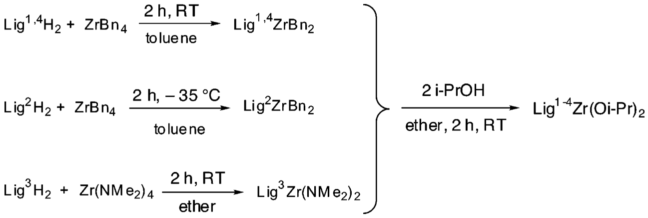
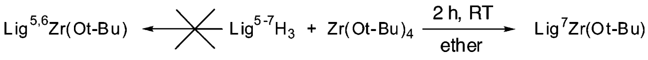
Scheme 2. Synthesis of Zirconium Isopropoxide Complexes $Lig^{1-4}Zr(O\text{-}i\text{-}Pr)_2$



Different approaches were employed for preparation of the zirconium complexes. The octahedral complexes of the type $Lig^{1-4}Zr(O\text{-}i\text{-}Pr)_2$ were synthesized by a two-step synthesis, so as to avoid the use of the ill-defined $Zr(O\text{-}i\text{-}Pr)_4$. Thus, the ligand precursors $Lig^{1-4}H_2$ were reacted with the well-defined monomeric $ZrBn_4$ and $Zr(NMe_2)_4$, and the respective intermediate dibenzyl complexes or bis(dimethylamide) complexes were reacted with 2 equiv of isopropyl alcohol to yield the corresponding diisopropoxide complexes $Lig^{1-4}Zr(O\text{-}i\text{-}Pr)_2$ (Scheme 2). We have previously reported that amine−bis(phenolate) ligand precursors bearing nonbulky phenolate substituents react with $ZrBn_4$, giving a high relative proportion of the bis(homoleptic) complex Lig_2Zr, which is inactive in polymerization of α-olefins because it does not carry any labile groups.[15e] The reaction between the bulky Lig^1H_2 and $Zr(NMe_2)_4$ gave a substantial amount of the bis(homoleptic) complex; however, the reaction with $ZrBn_4$ gave the desired Lig^1ZrBn_2 selectively, as previously observed. The less bulky ligand precursor Lig^2H_2 yielded a substantial proportion of the bis(homoleptic) complex with both zirconium reagents [for characterization of the bis(homoleptic) complex $Lig^2{}_2Zr$, see the Experimental Section]. However, we found that the reaction with $ZrBn_4$ proceeds smoothly even at −35 °C, giving a much higher proportion of the desired Lig^2ZrBn_2 complex.[19] The complexes $Lig^{1-4}Zr(O\text{-}i\text{-}Pr)_2$ are all proposed to be hexacoordinate and of approximate octahedral geometry (vide infra).

The synthesis of pentacoordinate zirconium complexes, i.e., those derived from amine−tris(phenolate) ligands, is expected to be more difficult because of the relatively large size of zirconium favoring higher coordination numbers. It was previously reported that the bulky ligand precursor Lig^7H_3 led to a pentacoordinate complex, whereas the less protected Lig^5H_3 led to a zwitterionic bis(homoleptic) complex upon reaction with $Zr(O\text{-}i\text{-}Pr)_4{\cdot}i\text{-}PrOH$.[20] In an attempt to obtain the well-defined pentacoordinate $Lig^{5-7}Zr(OR)$-type complexes, we reacted the ligand precursors with the bulky $Zr(O\text{-}t\text{-}Bu)_4$ precursor. As it turned out, even with this bulky precursor, only Lig^7H_3 led to the desired pentacoordinate complex [$Lig^7Zr(O\text{-}t\text{-}Bu)$] cleanly, whose structure was analyzed by X-ray diffraction (vide infra), whereas the less bulky ligands led to undefined products, which may be of the zwitterionic homoleptic type previously described (Scheme 3). It thus seems that a pentacoordinate amine−tris(phenolate) zirconium complex is stable only for bulky ligands.

Scheme 3. Attempted Synthesis of Pentacoordinate Zirconium *tert*-Butoxide Complexes $Lig^{5-7}Zr(O\text{-}t\text{-}Bu)$



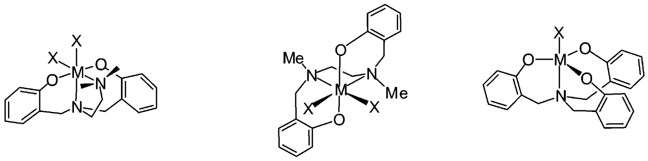


Figure 2. Typical wrapping modes and symmetries of the three families of ligands around group IV metals (phenolate substituents omitted; X = labile group): (left) amine−bis(phenolates), C_s symmetry; (middle) diamine−bis(phenolates), C_2 symmetry; (right) amine−tris(phenolates), C_3 symmetry.

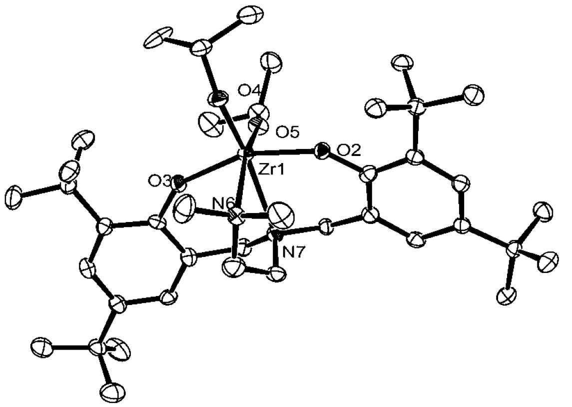


Figure 3. ORTEP representation of $Lig^1Zr(O\text{-}i\text{-}Pr)_2$, with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−O2, 2.038(4); Zr−O3, 2.044(4); Zr−O4, 1.955(4); Zr−O5, 1.925(4); Zr−N6, 2.493(4); Zr−N7, 2.447(5); O4−Zr−O5, 106.0(2); Zr−O4−C29, 151.3(3); Zr−O5−C26, 167.7(3).

We have previously reported that the typical wrapping modes of the three families of ligands around metal centers lead to complexes of different symmetries (Figure 2). The complexes described herein were found to fit the typical symmetries previously reported for their respective families.

The titanium and zirconium complexes of the amine−bis(phenolate) ligands Lig^1 and Lig^2 featured C_s symmetry in solution, with the symmetry plane reflecting the phenolate rings and including the side-arm nitrogen donor and the labile alkoxide groups, as revealed from their ^1H NMR spectra. Crystals of $Lig^1Zr(O\text{-}i\text{-}Pr)_2$ suitable for X-ray structural determination were grown from cold pentane. The molecular structure of $Lig^1Zr(O\text{-}i\text{-}Pr)_2$ and several selected bond lengths and angles are described in Figure 3. The X-ray structure features a slightly distorted octahedral geometry, in which the two oxygen atoms of the phenolate rings are in a trans configuration and the two isopropoxide groups are in a cis configuration consistent with the NMR data. The same geometry was previously described for $Lig^1Ti(O\text{-}i\text{-}Pr)_2$ (that structure was of low quality)[15b] and for related amine−bis(phenolate) alkoxotitanium complexes,[15a,c] as well as for $Lig^1Zr(Bn)_2$[15d] and for related amine−bis(phenolate) dibenzylzirconium complexes.[15e,f] The very broad bond angles of the

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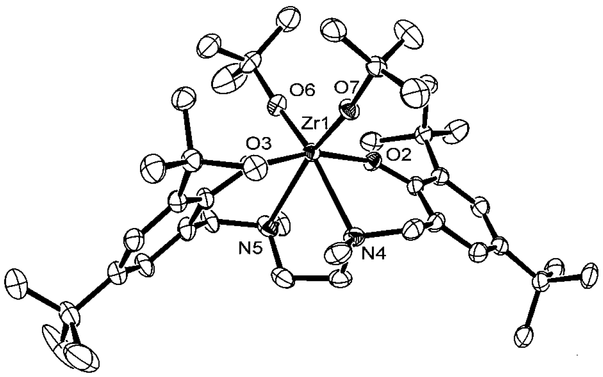

Figure 4. ORTEP representation of $Lig^3Zr(O\text{-}t\text{-}Bu)_2$, with 50% probability ellipsoids and hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−O2, 2.044(2); Zr−O3, 2.041(2); Zr−O6, 1.933(2); Zr−O7, 1.930(2); Zr−N4, 2.486(3); Zr−N5, 2.487(3); O3−Zr−O2, 163.01(9); N4−Zr−N5, 71.44(9); O7−Zr−O6, 107.76(9); C46−O6−Zr, 160.9(2); C42−O7−Zr, 166.8(2).

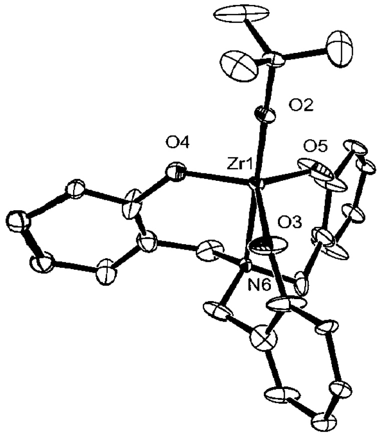

Figure 5. ORTEP representation of $Lig^7Zr(O\text{-}t\text{-}Bu)$, with 50% probability ellipsoids and hydrogen atoms and *tert*-butyl−phenolate substituents omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr−O2, 1.921(5); Zr−O3, 1.955(7); Zr−O4, 1.993(7); Zr−O5, 1.940(7); Zr−N6, 2.439(7); Zr−O2−C28, 177.6(5).

isopropoxo oxygens [Zr−O4−C29, 151.3(3); Zr−O5−C26, 167.7(3)] signify a substantial π bonding to the zirconium. The almost identical Zr−N bond distances [Zr−N6, 2.493(4); Zr−N7, 2.447(5)] signify a strong binding of the side-arm nitrogen donor to the zirconium.

The titanium and zirconium complexes of the diamine−bis(phenolate) ligands Lig^3 and Lig^4 featured C_2 symmetry according to their ^{1}H NMR spectra, in each of which the two isopropoxide groups and the two *N*-methyl groups were symmetry related. The X-ray structure of the titanium dipropoxide complex $Lig^4Ti(OPr)_2$ was recently described.[15i] The X-ray structure of the related zirconium di-*tert*-butoxide complex $Lig^3Zr(O\text{-}t\text{-}Bu)_2$ was solved and is outlined in Figure 4, together with selected bond lengths and angles. The wrapping of the tetradentate [ONNO]-type ligands in these two alkoxo complexes is identical with the one reported for the dibenzylzirconium complex,[15h] i.e., a *fac*−*fac* geometry. The very broad bond angles of the oxygens of the *tert*-butoxy ligand [Zr−O6−C46, 160.9(2); Zr−O7−C42, 166.8(2)] signify a substantial π bonding to the zirconium in these types of complexes as well. In comparison, the respective angles around the propoxo oxygen in $Lig^4Ti(OPr)_2$ were considerably narrower [Ti−O8−C12, 129.2(2); Ti−O9−C15, 129.5(2)].[15i]

We previously observed that titanium complexes of the tripodal amine−tris(phenolate) ligands are rigid chiral conformers having C_3 symmetry at room temperature, as can be detected from the AX spin system of the methylene protons.[15k] When the complexes were heated to high temperature, a coalescence occurred; the barrier for exchange of the titanium complex $Lig^7Ti(O\text{-}i\text{-}Pr)$ was found to be $\Delta G^{\ddagger}_{386\,K} = 74.4$ kJ mol^{-1}. In contrast, the complex $Lig^7Zr(O\text{-}t\text{-}Bu)$ is not rigid at room temperature, and the AX spin system for the methylene protons appears in the ^{1}H NMR spectrum as a very broad singlet. Variable-temperature NMR experiments indicated that coalescence occurred below room temperature, at 278 K (200 MHz). The barrier for the exchange was found to be $\Delta G^{\ddagger}_{278\,K} = 54.2$ kJ mol^{-1}. This result is consistent with the larger radius of the zirconium, leading to a less rigid structure. Crystals of $Lig^7Zr(O\text{-}t\text{-}Bu)$ suitable for X-ray structural analysis were grown from cold pentane; the molecular structure and several selected bond lengths and angles are described in Figure 5. As predicted from the spectroscopic data, $Lig^7Zr(O\text{-}t\text{-}Bu)$ is a mononuclear complex, having slightly distorted trigonal-bipyramidal geometry around the zirconium. The zirconium atom lies 0.33 Å above the plane defined by the three oxygen atoms of the phenolate rings. The very broad Zr−O2−C28 angle, which approaches linearity, signifies a substantial π-donating ability of the axial oxygen to the zirconium metal; however, no substantial decrease in the O−Zr bond length relative to the zirconium complexes described above is observed. A similar structure including an axial isopropoxo group was recently described by Davidson and co-workers and exhibited a similar broad angle of 177.3(3)°.[20a] In comparison, the isopropoxotitanium complex $Lig^7Ti(O\text{-}i\text{-}Pr)$ featured a somewhat narrower angle of 164.4(6)°.[15k]

Lactide Polymerization Activity. The various alkoxotitanium and -zirconium complexes outlined above were employed as catalysts in lactide polymerization. We aimed at unraveling the effect of the structural parameters, i.e., nature of the metal, metal coordination number, ligand type, and ligand substituents on the activity of the corresponding catalysts. For this study, we employed the optically pure monomer (L-lactide) because it is expected to lead to an isotactic polymer, independently of the catalyst being used. The polymerizations were run in the neat monomer at 130 °C, employing a 300:1 ratio of lactide to catalyst. The polymerizations of lactide by the titanium complexes $Lig^1Ti(O\text{-}i\text{-}Pr)_2$−$Lig^7Ti(O\text{-}i\text{-}Pr)$ and those catalyzed by the zirconium complexes $Lig^1Zr(O\text{-}i\text{-}Pr)_2$−$Lig^4Zr(O\text{-}i\text{-}Pr)_2$ and $Lig^7Zr(O\text{-}t\text{-}Bu)$ are summarized in Tables 1 and 2, respectively.

Several structure−activity trends may be drawn from Table 1. The complexes $Lig^1Ti(O\text{-}i\text{-}Pr)_2$ and $Lig^3Ti(O\text{-}i\text{-}Pr)_2$ that correspond to two different ligand families are structural isomers featuring the same phenolate substituents (*tert*-butyl). These two complexes showed similar activities, and the

Table 1. Polymerization Data for the Titanium Complexes[a]

entry	catalyst	time (h)	yield (%)	activity[b]	M_w[c]	M_n[c]	M_w/M_n[c]	M_n(NMR)[d]
1	Lig^{1}Ti(O-*i*-Pr)$_2$	53	31	0.25	9000	7000	1.28	7200
2	Lig^{2}Ti(O-*i*-Pr)$_2$	28	6	0.09	5300	4400	1.21	5200
3	Lig^{3}Ti(O-*i*-Pr)$_2$	29	16	0.23	6000	5400	1.11	3800
4	Lig^{4}Ti(O-*i*-Pr)$_2$	71	19	0.11	8000	6800	1.18	5400
5	Lig^{5}Ti(O-*i*-Pr)	26	55	0.91	26100	18100	1.44	19500
6	Lig^{6}Ti(O-*i*-Pr)[e]	22	55	1.1	23300	17600	1.32	21400
7	Lig^{7}Ti(O-*i*-Pr)	48	43	0.38	16100	12500	1.29	15700

[a] Polymerization conditions: 2 g of L-lactide, oil bath temperature = 130 ± 2 °C, lactide/M = 300, no solvent used. [b] $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$. [c] Measured by GPC relative to polystyrene standards; no correction parameter employed.[21] [d] Calculated from isopropoxy end-group integration in 500-MHz ^{1}H NMR spectra.[22] [e] Only 1.5 g of L-lactide was employed.

Table 2. Polymerization Data for Zirconium Complexes[a]

entry	catalyst	time (h)	yield (%)	activity[b]	M_w[c]	M_n[c]	M_w/M_n[c]	M_n(NMR)[d]
1	Lig^{1}Zr(O-*i*-Pr)$_2$	5.3	21	1.7	14 100	11 900	1.19	nd
2	Lig^{2}Zr(O-*i*-Pr)$_2$	1	75	32.4	22 400	14 300	1.56	22 200
3	Lig^{3}Zr(O-*i*-Pr)$_2$	8	40	2.2	13 200	11 300	1.17	10 600
4	Lig^{4}Zr(O-*i*-Pr)$_2$	1.3	71	27.0	22 700	14 600	1.53	25 300
5	Lig^{7}Zr(O-*t*-Bu)	3	50	6.6	31 700	24 200	1.31	nd

[a] Polymerization conditions: 2 g of L-lactide, oil bath temperature = 130 ± 2 °C, lactide/M = 300, no solvent used. [b] $g_{pol}\ mmol_{cat}^{-1}\ h^{-1}$. [c] Measured by GPC relative to polystyrene standards; no correction parameter employed.[21] [d] Calculated from isopropoxy end-group integration in 500-MHz ^{1}H NMR spectra.[22]

polymers obtained had similar molecular weights and PDIs.[21,22] The relatively narrow PDI values support living polymerization catalysis for both of these complexes (entries 1 and 3). The complexes Lig^{2}Ti(O-*i*-Pr)$_2$ and Lig^{4}Ti(O-*i*-Pr)$_2$ are also structural isomers of these ligand families featuring the same phenolate substituents (Cl). They also feature similar activities (entries 2 and 4). We have recently shown that titanium complexes of these two ligand families exhibited higher activities in the polymerization of linear α-olefins when the *tert*-butyl−phenolate substituents were replaced with electron-withdrawing groups.[15g,j] In contrast, Lig^{2}Ti(O-*i*-Pr)$_2$ and Lig^{4}Ti(O-*i*-Pr)$_2$ exhibited somewhat lower activities in lactide polymerization relative to Lig^{1}Ti(O-*i*-Pr)$_2$ and Lig^{3}Ti(O-*i*-Pr)$_2$; i.e., the electron-withdrawing substituents carry no beneficial effect on the activity of the octahedral titanium complexes. The tripodal complex Lig^{5}Ti(O-*i*-Pr)[15k] exhibited an activity that was an order of magnitude higher than that of the octahedral complexes (entry 5). This activity was somewhat lower than that previously reported by Verkade for that complex.[16a] The new tripodal complex featuring the chloro−phenolate substituents Lig^{6}Ti(O-*i*-Pr) showed a similar activity (entry 6). The tripodal complex featuring the amine−tris(phenolate) ligand bearing the most bulky substituents Lig^{7}Ti(O-*i*-Pr) showed lower activity than the two other tripodal titanium complexes in lactide polymerization. This finding is consistent with the blocking of the metal center that was previously reported to lead to the relative inertness of the complex.[15k]

Several clear-cut structure−activity relationships regarding the lactide polymerization by the zirconium complexes may be drawn from Table 2. Again, complexes of isomeric ligands bearing the same phenolate substituents but belonging to different families showed very similar activities. Thus, Lig^{1}Zr(O-*i*-Pr)$_2$ and Lig^{3}Zr(O-*i*-Pr)$_2$ exhibited very similar activities, and the polymers obtained were of similar molecular weights and PDIs (entries 1 and 3).[21,22] The same similarity was observed for the pair Lig^{2}Zr(O-*i*-Pr)$_2$ and Lig^{4}Zr(O-*i*-Pr)$_2$ (entries 2 and 4). However, in contrast to the titanium series, a clear difference in activities was observed between the two pairs: the activities of the zirconium complexes featuring the chloro−phenolate ligands were 10−20 times higher than those of the other pair. The PDIs of the poly(lactide) samples obtained from the most active zirconium catalysts were broader, signifying a decrease in the living character of the polymerization process.[23] The pentacoordinate zirconium complex bearing *tert*-butyl−phenolate substituents Lig^{7}Zr(O-*t*-Bu) was ca. 3 times more active than the octahedral complexes Lig^{1}Zr(O-*i*-Pr)$_2$ and Lig^{3}Zr(O-*i*-Pr)$_2$ bearing the same phenolate substituents (entry 5 vs entries 1 and 3), signifying that, as was observed for the titanium series, a lower coordination number leads to higher activity in lactide polymerization. Most significantly, a comparison of Tables 1 and 2 shows that, for a given ligand, the activity of the resulting zirconium complex is considerably higher than that of the corresponding titanium complex. The ratio of zirconium-to-titanium activities was ca. 10-fold for the ligands bearing *tert*-butyl substituents, i.e., Lig^{1}M-

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(21) A parameter of 0.58 is recommended for obtaining the correct PLA molecular weights relative to polystyrene standards:[22] Biela, T.; Duda, A.; Penczek, S. *Macromol. Symp*. **2002**, *183*, 1.

(22) Calculating M_n(NMR) by end-group NMR analysis is expected to give correct results when every polymer chain carries the alkoxide group that was originally bound to the metal (e.g., isopropoxide); otherwise, the M_n(NMR) values will be higher than the correct ones.

(23) Examination of Tables 1 and 2 shows that higher molecular weights are obtained from the pentacoordinate complexes relative to the octahedral complexes for both the titanium and zirconium series. A possible explanation for this phenomenon is that a single polymer chain may grow on the former, whereas the two labile groups in the latter may give rise to two growing polymer chains. For example, a PDI of 1.0 and a single polymer chain for every metal center would yield a calculated M_n of 6900 (16% × 300 × 144) for the polymer derived from Lig^{3}Ti(O-*i*-Pr)$_2$ (Table 1, entry 3), whereas the M_n values obtained from GPC (0.58 × 5400 = 3100)[21] and from NMR (3800) are considerably lower, supporting the possibility of two growing polymer chains for the metal center. The broadening of PDIs and lower than expected molecular weights may be indicative of trans-esterification processes.

(OR)$_2$, Lig^{3}M(OR)$_2$, and Lig^{7}M(OR) (M = Zr, Ti; R = *i*-Pr, *t*-Bu) but reached more than 200-fold for Lig^{2}M(O-*i*-Pr)$_2$ and Lig^{4}M(O-*i*-Pr) bearing the chloro substituents. We tentatively attribute the higher activities observed in the zirconium series to the less crowded site for this larger metal center, enabling a facile approach and coordination of the lactide.

Conclusions

Well-defined alkoxotitanium and -zirconium complexes of tetradentate amine−phenolate ligands were synthesized by following several protocols. While hexacoordinate complexes of both titanium and zirconium were easily obtained and pentacoordinate complexes could be easily obtained for titanium, the only pentacoordinate complex that was obtained for zirconium by this route corresponded to the bulkiest ligand. All complexes were found to be active catalysts in lactide polymerization, and the activity was found to depend on the metal, its coordination number, and the substituents on the phenolate rings of the ligands. The structural effects on reactivity were more pronounced in the zirconium series relative to the titanium series. The activities of complexes derived from the dianionic ligands depended on the phenolate substituents but not on the ligand backbone. Pentacoordinate complexes were more active than hexacoordinate complexes bearing the same phenolate substituents. Zirconium complexes were substantially more active than the corresponding titanium complexes. All of these findings indicate that a more open metal site leads to higher activity in lactide polymerization.

Experimental Section

General Procedures. All reactions with air- and/or water-sensitive compounds were carried out under dry nitrogen in a glovebox. Ether and tetrahydrofuran (THF) were purified by reflux and distillation under a dry argon atmosphere from sodium benzophenone. Pentane was washed with HNO_3/H_2SO_4 prior to distillation from sodium benzophenone/tetraglyme. Toluene was refluxed over sodium and distilled. Benzylmagnesium chloride and titanium(IV) isopropoxide were purchased from Aldrich Inc. Tetrabenzylzirconium[24] and tetrakis(dimethylamino)zirconium[25] were synthesized according to published procedures. The complexes Lig^{1}Ti(O-*i*-Pr)$_2$,[15b] Lig^{3}Ti(O-*i*-Pr)$_2$,[26] Lig^{5}Ti(O-*i*-Pr),[15k] Lig^{7}Ti(O-*i*-Pr),[15k] Lig^{1}ZrBn$_2$,[15d] Lig^{2}ZrBn$_2$,[20] and Lig^{4}ZrBn$_2$[15j] were synthesized according to previously published procedures. The NMR data were recorded on Bruker AC-200, Avance AC-400, and ARX-500 spectrometers and referenced to protio impurities in benzene-d_6 (δ 7.15) or tetramethylsilane in $CDCl_3$ (δ 0.00). Elemental analyses were performed in the microanalytical laboratory in the Hebrew University of Jerusalem. PLA molecular weights were determined by gel permeation chromatography (GPC) using TSKgel GMHHR-M and TSKgel G 3000 HHR columns set on a Jasco instrument equipped with a refractive index detector. Molecular weight determination was carried out relative to polystyrene standards using THF (high-performance liquid chromatography grade, distilled and filtered under vacuum prior to use) as the eluting solvent. The X-ray diffraction measurements were performed on a Nonius Kappa CCD diffractometer system, using Mo Kα (λ = 0.7107 Å radiation). The analyzed crystals were embedded within a drop of viscous oil and freeze-cooled to ca. 110 K. The structures were solved by a combination of direct methods and Fourier techniques using the SIR-92 software[27] and were refined by full-matrix least squares with *SHELXL-97*.[28] See Table 3 for crystallographic experimental details.

Table 3. Crystallographic Experimental Details

	Lig^{1}Zr(O-*i*-Pr)$_2$	Lig^{3}Zr(O-*t*-Bu)$_2$	Lig^{7}Zr(O-*t*-Bu)^a
formula	$C_{40}H_{68}N_2O_4Zr$	$C_{46}H_{82}N_2O_5Zr$	$C_{54}H_{87}NO_4Zr$
fw	732.18	834.36	905.47
a (Å)	12.6310(3)	12.3186 (2)	14.5900(4)
b (Å)	19.6250(6)	15.3071 (2)	14.5900(4)
c (Å)	16.5810(3)	25.6619 (4)	25.4060(7)
α (deg)	90.00	90.00	90.00
β (deg)	96.5500(15)	93.8574 (7)	90.00
γ (deg)	90.00	90.00	90.00
cryst syst	monoclinic	monoclinic	tetragonal
space group	*P*21/*c*	*P*21/*c*	P4$_1$
V (Å^3)	4083.33(17)	4827.90 (13)	5408.1(3)
D_c (g cm^{-3})	1.191	1.148	1.112
μ (cm^{-1})	0.308	0.269	0.244
Z	4	4	4
no. of measd reflns	9778	11413	8708
no. of reflns [$I > 2\sigma(I)$]	6066	6910	6793
R1 [$I > 2\sigma(I)$]	0.0588	0.0621	0.0837
wR2 [$I > 2\sigma(I)$]	0.1414	0.1448	0.2066
GOF	0.963	1.058	0.993

[a] The structure was refined as a racemic twin with a Flack parameter of 0.39(8) based on unmerged data, indicating that this compound has not been resolved upon crystallization and is consistent with the dynamic conformation of this compound.

Complex Lig^{2}Ti(O-*i*-Pr)$_2$. A solution of Lig^{2}H$_2$ (131 mg, 0.3 mmol) in ether (2 mL) was added dropwise to a solution of Ti(O^i-Pr)$_4$ (85 mg, 0.3 mmol) in ether (2 mL) at room temperature. The color changed immediately from colorless to yellow. The reaction mixture was stirred for 2 h and the volatiles were removed under reduced pressure. The crude product was washed with pentane to give Lig^{2}Ti(O-*i*-Pr)$_2$ as a yellow solid in a final yield of 93%. ^{1}H NMR (200 MHz, C_6D_6): δ 7.34 (d, *J* = 2.6 Hz, 2H), 6.72 (d, *J* = 2.6 Hz, 2H), 5.16 (hept, *J* = 6.1 Hz, 1H), 4.66 (hept, *J* = 6.1 Hz, 1H), 4.03 (d, *J* = 13.4 Hz, 2H), 2.48 (d, *J* = 13.5 Hz, 2H), 2.00 (s, 6H), 1.73 (m, 2H), 1.48 (d, *J* = 6.1 Hz, 6H), 1.40 (m, 2H), 1.06 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 158.6 (2C, *C*, arom), 130.7, 128.8 (4C, *C*H, arom), 127.1, 123.4, 121.8 (6C, *C*, arom), 80.4, 79.3 (2C, O*C*H(CH$_3$)$_2$), 64.1 (2C, *C*H$_2$), 58.7, 51.4 (2C, *C*H$_2$), 49.2 (2C, N(*C*H$_3$)$_2$), 26.7, 26.6 (4C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{24}H_{32}Cl_4N_2O_4Ti$: C, 47.88; H, 5.36; N, 4.65. Found: C, 48.52; H, 5.39; N, 4.62.

Complex Lig^{4}Ti(O-*i*-Pr)$_2$. The complex was prepared analogously to Lig^{2}Ti(O-*i*-Pr)$_2$ from Lig^{4}H$_2$ (92 mg, 0.21 mmol) and Ti(Oi-Pr)$_4$ (60 mg, 0.21 mmol). Prior to evaporation, the reaction mixture was filtered through Celite. Lig^{4}Ti(O-*i*-Pr)$_2$ was obtained as a yellow solid in a final yield of 57%. ^{1}H NMR (200 MHz, C_6D_6): δ 7.33 (d, *J* = 2.6 Hz, 2H), 6.61 (d, *J* = 2.6 Hz, 2H), 5.19 (hept, *J* = 6.1 Hz, 2H), 4.31 (d, *J* = 13.8 Hz, 2H), 2.40 (d, *J* = 13.9 Hz, 2H), 2.19 (d, *J* = 9.4 Hz, 2H), 1.96 (s, 6H), 1.33 (d, *J* = 6.1 Hz, 6H), 1.25 (d, *J* = 6.1 Hz, 6H), 0.88 (d, *J* = 9.5 Hz, 2H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 157.3 (2C, *C*, arom), 130.0, 129.0

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(4C, *C*H, arom), 127.0, 123.7, 122.0 (6C, *C*, arom), 79.9 (2C, O*C*H(CH$_3$)$_2$), 64.3 (2C, *C*H$_2$), 51.9 (2C, *C*H$_2$), 47.3 (2C, N*C*H$_3$), 27.0, 26.5 (4C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{24}H_{32}Cl_4N_2O_4Ti$: C, 47.88; H, 5.36; N, 4.65. Found: C, 48.19; H, 5.29; N, 4.66.

Complex Lig^{6}Ti(O-*i*-Pr). The complex was prepared analogously to Lig^{2}Ti(O-*i*-Pr)$_2$ from Lig^{6}H (66 mg, 0.12 mmol) and Ti(O-*i*-Pr)$_4$ (35 mg, 0.12 mmol). Lig^{6}Ti(O-*i*-Pr) was obtained as an orange solid in quantitative yield. ^{1}H NMR (400 MHz, C_6D_6): δ 7.17 (d, $J = 2.5$ Hz, 3H), 6.43 (d, $J = 2.5$ Hz, 3H), 5.20 (hept, $J = 6.1$ Hz, 1H), 2.50 (v br s, 6H), 1.60 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (100.58 MHz, C_6D_6): δ 157.9 9 (3C, *C*, arom), 130.0, 128.7 (6C, *C*H, arom), 127.0, 125.8, 123.1 (9C, *C*, arom), 85.1 (1C, O*C*H(CH$_3$)$_2$), 57.8 (3C, *C*H$_2$), 25.9 (2C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{24}H_{19}Cl_6NO_4Ti$: C, 44.62; H, 2.96; N, 2.17. Found: C, 44.88; H, 3.20; N, 1.99.

Complex Lig^{1}Zr(O-*i*-Pr)$_2$. A solution of *i*-PrOH (22 mg, 0.36 mmol) in ether (2 mL) was added dropwise to a solution of Lig^{1}ZrBn$_2$ (143 mg, 0.18 mmol) in ether (2 mL) at room temperature. The color changed immediately from yellow to colorless. The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure to give Lig^{1}Zr(O-*i*-Pr)$_2$ as a white solid in a final yield of 89%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.29 (d, $J = 2.5$ Hz, 2H), 7.05 (d, $J = 2.5$ Hz, 2H), 4.62 (hept, $J = 6.0$ Hz, 1H), 4.42 (d, $J = 13.1$ Hz, 2H), 4.43 (hept, $J = 6.1$ Hz, 1H), 2.92 (d, $J = 13.1$ Hz, 2H), 2.28 (m, 2H), 1.88 (s, 6H), 1.72 (s, 18H), 1.69 (m, 2H), 1.49 (d, $J = 6.0$ Hz, 6H), 1.43 (s, 18H), 1.22 (d, $J = 6.0$ Hz, 6H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 160.4, 139.3, 137.0, 129.0 (8C, *C*, arom), 125.6, 125.3 (4C, *C*H, arom), 72.1, 72.0 (2C, O*C*H(CH$_3$)$_2$), 66.2 (2C, *C*H$_2$), 59.7, 51.2 (2C, *C*H$_2$), 49.3 (2C, N(*C*H$_3$)$_2$), 36.3, 35.0 (4C, *C*(CH$_3$)$_3$), 32.8, 31.4 (12C, C(*C*H$_3$)$_3$), 28.7, 28.2 (4C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{40}H_{68}N_2O_4Zr$: C, 65.61; H, 9.36; N, 3.83. Found: C, 66.11; H, 9.16; N, 3.96.

Complex Lig^{2}Zr(O-*i*-Pr)$_2$. The complex was prepared analogoulsy to Lig^{1}Zr(O-*i*-Pr)$_2$ from *i*-PrOH (16 mg, 0.26 mmol) and Lig^{2}ZrBn$_2$ (92 mg, 0.13 mmol). Prior to evaporation, the reaction mixture was filtered through Celite. Lig^{2}Zr(O-*i*-Pr)$_2$ was obtained as a white solid in a quantitative yield. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.33 (d, $J = 2.6$ Hz, 2H), 6.71 (d, $J = 2.5$ Hz, 2H), 4.53 (hept, $J = 6.1$ Hz, 1H), 4.30 (hept, $J = 6.0$ Hz, 1H), 4.19 (d, $J = 13.3$ Hz, 2H), 2.40 (d, $J = 13.3$ Hz, 2H), 1.90 (s, 6H), 1.68 (m, 2H), 1.47 (d, $J = 6.1$ Hz, 6H), 1.27 (m, 2H), 1.16 (d, $J = 6.1$ Hz, 6H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 157.5 (2C, *C*, arom), 131.2, 129.4 (4C, *CH*, arom), 127.1, 124.6, 121.9 (6C, *C*, arom), 73.1, 72.7 (2C, O*C*H(CH$_3$)$_2$), 64.0, 59.0, 50.1 (4C, *C*H$_2$), 48.1 (2C, N*C*H$_3$), 28.0, 27.8 (4C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{24}H_{34}Cl_4N_2O_4Zr$: C, 44.65; H, 5.00; N, 4.34. Found: C, 45.28; H, 5.10; N, 4.34.

Complex Lig$^2{}_2$Zr. A solution of Lig^{2}H$_2$ (80 mg, 0.18 mmol) in THF (2 mL) was added to a solution of ZrCl$_4$ (21 mg, 0.09 mmol) and Et$_3$N (0.36 mmol) in THF (2 mL) at room temperature. White solid precipitated immediately. The reaction mixture was stirred for 2 h and filtered through Celite, and the volatiles were removed under reduced pressure to give Lig$^2{}_2$Zr in a final yield of 97%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.34 (d, $J = 2.6$ Hz, 2H), 7.21 (d, $J = 2.6$ Hz, 2H), 6.83 (d, $J = 2.6$ Hz, 2H), 6.56 (d, $J = 2.6$ Hz, 2H), 5.84 (d, $J = 13.7$ Hz, 2H), 4.53 (d, $J = 13.6$ Hz, 2H), 2.58 (d, $J = 13.7$ Hz, 2H), 2.33 (d, $J = 13.7$ Hz, 2H), 2.12−1.94 (16H), 1.41 (dd, $J_1 = 13.6$ Hz, $J_2 = 2.5$ Hz, 2H), 1.00 (dd, $J_1 = 13.6$ Hz, $J_2 = 2.6$ Hz, 2H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 156.48, 155.28 (4C, *C*, arom), 130.01, 130.00, 128.96 (6C, *C*H, arom), 128.97, 128.72, 123.27, 122.38, 121.83, 121.73 (12C, *C*, arom), 64.98, 62.85 (4C, *C*H$_2$, AB system), 59.04, 52.16 (4C, *C*H$_2$), 49.86, 45.58 (4C, N(*C*H$_3$)$_2$).

Complex Lig^{3}Zr(NMe$_2$)$_2$. A solution of Lig^{3}H$_2$ (100 mg, 0.19 mmol) in ether (2 mL) was added dropwise to a solution of Zr(NMe$_2$)$_4$ (51 mg, 0.19 mmol) in ether (2 mL) at room temperature. The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure to give Lig^{3}Zr(NMe$_2$)$_2$ as a bright-yellow solid in a final yield of 89%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.62 (d, $J = 2.5$ Hz, 2H), 6.93 (d, $J = 2.5$ Hz, 2H), 4.34 (d, $J = 13.3$ Hz, 2H), 3.35 (s, 12H), 3.11 (d, $J = 8.4$ Hz), 2.71 (d, $J = 13.6$ Hz, 2H), 1.93 (s, 6H), 1.76 (s, 18H), 1.38 (s, 18H), 1.02 (d, $J = 9.0$ Hz, 2H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 157.9, 139.9, 137.4 (6C, *C*, arom), 125.5 (2C, *CH*, arom), 125.4 (2C, *C*, arom), 124.5 (2C, *C*H, arom), 65.3, 52.1 (4C, *C*H$_2$), 46.8 (2C, N*C*H$_3$), 46.0 (4C, N(*C*H$_3$)$_2$), 35.8, 34.4 (4C, *C*(CH$_3$)$_3$), 32.0, 30.7 (12C, C(*C*H$_3$)$_3$).

Complex Lig^{3}Zr(O-*i*-Pr)$_2$. The complex was prepared analogously to Lig^{1}Zr(O-*i*-Pr)$_2$ from *i*-PrOH (20 mg, 0.34 mmol) and Lig^{3}Zr(NMe$_2$)$_2$ (119 mg, 0.17 mmol). Lig^{3}Zr(O-*i*-Pr)$_2$ was obtained as a white solid in a final yield of 90%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.59 (d, $J = 2.5$ Hz, 2H), 6.90 (d, $J = 2.5$ Hz, 2H), 4.44 (d, $J = 13.2$ Hz, 2H), 4.45 (hept, $J = 6.0$ Hz, 2H), 2.82 (d, $J = 9.4$ Hz, 2H), 2.73 (d, 13.3 Hz, 2H), 2.05 (s, 6H), 1.76 (s, 18H), 1.39 (s, 18H), 1.31 (d, $J = 6.0$ Hz, 6H), 1.27 (d, $J = 6.0$ Hz, 6H), 1.04 (d, $J = 9.5$ Hz, 2H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 159.4, 139.3, 137.8 (6C, *C*, arom), 125.4, 124.8 (4C, *C*H, arom), 124.2 (2C, *C*, arom), 72.1 (2C, O*C*H(CH$_3$)$_2$), 65.9, 52.1 (4C, *C*H$_2$), 47.5 (2C, N*C*H$_3$), 36.3, 35.0 (4C, *C*(CH$_3$)$_3$), 32.8, 31.2 (12C, C(*C*H$_3$)$_3$), 28.4, 28.3 (4C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{40}H_{68}N_2O_4Zr$: C, 65.61; H, 9.36; N, 3.83. Found: C, 65.86; H, 9.26; N, 3.95.

Complex Lig^{4}Zr(O-*i*-Pr)$_2$. The complex was prepared analogously to Lig^{1}Zr(O-*i*-Pr)$_2$ from *i*-PrOH (23 mg, 0.38 mmol) and Lig^{4}ZrBn$_2$ (136 mg, 0.19 mmol). Prior to evaporation, the reaction mixture was filtered through Celite. Lig^{4}Zr(O-*i*-Pr)$_2$ was obtained as a white solid in a final yield of 91%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.34 (d, $J = 2.6$ Hz, 2H), 6.57 (d, $J = 2.6$ Hz, 2H), 4.46 (hept, $J = 6.1$ Hz, 2H), 4.22 (d, $J = 13.6$ Hz, 2H), 2.32 (d, $J = 13.7$ Hz, 2H), 2.14 (d, $J = 9.7$ Hz, 2H), 1.96 (s, 6H), 1.35 (d, $J = 6.1$ Hz, 6H), 1.31 (d, $J = 6.1$ Hz, 6H), 0.82 (d, $J = 9.7$ Hz, 2H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 156.5 (2C, *C*, arom), 130.5, 129.0 (4C, *C*H, arom), 126.9, 124.9, 121.9 (6C, *C*, arom), 73.0 (2C, O*C*H(CH$_3$)$_2$), 63.6, 51.5 (4C, *C*H$_2$), 46.1 (2C, N*C*H$_3$), 27.9 (4C, OCH(*C*H$_3$)$_2$). Anal. Calcd for $C_{24}H_{32}Cl_4N_2O_4Zr$: C, 44.65; H, 5.00; N, 4.34. Found: C, 44.92; H, 4.99; N, 4.16.

Complex Lig^{7}Zr(O-*t*-Bu). A solution of Lig^{7}H$_2$ (100 mg, 0.15 mmol) in ether (2 mL) was added dropwise to a solution of Zr(O-*t*-Bu)$_4$ (57 mg, 0.15 mmol) in ether (2 mL) at room temperature. The color changed from clear yellow to white, and precipitation of a white solid was observed. The reaction mixture was stirred for 2 h, and the volatiles were removed under reduced pressure. The crude product was washed with pentane to give Lig^{7}Zr(O-*t*-Bu) as a white solid in a final yield of 63%. ^{1}H NMR (C_6D_6, 200 MHz): δ 7.46 (d, $J = 2.4$ Hz, 3H), 6.84 (d, $J = 2.4$ Hz, 3H), 3.25 (v br s, 6H), 1.73 (s, 9H), 1.64 (s, 27H), 1.33 (s, 27H). ^{13}C NMR (50.29 MHz, C_6D_6): δ 142.5, 137.1, 129.0 (9C, *C*, arom), 125.9 (3C, *C*H, arom), 125.2 (3C, *C*, arom), 124.4 (3C, *C*H, arom), 60.6 (1C, O*C*(CH$_3$)$_3$), 36.1, 35.1 (6C, *C*(CH$_3$)$_3$), 34.1 (3C, OC(*C*H$_3$)$_3$), 32.6, 30.7 (18C, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{49}H_{75}NO_4Zr$: C, 70.62; H, 9.07; N, 1.68. Found: C, 71.12; H, 9.21; N, 1.80.

General Polymerization Procedure. Lactide bulk polymerizations were carried out by heating the lactide (2 g, 13.9 mmol) and the catalyst in a 300:1 ratio in a closed glass vessel to 130 °C for a given period of time. The reaction was terminated by the addition of 5 mL of methanol. The polymer so obtained was dissolved in dichloromethane, and an excess of methanol was added. The resulting reprecipitated polymer was filtered, washed with methanol, dried in air, and weighed for calculating the yield. ^{1}H NMR analysis of the PLA samples (500 MHz, $CDCl_3$) indicated that no epimerization occurred during the polymerization and that the polymer was isotactic, as is evident from a quartet (5.16 ppm) and a doublet (1.57 ppm) in a ratio of 1:3. An isopropoxide end group was observed for all polymers resulting from the catalysts bearing isopropoxide labile groups, with its diastereotopic methyl groups appearing as two partially overlapping doublets (1.23 and 1.25 ppm). In contrast, no appreciable peaks attributable to an amine−phenolate ligand could be detected in the ^{1}H NMR spectra of the polymer samples. These findings indicate that the M−O−*i*-Pr bond and not the M−O(ligand) bond is the site of initiation and that the polymer is linear. Molecular weight analysis was done by GPC employing the setup described above and by isopropoxide end-group analysis.[22]

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Supporting Information Available: ^{1}H NMR spectrum of a typical PLA sample prepared with the above catalysts and X-ray crystallographic files (in CIF format) for the structural determinations of complexes $Lig^1Zr(O\text{-}i\text{-}Pr)_2$, $Lig^3Zr(O\text{-}t\text{-}Bu)_2$, and $Lig^7Zr(O\text{-}t\text{-}Bu)$. This material is available free of charge via the Internet at http://pubs.acs.org.

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