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Synthesis, Characterization, and Lactide Polymerization Activity of Group 4 Metal Complexes Containing Two Bis(phenolate) Ligands

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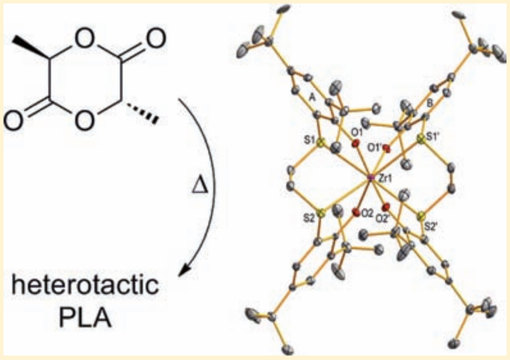
Supporting Information

ABSTRACT: A series of group 4 metal complexes **Zr-(1)$_2$**, **Zr-(2)$_2$**, **Zr-(3)$_2$**, **Zr-(4)$_2$**, **Zr-(5)$_2$**, **Hf-(1)$_2$**, and **Hf-(4)$_2$** containing two bridged bis(phenolate) ligands of the (OSSO)-type were prepared by the reaction of the corresponding bis(phenol) and group 4 metal precursor MX_4 (X = O^{i}Pr, CH_2Ph) and isolated as robust, colorless crystals. NMR spectra indicate D_2 symmetry, in agreement with the solid state structure determined by single crystal X-ray diffraction study of the complexes **Zr-(1)$_2$**, **Hf-(1)$_2$**, **Zr-(3)$_2$**, **Zr-(4)$_2$**, and **Zr-(5)$_2$**. The complexes with the 1,4-dithiabutanediyl bridged ligands exhibit a highly symmetric coordination around the metal center. The introduction of the rigid *trans*-1,2-cyclohexanediyl bridged ligands led to a distorted coordination around the metal center in **Zr-(4)$_2$** and **Zr-(5)$_2$** when the *ortho* substituent is *tert*-butyl and the *para* substituent is larger than methyl. The complexes **Zr-(1)$_2$**, **Zr-(2)$_2$**, **Zr-(3)$_2$**, **Zr-(4)$_2$** as well as **Hf-(1)$_2$** and **Hf-(4)$_2$** initiated the ring-opening polymerization of *meso*-lactide at 100 °C to give heterotactic polylactide with pronounced heterotacticity (>70%) and varying polydispersity ($1.05 < M_w/M_n < 1.61$). As shown by kinetic studies, zirconium complex **Zr-(1)$_2$** polymerized *meso*-lactide faster than the homologous hafnium complex **Hf-(1)$_2$**.



INTRODUCTION

Polylactide (PLA) is a biorenewable, biocompatible, and biodegradable polyester produced by ring-opening polymerization (ROP) of lactide. Polylactide possesses versatile physical properties and has been widely used in biomedical applications such as media for controlled drug release.[1−4] ROP of lactide by single-site initiators is the most efficient route to PLAs with predictable molecular weight and narrow molecular weight distribution. The past two decades have witnessed the rapid development of initiators for the improved control of polymer stereochemistry which is one of the critical factors in determining the physical and mechanical properties of a polymeric material.[5−8] Various initiators with good stereocontrol during the propagation step have been introduced.[9−15]

Postmetallocene complexes of group 4 metals containing multidentate ligands, widely studied as single-site catalyst precursors for the polymerization of α-olefins,[16,17] could offer versatile platforms for stereoselective initiators for ROP of lactide. Davidson et al.,[18a] Eisen et al.,[18b] and Kobayashi et al.[18c] have recently reported complexes of titanium(IV) and zirconium(IV) with two bidentate ligands, while Harada et al.,[19a] and Mountford et al.,[19b,c] obtained group 4 complexes with a tridentate ligand. Titanium(IV) and zirconium(IV) complexes with two (ONO)-[23a] or (OSO)-type[23b] ligands were also reported. Kol et al.[20a−d] introduced a series of group 4 metal complexes with a tetradentate ligand, whereas Rheingold et al.[20e] described zirconium(IV) complexes with two salen-type (ONNO) ligands. Davidson et al. reported a zirconium complex with two (ONNO) ligands as the only isolable product of the reaction of [Zr(O^{i}Pr)$_4$(^{i}PrOH)] and varying amounts of (ONNO) ligand precursor along with its application in the ROP of *rac*-lactide monomer.[13d] We have previously found that structurally defined initiators based on group 4 metal complexes containing one bis(phenolate) ligand of (OSSO)-type initiate the ring-opening polymerization of lactide monomers efficiently and in a controlled fashion.[21] We report here the synthesis and characterization of group 4 metal complexes containing two bis(phenolate) (OSSO)-type ligands and their activity in lactide polymerization. These coordinatively saturated complexes (VEN ≥ 16) are thermodynamically favored and easily form from mono(ligand) complexes containing one bis(phenolate) ligand through ligand exchange or during unintentional hydrolysis.[20f]

RESULTS AND DISCUSSION

Synthesis and Characterization. Bis(phenols) and complexes discussed in this work are shown in Scheme 1. Complexes **Zr-(1)$_2$**, **Zr-(2)$_2$**, **Zr-(3)$_2$** were synthesized by the reaction of [Zr(O^{i}Pr)$_4$(^{i}PrOH)] with 2 equiv of the linked bis(phenol) (H$_2$)-**1**,[17a] (H$_2$)-**2**,[17b] or (H$_2$)-**3**[17c] in toluene at 50 °C. Complex **Zr-(4)$_2$** was synthesized by the reaction of

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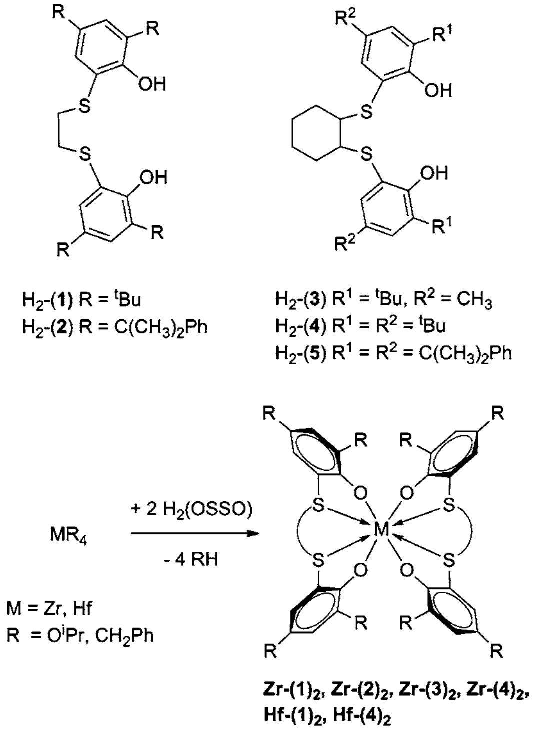
Scheme 1. Bis(phenols) and Bis(ligand) Complexes of Zirconium and Hafnium



$[Zr(CH_2Ph)_4]$ with 2 equiv of racemic (H_2)-**4**[17d] in toluene at 50 °C for 13 h. Complex **Zr-(5)$_2$** had originally been obtained as single crystals during the crystallization of [(**5**)Zr(*O*-acetylmandelate)$_2$]. The complexes **Hf-(1)$_2$** and **Hf-(4)$_2$** were synthesized by the reaction of 2 equiv of proligand (H_2)-**1** or (H_2)-**4** with $[Hf(O^iPr)_4(^iPrOH)]$ in toluene at 50 or 100 °C for 16 h, respectively. All complexes except for **Zr-(5)$_2$** were isolated as colorless crystals in 65−85% yield and are soluble in common organic solvents. They are thermally robust (mp = 210.7 °C for **Zr-(1)$_2$**; mp = 204.9 °C for **Hf-(1)$_2$**) and stable against air and moisture, even in most solvents at elevated temperatures.

The ^1H NMR spectrum of complex **Zr-(1)$_2$** in benzene-d_6 is in agreement with high symmetry and features four doublets for the eight aryl-C*H* protons at 7.49, 7.39, 7.30, and 7.11 ppm ($^4J_{HH}$ = 2.5 Hz).

The eight protons of the two bridges give two multiplets between 2.20 and 2.30 and between 2.40 and 2.55 ppm. The $^{13}C\{^1H\}$ NMR spectrum shows two signals for the four C1-O at 166.63 and 166.45 ppm. The four carbon atoms of the bridge are observed as two signals at 38.36 and 38.11 ppm. The ^1H NMR spectrum of **Hf-(1)$_2$** shows similar resonances for the aromatic and the *tert*-butyl protons. The bridge protons are observed as two multiplets between 2.15 and 2.55 ppm.

In complex **Zr-(2)$_2$** the bridge protons appear as two doublets ($^3J_{HH}$ = 10.0 Hz); the CH_3 protons give rise to four singlets. The ^1H NMR spectrum of complex **Zr-(3)$_2$** in chloroform-d_1 shows two doublets for the eight aryl-C*H* protons at 6.95 and 6.78 ppm ($^4J_{HH}$ = 1.6 Hz). The eight CH_2 protons of the *trans*-1,2-cyclohexanediyl bridge are observed as four multiplets at 0.80−2.05 ppm. Four C*H* protons of the *trans*-1,2-cyclohexanediyl bridge are observed as multiplets at 2.20 to 2.25 ppm. Two sharp singlets at 1.47 and at 2.15 ppm are due to the CH_3 protons of the *tert*-butyl and the methyl groups.

In the ^1H NMR spectrum of complex **Zr-(4)$_2$** the four C*H* protons of the *trans*-1,2-cyclohexanediyl bridge are observed as multiplets at 2.50−2.61 ppm. The ^1H NMR spectrum of complex **Zr-(5)$_2$** features the diagnostic pattern with three singlets for the 16 CH_3 groups of the 8 C(CH_3)$_2$Ph substituents at 2.08, 1.95, and 1.56 ppm. The four methylene protons appear as a multiplet between 1.83 and 1.88 ppm. The ^1H NMR spectrum of **Hf-(4)$_2$** is similar to the spectrum of complex **Hf-(1)$_2$** with additional signals for the *trans*-1,2-cyclohexanediyl bridge. The ^1H NMR spectrum in benzene-d_6 features four doublets for the eight aryl-C*H* at 7.59 and 7.21 ppm ($^4J_{HH}$ = 2.5 Hz). The eight *tert*-butyl groups appear as four singlets, the CH_2 protons of the *trans*-1,2-cyclohexanediyl bridge are multiplets from 0.37 to 1.83 and the C*H* protons are detected as a doublet between 2.43 and 2.58 ppm.

Crystallography. Colorless crystals of complexes **Zr-(1)$_2$** and **Hf-(1)$_2$** were grown from a benzene or toluene solution. The molecular structures of **Zr-(1)$_2$** and **Hf-(1)$_2$** are shown in Figure 1 and Supporting Information, Figure S8. Selected average bond lengths and angles for the complexes are collated in Table 1. The X-ray structures reveal that the metal center in each complex **Zr-(1)$_2$** and **Hf-(1)$_2$** shows an eight-coordinated metal center with two tetradentate bis(phenolate) (OSSO)-type ligands. The coordination geometry can be regarded as a

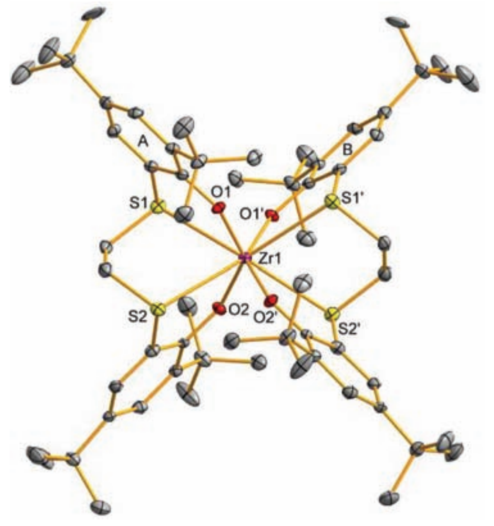


Figure 1. Molecular structure of **Zr-(1)$_2$**. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 2.041(3), Zr1−O2 2.040(3), Zr1−S1 2.9422(11), Zr1−S2 2.9279(11) O1−Zr1−O2 138.95(10), S1−Zr1−S2 72.28(3).

Table 1. Average Bond Lengths (Å) and Angles (deg) for M-(1)$_2$

	compound	
	Zr-(1)$_2$	**Hf-(1)$_2$**
	Bond Lengths	
M−O	2.041	2.034
M−S	2.935	2.906
	Bond Angles	
O1−M−O2	138.95(10)	139.55(14)
S1−M−S2	72.28(3)	72.53(4)

distorted square antiprism with point group D_2. The two oxygen donors of the bis(phenolate) ligand are arranged *trans* to each other. The average M−O bond distances for **Zr-(1)**$_2$ and **Hf-(1)**$_2$ are similar (2.041 Å and 2.034 Å respectively) and correspond to the literature range for four coordinated complexes with phenolate ligands (Zr(IV), 1.948−2.047 Å,[20−212223] Hf(IV), 1.966−2.074 Å[16c,24]). The average Zr−S bond length (2.936 Å) is slightly longer than the range reported in the literature (2.837−2.877 Å).[21,23e]

Colorless crystals of complexes **Zr-(3)**$_2$, **Zr-(4)**$_2$, and **Zr-(5)**$_2$ were grown from a hexane solution. The molecular structures of **Zr-(3)**$_2$ and **Zr-(5)**$_2$ are depicted in the Supporting Information, Figure S9 and **Zr-(4)**$_2$ in Figure 2. Selected average bond lengths and angles for the complexes are collated in Table 2.

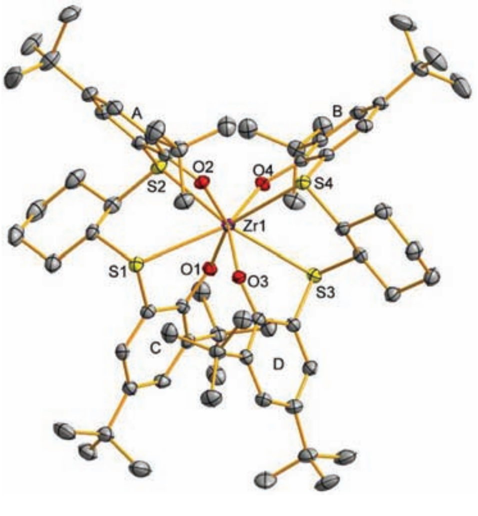


Figure 2. Molecular structure of **Zr-(4)**$_2$. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−O1 2.0574(15), Zr1−O2 2.0275(15), Zr1−O3 2.0528(15), Zr1−O4 2.0238(15), Zr1−S1 2.9398(6), Zr1−S2 2.8742(6), Zr1−S3 2.9493(6), Zr1−S4 2.8488(6); O1−Zr1−O2 142.77(6) and S1−Zr1−S2 69.602(17).

Table 2. Average Bond Lengths (Å) and Angles (deg) for Zr-(L)$_2$

	compound		
	Zr-(3)$_2$	**Zr-(4)**$_2$	**Zr-(5)**$_2$
Bond Lengths			
Zr−O	2.050	2.040	2.074
Zr−S	2.838	2.903	2.795
Bond Angles			
O1−Zr−O2	139.15(9)	142.77(6)	141.89(6)
S1−Zr−S2	73.03(3)	69.602(17)	73.92(2)

The molecular structures in the solid state reveal that the metal center in each complex adopts a distorted square antiprism geometry, isostructural to the 1,4-dithiabutanediyl bridged complexes **Zr-(1)**$_2$ and **Hf-(1)**$_2$. The racemic complexes have the (*RR,RR*) or (*SS,SS*) configuration of the ligands and both enantiomers are present in the unit cell. In the complex **Zr-(3)**$_2$, the average Zr−O bond length (2.050 Å) is similar to the one derived from the mono(ligand) dibenzyl complex [(**5**)Zr(CH$_2$Ph)$_2$] (Zr−O 2.0182 Å). The O1−Zr1−O2 angle of 139.15° is smaller (O−Zr−O is 149.36° in [(**5**)Zr(CH$_2$Ph)$_2$]), although **Zr-(3)**$_2$ is eight-coordinate and the benzyl complex is six-coordinate.[25] The average Zr−O bond length is similar in all the zirconium complexes (2.050 Å for **Zr-(3)**$_2$, 2.040 Å for **Zr-(4)**$_2$ and 2.074 Å for **Zr-(5)**$_2$, respectively) and close to the range reported for tetravalent zirconium complexes (1.948−2.047 Å).[21,23] However, the average Zr−S bond length (2.903 Å for **Zr-(4)**$_2$) is slightly longer than in the other zirconium complexes (2.838 Å for **Zr-(3)**$_2$ and 2.795 Å for **Zr-(5)**$_2$ respectively) and longer than the literature values.[21,23e] For complexes **Zr-(4)**$_2$ and **Zr-(5)**$_2$, the coordination geometry of the metal center in the solid state is of lower symmetry than for **Zr-(3)**$_2$. Given that the only difference between proligand H$_2$-**3** and H$_2$-**4** is the *para*-substituent on the phenolate rings (H$_2$-**3** R_{para} = Me, H$_2$-**4** R_{para} = *tert*-butyl), we attribute this finding to the larger steric stress induced by the *tert*-butyl group. The lower symmetry of **Zr-(4)**$_2$ and **Zr-(5)**$_2$ is also highlighted by the distance between the opposing phenyl rings A and B (ctA-ctB 6.873 Å for **Zr-(4)**$_2$ and **Zr-(5)**$_2$ ctA-ctB 6.288 Å). This distance is far larger than in the undistorted case **Zr-(3)**$_2$ (ctA-ctB 5.392 Å). The S1−Zr−S2 angles in **Zr-(4)**$_2$ (69.60(2)°) are smaller than in the other zirconium complexes (73.03(3)° for **Zr-(3)**$_2$ and 73.92(2)° for **Zr-(5)**$_2$ respectively).

Polymerization of *meso*-Lactide. When *meso*-lactide is polymerized under ring-opening using metal initiators, either syndiotactic or heterotactic polylactide can be formed (Scheme 2).[21a] The bis(bis(phenolate)) complexes of zirconium and hafnium (except for **Zr-(5)**$_2$) were tested in the polymerization of *meso*-lactide in toluene at 100 °C over a period of 48 h. The results are shown in Table 3. With an initiator/monomer ratio of 1:100, the polylactides obtained were highly heterotactic (>70%) with varying polydispersities (1.05 < M_w/M_n < 1.61). The efficiency was in the range of 0.38 < *f* < 0.68, indicating that not all catalyst molecules are active in the ROP of *meso*-

Scheme 2. Ring-Opening Polymerization of *meso*-Lactide

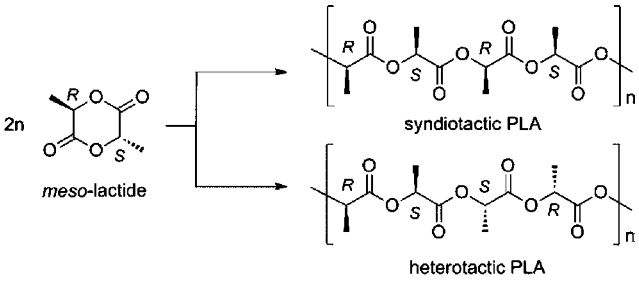


Table 3. Polymerization Data of *meso*-Lactide[a]

entry	init.	conv.[b] [%]	$M_{n,exp}$[c] [g/mol]	f[d]	M_w/M_n[c]	P_s[e]
1	**Zr-(1)**$_2$	79	17 000	0.67	1.33	0.18
2	**Zr-(2)**$_2$	81	22 500	0.52	1.29	0.10
3[f]	**Hf-(1)**$_2$	40	8 537	0.68	1.61	0.26
4	**Zr-(3)**$_2$	75	23 250	0.46	1.48	0.11
5	**Zr-(4)**$_2$	91	20 500	0.64	1.05	0.21
6	**Hf-(4)**$_2$	67	25 500	0.38	1.36	0.27

[a] Polymerization conditions: $[LA]_0/[Init]_0$ = 100, $[LA]_0$ = 0.520 M, 48 h, toluene, 2 mL, 100 °C. [b] Conversion of monomer (($[LA]_0$ − $[LA]_t$)/$[LA]_0$). [c] Measured by GPC with polystyrene standards in THF.[15] [d] Efficiency calculated using $f = M_{n,theo}/M_{n,exp}$ ($M_{n,theo} = [LA]_0/[init]_0 \times M_{LA} \times$ conv.). [e] P_s is the probability of a new *s* dyad.[26] [f] In C_6D_6, 0.5 mL.

lactide. Using complexes **Zr-(2)**$_2$ and **Zr-(3)**$_2$, the heterotacticity reached 90%, but the control over the molecular weight was lost ($f = 0.52$ for **Zr-(2)**$_2$, entry 2; $f = 0.46$ for **Zr-(3)**$_2$, entry 4). These values are comparable to those reported when titanium mono(bis(phenolate)) complexes were used.[21b] Upon changing the metal from zirconium in **Zr-(1)**$_2$, to hafnium in **Hf-(1)**$_2$, the heterotacticity of the polymer decreased from $P_s = 0.18$ to $P_s = 0.26$. The increased steric bulk of the *para*-substituents on the aromatic rings appear to limit transesterification reactions. The polymers obtained with **Zr-(4)**$_2$ have lower polydispersities than those polymerized using **Zr-(3)**$_2$ ($M_w/M_n = 1.05$ versus 1.48). The efficiency was $f = 0.64$ and 0.46, respectively. These values are lower than those previously reported for zirconium mono(bis(phenolate)) complexes ($f < 1.04$).[21c] At 100 °C and in moist benzene-d_6, complex **Hf-(1)**$_2$ was shown to be still active in the polymerization of *meso*-lactide. With an initiator (**Hf-(1)**$_2$)/monomer ratio of 1:100, 98% conversion was obtained after 48 h ($f = 0.99$). Polymer showed $M_w/M_n = 1.03$ and $P_s = 0.27$.

To study the difference in the polymerization activity between zirconium and hafnium, **M-(1)**$_2$ (M = Zr or Hf), polymerization kinetics were carried out with an initiator/monomer ratio of 1:100 at 100 °C in toluene. The results are shown in Figure 3. The observed propagation rates, k_{obs}, were determined by analysis of a semilogarithmic plot of $\ln([LA]_0/[LA]_t)$ vs time, where $[LA]_0 = 0.520$ mol/L.[27]

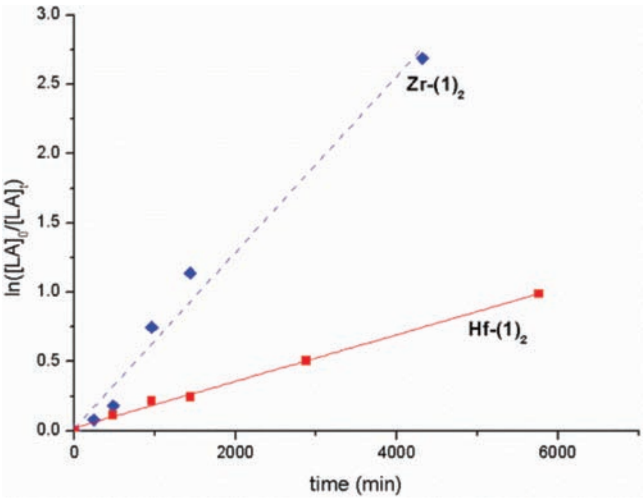


Figure 3. Semilogarithmic plots of lactide monomer conversion vs time, $[LA]_0/[Init]_0 = 100$, $[LA]_0 = 0.52$ M, $T = 100$ °C, toluene (2 mL): *meso*-lactide polymerization using **Zr-(1)**$_2$ (blue filled diamonds), **Hf-(1)**$_2$ (red filled squares).

As can be seen in Figure 3, **Zr-(1)**$_2$, is more active ($k_{obs} = 3.84 \times 10^{-2}$ h^{-1}) toward *meso*-lactide polymerization than the homologous complex **Hf-(1)**$_2$ ($k_{obs} = 1.02 \times 10^{-2}$ h^{-1}).

At 100 °C in melt, **Hf-(1)**$_2$ polymerized *meso*-lactide with a conversion of 16% after 24 h affording PLA with a similar tacticity ($P_s = 0.30$) as that obtained in solution. The molecular weight was $M_{n,exp} = 32\,700$ g/mol and $M_w/M_n = 1.17$.

Polymerization of *rac*-lactide was carried out with an initiator (**Zr-(4)**$_2$)/monomer ratio of 1:50 at 50 °C for 72 h and gave an atactic poly(lactide) ($M_{n,exp} = 23\,500$ g/mol and $M_w/M_n = 1.01$) with 64% conversion.[28]

The polylactides synthesized from *meso*-lactide using zirconium complexes showed high heterotacticity. Coates et al. had previously reported the formation of heterotactic polylactide from *meso*-lactide using the racemic chiral aluminum initiator [Al(SalBinap)(OR)].[8a] The formation of heterotactic polylactides from *meso*-lactide was explained by a mechanism involving "polymer exchange". We have shown that the chirality of the backbone has no influence on the stereocontrol, as both achiral and chiral complexes polymerized *meso*-lactide to give PLA with similar tacticity.[12d] At this point, we can only speculate that the somewhat unusual alternating enchainment of *meso*-lactide from both diastereotopic sites is caused by the presence of two bis(phenolate) ligands, one of which may remain attached to the chain end as the result of initiation through the phenolate group. An analogous mechanism was proposed by Davidson et al. using a related group 4 metal initiator with two (ONNO)-type ligands.[13b]

■ CONCLUSION

Thermally robust bis(ligand) complexes of group 4 metals containing two (OSSO)-type bis(phenolate) ligands are easily accessible and were found to initiate the ring-opening polymerization of lactide monomers despite the coordinatively saturated ligand sphere. The zirconium and hafnium complexes polymerized *meso*-lactide to give heterotactic polylactide. As shown by kinetic studies, zirconium complexes polymerized *meso*-lactide faster than the homologous hafnium complexes.

■ EXPERIMENTAL SECTION

All operations were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Toluene, *n*-hexane, and tetrahydrofuran (THF) were distilled under argon from sodium/benzophenone ketyl prior to use. Benzene-d_6, chloroform-d_1, and other reagents were carefully dried and stored in a glovebox; [Zr(O^{i}Pr)$_4$(^{i}PrOH)] and [Hf(O^{i}Pr)$_4$(^{i}PrOH)] were purchased and used as received. [Zr(CH$_2$Ph)$_4$] was synthesized according to the literature.[29] *meso*-Lactide was kindly provided by Uhde Inventa-Fisher and was recrystallized from 2-propanol at −30 °C, washed with diethylether and dried under vacuum. Glassware and vials used in the polymerization were dried in an oven at 140 °C overnight and exposed to vacuum-argon cycle three times. Proligands were synthesized following the literature.[17a−d] Chemical shifts for ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker Avance II 400 MHz spectrometer or a Varian NMR 200 MHz spectrometer at room temperature in 5 mm NMR tubes. Chemical shifts were reported in parts per million and referenced against TMS using the residual proton signal of the solvent (^{1}H benzene-d_6, $\delta = 7.16$ ppm; chloroform-d_1, $\delta = 7.26$ ppm), (^{13}C{^{1}H} benzene-d_6, $\delta = 128.06$ ppm; chloroform-d_1, $\delta = 77.16$ ppm). Molecular weights and polydispersities were determined by size exclusion chromatography (SEC) in THF at 35 °C, at a flow rate of 1 mL/min utilizing an Agilent 1100 Series HPLC, G1310A isocratic pump, an Agilent 1100 Series refractive index detector and 8 × 600 mm, 8 × 300 mm, 8 × 50 mm PSS SDV linear M columns. Calibration standards were commercially available narrowly distributed linear polystyrene samples that cover a broad range of molar masses ($10^3 < M_n < 2 \times 10^6$ g/mol).

Crystallography. Single crystals were mounted on a glass fiber in viscous hydrocarbon oil. Crystals were quench-cooled to the temperature given in Supporting Information, Table S1. All data collections were carried out with a Bruker Apex II CCD diffractometer using ω scans and Mo−K$_\alpha$ radiation ($\lambda = 0.71073$ Å) from an INCOATEC microsource. The data analysis was performed with the program SAINT+ within the SMART software package.[30a] Absorption corrections were applied using MULABS (for **Zr-(1)**$_2$, **Zr-(5)**$_2$, and **Hf-(1)**$_2$) or SADABS (for **Zr-(3)**$_2$ and **Zr-(4)**$_2$).[30b,c] The structures were solved by direct methods using SIR-92 and refined against F^2 using all data with the SHELXL-97 software implied within the graphical interface WIN-GX.[30d−f] The crystals of **Zr-(3)**$_2$ contain clathrated toluene that is highly disordered. This was taken into account by the program SQUEEZE (within the program system PLATON).[30b] Graphics were generated with the program DIAMOND.[30g]

Polymerization Procedure. A solution of a specified amount of the initiator in 0.5 mL of toluene was added to a solution of 150 mg (1.04 mmol) of *meso*-lactide in 1.5 mL of toluene. After the desired time the polymerization mixture was quenched with drops of moist hexanes and added slowly to a cooled, stirred solution of hexanes (2.0 mL). The polymer was filtered over a Büchner funnel, washed with diethyl ether, and dried in vacuo.

Bis{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenolate)}zirconium (Zr-(1)$_2$). A solution of 2 equiv of (H$_2$)-**1** (0.101 g, 0.201 mmol) in benzene-d_6 (0.25 mL) was added to a solution of 1 equiv of $[\mathrm{Zr(O^iPr)_4(^iPrOH)}]$ (0.039 g, 0.100 mmol) in benzene-d_6 (0.25 mL) in a Young-Tap NMR tube. The colorless reaction mixture was heated to 50 °C for 16 h and turned to a yellow solution overnight. The volatiles were removed in vacuo, and **Zr-(1)$_2$** was obtained as a yellow solid in 85% yield (0.093 g, 0.085 mmol). ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 1.12 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 1.55 (s, 18H, $C(CH_3)_3$), 1.82 (s, 18H, $C(CH_3)_3$), 2.25 (d, 2H, $^3J_{HH}$ = 9.8 Hz, CH_2), 2.27 (d, 2H, $^3J_{HH}$ = 9.3 Hz, CH_2), 2.44 (d, 2H, $^3J_{HH}$ = 9.8 Hz, CH_2), 2.50 (d, 2H, $^3J_{HH}$ = 10.0 Hz, CH_2), 7.11 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.30 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.39 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.49 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}); $^{13}C\{^1H\}$ NMR (100.1 MHz, C_6D_6, 25 °C) δ (ppm): 30.38 ($C(CH_3)_3$), 30.96 ($C(CH_3)_3$), 31.63 ($C(CH_3)_3$), 31.84 ($C(CH_3)_3$), 34.29 ($C(CH_3)_3$), 34.49 ($C(CH_3)_3$), 35.49 ($C(CH_3)_3$), 35.79 ($C(CH_3)_3$), 38.11 (CH_2), 38.36 (CH_2), 119.19 (C_{ar}), 119.55 (C_{ar}), 125.80 (CH_{ar}), 126.05 (CH_{ar}), 127.32 (CH_{ar}), 127.34 (CH_{ar}), 137.81 (C_{ar}), 137.99 (C_{ar}), 141.48 (C_{ar}), 141.54 (C_{ar}), 166.45 (C_{ar}), 166.63 (C_{ar}). Mp. 210.7 °C. Anal. Calcd for $C_{60}H_{88}O_4S_4Zr$ (1092.82 g/mol): C 65.94, H 8.12; found: C 65.84, H 8.24.

Bis{1,4-dithiabutanediyl-2,2′-bis(4,6-di-2-phenyl-2-propylphenolate)}zirconium (Zr-(2)$_2$). A solution of (H$_2$)-**2** (0.388 g, 0.516 mmol) in toluene (2 mL) was added dropwise to a solution of $[\mathrm{Zr(O^iPr)_4(^iPrOH)}]$ (0.100 g, 0.258 mmol) in toluene (2 mL). The colorless solution was stirred for 18 h at 50 °C. The volatiles were removed under vacuum to afford **Zr-(2)$_2$** as colorless powder in 74% yield (0.302 g, 0.190 mmol). ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 1.59 (s, 12H, $C(CH_3)_2$), 1.60 (s, 12H, $C(CH_3)_2$), 1.63 (s, 12H, $C(CH_3)_2$), 1.82 (s, 12H, $C(CH_3)_2$), 1.85 (d, 4H, $^3J_{HH}$ = 10 Hz, CH_2), 2.24 (d, 4H, $^3J_{HH}$ = 10 Hz, CH_2), 6.92−6.97 (m, 8H, CH_{ar}), 7.00−7.08 (m, 16H, CH_{ar}), 7.14−7.17 (m, 8H, CH_{ar}), 7.19 (d, 4H, $^4J_{HH}$ = 2.8 Hz, CH_{ar}), 7.29 (d, 4H, $^4J_{HH}$ = 2.6 Hz, CH_{ar}), 7.32 (d, 4H, $^4J_{HH}$ = 2.6 Hz, CH_{ar}), 7.38 (d, 4H, $^4J_{HH}$ = 2.8 Hz, CH_{ar}). Anal. Calcd for $C_{100}H_{104}O_4S_4Zr$ (1589.38 g/mol): C 75.57, H 6.60; found: C 74.93, H 7.39.

Bis{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenolate)}hafnium (Hf-(1)$_2$). To a solution of $[\mathrm{Hf(O^iPr)_4(^iPrOH)}]$ (0.248 g, 0.06 mmol) in toluene (2 mL) was added a solution of (H$_2$)-**1** (0.500 g, 0.10 mmol) in toluene (2 mL). The initially colorless reaction mixture was heated to 50 °C for 16 h and turned into a slightly yellow suspension. The suspension was heated to 100 °C and was then cooled to 25 °C to give slightly yellow crystals. The mother liquor was removed by decantation, and the solid was dried in vacuo to afford **Hf-(1)$_2$** as a colorless powder in 65% yield (0.382 g, 0.401 mmol). ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 1.22 (s, 18H, $C(CH_3)_3$), 1.28 (s, 18H, $C(CH_3)_3$), 1.55 (s, 18H, $C(CH_3)_3$), 1.82 (s, 18H, $C(CH_3)_3$), 2.5−2.2 (m, 8H, CH_2), 7.11 (d, 2H, $^4J_{HH}$ = 2.4 Hz, CH_{ar}), 7.30 (d, 2H, $^4J_{HH}$ = 2.4 Hz, CH_{ar}), 7.40 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.51 (d, 2H, $^4J_{HH}$ = 2.4 Hz 2H, CH_{ar}); $^{13}C\{^1H\}$ NMR (100.1 MHz, C_6D_6, 25 °C) δ (ppm): 30.42 ($C(CH_3)_3$), 30.97 ($C(CH_3)_3$), 31.64 ($C(CH_3)_3$), 31.85 ($C(CH_3)_3$), 34.25 ($C(CH_3)_3$), 34.45 ($C(CH_3)_3$), 35.42 ($C(CH_3)_3$), 35.72 ($C(CH_3)_3$), 38.00 (CH_2), 38.22 (CH_2), 118.61 (C_{ar}), 119.03 (C_{ar}), 125.93 (CH_{ar}), 126.15 (CH_{ar}), 127.42 (CH_{ar}), 127.47 (CH_{ar}), 138.60 (C_{ar}), 138.78 (C_{ar}), 141.33 (C_{ar}), 141.39 (C_{ar}), 166.34 (C_{ar}), 166.64 (C_{ar}), Mp. 204.9 °C. Anal. Calcd for $C_{60}H_{88}HfO_4S_4$ (953.60 g/mol): C 61.07, H 7.52; found: C 61.23, H 7.78.

***rac*-Bis{dithiocyclohexanediyl-2,2′-bis(4-methyl-6-*tert*-butyl-phenolate)}zirconium (Zr-(3)$_2$).** A solution of *rac*-(H$_2$)-3 (0.400 g, 0.846 mmol) in toluene (4 mL) was added dropwise to a solution of $[\mathrm{Zr(O^iPr)_4(^iPrOH)}]$ (0.139 g, 0.423 mmol) in toluene (2 mL). The colorless solution was stirred for 14 h at 50 °C, and a colorless precipitate formed. All volatiles were removed under vacuum to afford **Zr-(3)$_2$** as a colorless powder in 45% yield (0.195 g, 0.211 mmol). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 0.89 (t, 4H, $^3J_{HH}$ = 9.8 Hz, cy), 1.34−1.43 (m, 4H, cy), 1.47 (s, 36H, $C(CH_3)_3$), 1.50−1.55 (m, 4H, cy), 1.97−2.06 (m, 4H, cy), 2.15 (s, 12H, CH_3), 2.20−2.25 (m, 4H, SCH), 6.78 (d, 4H, $^3J_{HH}$ = 1.5 Hz, CH_{ar}), 6.95 (d, 4H, $^3J_{HH}$ = 1.8 Hz, CH_{ar}). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25 °C) δ (ppm): 20.65 (CH_3), 25.65 (cy), 30.43 ($C(CH_3)_3$), 32.40 (cy), 34.83 ($C(CH_3)_3$), 51.85 (SCH), 115.39 (C_{ar}), 124.88 (C_{ar}), 129.59 (CH_{ar}), 133.39 (CH_{ar}), 137.77 (C_{ar}), 166.05 (C_{ar}).

***rac*-Bis{dithiocyclohexanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenolate)}zirconium (Zr-(4)$_2$).** A solution of 2 equiv of *rac*-(H$_2$)-4 (0.567 g, 1.00 mmol) in toluene (10 mL) was added dropwise to a solution of 1 equiv of $[\mathrm{Zr(CH_2Ph)_4}]$ (0.228 g, 0.500 mmol) in toluene (5 mL). The reaction mixture was stirred for 13 h at 50 °C. Then, the volatiles were removed in vacuo to afford **Zr-(4)$_2$** as a colorless powder in 80% yield (0.486 g). ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm) 0.41−0.59 (m, 4H, cy), 1.10−1.18 (m, 4H, cy), 1.22 (s, 18H, $C(CH_3)_3$), 1.33−1.37 (m, 20 H, cy and $C(CH_3)_3$), 1.55−1.61 (m, 20H, cy and $C(CH_3)_3$), 1.79−1.92 (m, 22 H, cy and $C(CH_3)_3$), 2.50−2.61 (m, 4H, SCH), 7.22 (d, 2H, $^4J_{HH}$ = 2.3 Hz, CH_{ar}), 7.41 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.46 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.52 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}); $^{13}C\{^1H\}$ NMR (100.1 MHz, C_6D_6, 25 °C) δ (ppm): 25.90 (cy), 26.09 (cy), 30.64 ($C(CH_3)_3$), 31.08 ($C(CH_3)_3$), 31.66 ($C(CH_3)_3$), 31.81 ($C(CH_3)_3$), 33.01 (cy), 33.08 (cy), 34.07 (cy), 34.25 (cy), 35.55 (cy), 35.72 (cy), 52.60 (SCH), 53.18 (SCH), 116.32 (C_{ar}), 116.58 (C_{ar}), 125.95 (CH_{ar}), 126.31 (CH_{ar}), 130.59 (CH_{ar}), 131.06 (CH_{ar}), 137.63 (CH_{ar}), 137.87 (CH_{ar}), 139.15 (CH_{ar}), 139.26 (CH_{ar}), 166.18 (C_{ar}), 166.94 (C_{ar}) ppm. Analysis calcd for $C_{68}H_{100}O_4S_4Zr$ (1201.00 g/mol): C 68.00, H 8.39; found: C 67.83, H 8.22.

***rac*-Bis{dithiocyclohexanediyl-2,2′-bis(4,6-di-2-phenyl-2-propyl-phenolate)}zirconium (Zr-(5)$_2$).** Complex **Zr-(5)$_2$** was obtained as single crystals from the crystallization of (**5**)Zr[(*O*-acetyl)mandelate]$_2$ from a toluene/pentane solution. ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 0.59−0.67 (m, 4H, cy), 0.90−0.98 (m, 4H, cy), 1.22−1.30 (m, 4H, cy), 1.49−1.52 (m, 4H, cy), 1.56 (s, 24H, $C(CH_3)_2$), 1.83−1.88 (m, 4H, SCH), 1.95 (s, 12H, $C(CH_3)_2$), 2.08 (s, 12H, $C(CH_3)_2$), 6.84 (d, 4H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.00−7.22 (m, 32H, CH_{ar}), 7.26 (d, 4H, $^4J_{HH}$ = 2.3 Hz, CH_{ar}), 7.29−7.34 (m, 8H, CH_{ar}).

***rac*-Bis{dithiocyclohexanediyl-2,2′-bis(4,6-di-*tert*-butyl-phenolato)}hafnium (Hf-(4)$_2$).** A solution of *rac*-(H$_2$)-4 (0.069 g, 0.12 mmol) in benzene-d_6 (0.25 mL) was added to a solution of $[\mathrm{Hf(O^iPr)_4(^iPrOH)}]$ (0.028 g, 0.067 mmol) in benzene-d_6 (0.25 mL). The reaction mixture was heated for 18 h at 50 °C. The volatiles were removed in vacuo to give **Hf-(4)$_2$** as a colorless powder in 75% yield (0.065 g, 0.050 mmol). ^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ (ppm): 0.38−0.60 (m, 4H, cy), 1.03−1.17 (m, 4H, cy), 1.22 (s, 18H, $C(CH_3)_3$), 1.24−1.33 (m, 2H, cy), 1.36 (s, 18H, $C(CH_3)_3$), 1.43−1.58 (m, 2H, cy), 1.59 (s, 18H, $C(CH_3)_3$), 1.76−1.83 (m, 4H, cy), 1.85 (s, 18H, $C(CH_3)_3$) 2.43−2.58 (m, 4H, SCH), 7.21 (d, 2H, $^4J_{HH}$ = 2.4 Hz, CH_{ar}), 7.42 (d, 2H, $^4J_{HH}$ = 2.3 Hz, CH_{ar}), 7.45 (d, 2H, $^4J_{HH}$ = 2.5 Hz, CH_{ar}), 7.59 (d, 2H, $^4J_{HH}$ = 2.7 Hz, CH_{ar}); $^{13}C\{^1H\}$ NMR (100.1 MHz, C_6D_6, 25 °C) δ (ppm): 25.89 (cy), 26.18 (cy), 30.74 ($C(CH_3)_3$), 31.16 ($C(CH_3)_3$), 31.73 ($C(CH_3)_3$), 31.88 ($C(CH_3)_3$), 33.14 (cy), 33.24 (cy), 34.10 (cy), 34.28 (cy), 35.54 (cy), 35.72 (cy), 52.49 (SCH), 53.09 (SCH), 115.89 (C_{ar}), 116.14 (C_{ar}), 126.08 (CH_{ar}), 126.48 (CH_{ar}), 130.75 (CH_{ar}), 131.23 (CH_{ar}), 138.49 (CH_{ar}), 137.73 (CH_{ar}), 139.11 (CH_{ar}), 139.18 (CH_{ar}), 166.08 (C_{ar}), 166.95 (C_{ar}). Anal. Calcd for $C_{68}H_{100}HfO_4S_4$ (1288.27 g/mol): C 63.40, H 7.82; found: C 63.41, H 7.39.

■ ASSOCIATED CONTENT

Supporting Information

NMR spectra for all compounds and cif-files for compounds **Zr-(1)$_2$**, **Zr-(3)$_2$**, **Zr-(4)$_2$**, **Zr-(5)$_2$**, and **Hf-(1)$_2$**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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