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Salen Complexes of Zirconium and Hafnium: Synthesis, Structural Characterization, Controlled Hydrolysis, and Solvent-Free Ring-Opening Polymerization of Cyclic Esters and Lactides

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Supporting Information

ABSTRACT: Dinuclear salen compounds of zirconium and hafnium are efficient initiators for the solvent-free ring-opening polymerization of cyclic ester monomers and lactides. There is a correlation between the theoretical and experimental number-average molecular weights (M_n's) in these polymerizations. Polymerization of β-butyrolactone gives poly(3-hydroxybutyrate) with a good M_n and molecular weight distribution.

The nonrenewable and rapidly depleting petrochemical resources have manifested a mandatory impact on expediting research toward the search for new polymeric materials that are derived from renewable feedstock.[1] These polymers are synthesized from annually renewable natural resources such as corn and sugar beet.[2] These polymers have found vital applications in biomedical and pharmaceutical sectors such as drug delivery, fabrication of implants, and scaffolds for tissue engineering.[3] In addition, the film and fiber industry have also benefited by employing such polymers in suitable applications.[4] Such an impact is the result of their permeability, biocompatibility, and biodegradability.[5] The most common and rapidly used strategy in the synthesis of such polymers is the catalytic ring-opening polymerization of suitable cyclic ester monomers and lactides that are mediated by metal catalysts.[6] Among several options available for ring-opening polymerization, coordination−insertion polymerization has been extensively popular because of its capability of producing high polymers with narrow molecular weight distributions (MWDs).[6] The polymerization initiates rapidly, and there are minimal risks of unwanted transesterification reactions. The synthesis of new metal catalysts containing rigid and polydentate ancillary ligands with suitable pendant substituents as initiating groups has been the common methodology of choice for catalyst construction.[6] It is understood that the nuclearity of the metal catalyst is controlled by this ancillary ligand and that the catalyst nuclearity plays a vital role in the coordination−insertion growth mechanism. This often has an influence on the proximity of observed number-average molecular weights (M_n's) to that of theoretical M_n's. We were interested in group 4 metals for the catalyst development toward the synthesis of green polymers.[7] Our ongoing studies are aimed at understanding the role of the pendant ligand in controlling M_n's and MWDs. With zirconium(IV) and hafnium(IV), a few initiators have already been reported.[8] The direct reactions of the (*R*,*R*)-(−)-*N*,*N*′-bis(3,5-di-*t*-butylsalicylidene)-1,2-cyclohexanediamine (salen) ligand and their derivatives are known with group 4 metal halides, resulting in the synthesis of mononuclear metal complexes.[9] However, the synthesis of dinuclear complexes with such ligands and zirconium(IV) and hafnium(IV) alcoholates still remains unexplored. We surmised that the dinuclear structure of the metal precursors must have an impact on controlling the nuclearity of the new complexes.[7a,10] Herein, we report the synthesis and structural characterization of new zirconium and hafnium compounds containing the salen ligand backbone. These compounds are potent initiators for the solvent-free ring-opening polymerization of *rac*-lactide (*rac*-LA), L-lactide (L-LA), ε-caprolactone (CL), δ-valerolactone (VL), and β-butyrolactone (BL). The theoretical M_n's match very well with the observed M_n's in these polymerizations. With *rac*-LA, the resulting polymer is atactic. Using our derivatives, the polymerization of BL results in the formation of poly(3-hydroxybutyrate). We have done controlled hydrolysis studies on these compounds and successfully characterized the hydrolysis product from the hafnium compound. This product is also a viable initiator for the polymerization of the above-mentioned monomers.

The salen ligand was reacted with $\mathrm{Zr(O^{\mathit{i}}Pr)_4(HO^{\mathit{i}}Pr)}$ or $\mathrm{Hf(O^{\mathit{t}}Bu)_4}$ in a 1:2 stoichiometric ratio, leading to the formation of **1** and **2** (Scheme 1; see also the Supporting Information, SI).

These compounds were purified by crystallization from toluene and isolated as yellow crystalline solids in high yields and purity. A stoichiometric reaction between salen and $\mathrm{Zr(O^{\mathit{i}}Pr)_4(HO^{\mathit{i}}Pr)}$ or $\mathrm{Hf(O^{\mathit{t}}Bu)_4}$ revealed the formation of the required product **1** or **2** along with the presence of an unreacted ligand. The compounds were completely characterized using various spectroscopic techniques, and their purity was assured by the correct elemental analysis results. The ^{1}H and ^{13}C NMR clearly reveal signals corresponding to the terminal and bridging alkoxy groups. Electrospray ionization mass spectrometry (ESI-MS) spectra reveal that these compounds have a dinuclear structure (see the SI).

A single-crystal X-ray structure of **1** (Figure 1; see also the SI) proves that the complex is dinuclear in the solid state and each Zr center adopts a distorted octahedral geometry. The two N centers from the ligand are coordinated to the Zr centers. The two metal centers are bridged by two $-\mathrm{O^{\mathit{i}}Pr}$ moieties, resulting in the formation of a dinuclear core that resembles the one from the starting material $\mathrm{Zr(O^{\mathit{i}}Pr)_4(HO^{\mathit{i}}Pr)}$.[7a,9b] All bond lengths and angles are in agreement with literature precedents.[8g,h]

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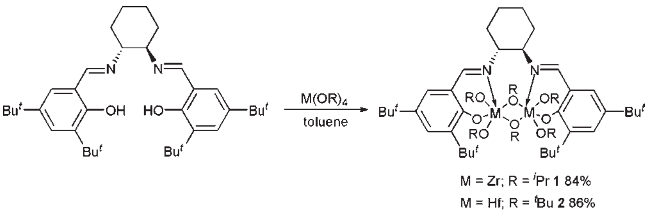
Scheme 1. Binuclear salen Complexes of Zirconium and Hafnium



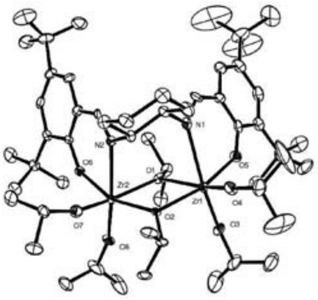


Figure 1. Molecular structure of **1**: thermal ellipsoids drawn at 30% probability level; H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Zr1−Zr2 3.537(11), Zr1−O1 2.189(7), Zr1−O2 2.177(6), Zr1−O3 1.908(7), Zr1−O4 1.950(7), Zr1−N1 2.503(8); O1−Zr1−O2 71.6(2), Zr1−O1−O2 107.3(3), N1−Zr1−O4 86.13.

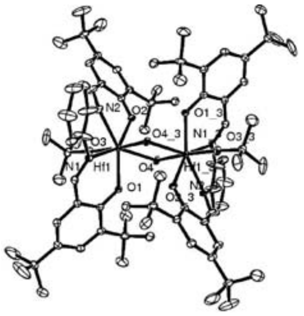


Figure 2. Molecular structure of **3**: thermal ellipsoids drawn at 30% probability level; H atoms omitted for clarity. Selected bond lengths (Å) and angles (deg): Hf1−O1 2.099(4), Hf1−O2 2.102(4), Hf1−O3 1.925(5), Hf1−O4 2.193(4), Hf1−N1 2.352(5), Hf1−N2 2.346(6); O3−Hf1−O2 87.6(2), N1−Hf1−N2 68.3(2), N1−Hf1−O3 89.2(2).

Controlled hydrolysis of **1** and **2** with water as a synthon was carried out next. A stoichiometric reaction of **1** with water in toluene resulted in the formation of intractable products. However, **2** resulted in the formation of a dimeric product **3** (Figure 2; see also the SI). Compound **3** was unambiguously characterized using various spectroscopic techniques, and their purity was assured by the correct elemental analysis results. An ESI-MS spectrum of **3** reveals that it is dimeric in the solid state (see the SI).

Single-crystal X-ray diffraction studies on **3** prove that the compound is a symmetric dimer in the solid state consisting of two mononuclear Hf centers containing the ligand that are joined by a μ-oxo bridge. The two Hf centers are in a distorted octahedral state. Bond lengths and angles agree well with the literature.[8j,10]

Table 1. Polymerization Data for *rac*-LA, L-LA, CL, VL, and *rac*-BL with 1−3 in the Ratio [M]/[C]^a = 200

					M_n (kg/mol)		
entry	initiator	monomer	temp (°C)	time^b (min)	observed^c	theoretical^d	M_w/M_n
1	1	*rac*-LA	140	48	29.5	28.9	1.02
2	1	L-LA	140	35	29.7	28.9	1.03
3	1	CL	80	55	23.5	22.9	1.05
4	1	VL	80	57	21.3	20.1	1.04
5	1	*rac*-BL	80	95	18.2	17.3	1.01
6	2	*rac*-LA	140	66	29.7	28.9	1.02
7	2	L-LA	140	62	30.7	28.9	1.01
8	2	CL	80	80	24.1	22.9	1.05
9	2	VL	80	75	22.4	20.1	1.06
10	2	*rac*-BL	80	95	18.9	17.3	1.08
11	3	*rac*-LA	140	58	29.4	28.9	1.01
12	3	L-LA	140	62	30.3	28.9	1.02
13	3	CL	80	72	23.9	22.9	1.04
14	3	VL	80	65	25.0	20.1	1.05
15	3	*rac*-BL	80	78	19.1	17.3	1.03

[a] [M]/[C] = wt of monomer × mol wt of complex/wt of complex × mol wt of monomer. [b] Time of polymerization measured by quenching the polymerization reaction when all of the monomer was found to be consumed at 100% conversion. [c] Measured by gel permeation chromatography at 27 °C in tetrahydrofuran relative to polystyrene standards with Mark−Houwink corrections for LA and CL polymerizations. [d] M_n(theoretical) at 100% conversion = $[M]_0/[C]_0 \times$ mol wt(monomer) + $(M)_{\text{end groups}}$.

Compounds **1**−**3** are powerful initiators for the polymerization of different cyclic ester monomers and lactides (Table 1). The polymerizations were performed under solvent-free conditions. These polymerizations have a great degree of control, and the close proximity of the theoretical M_n's with the observed M_n's is a noteworthy observation. Such control is rare and greatly signifies another important application of salen as a privileged ligand in chemical synthesis.[11] Variations of M_n's and MWDs with the $[M]_0/[Cat]_0$ ratio using **1**−**3** for the polymerizations with different monomers were studied. The plots are linear, indicating that there is a continual rise in the M_n's with an increase in the $[M]_0/[Cat]_0$ ratio (see the SI). Variations of the MWDs with different $[M]_0/[Cat]_0$ ratios for a given monomer are almost invariable. The polymerization continues when monomer is added externally. Analysis of the low-molecular-weight oligomers of lactide catalyzed by these complexes using ^{1}H NMR and MALDI-TOF indicates that the pendant alcoholate group on the metal initiates the polymerizations. MALDI-TOF results show extensive transesterification reaction (see the SI). The ligand is virtually a spectator but influences the observed M_n's in these polymerizations. These results are complementary to our observations with the bis(imino)phenoxide complexes of zirconium, where the observed M_n's were found to be much greater than the theoretical M_n's.[7b] Polymerization of BL results in poly(3-hydroxybutyrate). The poly(3-hydroxybutyrate) samples from entries 5, 10, and 15 (Table 1) show a very strong contribution from the *r*-centered diad (see the SI). The methylene region reveals one prominent signal corresponding to the *rr* triad. The polymerization of *rac*-LA results in atactic polymer (see the SI). These results are in contrast to those reported for analogous aluminum systems.[12] The dinuclearity of these complexes may be the reason for the loss of stereocontrol because chain growth is possible simultaneously from both centers.

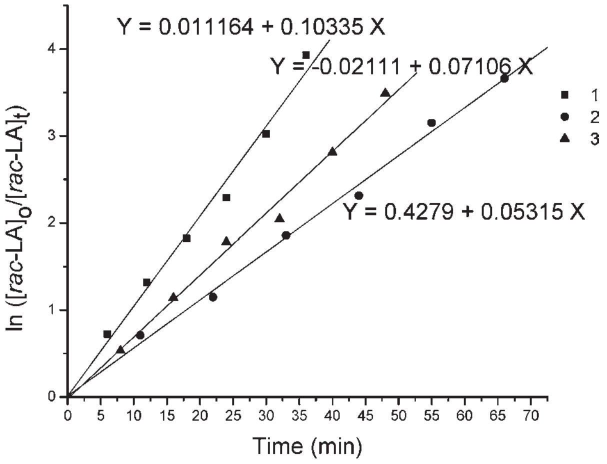


Figure 3. Semilogarithmic plots of *rac*-LA conversion in time initiated by **1**−**3**: $[\text{rac-LA}]_0/[\text{Cat}]_0$ = 200 at 140 °C.

The kinetic studies for the polymerization of *rac*-LA using **1**−**3** were studied next. The polymerization of *rac*-LA in the ratio $[rac\text{-LA}]_0/[\text{Cat}]_0 = 200$ was performed at 140 °C. The results are depicted in Figure 3. The plots suggest that there is a first-order dependence of the rate of polymerization on the monomer concentration. There is no induction period. The $\ln([rac\text{-LA}]_0/[rac\text{-LA}]_t)$ versus time plots exhibit linear variation. From the slope of the plots, the values of the apparent rate constants (k_{app}) for *rac*-LA polymerizations initiated by **1**−**3** were found to be 0.1034, 0.0532, and 0.0711 min^{-1}, respectively.

We have synthesized and structurally characterized new dinuclear complexes of zirconium and hafnium containing the salen backbone. These compounds are versatile initiators for the polymerization of cyclic ester monomers and lactides. These results are based upon a simplified approach to ring-opening polymerization with mild Lewis acids as initiators. The methodology employed and the concepts discussed may be considered crucial for bulk-scale procedures.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Crystallographic data in CIF format and full experimental details including spectroscopic, crystallographic, and polymerization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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