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Synthesis and Characterization of Zirconium and Hafnium Aryloxide Compounds and Their Reactivity Towards Lactide and ε-Caprolactone Polymerization

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Reactions of 2 equiv. pyrrole with $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$ in toluene generated tetra-pyrrolyl metal compounds $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(C_4H_4N)_2$ (**3**, M = Zr; **4**, M = Hf) in moderate yields. Similarly, treatment of metal amides $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$ with 2,6-dimethylphenol or 2,6-diisopropylphenol in heptane resulted in the elimination of diethylamine along with the formation of the corresponding metal alkoxides $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(OR)_2$ (**5**, M = Zr, R = C_6H_3-2,6-Me_2; **6**, M = Hf, R = C_6H_3-2,6-Me_2; **7**, M = Zr, R = C_6H_3-2,6-*i*Pr_2; **8**, M = Hf, R = C_6H_3-2,6-*i*Pr_2) in moderate yields. All the new compounds were characterized by ^1H and ^{13}C NMR spectroscopy and the structures of **3**, **4**, **6**, **7**, and **8** have also been determined by X-ray crystallographic studies. The aryloxides and the substituted pyrrolyl ligands in both compounds **5** and **6** show fluxionality as observed by ^1H NMR signals. A kinetic study on the ring-opening polymerization of lactide exhibits a first-order reaction of lactide monomer with compound **8**. The catalytic properties of all the metal complexes have been studied for the ring-opening polymerization of ε-caprolactone.

Introduction

Poly-ε-caprolactone (PCL) and polylactide (PLA) are considered as biodegradable polyesters for medical and ecological applications.[1–4] PCL and PLA are mainly synthesized by ring-opening polymerization using $Sn(OR)_2$ as catalysts.[5–8] However, the study of polyesters generated from ring-opening polymerization using non-tin metal alkoxides as catalysts has just started to attract researchers' attention. Among those metal alkoxides, aluminum,[9–15] lithium,[16,17] titanium,[18–21] and some lanthanide metals[22–27] have been studied by different groups. We have previously examined the ring-opening polymerization of ε-caprolactone and lactide with aluminum alkoxides supported by monoanionic bidentate ketiminate ligands.[28] Herein we report the synthesis and characterization of zirconium and hafnium metal complexes containing substituted pyrrolyl ligands and their applications as catalysts on the ring-opening polymerization of ε-caprolactone and lactide.

Results and Discussion

Synthesis of Compounds 1–8

The zirconium and hafnium amide complexes $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(NEt_2)_2$ (**1**, M = Zr; **2**, M = Hf) were prepared following the published procedures (see experimental section) by treatment of $M(NEt_2)_4$ with 2 equiv. of substituted pyrrolyl ligands (Scheme 1). Reactions of 2 equiv. pyrrole with **1** and **2** in toluene generated tetrapyrrolyl metal compounds $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(C_4H_4N)_2$ (**3**, M = Zr; **4**, M = Hf) in moderate yields. Similarly, treatment of metal amides **1** and **2** with a stoichiometric amount of 2,6-dimethylphenol or 2,6-diisopropylphenol in heptane resulted in the elimination of diethylamine with the formation of the corresponding metal alkoxides $[C_4H_3N(CH_2NMe_2)\text{-}2]_2M(OR)_2$ (**5**, M = Zr, R = C_6H_3-2,6-Me_2; **6**, M = Hf, R = C_6H_3-2,6-Me_2; **7**, M = Zr, R = C_6H_3-2,6-*i*Pr_2; **8**, M = Hf, R = C_6H_3-2,6-*i*Pr_2) in moderate yields (Scheme 1). The resulting metal alkoxide compounds **3**–**8** were characterized by ^1H and ^{13}C NMR spectroscopy.

Molecular Structures for Compounds 3, 4, 6, 7, and 8

Compounds **3**, **4**, **6**, **7**, and **8** were structurally characterized and selected bond lengths and angles are listed in Table 1. The molecular geometries are shown in Figure 1, Figure 2, Figure 3, Figure 4, and Figure 5 where the molecular geometries are highly dependent on the steric hindrance of the ligands. Compounds **3**, **4**, **6**, and **8** all contain solvent molecules in their unit cells. For compound **4**, there are two independent molecules in the asymmetrical unit. However, the bond lengths and angles of the two molecules are very similar; therefore, only one molecule is discussed

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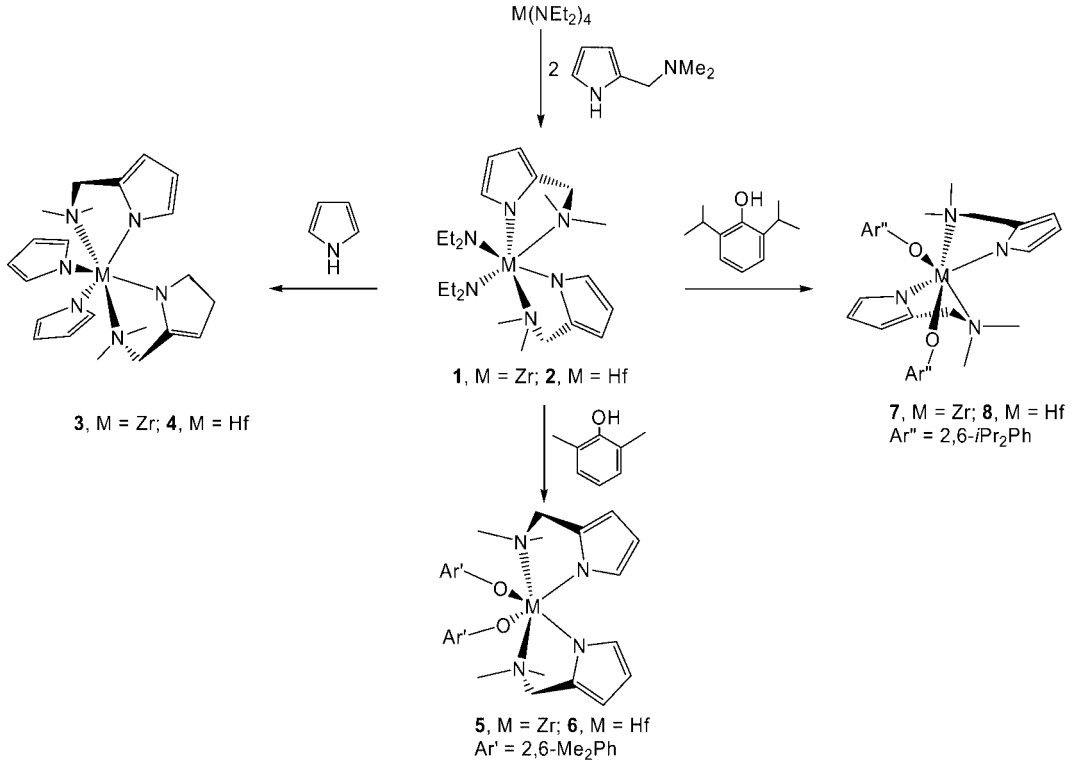

Scheme 1.

Table 1. Selected bond lengths [Å] and angles [°] for compounds **3**, **4**, **6**, **7**, and **8**.

	3		
Zr(1)–N(1)	2.1445(16)	Zr(1)–N(2)	2.3824(16)
Zr(1)–N(3)	2.1393(16)	Zr(1)–N(4)	2.3957(16)
Zr(1)–N(5)	2.1611(16)	Zr(1)–N(6)	2.1577(16)
N(1)–Zr(1)–N(6)	143.09(6)	N(3)–Zr(1)–N(5)	143.47(6)
N(2)–Zr(1)–N(4)	163.05(6)	N(1)–Zr(1)–N(2)	71.07(6)
N(3)–Zr(1)–N(4)	72.62(6)		
	4		
Hf(1)–N(1)	2.134(6)	Hf(1)–N(2)	2.381(6)
Hf(1)–N(3)	2.133(7)	Hf(1)–N(4)	2.359(6)
Hf(1)–N(5)	2.140(6)	Hf(1)–N(6)	2.112(7)
N(1)–Hf(1)–N(5)	143.5(2)	N(2)–Hf(1)–N(4)	162.1(2)
N(3)–Hf(1)–N(6)	143.8(2)	N(1)–Hf(1)–N(2)	73.2(2)
N(3)–Hf(1)–N(4)	70.6(2)		
	6		
Hf(1)–N(1)	2.190(5)	Hf(1)–N(2)	2.391(5)
Hf(1)–N(3)	2.182(5)	Hf(1)–N(4)	2.389(5)
Hf(1)–O(1)	1.975(4)	Hf(1)–O(2)	1.945(5)
N(1)–Hf(1)–N(2)	71.87(18)	N(3)–Hf(1)–N(4)	71.8(2)
N(4)–Hf(1)–N(2)	159.24(19)	N(1)–Hf(1)–O(1)	142.54(19)
O(2)–Hf(1)–N(3)	139.59(18)		
	7		
Zr(1)–O(1)	1.924(2)	Zr(1)–N(1)	2.535(3)
Zr(1)–N(2)	2.137(3)		
N(1)–Zr(1)–N(2)	69.68(10)	O(1)–Zr(1)–N(1A)	168.04(10)
N(2)–Zr(1)–N(2A)	141.17(15)		
	8		
Hf(1)–O(1)	1.9446(16)	Hf(1)–N(1)	2.162(2)
Hf(1)–N(2)	2.508(2)		
N(1)–Hf(1)–N(2)	70.87(7)	O(1A)–Hf(1)–N(2)	170.47(7)
N(1)–Hf(1)–N(1A)	140.28(11)		

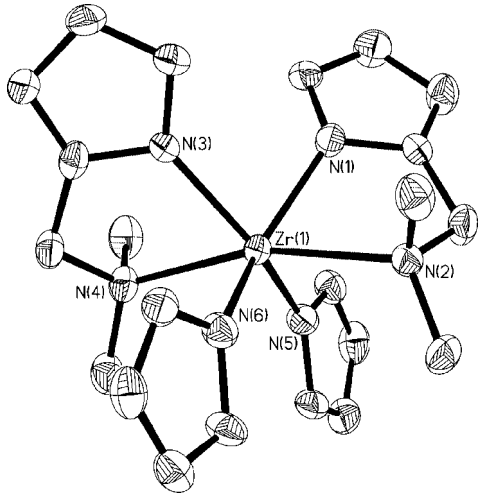

Figure 1. The molecular structure for compound **3**; thermal ellipsoids were drawn at 50% probability level. Toluene and hydrogen atoms were omitted for clarity.

here. The structures for compounds **3**, **4**, and **6**, with less steric congestion, are quite similar and show a highly distorted octahedral geometry, which can also be described as an *anti*-trigonal prism. The two nitrogen atoms of the dimethylamino fragments in compounds **4** and **6** have *trans* positions with bond angles of 162.1(2)° and 159.24(19)°, respectively. The sterically congested compounds **7** and **8** exhibit regular octahedral geometries. For the sterically congested compound **8**, the aryloxide ligands are *trans* to the dimethylamino fragments and the two pyrrolyl fragments are *trans* to each other; where the bond angles of the three axes for the octahedral geometry are 170.47(7)°,

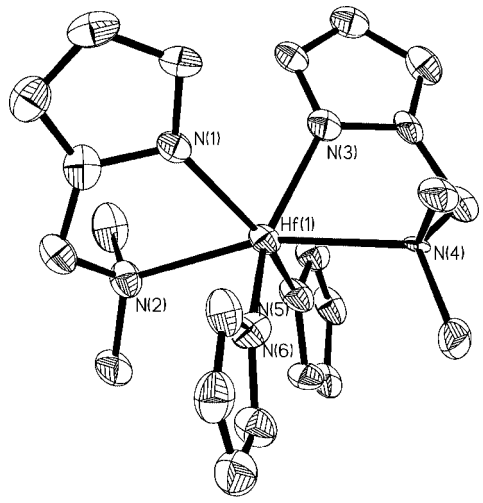

Figure 2. One of two independent molecular structures of compound **4**; thermal ellipsoids were drawn at 50% probability level. Toluene and hydrogen atoms were omitted for clarity.

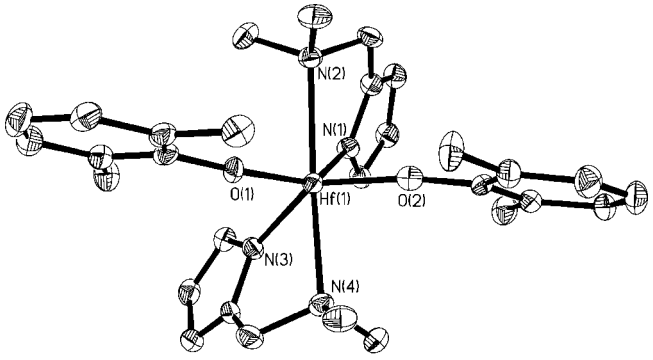

Figure 3. The molecular structure for compound **6**; thermal ellipsoids were drawn at 50% probability level. Methylene chloride molecule and hydrogen atoms were omitted for clarity.

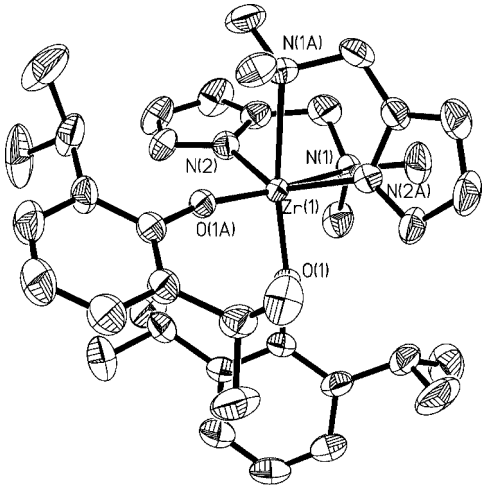

Figure 4. The molecular structure for compound **7**; thermal ellipsoids were drawn at 30% probability level. Hydrogen atoms were omitted for clarity.

170.47(7)°, and 140.28(11)°, respectively. The bond lengths of metal to pyrrolyl nitrogen atoms and metal to dimethylamino nitrogen atoms are very similar despite the differences in steric effect for compounds **4**, **6**, and **8**.[29–34]

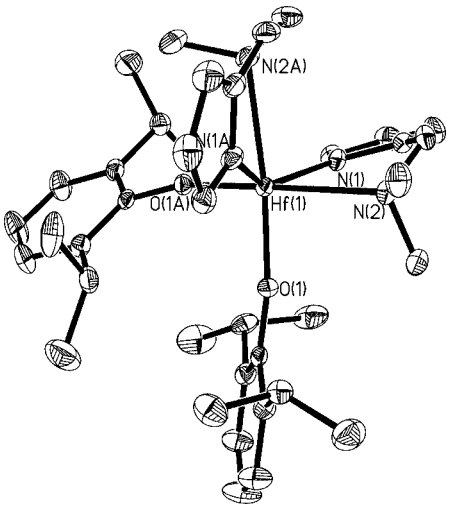

Figure 5. The molecular structure for compound **8**; thermal ellipsoids were drawn at 50% probability level. Methylene chloride and hydrogen atoms were omitted for clarity.

NMR Study of the Structures in Solution

For compounds **3** and **4**, the ^{1}H NMR spectra of the 2-[(dimethylamino)methyl] fragments at room temperature exhibit sharp singlets for the methylene and methyl protons at δ = 3.60 and 2.43 ppm for **3** and δ = 3.18 and 1.87 ppm for **4**. The proton-coupled ^{13}C NMR spectra of the methylene fragments for compounds **3** and **4** both show a triplet resonance at δ = 62.6 and 62.5 ppm with $^1J_{CH}$ coupling constants of 136 and 139 Hz, respectively. In the solid-state structures of **3** and **4**, there is nonsymmetrical geometry; the NMe_2 and the NCH_2 of the substituted pyrrolyl ligands, and the NCH and CCHC of the pyrrolide anion should have different resonance signals. However, the room temperature NMR spectroscopic data for **3** and **4** indicate either the solution structures are different from the solid ones and/or equilibria are occurring. In order to elucidate eventual dynamic phenomena (rotation of the pyrrolide anions) and/or the *cis*/*trans* isomerization of the complex, a variable temperature NMR investigation and ^{1}H–^{1}H NOESY spectra were carried out. The results show the resonance signals for the substituted pyrrolyl ligands and pyrrolides remain unchanged at 250 K, which indicates a fast rotation of the pyrrolide anions and a fast equilibrium of the *cis*/*trans* isomerization must exist at the same time.

The bulkiness of the aryloxide groups indeed affects the M–O bond rotation rate and the fluxionality of the substituted pyrrolyl ligands. The methyl fragments of the aryloxides and the dimethylaminomethyl groups in compounds **5** and **6** show broad ^{1}H NMR signals at room temperature. Use of bulkier 2,6-diisopropylphenyl groups in compounds **7** and **8** results in greater stereorigidity of the molecular structures in which the methyl groups of the isopropyl fragments were split into four doublet signals, whereas the methyl groups of the dimethylamino fragments were split into two singlets. For compound **6**, ^{1}H, ^{13}C and ^{1}H–^{13}C HSQC NMR spectra were recorded in the range of 320–250 K in $CDCl_3$ with a 300 MHz NMR spectrometer in

order to resolve its structure in solution at various temperatures. Variable temperature ^{1}H NMR spectra of compound **6** are shown in Figure 6. The ^{1}H and ^{1}H–^{13}C HSQC NMR spectra clearly identified that the methyl groups of aryloxides and dimethylamino fragments appeared as sharp singlets at δ = 2.22 and 2.46 ppm, respectively, at 320 K. The methylene protons of the CH_2NM_2 fragments also show a sharp singlet at 320 K. The methyl groups of the aryloxides and dimethylamino fragments were split into complicated singlets at δ = 2.45, 2.58, 2.51, 2.30, 2.02, and 1.40 when the temperature was lowered to 250 K. Similarly, the methylene protons of the CH_2NM_2 fragments showed splitting of signal from a sharp singlet at δ = 3.87 to a complicated overlapping of two doublets and a broad singlet when the temperatures were lowered from 320 to 250 K. The observed patterns at 250 K are indicative of complex solution dynamics. As far as the NCH_2 signal is concerned, the splitting of the singlet at room temperature into two doublets and a singlet at low temperature could indicate that two isomers, namely *cis* and *trans*, may be present in solution at low temperature. The two doublets may result from a solution structure similar to the solid state one (the *cis* form) and the singlet may result from a more symmetrical solution structure such as a more symmetrical pseudo-C_2 symmetry of *trans* geometry (the *trans* form with the phenoxide anions in an axial arrangement and the bidentate ligands in the equatorial plane with an unpredictable mutual arrangement). Interestingly, in accordance with this, six methyl resonances are observed and assignable to (i) the two nonequivalent methyls of the phenoxide anions; (ii) the two nonequivalent NMe_2 methyls of the *cis* isomers; and (iii) the NMe_2 moiety and the two equivalent methyls of the reasonably freely rotating phenoxide of the *trans* isomer. A ^{1}H NOESY experiment of **6** was performed at 250 K; however, because of the complication of methyl resonances we are unable to determine the *cis* and *trans* forms of **6**.[35]

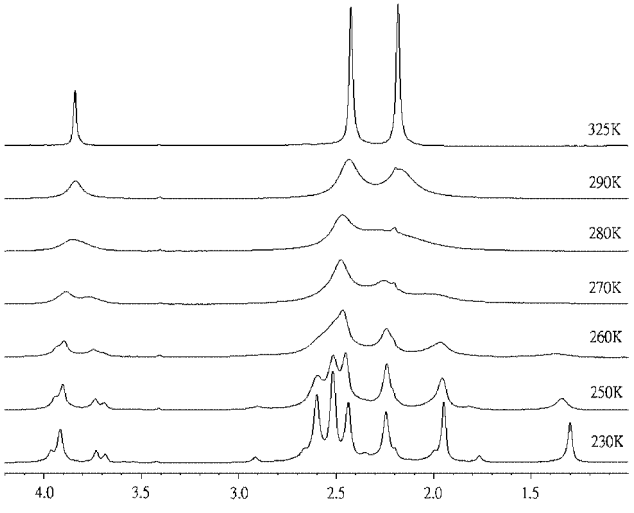

Figure 6. Variable ^{1}H NMR spectra of compound **6** in $CDCl_3$ using a 300 MHz NMR spectrometer. Spectra ranges are drawn in the range of δ = 1.0–4.2.

Kinetic Study of Lactide Polymerization Initiated by 8

The reactions of **8** with *rac* lactides proceeded in $CDCl_3$ at 70 °C and were monitored with a ^{1}H NMR spectrometer. The consumptions of lactide were measured from the integration of the ^{1}H NMR signals. Plots of ln([lactide]$_0$/[lactide]) versus time give straight lines (Figure 7), indicating the lactide polymerization is first-order with respect to the monomer.[36]

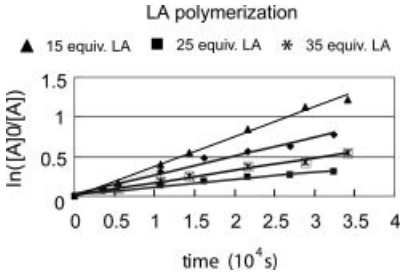

Figure 7. Plot of ln([lactide]$_0$/[lactide]) vs. time for the reaction of **8** with *rac* lactide in $CDCl_3$ at 70 °C.

Polymerization of ε-Caprolactone

Polymerizations of ε-caprolactone by using zirconium or hafnium complexes as catalysts have been seen in the literature.[37–39] Here we use the synthesized metal complexes as catalysts to study their reactivity toward ε-caprolactone. All the compounds have been studied as catalysts for the ring-opening polymerization of ε-caprolactone. The results of polymerization studies of ε-caprolactone initiated by compounds **3**–**8** are shown in Table 2. It is found that compounds **3**–**8** catalyzed the ring-opening polymerization of ε-caprolactone to give a moderate molecular weight of PCL (range 11000–53000) with a rather broad molecular weight distribution (PDI = 1.38–2.63). There are no noticeable differences toward the ring-opening polymerization relating to metals (Zr or Hf) or bulkiness of the substituted aryloxides and pyrrolyl ligands of compounds **3**–**8**.

Table 2. Ring-opening polymerization of ε-caprolactone initiated by complexes **3**–**8**.

Entry	Catalyst	[M]/[cata]	*T* (°C)	Yield (%)	Mn	PDI
1	**3**	100	25	96	18457	2.63
2	**3**	100	65	98	15612	2.38
3	**4**	100	25	99	52962	1.45
4	**4**	100	65	97	26416	2.10
5	**5**	100	50	76	21219	1.55
6	**6**	100	50	75	17727	1.38
7	**7**	100	50	93	14764	1.38
8	**8**	100	50	94	10907	1.23

Experimental Section

General Procedure: All reactions were performed under dry nitrogen using standard Schlenk techniques or in a glovebox. Toluene, heptane, diethyl ether, and tetrahydrofuran were dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried with P_2O_5.

All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker AC 200 or an Avance 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C spectra were recorded in ppm relative to the residual protons and ^{13}C of $CDCl_3$ (δ = 7.24, 77.0) and C_6D_6 (δ = 7.16, 128.0). Elemental analyses were performed with a Heraeus CHN-OS Rapid Elemental Analyzer at the Instrument Center, NCHU. $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(NEt_2)_2$, $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NEt_2)_2$,[40,41] $C_4H_3NH(CH_2NMe_2)\text{-}2$,[42,43] and $M(NEt_2)_4$ (M = Zr, Hf)[44] were prepared according to previously reported procedures.

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(NC_4H_4)_2$ (3): Pyrrole (0.1 mL, 1.44 mmol) was added to a solution of $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(NEt_2)_2$ (0.345 g, 0.72 mmol) in toluene (15 mL) at 0 °C with a micro syringe. The solution was stirred at room temperature for 10 h after the addition was completed. The volatiles were removed under vacuum, and the residue was recrystallized from a toluene solution to yield 0.181 g of colorless crystals in 53.9% yield. ^{1}H NMR ($CDCl_3$): δ = 2.43 (s, 12 H, N*Me*$_2$), 3.60 (s, 4 H, C*H*$_2$N), 5.97 (m, 2 H, pyrrolyl C*H*), 6.17 (m, 6 H, pyrrolyl C*H*), 6.70 (m, 4 H, pyrrolyl C*H*), 6.97 (m, 2 H, pyrrolyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 47.1 (q, J_{CH} = 138 Hz, N*Me*$_2$), 62.6 (t, J_{CH} = 136 Hz, *C*H$_2$N), 104.2 (d, J_{CH} = 167 Hz, pyrrolyl *C*H), 109.2 (d, J_{CH} = 168 Hz, pyrrolyl *C*H), 125.5 (d, J_{CH} = 179 Hz, pyrrolyl *C*H), 127.7 (d, J_{CH} = 190 Hz, pyrrolyl *C*H), 135.9 (s, pyrrolyl *C*$_{ipso}$) ppm. One pyrrolyl carbon resonance was not observed because of overlapping (δ = 109.2 ppm). $C_{22}H_{30}N_6Zr$ (467.74): calcd. C 56.25, H 6.44, N 17.89; found C 55.83, H 6.53, N 17.85.

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NC_4H_4)_2$ (4): This compound was prepared in a manner analogous to that described for the synthesis of **3** using $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NEt_2)_2$ (1.0 g, 1.76 mmol) and pyrrole (0.248 mL, 3.52 mmol) as starting material. Colorless crystals of **4** were obtained from a toluene solution (0.812 g, 83% yield). ^{1}H NMR (C_6D_6): δ = 1.87 (s, 12 H, N*Me*$_2$), 3.18 (s, 4 H, C*H*$_2$N), 6.12 (m, 2 H, pyrrolyl C*H*), 6.40 (m, 4 H, pyrrolyl C*H*), 6.49 (m, 4 H, pyrrolyl C*H*), 6.68 (m, 2 H, pyrrolyl C*H*) ppm. ^{13}C NMR (C_6D_6): δ = 46.5 (q, J_{CH} = 138 Hz, N*Me*$_2$), 62.5 (t, J_{CH} = 139 Hz, *C*H$_2$N), 105.6 (d, J_{CH} = 166 Hz, pyrrolyl *C*H), 110.4 (d, J_{CH} = 168 Hz, pyrrolyl *C*H), 111.0 (d, J_{CH} = 171 Hz, pyrrolyl *C*H), 126.9 (d, J_{CH} = 180 Hz, pyrrolyl *C*H), 128.5 (d, J_{CH} = 181 Hz, pyrrolyl *C*H), 136.1 (s, pyrrolyl *C*$_{ipso}$) ppm.

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(OC_6H_3Me_2\text{-}2,6)_2$ (5): A solution of 2,6-dimethylphenol (0.254 g, 2.08 mmol) in heptane (15 mL) was added to a heptane solution (20 mL) of $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(NEt_2)_2$ (0.50 g, 1.04 mmol) dropwise over 10 min. The solution was stirred at room temperature for 3 h after the addition was completed. The volatiles were removed under vacuum, and the residue was recrystallized from a dichloromethane solution to yield 0.45 g of colorless crystals in 73.8% yield. ^{1}H NMR ($CDCl_3$): δ = 2.23 (br. s, 12 H, N*Me*$_2$), 2.47 (br. s, 12 H, Ph-*Me*), 3.87 (br. s, 4 H, C*H*$_2$N), 5.29 (s, 2 H, C*H*$_2$Cl$_2$), 6.02 (m, 2 H, pyrrolyl C*H*), 6.16 (m, 2 H, pyrrolyl C*H*), 6.70 (m, 2 H, pyrrolyl C*H*), 6.93 (m, 4 H, *Ph*), 7.33 (br., 2 H, *Ph*) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.8 (q, J_{CH} = 126 Hz, Ph-*Me*), 48.2 (q, J_{CH} = 140 Hz, N*Me*$_2$), 61.6 (t, J_{CH} = 137 Hz, *C*H$_2$N), 104.5 (d, J_{CH} = 168 Hz, pyrrolyl *C*H), 108.2 (d, J_{CH} = 166 Hz, pyrrolyl *C*H), 120.2 (d, J_{CH} = 162 Hz, *Ph*), 126.5 (s, Ph *C*$_{ipso}$), 128.6 (d, J_{CH} = 158 Hz, *Ph*), 128.8 (d, J_{CH} = 180 Hz, pyrrolyl *C*H), 136.3 (s, pyrrolyl *C*$_{ipso}$), 159.2 (s, Ph *C*$_{ipso}$) ppm. $C_{30}H_{40}N_4O_2Zr{\cdot}CH_2Cl_2$ (664.82): calcd. C 56.00, H 6.37, N 8.43; found C 55.72, H 6.54, N 8.43.

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(OC_6H_3Me_2\text{-}2,6)_2$ (6): This compound was prepared in a manner analogous to that described for the synthesis of **5** using $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NEt_2)_2$ (1.0 g, 1.76 mmol) and 2,6-dimethylphenol (0.429 g, 3.52 mmol) as starting material. Colorless crystals of **6** were obtained from a CH_2Cl_2 solution (0.74 g, 63.2% yield). ^{1}H NMR ($CDCl_3$): δ = 2.25 (br. s, 12 H, Ph-*Me*), 2.50 (br. s, 12 H, N*Me*$_2$), 3.90 (br. s, 4 H, C*H*$_2$N), 5.29 (s, 2 H, C*H*$_2$Cl$_2$), 6.09 (m, 2 H, pyrrolyl C*H*), 6.22 (m, 2 H, pyrrolyl C*H*), 6.69 (m, 2 H, pyrrolyl C*H*), 6.95 (m, 4 H, *Ph*), 7.39 (br., 2 H, *Ph*) ppm. ^{13}C NMR ($CDCl_3$): δ = 17.9 (q, J_{CH} = 128 Hz, Ph-*Me*), 48.4 (q, J_{CH} = 145 Hz, N*Me*$_2$), 53.5 (t, J_{CH} = 177 Hz, *C*H$_2$Cl$_2$), 61.6 (t, J_{CH} = 137 Hz, *C*H$_2$N), 105.1 (d, J_{CH} = 166 Hz, pyrrolyl *C*H), 109.1 (d, J_{CH} = 166 Hz, pyrrolyl *C*H), 120.0 (d, J_{CH} = 161 Hz, *Ph*), 126.8 (s, Ph *C*$_{ipso}$), 128.6 (d, J_{CH} = 155 Hz, *Ph*), 129.4 (d, J_{CH} = 179 Hz, pyrrolyl *C*H), 136.5 (s, pyrrolyl *C*$_{ipso}$), 159.0 (s, Ph *C*$_{ipso}$) ppm. $C_{30}H_{40}HfN_4O_2{\cdot}CH_2Cl_2$ (752.09): calcd. C 49.51, H 5.63, N 7.45; found C 49.80, H 5.65, N 7.48.

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(OC_6H_3iPr_2\text{-}2,6)_2$ (7): This compound was prepared in a manner analogous to that described for the synthesis of **5** using $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Zr(NEt_2)_2$ (1.0 g, 2.08 mmol) and 2,6-diisopropylphenol (0.74 g, 4.16 mmol) as starting material. Colorless crystals of **7** were obtained from a CH_2Cl_2 solution (0.85 g, 59.2% yield). ^{1}H NMR ($CDCl_3$): δ = 0.72 (d, 6 H, CH*Me*$_2$), 0.82 (d, 6 H, CH*Me*$_2$), 1.27 (d, 6 H, CH*Me*$_2$), 1.47 (d, 6 H, CH*Me*$_2$), 2.12 (s, 6 H, N*Me*$_2$), 2.31 (s, 6 H, N*Me*$_2$), 3.45 (d, 2 H, C*H*$_a$H$_b$NMe$_2$), 3.51 (m, 2 H, C*H*Me$_2$), 4.00 (m, 2 H, C*H*Me$_2$), 4.21 (d, 2 H, CH$_a$*H*$_b$NMe$_2$), 5.27 (s, C*H*$_2$Cl$_2$), 6.00 (d, 2 H, pyrrolyl C*H*), 6.13 (d, 2 H, pyrrolyl C*H*), 6.85 (m, 4 H, pyrrolyl + phenyl C*H*), 7.07 (m, 2 H, phenyl C*H*), 7.38 (m, 2 H, phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 23.0 (q, J_{CH} = 126 Hz, CH*Me*$_2$), 24.2 (q, J_{CH} = 122 Hz, CH*Me*$_2$), 25.56 (q, J_{CH} = 127 Hz, CH*Me*$_2$), 25.61 (q, J_{CH} = 127 Hz, CH*Me*$_2$), 25.63 (d, J_{CH} = 123 Hz, *C*HMe$_2$), 26.8 (d, J_{CH} = 123 Hz, *C*HMe$_2$), 47.2 (q, J_{CH} = 137 Hz, N*Me*$_2$), 50.3 (q, J_{CH} = 140 Hz, N*Me*$_2$), 54.3 (t, J_{CH} = 177 Hz, *C*H$_2$Cl$_2$), 61.9 (t, J_{CH} = 135 Hz, *C*H$_2$N), 105.3 (d, J_{CH} = 165 Hz, pyrrolyl *C*H), 108.3 (d, J_{CH} = 167 Hz, pyrrolyl *C*H), 121.2 (d, J_{CH} = 161 Hz, phenyl *C*H), 123.6 (d, J_{CH} = 151 Hz, phenyl *C*H), 123.7 (d, J_{CH} = 151 Hz, phenyl *C*H), 127.7 (d, J_{CH} = 180 Hz, pyrrolyl *C*H), 135.8 (s, phenyl *C*$_{ipso}$), 136.1 (s, pyrrolyl *C*$_{ipso}$), 139.2 (s, phenyl *C*$_{ipso}$), 155.8 (s, phenyl *C*$_{ipso}$). $C_{38}H_{56}N_4O_2Zr{\cdot}0.5CH_2Cl_2$ (734.57): calcd. C 62.95, H 7.82, N 7.63; found C 62.31, H 8.09, N 7.34.

$[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(OC_6H_3iPr_2\text{-}2,6)_2$ (8): This compound was prepared in a manner analogous to that described for the synthesis of **5** using $[C_4H_3N(CH_2NMe_2)\text{-}2]_2Hf(NEt_2)_2$ (0.3 g, 0.53 mmol) and 2,6-diisopropylphenol (0.19 g, 1.06 mmol) as starting material. Colorless crystals of **8** were obtained from a CH_2Cl_2 solution (0.20 g, 44% yield). ^{1}H NMR ($CDCl_3$): δ = 0.67 (d, 6 H, CH*Me*$_2$), 0.78 (d, 6 H, CH*Me*$_2$), 1.24 (d, 6 H, CH*Me*$_2$), 1.45 (d, 6 H, CH*Me*$_2$), 2.13 (s, 6 H, N*Me*$_2$), 2.31 (s, 6 H, N*Me*$_2$), 3.47 (m, 4 H, C*H*$_a$H$_b$NMe$_2$ + C*H*Me$_2$), 3.96 (m, 2 H, C*H*Me$_2$), 4.15 (m, 2 H, CH$_a$*H*$_b$NMe$_2$), 6.02 (m, 2 H, pyrrolyl C*H*), 6.12 (m, 2 H, pyrrolyl C*H*), 6.83 (m, 4 H, pyrrolyl + phenyl C*H*), 7.03 (m, 2 H, phenyl C*H*), 7.33 (s, 2 H, phenyl C*H*) ppm. ^{13}C NMR ($CDCl_3$): δ = 22.8 (q, J_{CH} = 127 Hz, CH*Me*$_2$), 24.3 (q, J_{CH} = 126 Hz, CH*Me*$_2$), 25.5 (d, J_{CH} = 131 Hz, CH*Me*$_2$), 25.7 (q, J_{CH} = 123 Hz, CH*Me*$_2$), 25.8 (d, J_{CH} = 126 Hz, *C*HMe$_2$), 26.6 (d, J_{CH} = 126 Hz, *C*HMe$_2$), 47.2 (q, J_{CH} = 141 Hz, N*Me*$_2$), 50.7 (q, J_{CH} = 141 Hz, N*Me*$_2$), 61.9 (t, J_{CH} = 137 Hz, *C*H$_2$N), 105.8 (d, J_{CH} = 167 Hz, pyrrolyl *C*H), 109.0 (d, J_{CH} = 167 Hz, pyrrolyl *C*H), 120.9 (d, J_{CH} = 160 Hz, phenyl *C*H), 123.6 (d, J_{CH} = 155 Hz, phenyl *C*H), 123.7 (d, J_{CH} = 155 Hz, phenyl *C*H), 128.7 (d, J_{CH} = 181 Hz, pyrrolyl *C*H), 136.1 (s, phenyl *C*$_{ipso}$), 136.4 (s, pyrrolyl *C*$_{ipso}$), 139.1 (s, phenyl *C*$_{ipso}$), 155.5 (s, phenyl *C*$_{ipso}$). $C_{38}H_{56}HfN_4O_2{\cdot}CH_2Cl_2$ (864.30): calcd. C 54.20, H 6.76, N 6.48; found C 54.13, H 6.63, N 6.06.

Table 3. The summary of data collections for compounds **3**, **4**, **6**, **7**, and **8**.

	3·0.5C_7H_8	**4**·0.75C_7H_8	**6**·CH_2Cl_2	**7**	**8**·CH_2Cl_2
Empirical formula	$C_{25.5}H_{34}N_6Zr$	$C_{27.25}H_{36}HfN_6$	$C_{31}H_{42}Cl_2HfN_4O_2$	$C_{38}H_{56}N_4O_2Zr$	$C_{39}H_{58}Cl_2HfN_4O_2$
Formula mass	515.81	626.11	752.08	692.09	864.28
T [K]	293	150(2)	150(2)	298(2)	150(2)
Crystal system	triclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2/n$
a [Å]	9.5756(6)	9.6927(15)	11.253(3)	20.950(2)	10.7842(3)
b [Å]	10.8727(7)	17.163(3)	12.453(3)	10.8831(10)	10.9035(3)
c [Å]	13.1039(9)	18.581(3)	13.726(4)	18.3747(18)	17.5344(5)
α [°]	94.1730(10)	64.774(3)	113.833(4)	90	90
β [°]	111.0280(10)	84.135(3)	97.283(4)	113.258(2)	107.8480(10)
γ [°]	95.7100(10)	74.502(2)	111.359(4)	90	90
V [Å^3]/Z	1258.44(14)/2	2694.3(7)/4	1551.6(7)/2	3849.1(6)/4	1962.56(10)/2
D_{calcd} [mg/m^3]	1.361	1.543	1.610	1.194	1.463
μ [mm^{-1}]	0.461	3.898	3.568	0.321	2.831
Reflections collected	7996	16456	15047	12112	20865
No. of independent reflections	5548 [R(int) = 0.025]	11773 [R(int) = 0.0403]	6813 [R(int) = 0.0478]	4394 [R(int) = 0.0752]	4526 [R(int) = 0.0408]
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0285	R_1 = 0.0428	R_1 = 0.0428	R_1 = 0.0414	R_1 = 0.0270
	wR_2 = 0.0578	wR_2 = 0.0953	wR_2 = 0.1337	wR_2 = 0.0623	wR_2 = 0.0475
R indices (all data)	R_1 = 0.0398	R_1 = 0.0800	R_1 = 0.0490	R_1 = 0.1158	R_1 = 0.0335
	wR_2 = 0.0606	wR_2 = 0.1031	wR_2 = 0.1379	wR_2 = 0.0.0722	wR_2 = 0.0480
Largest diff. peak and hole [e/Å^3]	0.576 and –0.431	2.087 and –2.927	4.065 and –1.930	0.379 and –0.734	2.070 and –1.651

X-ray Structure Determination of Compounds 3, 4, 6, 7, and 8: The crystals were sealed in glass fibers under nitrogen and transferred to a goniostat. Data were collected with a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation with a radiation wavelength of 0.71073 Å at 293(2) K. Structural determinations were made using the SHELXTL package of programs. A SADABS absorption correction was made. All refinements were carried out by full-matrix least-squares using anisotropic displacement parameters for all non-hydrogen atoms. All the hydrogen atoms are placed with the use of a riding model. The crystal data are summarized in Table 3.

CCDC-279540 (for **3**), -279541 (for **4**), -279543 (for **6**), -279542 (for **7**), and -279544 (for **8**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Kinetic Study of *rac*-Lactide Polymerization Initiated by 8: Compound **8** and lactides were placed in a J-Young NMR tube and $CDCl_3$ (0.5 mL) was added. The solution was placed in a preheated oil bath (70 °C) and reactions were monitored by a ^{1}H NMR spectrometer constantly.

General Procedure for the Polymerization of ε-Caprolactone: General procedures for ε-caprolactone polymerization catalyzed by the new zirconium and hafnium complexes are as follows. In a glovebox, the monomer (ε-caprolactone) and catalyst were placed in separate Schlenk flasks and then moved out of the glovebox. Toluene (10 mL) was added with a syringe to the catalyst and heated to the desired temperature followed by the addition of the monomer. The reactions proceeded in the desired conditions and were quenched with methanol. Solids were obtained by filtration, washed with methanol to remove excess metal catalysts, and dried under vacuum.

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