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Cerium(IV) Catalysts for the Ring-Opening Polymerization of Lactide

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A rare example of a cerium(IV) alkoxide catalyst for lactide polymerization is reported. The lactide polymerization activity of the new cerium(IV) complex supported by a ferrocene Schiff base ligand, salfen, is compared to the activity of the yttrium analogue and to that of $Ce(O^tBu)_4(THF)_2$. The complex $Ce(salfen)(O^tBu)_2$ is less active than $Ce(O^tBu)_4(THF)_2$ and the corresponding yttrium(III) alkoxide, $Y(salfen)(O^tBu)(THF)$. The different activity was correlated with the Mulliken charges calculated by density functional theory for the two complexes.

Introduction

Polyesters are a major class of biodegradable polymers[1] that are obtained in a defined manner from the ring-opening polymerization (ROP) of cyclic esters. Polymer characteristics can be controlled when metal-based[2,3] or organic[4−7] catalysts are employed. Among the cyclic esters used as monomers, lactide is one of the most studied examples and is often used as a benchmark in developing new catalysts.[3] The quest to find more active catalysts than group 13,[8−12] zinc,[13−16] and rare earth[17−19] complexes is motivated by the goal of combining all desired properties in one new catalyst: high activity, low toxicity, high enantioselectivity, and functional group tolerance.

Although rare earth alkoxides have been studied extensively as catalysts for the ROP of cyclic esters,[20−23] cerium(IV) examples are virtually unknown. One report shows the use of $Ce(OTf)_4$ ($OTf = CF_3SO_3$) in combination with ionic liquids for the polymerization of ε-caprolactone,[24] but studies of cerium alkoxide complexes are absent from the literature. Herein we report the first examples of cerium(IV) alkoxides as catalysts for the polymerization of lactide.

Results and Discussion

We are interested in developing the chemistry of d^0f^n metal complexes supported by non-metallocene ligands.[25−28] Ferrocene-based ligands are capable of blocking one side of the metal coordination sphere and have the ability to accommodate changes in the electronic density at the d^0f^n metal center by varying the geometry around iron. A ferrocene Schiff base

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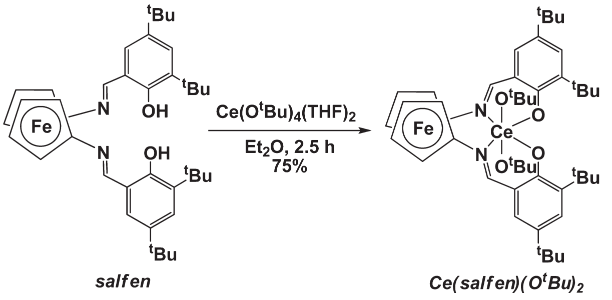
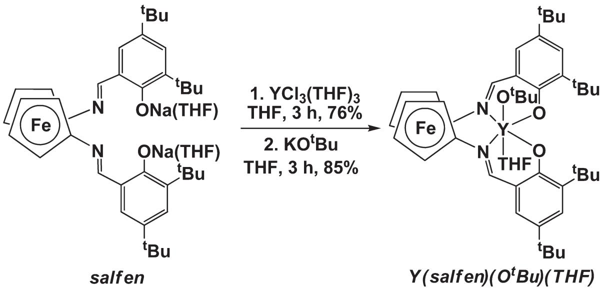
(salfen), previously reported by Arnold et al.,[29] has been chosen as the ancillary ligand for cerium(IV) because it combines the properties of ferrocene and of Schiff bases, which have proven successful in supporting metal alkoxides used as ROP catalysts.[2,3,30] An additional feature of salen-derived ligands is that they allow axial access of the incoming substrate, whereas most existing systems encapsulate the metal center.[2,3]



(1)

Synthesis and Characterization of Salfen Complexes. The reaction between Ce(O^{t}Bu)$_4$(THF)$_2$[31] and salfen in diethyl ether, at room temperature, led to the desired cerium product, Ce(salfen)(O^{t}Bu)$_2$, in 75% yield (eq 1). ^{1}H NMR spectroscopy data confirmed that Ce(salfen)(O^{t}Bu)$_2$ is diamagnetic and oxidation of the ferrocene backbone by the cerium(IV) center did not occur. The synthesis of Ce(salfen)(O^{t}Bu)$_2$ from Ce(O^{t}Bu)$_4$(THF)$_2$ gave better results than that from Ce(O^{t}Bu)$_2$(NO$_3$)$_2$(THF)$_2$[31] and [K(THF)]$_2$(salfen).



(2)

Since cerium(IV) alkoxides have not been previously evaluated as catalysts for the ROP of lactide, it was important to compare their activity with analogous yttrium complexes. Such complexes show high activity[18,19,22,23,32,33] and the ionic radii of six-coordinate cerium(IV) (0.87 Å) and yttrium(III) (0.90 Å) are very close.[34] Synthesis of Y(salfen)(O^{t}Bu)(THF) was accomplished by treating YCl$_3$(THF)$_3$ with [Na(THF)]$_2$(salfen), followed by a reaction with KO^{t}Bu (eq 2). Crystallization of Y(salfen)(O^{t}Bu)(THF) from hexanes allowed its purification and isolation in 85% yield.

Both complexes, Ce(salfen)(O^{t}Bu)$_2$ and Y(salfen)(O^{t}Bu)(THF), were characterized by X-ray crystallography. The solid-state structure of Ce(salfen)(O^{t}Bu)$_2$ (Figure 1) shows the expected trans arrangement of the two *t*-butoxide ligands. The Ce−O$_{\mathrm{OtBu}}$ distances of 2.085(3) and 2.087(3) Å compare well to other Ce−O$_{\mathrm{OtBu}}$ distances in neutral complexes: 2.026(5) and 2.023(5) Å in Ce(O^{t}Bu)$_2$(NO$_3$)$_2$(HO^{t}Bu)$_2$[31] and 2.045(3) in Cp$_3$Ce(O^{t}Bu).[35] The Ce−O$_{\mathrm{salfen}}$ distances (2.221(2) and 2.224(2) Å) are longer than the Ce−O$_{\mathrm{OtBu}}$ distances by about 0.14 Å. Although these distances are outside the range for cerium(IV) alkoxides (2.025(5)−2.133(10) Å),[36,37] they are comparable to Ce−O distances in other cerium(IV) Schiff base complexes (2.164(2)−2.258(4) Å).[38−40] The Ce−N distances (2.484(3) and 2.487(3) Å) are shorter than Ce−N distances in other cerium(IV) Schiff base complexes (2.536(2)−2.774(2) Å),[38−40] but the cerium coordination numbers are different in those complexes.

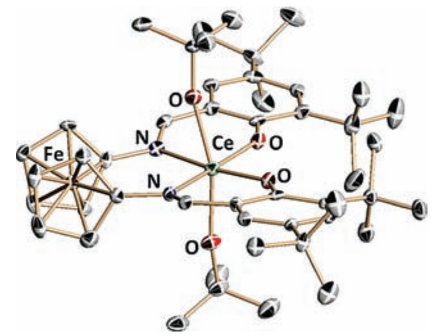


Figure 1. Thermal ellipsoid (50% probability) representation of Ce(salfen)(O^{t}Bu)$_2$; H atoms were removed for clarity.

The solid-state structure of Y(salfen)(O^{t}Bu)(THF) (Figure 2) shows that the yttrium atom is slightly displaced from the plane formed by the donor atoms of the salfen ligand: the torsion angle between the NYN and the NNO planes is 19.5°, and the sum of the angles around yttrium (not considering the axial ligands) is 355.8°. By comparison, the same torsion angle is 3.1°, and the analogous sum of the angles around cerium is 359.8°. However, the yttrium-donor atom distances are similar to those for cerium if the 0.03 Å difference between yttrium and cerium is taken into account: Y−O$_{\mathrm{OtBu}}$ is 2.046(3) Å, Y−O$_{\mathrm{salfen}}$ are 2.170(2) and 2.176(3) Å, and Y−N are 2.426(3) and 2.461(3) Å. A comparison with analogous yttrium distances in other *t*-butoxide[30,41−44] or Schiff base complexes[45−48] shows that these distances fall in the expected range for such compounds.

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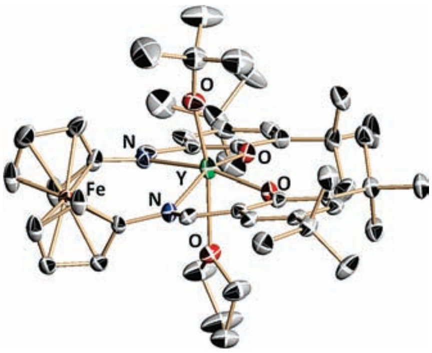


Figure 2. Thermal ellipsoid (50% probability) representation of Y(salfen)(O^{t}Bu)(THF); H atoms were removed for clarity.

Density Functional Theory (DFT) Calculations. Interestingly, the angles at the alkoxide oxygen donors (CeOC, YOC) are close to 180° (165.5(2) and 165.0(2)° for Ce(salfen)(O^{t}Bu)$_2$ and 166.0(3)° for Y(salfen)(O^{t}Bu)(THF)). Analogous angles in neutral *t*-butoxide complexes are similar in value: 168.9 and 170.1° in Ce(O^{t}Bu)$_2$(NO$_3$)$_2$(HO^{t}Bu)$_2$,[31] 176.3° in Cp$_3$Ce(O^{t}Bu),[35] 178.4 and 176.2° in [(C$_5$Me$_5$)Y(μ-OCMe$_3$)(OCMe$_3$)]$_2$[41] and 179.1, 178.3, and 164.0° in Y$_3$(μ-OCMe$_3$)(μ-Cl)(μ-OCMe$_3$)$_3$(OCMe$_3$)$_4$(THF)$_2$.[42] It is possible that these angles are indicative of π donation from the oxygen lone pairs to the cerium(IV) centers. To verify this proposal, DFT calculations were performed on complexes modeling Ce(salfen)(O^{t}Bu)$_2$ and Y(salfen)(O^{t}Bu)(THF). Calculations for a Ce(O^{t}Bu)$_2$(NO$_3$)$_2$(HO^{t}Bu)$_2$ model were also carried out since this complex also shows almost 180° angles at the alkoxide oxygen donors and does not contain the salfen ligand. A comparison between the experimental and calculated metrical parameters is presented in Table 1 and indicates that the models can be used to describe the actual complexes. For all model complexes, the calculated bond distances are consistently larger than the experimental values, with a better agreement for the yttrium than for the cerium salfen complex. However, the calculations reproduce the almost linear arrangement around the *t*-butoxide oxygen atoms and the relative displacement of yttrium versus cerium out of the salfen donor atom plane (Table 1).

DFT calculations support the existence of π donation from oxygen to cerium in Ce(salfen)(O^{t}Bu)$_2$, five occupied molecular orbitals being found to show such interactions (Figure 3, only 4 orbitals shown; see the Supporting Information for other orbitals). In all these orbitals the cerium contribution is between 5 and 8%, but the contribution from the oxygen p orbitals is much greater (up to 31% for one oxygen atom). In the case of the yttrium model complex, such bonds were found for HOMO-5 and HOMO-6 (Figure 4). For the yttrium model complex, the contribution from the *t*-butoxide oxygen donor is almost as great as the sum of the corresponding contributions for the cerium complex, and the yttrium orbital contribution is slightly smaller (4.2 and 4.4%) than the orbital contribution of cerium. The model complex Ce(O^{t}Bu)(NO$_3$)$_2$(HO^{Me})$_2$ also has orbitals showing the π donation from oxygen to cerium (orbital pictures and contributions are given in the Supporting Information). Slightly increased orbital contributions from cerium and decreased orbital contributions from the two oxygen donors were calculated, but they were comparable to those found for Ce(salfen)(O^{t}Bu)$_2$.

Table 1. Experimental Metrical Parameters for Ce(salfen)(O^{t}Bu)$_2$, Y(salfen)(O^{t}Bu)(THF), and Ce(O^{t}Bu)(NO$_3$)$_2$(HO^{t}Bu)$_2$ and Calculated Values for Their Respective Model Complexes[a]

complex	parameter	experimental	calculated
Ce(salfen)(O^{t}Bu)$_2$	Ce$-$O$_{OtBu}$	2.085	2.184
		2.087	2.185
	Ce$-$O$_{salfen}$	2.221	2.335
		2.224	2.336
	Ce$-$N	2.484	2.593
		2.487	2.597
	CeOC$_{OtBu}$	165.5	163.1
		165.0	167.1
	NCeNO	3.1	1.9
Y(salfen)(O^{t}Bu)(THF)	Y$-$O$_{OtBu}$	2.046	2.082
	Y$-$O$_{salfen}$	2.170	2.236
		2.176	2.239
	Y$-$O$_{THF}$	2.458	2.751
	Y$-$N	2.426	2.519
		2.461	2.529
	YOC$_{OtBu}$	166.0	163.9
	NYNO	19.5	20.5
Ce(O^{t}Bu)(NO$_3$)$_2$(HO^{t}Bu)$_2$	Ce$-$O$_{OtBu}$	2.023	2.130
		2.025	2.134
	Ce$-$O(H)^{t}Bu	2.520	2.675
		2.527	2.685
	Ce$-$O$_{ONO}$	2.515	2.578
		2.529	2.593
		2.583	2.631
		2.593	2.642
	CeOC$_{OtBu}$	168.9	160.9
		170.1	167.3

[a] Distances are given in angstrom and angles in degrees.

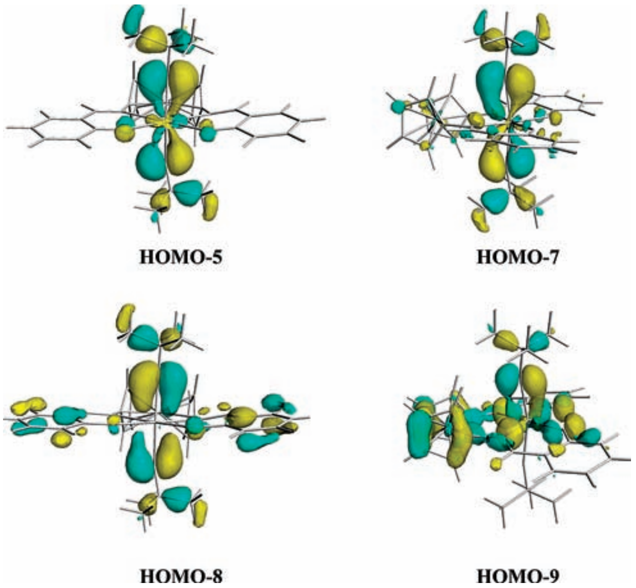


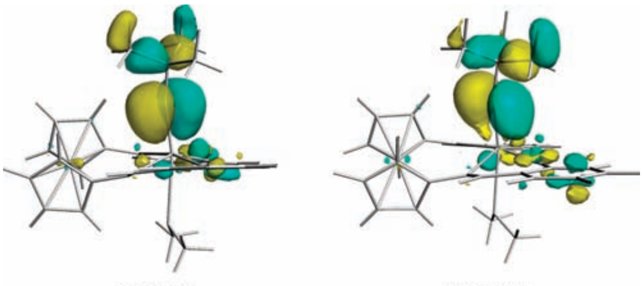
Figure 3. Orbitals showing the π interaction between cerium and the *t*-butoxide oxygen atoms in a Ce(salfen)(O^{t}Bu)$_2$ model compound (salfen ^{t}Bu groups were replaced by H atoms). Orbital components (%): HOMO-5, 30.6 O$_{OtBu}$, 29.9 O$_{OtBu}$, 6.3 Ce; HOMO-7, 25.6 O$_{OtBu}$, 21.9 O$_{OtBu}$, 8.2 Ce; HOMO-8, 23.7 O$_{OtBu}$, 22.0 O$_{OtBu}$, 5.0 Ce; HOMO-9, 12.5 O$_{OtBu}$, 6.3 Ce.

Polymerization studies. With Ce(salfen)(O^{t}Bu)$_2$ and Y(salfen)(O^{t}Bu)(THF) in hand, we became interested in evaluating their activity as catalysts for the ROP of cyclic esters (Table 2). The complex Ce(salfen)(O^{t}Bu)$_2$ reacts with ε-caprolactone and L-lactide at 70 °C, but not with β- or γ-butyrolactone. The reaction with 100 equiv of ε-caprolactone takes 4 h to reach 80% conversion, while

Table 2. Data for the ROP of Lactide by Ce(salfen)(O^tBu)$_2$ (70 °C), Ce(O^tBu)$_4$(THF)$_2$, and Y(salfen)(O^tBu)(THF) (Room Temperature)

catalyst	eq LA	time (min)	conversion (%)	Mn (kg/mol)[a]	PDI
Ce(salfen)(O^tBu)$_2$	100	20	94	32.7	1.45
	200	20	90	53.4	1.36
	300	35	89	58.4	1.39
	400	35	94	47.4	1.55
	500	48	88	64.7	1.27
Ce(O^tBu)$_4$(THF)$_2$	100	20	96	5.8	1.54
	200	20	89	13.5	1.34
	300	20	92	24.8	1.67
	400	40	82	23.7	1.15
	500	40	98	17.5	1.24
Y(salfen)(O^tBu)(THF)	100	5	97	17.9	1.21
	200	5	98	42.1	1.15
	300	15	98	59.1	1.19
	400	40	86	66.3	1.17
	500	40	90	92.9	1.13

[a] Molecular weights were corrected by a Mark−Houwink factor of 0.58 (PS standards were used).[49,50]



HOMO-5 HOMO-6

Figure 4. Orbitals showing the π interaction between yttrium and the *t*-butoxide oxygen atoms in a Y(salfen)(O^tBu)(THF) model compound (salfen ^tBu groups were replaced by H atoms and THF was replaced by OMe_2). Orbital components (%): HOMO-5, 51.5 O_{OtBu}, 4.4 Y; HOMO-6, 56.2 O_{OtBu}, 4.2 Y.

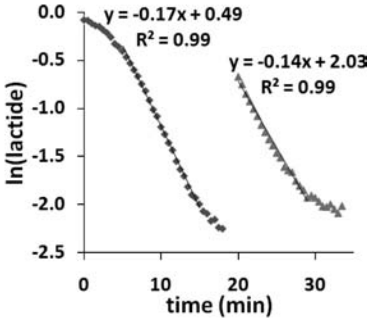


Figure 5. Successive additions of 100 equiv lactide to Ce(salfen)(O^tBu)$_2$ (C_6D_6, 70 °C, $[LA]_0$ = 0.2 M).

the reaction with 100 equiv of L-lactide requires only 20 min. In general, ROP of ε-caprolactone is more facile than that of lactide; a reasonable explanation for our observation has not been found yet.

No epimerization of L-lactide was observed and the polymers obtained were isotactic (see the Supporting Information for the corresponding NMR spectra). The reactions with L-lactide were monitored by in situ ^{1}H NMR spectroscopy measurements to gain more understanding about the polymerization process. Plots of ln[lactide] versus time are linear (Figure 5), giving, at first, an indication of a well-behaved system; however, the polymerization data (see below) suggest a more complicated system than initially assumed.

Once the activity of Ce(salfen)(O^tBu)$_2$ versus lactide was established, a comparison with the simple alkoxide Ce(O^tBu)$_4$(THF)$_2$ was undertaken, since it is the starting material used in the synthesis of Ce(salfen)(O^tBu)$_2$. The complex Ce(O^tBu)$_4$(THF)$_2$ was more active than the salfen complex; it polymerized 500 equiv of L-lactide at room temperature in 40 min. When 100 equiv of lactide was added to Ce(O^tBu)$_4$(THF)$_2$, a long induction period (18 min, 20% conversion) was observed at room temperature, after which the polymerization was complete in a few minutes; a second 100 equiv of lactide was converted within minutes as well.

Reactions between Y(salfen)(O^tBu)(THF) and L-lactide showed that the yttrium complex was also more active than Ce(salfen)(O^tBu)$_2$: ROP occurred at room temperature within minutes (Table 2). Analysis of the polymer molecular weights showed that the reactions are better behaved with the yttrium than with the cerium salfen complex, since a linear increase of M_n with the number of equivalents of monomer used and lower PDI than for Ce(salfen)(O^tBu)$_2$ were observed.

To determine if there was still active catalyst after the polymerization reaction with Ce(salfen)(O^tBu)$_2$, a second 100 equiv of lactide was added after the reaction with the first 100 equiv was complete. Similar observed rate constants (k_{first} = 0.17 s^{-1} M^{-1} and k_{second} = 0.14 s^{-1} M^{-1}, Figure 5) were obtained, and the results were reproducible. However, analysis of the polymer molecular weights (Table 2) showed that even though the polymerization was relatively well behaved (PDI = 1.2−1.6), the molecular weights of the polymers did not increase linearly with the number of lactide equivalents used, indicating that Ce(salfen)(O^tBu)$_2$ did not promote a controlled-living polymerization under those conditions. Such behavior is similar to that reported for some aluminum alkoxides supported by salen-like ligands by Carpentier et al.,[51] in which case it was attributed to transfer reactions.

To probe this hypothesis, reactions with D,L-lactide were conducted, and the ^{13}C NMR spectra of the obtained polymers were studied.[52−54] The polymers

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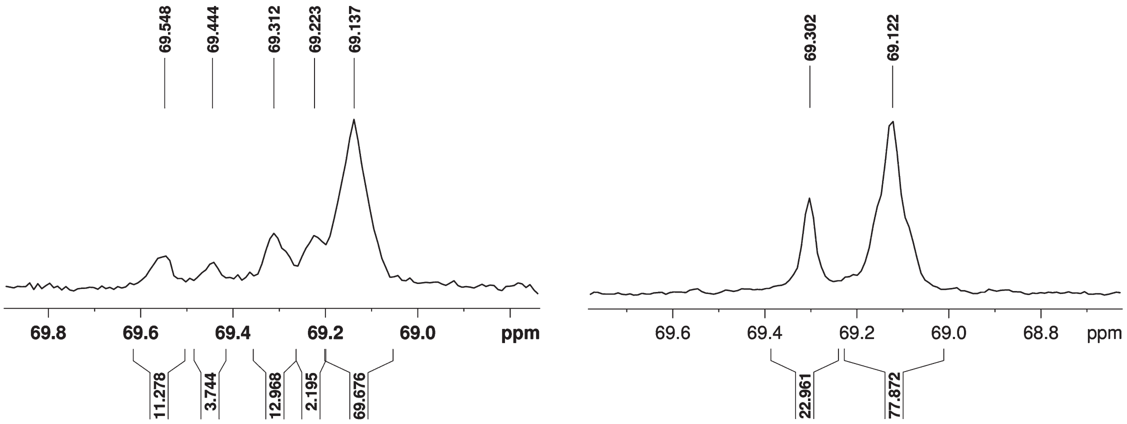

Figure 6. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for the polymers obtained from D,L-lactide. Left: 100 equiv and $Ce(O^tBu)_4(THF)_2$ (toluene, 25 °C, $[LA]_0 = 0.2$ M); right: 500 equiv and $Ce(salfen)(O^tBu)_2$ (toluene, 70 °C, $[LA]_0 = 0.2$ M).

obtained were atactic (see the Supporting Information for the corresponding NMR spectra). It has been observed that chain-transfer reactions can be identified on the basis of a specific triad formation, which can occur with D,L-lactide, but not L-lactide. The investigation of the ^{13}C NMR spectra of the polymers obtained from reactions with 100 or 500 equiv of D,L-lactide showed that chain transfer occurred for $Ce(O^tBu)_4(THF)_2$, but neither for $Y(salfen)(O^tBu)(THF)$ nor for $Ce(salfen)(O^tBu)_2$ (Figure 6, see the Supporting Information for all the spectra).

Therefore, the reactions with D,L-lactide indicate that coordinating the salfen ligand to the metal center prevents chain transfer. To explain the molecular weights of the polymers obtained in the reactions with $Ce(salfen)(O^tBu)_2$ and more than 300 equiv of lactide, we propose that chain termination occurred. Chain termination processes[55] are not well understood for the ROP of cyclic esters, but it is possible that transfer of one of the *t*-butoxide groups takes place from one metal center to the propagating species or that backbiting occurs. Unfortunately, it was not possible to differentiate the signals corresponding to the *t*-butoxide groups to probe chain termination processes. However, this explanation is in agreement with the fact that the molecular weights of the polymers obtained from reactions in which more than 300 equiv of lactide was used are lower than the theoretical values, since those reactions also required more time for completion (Table 2). In addition, a reaction with $Ce(salfen)(O^tBu)_2$ and 500 equiv of lactide is no longer active. When an additional 100 equiv was added to the reaction, no conversion occurred.

The different activities of the cerium(IV) and yttrium (III) salfen complexes might be explained on the basis of the electrophilicity of the metal center. Mulliken charges are usually correlated with the "real" charge of an atom in a molecule and have been used as an indicator for the electrophilicity of metal centers.[56−59] Investigation of Mulliken charges in the model complexes showed that yttrium had a higher charge (1.92) than cerium (1.64) in the respective salfen complexes. The same trend was observed for the *t*-butoxide oxygen charges: −0.87 for the yttrium and −0.66 (average value) for the cerium salfen model complex. This comparison supports the higher reactivity of the yttrium than that of the cerium complex toward lactide.

Conclusions

The first evaluation of the activity of cerium(IV) alkoxides as catalysts for the ROP of L-lactide has been reported. The polymerization of lactide with $Ce(salfen)(O^tBu)_2$ was monitored and the results, along with the polymer molecular weights, suggest a complicated mechanism of polymerization. The decreased activity of $Ce(salfen)(O^tBu)_2$ versus $Y(salfen)(O^tBu)(THF)$ was explained on the basis of the Mulliken charges calculated by DFT for the two complexes that indicate that the yttrium center is more electrophilic than the cerium one and that the alkoxide oxygen donors are more nucleophilic in $Y(salfen)(O^tBu)(THF)$ than in $Ce(salfen)(O^tBu)_2$.

Experimental Section

All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glovebox. Solvents were purified using a two-column solid-state purification system by the method of Grubbs[60] and transferred to the glovebox without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Compounds $Ce(O^tBu)_4(THF)_2$,[31] H_2salfen, and $[Na(THF)]_2$(salfen)[29] were prepared following published procedures; D,L-lactide and L-lactide were recrystallized twice from hot isopropanol and hot toluene. ε-Caprolactone was distilled from CaH_2 and stored in the glovebox; all other materials were used as received. ^1H NMR spectra [This material is based upon work supported by the NSF grant CHE-9974928] were recorded on Bruker300 or Bruker500 spectrometers at room temperature in C_6D_6 unless otherwise specified. Chemical shifts are reported with respect to internal solvent, 7.16 ppm (C_6D_6). CHN analyses were performed by UC Berkeley Micro-Mass facility, 8 Lewis Hall, College of Chemistry, University of California, Berkeley, CA 94720. Gel permeation chromatography was

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conducted on a Shimadzu HPLC system equipped with a refractive index detector RID-10A, one Polymer Laboratories PLgel guard column, and two Polymer Laboratories PLgel 5 μm mixed D columns. Tetrahydrofuran (THF) at 23 °C was used as the eluent (flow rate: 0.80 mL/min), and near-monodisperse polystyrene standards from Polymer Laboratories were used for calibration. Chromatograms were processed using the EZStart 7.2 chromatography software.

Synthesis of Ce(salfen)(O^{t}Bu)$_2$. A 5 mL diethyl ether solution of H$_2$salfen (0.241 g, 0.371 mmol) was added dropwise to a stirring diethyl ether solution (4 mL) of Ce(O^{t}Bu)$_4$(THF)$_2$ (0.214 g, 0.371 mmol). After stirring for 2.5 h, the ether was removed, and the product was extracted with hexanes. A concentrated solution of the product produced a fine, orange powder. Yield: 0.258 g (75%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C). δ, ppm: 8.29 (broad s, 2H, N=C*H*), 7.82 (broad s, 2H, Ar-*H*), 7.07 (broad s, 2H, Ar*H*), 4.43 and 4.08 (broad s, 8H, Cp-*H*), 1.95 and 1.80 (broad s, 18H, CC*H*$_3$), 1.33 (broad s, 18H, CC*H*$_3$), 1.24 and 1.10 (broad s, 18H, CC*H*$_3$). ^{1}H NMR (C_6D_6, 300 MHz, 50 °C). δ, ppm: 8.35 (s, 2H, N=C*H*), 7.78 (s, 2H, Ar-*H*), 7.09 (s, 2H, Ar*H*), 4.45 (broad s, 4H, Cp-*H*) and 4.11 (s, 4H, Cp-*H*), 1.84 (s, 18H, CC*H*$_3$), 1.34 (s, 18H, CC*H*$_3$), 1.16 (s, 18H, CC*H*$_3$). ^{13}C NMR (C_6D_6, 75 MHz, 25 °C). δ, ppm: 169.58, 167.20, 137.75, 130.81, 129.76, 124.92, 104.65, 84.64, 69.19, 68.28, 64.87, 36.15, 33.60, 31.85, and 30.69. Anal. for $C_{48}CeH_{68}FeN_2O_4$. Calcd: C, 61.79%; H, 7.35%, N, 3.00%. Found: C, 61.45%, H, 7.62%, N, 3.15%.

Synthesis of Y(salfen)Cl(THF). A THF solution (6 mL) of [Na(THF)]$_2$(salfen) (0.568 g, 0.664 mmol) was added dropwise to a stirring THF slurry (8 mL) of YCl$_3$(THF)$_3$ (0.273 g, 0.664 mmol) at room temperature. After 3 h, the solvent was removed and the product was extracted with toluene. Yield: 0.425 g (76%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C). δ, ppm: 8.07 (broad s, 2H, N=C*H*), 7.68 (broad s, 2H, Ar-*H*), 6.98 (broad s, 2H, Ar*H*), 5.24, 3.85, and 3.80 (broad s, 8H, Cp-*H*), 1.69 (broad s, 18H, CC*H*$_3$), 1.29 (broad s, 18H, CC*H*$_3$).

Note: The complex Y(salfen)Cl(THF) was not soluble enough in C_6D_6 to allow the acquisition of a ^{13}C NMR spectrum. Its low solubility in hydrocarbons and diethyl ether also prevented its required purification for elemental analysis.

Synthesis of Y(salfen)(O^{t}Bu)(THF). A THF solution (5 mL) of KO^{t}Bu (0.024 g, 0.218 mmol) was added dropwise to a stirring THF slurry (10 mL) of Y(salfen)Cl(THF) (0.168 g, 0.218 mmol) at room temperature. After 3 h, the solvent was removed, and the product was extracted with hexane. Yield: 0.150 g (85%). ^{1}H NMR (C_6D_6, 300 MHz, 25 °C). δ, ppm: 8.00 (s, 2H, N=C*H*), 7.69 (s, 2H, Ar-*H*), 7.03 (broad s, 2H, Ar*H*), 5.07, 4.04, 4.00, and 3.93 (broad s, 8H, Cp-*H*), 3.53 (t, 4H, OC*H*$_2$), 1.88 (s, 18H, CC*H*$_3$), 1.39 (s, 18H, CC*H*$_3$), 1.34 (s, 18H, CC*H*$_3$), 1.34 (t, 4H, OCH$_2$C*H*$_2$). ^{13}C NMR (C_6D_6, 75 MHz, 25 °C). δ, ppm: 171.35, 166.46, 140.04, 136.10, 130.56, 130.08, 122.50, 109.84, 71.31, 69.74, 68.06, 65.79, 62.61, 36.13, 34.16, 31.79, 30.30, and 25.27. Anal. for $C_{48}H_{67}FeN_2O_4Y$. Calcd: C, 65.39%; H, 7.72%, N, 3.17%. Found: C, 64.91%, H, 7.71%, N, 3.47%.

NMR Scale Polymerization of L-Lactide Using Ce(salfen)(O^{t}Bu)$_2$. In a Teflon sealed NMR tube, 0.12 mL of catalyst in C_6D_6 (0.0066 M, 0.0008 mmol) was added to a solution of L-lactide (11.5 mg, 0.08 mmol) in 0.2 mL C_6D_6 and a solution of the internal standard hexaethylbenzene (4.9 mg, 0.02 mmol) in 0.08 mL C_6D_6. The NMR tube was inserted into the instrument (Bruker AV 300) and heated to 70 °C. The polymerization was monitored until about 88% conversion.

Large Scale Polymerization of L-Lactide Using Ce(salfen)(O^{t}Bu)$_2$. In a 50 mL Schlenk tube, a 0.47 mL toluene solution of catalyst (6.5 mg, 0.0069 mmol) was added dropwise to a stirring 3 mL toluene solution of L-lactide (100 mg, 0.69 mmol). The reaction was heated to 70 °C and monitored by taking aliquots until about 88% conversion. The solvent was removed, and the polymeric material was dissolved in minimal CH$_2$Cl$_2$. Cold wet methanol (dry ice/acetone bath, 40 mL) was added to the stirring CH$_2$Cl$_2$ solution. The polymer crashed out of solution and was collected by filtering through Celite. The polymer was washed with CH$_2$Cl$_2$ and dried. The polymer was precipitated two more times before analysis.

X-ray Crystal Structures. X-ray quality crystals were obtained from various concentrated solutions placed in a −35 °C freezer in the glovebox. Inside the glovebox, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glovebox. The X-ray data collections were carried out on a Bruker AXS single crystal X-ray diffractometer using Mo Kα radiation and a SMART APEX CCD detector. The data was reduced by SAINTPLUS, and an empirical absorption correction was applied using the package SADABS. The structures were solved and refined using SHELXTL (Bruker 1998, SMART, SAINT, XPREP AND SHELXTL, Bruker AXS Inc., Madison, Wisconsin, U.S.A.). All atoms were refined anisotropically, and hydrogen atoms were placed in calculated positions unless specified otherwise. Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the bond lengths and angles, and with anisotropic displacement parameters are listed in the cif files.

Ce(salfen)(O^{t}Bu)$_2$. X-ray quality crystals were obtained from a concentrated Et$_2$O solution placed in a −35 °C freezer in the glovebox. A total of 82686 reflections ($-13 \leq h \leq 13$, $-34 \leq k \leq 34$, $-46 \leq l \leq 46$) were collected at T = 100(2) K with $2\theta_{max}$ = 56.44°, of which 78617 were unique (R_{int} = 0.0406). The residual peak and hole electron density were 1.15 and −2.23 e A^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0749 and GOF = 1.137. Crystal and refinement data for **Ce(salfen)(O^{t}Bu)$_2$**: formula $C_{48}H_{68}N_2O_4$-FeCe, space group *Pbca*, a = 10.2609, b = 25.8325, c = 35.1187, α = β = γ = 90 °, V = 9308.73 Å^3, Z = 8, μ = 1.32 mm^{-1}, F(000) = 3888, R_1 = 0.0489 and wR_2 = 0.0898 (based on all 11428 data, $I > 2\sigma(I)$).

Y(salfen)(O^{t}Bu)(THF). X-ray quality crystals were obtained from a concentrated pentane solution placed in a −35 °C freezer in the glovebox. A total of 41828 reflections ($-25 \leq h \leq 25$, $-13 \leq k \leq 13$, $-32 \leq l \leq 32$) were collected at T = 110(2) K with $2\theta_{max}$ = 56.57°, of which 40635 were unique (R_{int} = 0.0781). The residual peak and hole electron density were 3.66 and −1.50 e A^{-3}. The least-squares refinement converged normally with residuals of R_1 = 0.0640 and GOF = 1.021. Crystal and refinement data for **Y(salfen)(O^{t}Bu)(THF)**: formula $C_{48}H_{67}N_2O_4FeY$, space group *P*2(1)/*n*, a = 19.3788, b = 10.4326, c = 24.5665, α = 73.400, β = 87.716, γ = 66.498°, V = 4653.93 Å^3, Z = 4, μ = 1.59 mm^{-1}, F(000) = 1864, R_1 = 0.1176 and wR_2 = 0.1546 (based on all 11496 data, $I > 2\sigma(I)$).

Computational Details. The Amsterdam Density Functional (ADF) package (version ADF2007.01) was used to do a full geometry optimization on Cartesian coordinates of the model compounds specified in the text. Standard triple-ζ STA basis sets from the ADF database ZORA TZP were used with 1s-4d (Ce), 1s-3p (Fe), 1s-2s (Si), 1s (C, N, O) electrons treated as frozen cores. The BP functional was employed together with the exchange and correlation corrections used by default in the ADF2007.01 program suite.

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Supporting Information Available: Experimental details for compound syntheses and characterization, full crystallographic descriptions (as cif), and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.