Fluorinated β-Ketoiminate Zinc Complexes: Synthesis, Structure and Catalytic Activity in Ring Opening Polymerization of Lactide

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Dedicated to Prof. H. Schnöckel on the occasion of his 80th birthday.

Complexes \( \text{L}_2\text{Zn}(\text{thf})_2 \) (3) were synthesized and analyzed by NMR \((^1\text{H}, ^{13}\text{C}, ^{19}\text{F})\) and IR spectroscopy, elemental analysis, and single crystal X-ray diffraction. Complexes 1 and 2 are dinuclear in the solid state but monomeric in toluene solution according to diffusion-ordered spectroscopy (DOSY-NMR). They showed poor activity in the ring opening polymerization (ROP) of lactide (LA) but moderate activity in the presence of benzyl alcohol (BnOH), yielding polymers with high number average molecular weight \((M_n)\) and moderately controlled molecular weight distribution (PDI). Homonuclear-decoupled \(^1\text{H}\) NMR analysis of polyactic acid (PLA) obtained from rac-LA showed isotactic enrichment of the polymer microstructure, and kinetic studies of the ROP of LA with complex 2 showed a first order dependence of the monomer concentration. Analyses of low molecular weight polymers by \(^1\text{H}\) NMR and MALDI-ToF mass spectrometry demonstrated the coordination-insertion mechanism (CIM).

Introduction

Polyactic acid (PLA) is a renewable, biodegradable and biocompatible polymer with potential application as sustainable replacement to petrochemical-based polymers in packaging, tissue engineering, drug delivery, bio-medical and agricultural fields.[1] PLA is typically formed by ring opening polymerization (ROP) of the cyclic lactide (LA), for which a large number of metal complexes and organocatalysts have been developed.[2] Metal complexes containing monoanionic \(\beta\)-diketiminate as well as \(\beta\)-ketoiminate ligands showed promising properties in the ROP of lactide, since their electronic and steric properties, and subsequently their catalytic activity and selectivity can be modified to a large extent.[3] \(\beta\)-Ketoiminate metal complexes showed excellent activities to the ROP of cyclic esters under mild reaction condition in solution.[4]

In recent years we reported on homo- and heteroleptic \(\beta\)-ketoiminate zinc complexes and showed that heteroleptic phenoxide complexes \(\text{L}_n\text{ZnOAr} \) (type A, scheme 1) are highly active catalysts for the ROP of LA.[5] In addition, \(\beta\)-diketiminate complexes \(\text{LZn} = \text{alkyl, alkoxy OR, amide N(SiMe}_3\text{)}_2\) were also found to be active catalysts for the ROP of cyclic esters.[6] The stereoelectronic properties of these ligands can be modified by introduction of imine substituents with different sizes and by electron donating or withdrawing groups at the imine and the \(\beta\)-carbon position of the ligand backbone. The introduction of electron withdrawing groups to the ligand backbone often resulted in a decreasing catalytic activity of the resulting metal complexes in the ROP of lactide as was shown for heteroleptic amino-quinoline-substituted ketoiminate complexes with fourfold-coordinated zinc atom (type B),[7] homo- leptic sixfold-coordinated ketoiminate complexes \(\text{L}_n\text{M} (\text{M} = \text{Mg}, \text{Zn})\), of type C, and for tridentate N,O-aminophenolate zinc ethyl complexes, respectively.[8] In contrast, Rieger et al. reported an increasing catalytic activity in the ROP of lactones

![Scheme 1. Non-fluorinated β-ketoiminate (type A) and partially fluorinated β-ketoiminate (type B, C) as well as β-diketiminate metal complexes (type D).](image-url)
by introduction of trifluoromethyl groups to the ligand backbone in heteroleptic β-diketiminate zinc complexes L\textsubscript{2}ZnEt (type D), which was attributed to the increased Lewis acidity of the zinc center.\textsuperscript{10} Introduction of 4-fluoro-phenyl substituents at the imine nitrogen atom of mononuclear Schiff base zinc complexes also resulted in an increased catalytic activity in the ROP of lactide, again due to the higher Lewis acidity of the metal center,\textsuperscript{11} and a similar trend was observed for binuclear Schiff base zinc complexes containing tridentate ketoiminate ligands with 4-fluoro-phenyl substituents in β-C(O) position.\textsuperscript{12}

We recently reported on fluorinated β-diketiminate Cu(I) carbonyl complexes L\textsubscript{2}CuCO (L\textsuperscript{2} = HCIC\textsubscript{2}F\textsubscript{5}N(C\textsubscript{6}H\textsubscript{4}F\textsubscript{3})\textsubscript{2})\textsuperscript{13} and showed the reduced electron-donating properties of fluorinated substituents in such complexes compared to non-fluorinated analogues. To investigate the effect of less electron-donating ketoiminate ligands in the ROP of lactide, we herein report on the synthesis and catalytic activity of heteroleptic LZnR (R = Me 1, Et 2) and homoleptic zinc complexes L\textsubscript{2}Zn(thf)\textsubscript{3} 3.

Results and Discussion

Synthesis and Characterization. Heteroleptic complexes L\textsubscript{2}ZnMe and L\textsubscript{2}ZnEt were synthesized in high yields by alkane elimination reactions of LH with one equivalent of dialkylzinc (ZnMe\textsubscript{2}; 1.3 M in toluene; ZnEt\textsubscript{2}; 0.9 M in n-hexane). Complexes 1 and 2 were purified by re-crystallization from saturated solutions in toluene at −30 °C (Scheme 2). Since heteroleptic zinc alkoxide complexes typically show enhanced catalytic activity in the ROP of lactones compared to the corresponding zinc alkyl complexes,\textsuperscript{16} we reacted L\textsubscript{2}ZnEt 2 with one equivalent of phenol ArOH (Ar = 2,6-Me\textsubscript{2}-C\textsubscript{6}H\textsubscript{4}) in toluene. However, after crystallization from a saturated solution in THF at 0 °C, the homoleptic thf-coordinated complex L\textsubscript{2}Zn(thf)\textsubscript{3} (Scheme 2) was obtained as was proven by \textsuperscript{1}H NMR spectroscopy and single crystal X-ray diffraction. Complex 3 also formed in an analogous reaction of complex 2 with benzyl alcohol (BnOH) under identical reaction conditions as was proven by \textsuperscript{1}H and \textsuperscript{19}F NMR spectroscopy (Figure S16 and S17). A similar reaction was previously observed in the reaction of a β-diketiminate zinc complex \textsuperscript{16}F\textsubscript{na}c\textsubscript{2}ZnEt with ArOH (Ar = 2,6-Me\textsubscript{2}-C\textsubscript{6}H\textsubscript{4})\textsuperscript{14}.

Complexes 1–3 were characterized by heteronuclear NMR (\textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F) and IR spectroscopy and their purity demonstrated by elemental analysis. The \textsuperscript{1}H NMR spectra show the expected resonances of the C-H (1: 5.96 ppm, 2: 5.97 ppm, 3: 5.88 ppm) and the zinc methyl (δ = −0.72 ppm) and ethyl groups (δ = 0.96, 0.22 ppm), respectively. Complex 3 only shows resonances of the ketoiminate ligands and the coordinated THF molecules, which are shifted to higher field compared to free THF.\textsuperscript{15} The \textsuperscript{19}F NMR spectra show two signals for the trifluoromethyl group in the ligand backbone (δ = −67.78, −75.24 ppm; δ = −67.64, −75.15 ppm), while the C\textsubscript{6}F\textsubscript{5} substituent shows the expected three signals for the ortho- (δ = −147.76, δ = −22.0 Hz, 4F 1; δ = −147.75, dt, δ = 8.4 Hz, 1JFF = 7.3 Hz, 4F 2, δ = −149.39, 1JFF = 31.6 Hz, 4F 3), para- (δ = −155.35, t, 1JFF = 21.5 Hz, 2F 1; δ = −155.46, t, 1JFF = 32.8 Hz, 2F 2; δ = −157.60, t, 1JFF = 32.2 Hz, 2F 3) and meta- F atoms (δ = −161.90, t, 1JFF = 20.3 Hz, 4F 1; δ = −161.86, td, 1JFF = 24.9 Hz, 2JFF = 12.4 Hz, 4F 2; δ = −161.86, m, 4F, 3).

Single crystal X-ray diffraction. Single crystals of complexes 1–3 were obtained upon storage of saturated solutions in toluene at 0 °C for 24 h (1, 2) and from a saturated solution in THF at 0 °C within 24 h (3), respectively. (Figure 1) crystallizes in the triclinic space group \textit{P}\textsuperscript{T} whereas 2 (Figure 2) and 3 (Figure 3) in the monoclinic space group \textit{P}\textsubscript{2}\textsubscript{1}/c, respectively. Selected bond lengths and angles are given in Table 1.

In the solid state, both complexes 1 and 2 adopt centrosymmetric dimeric structures with tetrahedrally coordinated zinc atoms due to coordination to one \textit{N},\textit{O}-chelating ketoiminate ligand, the alkyl group and an additional oxygen atom of the symmetry equivalent \textit{β}-ketoiminate ligand, resulting in the formation of a four-membered Zn\textsubscript{2}O\textsubscript{2} ring. The six-membered ZnNC\textsubscript{6}O\textsubscript{3} rings clearly deviate from planarity (0.7715(2)/

![Scheme 2. Synthesis of hetero- and homoleptic fluorinated β-ketoiminate zinc complexes 1–3.](image)

![Figure 1. ORTEP representation of solid-state structure of complex 1. Displacement ellipsoids are shown with 50% probability level. Parts generated by symmetry are displayed in pale colors. Only one of the two independent molecules is shown.](image)
0.7947(12) Å 1; 0.7442(11) Å 2). The combination of chelating co-ordination and dimer formation results in a tri-cyclic core of the molecule. Compared to the non-fluorinated complexes of types A[5a] and B[65] (Scheme 1) the fluorinated β-ketoiminate complexes 1 and 2 show elongated Zn–O (R = Me: 2.0240(9) Å A; 2.0233(7)/2.0433(8) Å 1; R = Et: 2.0169(9) B; 2.0439(7) Å 2) and the Zn–N bonds (R = Me: 2.0291(11) Å A; 2.0750(9)/2.0744(9) Å 1; R = Et: 2.0373(10) Å B; 2.0704(8) Å 2), which is accompanied by more acute O–Zn–N angles (R = Me: 90.87(4)° A; 87.35(3)/86.68(3)° 1; R = Et: 91.30(4)° B; 86.56(3)° 2) in 1 and 2, whereas the zinc alkyl bonds in 1 and 2 (Zn–C: 1.9293(12)/1.9339(13) Å 1; 1.9467(11) Å 2) are shorter compared to those in complexes A and B (Zn–C: 1.9613(15) Å A; 1.983(2) Å B), respectively.

The molecule of 3 is also centrosymmetric with the zinc placed on a special position. The zinc atom adopts a barely distorted octahedral coordination geometry due to coordination of a chelating β-ketoiminate ligands, one THF molecule as well as their symmetry-equivalents, respectively. The β-ketoiminate ligands occupy the equatorial positions with trans-oriented (centrosymmetry) nitrogen and oxygen atoms and the thf molecule in the axial positions. The six-membered ZnNC3O rings in 3 deviate from planarity (0.1959(20) Å) as was observed for complexes 1 and 2. The Zn–O bond length to the β-ketoiminate oxygen atom (1.998(3) Å) is shorter compared to those of the coordinated THF molecules (2.1842(12) Å) and to those of the heteroleptic complexes 1 and 2, while the Zn–N bond lengths in 3 (2.1842(12) Å) is elongated compared to 1 and 2, respectively.

The diffusion coefficients (D) of complexes 1 (1.24·10⁻⁹ m²s⁻¹) and 2 (1.12·10⁻⁹ m²s⁻¹) were determined by diffusion-ordered NMR spectroscopy (DOSY, Figure S18, S19) in non-coordinating solvents (toluene-d₈), and the hydrodynamic radii (Rₑ) calculated using the Stokes-Einstein equation.[16] The calculated Rₑ values of 3.25 Å (1) and 3.60 Å (2) in solution are very adjacent to half of the hydrodynamic radii of 6.70 Å (1) and 7.69 Å (2) as obtained from the single crystal X-ray analyses, indicating that complexes 1 and 2 adopt monomeric structures in solution.

**Polymerization Experiments.** Complexes 1–3 were tested in the ROP of lactide in toluene at 100 °C under argon atmosphere (Table 2). We first studied the polymerization activity towards L-lactide (L-PLA) using complexes 1–3 in a 200:1 [M]₀/[C]₀ molar ratio. The conversion of L-PLA was examined by ¹H NMR spectroscopy, and the resulting polymer was characterized by gel permeation chromatography (GPC). Complexes 1 and 2 showed poor activities with low conversion (15% 1, 25% 2) after 48 h, giving atactic PLA (Figure S20), L-PLA obtained with complex 2 due to epimerization of L-PLA during polymerization, whereas complex 3 is completely inactive (Table 2, entries 1, 2 and 3). We therefore tested the ROP activity of complexes 1 and 2 in the presence of benzyl alcohol (BnOH) as co-initiator in toluene at 100 °C with a [monomer]:[cat.]:[BnOH] molar ratio of 200:1:2 (Table 2, entries 4, 5 and 6). Reactions of complexes 1 and 2 with BnOH are expected to yield LZnOBn, in which the poorly nucleophilic alkyl initiator groups (Me 1, Et 2) are replaced by the stronger nucleophilic alkoxide (OBn) initiator. Complexes 1 and 2 showed moderate catalytic activities with virtually identical conversion rates of 84% (1) and 87% (2) after 30 h, producing L-PLA with moderately controlled molecular weight and narrow polydispersity, whereas complex 3 still did not show any catalytic activity. These findings demonstrate that the reaction rates of the alcoholysis reaction of 1 and 2 with BnOH are comparable. Comparing the catalytic activity of fluorinated β-ketoiminate zinc complex 2 in the ROP of lactide with that of non-fluorinated β-ketoiminate zinc analogues[5a] clearly shows, that the introduction of electron-withdrawing CF₃
and C_{F_2} groups to the $\beta$-ketoiminate ligand backbone reduces the catalytic activity.

The polymerization of L-LA with complex 2 was also performed in the presence of one equivalent of BnOH ([monomer]:[cat.]:[BnOH] molar ratio of 200:1:1) in toluene at 100°C. 52% conversion was achieved after 30 h and the homonuclear decoupled $^{1}H$ NMR spectrum of the polymer showed the formation of isotactically-enriched PLA with $P_{m}$ values of 0.66 (1) and 0.68 (2), proving a moderate iso-selectivity of complexes 1 and 2 in the ROP of rac-LA. Moreover, polymerization reactions with enantiomeric pure L-LA using complex 2 (Table 2, entry 5) produced completely pure isotactic PLLA ($P_{m}$ = 1, Figure S21), revealing that epimerization reactions do not occur in the polymerization process.

The ROP of L-LA with complex 2 ([monomer]:[cat.]:[BnOH] molar ratio of 200:1:2) was further monitored by $^{1}H$ NMR spectroscopy, and the conversion (%) was determined from the integration of the polymer and monomer resonances. The linear dependency of $\ln[M]_0/[M]_t$ vs time (Figure 4) illustrates that the overall rate of polymerization is first order with respect to the monomer concentration. The rate constant ($k_{app}$) for the polymerization reaction was found to be $6.785 \times 10^{-3}$ h$^{-1}$. To understand the reaction mechanism, a low molecular weight oligomer of PLA was synthesized by reaction of L-LA with complex 2 with a [monomer]:[cat.]:[BnOH] molar ratio of 100:1:2 at 100°C in toluene. The solvent was removed under vacuum and the residue was dissolved in a minimum amount of THF using polystyrene standards. $P_{m}$ was the probability of mesomerism, determined from the methine region of the homonuclear decoupled $^{1}H$ NMR spectrum analysis (Bernoullian statistics).

### Table 2. Polymerization data of lactide using complexes 1–3 in toluene at 100°C[a]

| Entry | Catalyst | Monomer | [LA]:[I]:[BnOH] | Time [h] | conversion [%][b] | $M_n$ [kg/mol][c] | $M_n$ [GPC] [kg/mol][d] | $\Delta$ | $P_m$ [e] |
|-------|----------|---------|-----------------|---------|------------------|-----------------|-------------------|------|--------|
| 1     | L-Zn1    | L-LA    | 200:1:0         | 48      | 15               | 4.2             | 2.7               | 1.5  |        |
| 2     | L-Zn1    | L-LA    | 200:1:0         | 48      | 25               | 7.2             | 4.0               | 1.4  |        |
| 3     | L-Zn1    | L-LA    | 200:1:0         | 48      | –                | –               | –                 | –    |        |
| 4     | L-Zn1    | L-LA    | 200:1:2         | 30      | 84               | 12.1            | 12.7              | 1.16 |        |
| 5     | L-Zn1    | L-LA    | 200:1:2         | 30      | 87               | 12.5            | 13.4              | 1.14 |        |
| 6     | L-Zn1    | L-LA    | 200:1:2         | 30      | –                | –               | –                 | –    |        |
| 7     | rac-LZn1 | rac-LA  | 200:1:2         | 30      | 80               | 11.5            | 10.3              | 1.17 | 0.66   |
| 8     | rac-LZn1 | rac-LA  | 200:1:2         | 30      | 83               | 11.9            | 10.7              | 1.16 | 0.68   |

[a] Reaction conditions: polymerization reactions were performed in toluene at 100°C. [b] Conversion was determined by $^{1}H$ NMR. [c] $M_n$ [GPC] values were determined by GPC analysis in THF using polystyrene standards. [d] $P_m$ is the probability of mesomerism, determined from the methine region of the homonuclear decoupled $^{1}H$ NMR spectrum analysis (Bernoullian statistics).
of CH₂Cl₂ and precipitated by pouring into cold ethanol. The resulting polymer was dried and characterized by NMR and IR spectroscopy as well as MALDI-TOF mass spectroscopy. The ¹H NMR spectrum (Figure S24) of the oligomer revealed that the PLA chain is linear and end-capped by a BnO (PhCH₂O) group. These results were confirmed by MALDI-TOF mass spectroscopy analyses of the oligomer (Figure S25), which showed a sequence of peaks with regular mass intervals of 72 au, which corresponds to half of the molecular weight of the lactide monomer. All peaks were assigned to the Na⁺ adducts bearing the benzyl and hydroxyl groups at the end chain. The presence of a hydroxyl group in the end chain of the polymer was confirmed by the characteristic ν(H–O) band at 3337 cm⁻¹ in the IR spectrum (Figure S26), showing that the polymerization proceeds via the "coordination-insertion" (CIM) pathway.

Conclusions

Heteroleptic zinc complexes 1 and 2 form dimers in the solid state whereas they are monomeric in solution according to diffusion-ordered spectroscopy (DOSY) NMR analysis. They showed poor activity in the ring opening polymerization (ROP) of lactide (LA) in toluene at 100 °C, which increased upon addition of BnOH as co-initiator, resulting in the formation of polymers with controlled average molecular weight (Mₐ) and molecular weight distribution (D). Kinetic studies showed first order dependences on the monomer concentration, and the polymerization occurs via CIM pathway. Polymerization of rac-LA with complexes 1 and 2 in the presence of BnOH produced isotactically-enriched PLA. The findings clearly demonstrate that the catalytic activity of heteroleptic β-ketoiminate zinc complexes in the ROP of lactide decreases upon introduction of electron-withdrawing substituents to the β-ketoiminate ligand backbone.

Experimental Section

General experimental details. The reactions were performed under dry argon atmosphere using standard Schlenk and glovebox techniques. Argon gas was purged by passing the gas through preheated Cu₂O pellets and molecular sieves columns. Toluene and n-hexane were dried using a mBraun Solvent Purification System (SPS), degassed, and stored in Schlenk flasks under argon atmosphere. THF was dried by heating under reflux for 12 h over sodium and benzophenone and distilled fresh prior to use. Deuterated solvents were dried over activated molecular sieves (4 Å) and degassed prior to use. Karl Fischer titration of the dry solvents showed values below 2 ppm. Solvents for column chromatography (p.a. grade) were used as received. Exact molar ratios of the reactions and reaction conditions were optimized by monitoring several small-scale reactions, which were performed in J-Young NMR tubes in deuterated solvents under different reaction conditions, by in situ ¹H-NMR spectroscopy. ZnMe₂, ZnEt₂ and CaH₂ were commercially available and used without further purification. Lactide (rac-LA, L-LA) was sublimed twice and stored under argon atmosphere in a glove box. The ketoimine ligands were prepared according to literature procedures.¹¹¹ ¹H, ¹³C, and ¹⁹F NMR spectra were measured as 297 K in CDCl₃, CD₂Cl₂ and toluene-d₈ using a Bruker Avance 300 spectrometer with a QNP probe head (¹H: 300 MHz, ¹³C: 75 MHz, ¹⁹F: 282 MHz), a Bruker Avance 400 (¹H: 400 MHz, ¹³C: 100 MHz, 377 MHz) or a Bruker DRX 600 (¹H: 400 MHz, ¹³C: 100 MHz, ¹⁹F: 565 MHz) and referenced to the solvent shifts (CDCl₃; ¹H = 7.26 ppm, ¹³C = 77.16 ppm; CD₂Cl₂; ¹H = 5.32 ppm, ¹³C = 53.84 ppm; toluene-d₈: ¹H = 7.00 ppm, ¹³C = 128.33 ppm). IR spectra were recorded in a glovebox under Ar atmosphere using an ALPHA-T FT-IR spectrometer equipped with a single reflection ATR sampling module. Matrix-assisted laser desorption/ionization time of flight mass spectra (MALDI-TOF MS) were measured with a Bruker UltraflexTreme MALDI-TOF mass spectrometer (Bruker Daltonik). Samples were dissolved in THF (10 mg/mL) and dihydroxy benzoic acid was used as the matrix in THF (20 mg/mL). The reflective positive ion mode was used to acquire the mass spectra of the samples. The calibration was done externally with poly (methylmethacrylate) standards using the nearest neighbor positions. Microanalyses were determined by the Elementaranalyse Labor of the University of Duisburg-Essen with a Perkin Elmer Series 11 analyzer. Melting points were determined in sealed glass capillaries and are not corrected.

The number-average molecular weight (Mₐ), molecular weight distribution (Mₘ/Mₐ) and dispersity (Mₘ/Mₐ) of all polylactide polymers were determined by Gel Permeation Chromatography (GPC) on a 1260 Infinity instrument (Polymer Standard Service, Mainz) equipped with 3 SDV columns (pore sizes 10⁵, 10⁶, 10⁷ Å) and a SECCurity differential refractometer. The PLA was measured using HPLC grade THF as eluent at a flow rate of 1.0 mL/min at 40 °C (column oven TCC6000). A calibration setup was obtained using 12 narrow molecular weight polystyrene standards (Polymer Standard Service, Mainz) and the WinGPC UniChrom software. Number average molecular weights (Mₐ) and MWDs (Mₘ/Mₐ) of polymers were measured relative to polystyrene standards.

General synthesis of 1 and 2. In an inert argon atmosphere using standard Schlenk techniques, a solution of one equivalent of ZnR₂ in toluene was added dropwise at −78 °C to a stirred solution of one equivalent of LH (200 mg, 0.536 mmol) in 5 mL of toluene. The reaction mixture was stirred for 5 min at −78 °C and for additional 2 h at ambient temperature. The solvent was removed under reduced pressure to yield a light-yellow solid, which was recrystallized from a saturated solution in toluene at −30 °C, isolated by filtration and dried under vacuum.

LZnMe 1. 1.3 M ZnMe₂ (0.41 ml, 0.536 mmol). Yield: 225 mg (93 %). Mp 105 °C. Anal. Calcd for C₃₁H₄₆F₆₂O₇Zn·C₆: 31.85; H: 0.89; N: 3.10. Found: C: 31.90; H: 0.84; N: 3.14. ¹H NMR (400 MHz, 25 °C, tolu-d₈): δ = 5.96 (s, 2H, γ-H); −0.72 (s, 6H, CH₃); ¹³C(¹H) NMR (151 MHz, 25 °C, tolu-d₈): δ = 175.08 (s, CO), 163.83 (s, CN), 141.07 (s, o-C), 139.7 (s, p-C), 137.5 (s, m-C), 120.68 (s, i-C), 118.45 (s, CF, CN), 110.03 (s, CF, CN), 89.67 (d, J CF = 162.8 Hz, γ-C). ¹³C(¹H) NMR (100 MHz, 25 °C, tolu-d₈): δ = 118.45 (q, J CF = 28.56 Hz, CF, CN), 110.03 (q, J CF = 284.4 Hz, CF, CN), 89.67 (s, γ-C), −13.56 (s, CH₃). ¹⁹F NMR (556 MHz, 25 °C, tolu-d₈): δ = −67.78 (s, 6F, CF, CN), −75.24 (s, 6F, CF, CO), −147.76 (d, J FF = 22.0 Hz, 4F, o-F), −153.35 (d, J FF = 21.5 Hz, 2F, p-F), −161.90 (br t, J FF = 20.3 Hz, 4F, m-F). ATR-IR: ν = 2989, 2927, 2834, 1552, 1534, 1456, 1408, 1391, 1371, 1325, 1279,1262, 1204, 1170, 1097, 1063, 1028, 1000, 950, 938, 823, 870, 850, 777, 726, 665, 595, 568, 495, 439, 416 cm⁻¹.

LZnEt 2. 0.9 M ZnEt₂ (0.50 ml, 0.536 mmol). Yield: 235 mg (94 %). Mp 110 °C. Anal. Calcd for C₃₂H₅₀F₈₂O₇Zn·C₆: 33.47; H: 1.30; N: 3.00. Found: C: 33.27; H: 1.08; N: 2.82. ¹H NMR (400 MHz, 25 °C, tolu-d₈): δ = −5.97 (s, 2H, γ-H); 0.97 (s, t, J FF = 8.6 Hz, 6H, CH₃), 0.25-0.19 (m, 4H, CH₂), ¹³C(¹H) NMR (151 MHz, 25 °C, tolu-d₈): δ = 175.27 (s, CO), 163.77 (s, CN), 141.26 (s, o-C), 139.45 (s, p-C), 137.59 (s, m-C), 121.10 (s, i-C), 118.42 (s, CF, CO), 118.03 (s, CF, CN), 89.61 (d, J CF = 168.2 Hz, ν-C) 11.25 (d, J CF = 123.5 Hz, CH₃). ¹³C(¹H) NMR (100 MHz, 25 °C, tol-
Polymerization Studies

General procedure for the polymerization of lactide. A [mono-mer]:[cat.]:[BnOH] molar ratio of 200:1:2 was used for each polymerization study. 17.34 µmol of complexes 1-3, 0.5 g of rac-LA/L-LA, and 34.69 µmol of BnOH were dissolved in 5 ml of toluene and stirred at 100 °C for the desired time (Table 2). An excess of MeOH was added and all volatiles were removed under vacuum, yielding a viscous residue which was used to determine the conversion rate by 1H-NMR analysis. The resulting polymers were dissolved into a minimum amount of CHCl3 and poured into cold methanol. The precipitated polymer was isolated by filtration, dried under vacuum until constant weight was observed and subsequently used for GPC and NMR analysis. All polymerization reactions were performed twice.

General Procedure for the Polymerization Kinetics. A solution of L-lactide (0.504 g, 3.469 mmol), 17.34 µmol (16.18 mg) of complex 1 and 34.69 µmol of BnOH in 7 mL of toluene was stirred at 100 °C for the desired time. Small portions of aliquots were frequently removed from the mixture, poured into an NMR tube containing CDCl3, and analyzed by 1H NMR spectroscopy to determine the rate of conversion. The In([M]/[M0]) ratio was calculated by integration of the peak corresponding to the H-atom for the polymer and unreacted monomer. Apparent rate constants were obtained from the slopes of the kinetic plots. The contents of the quenched aliquots obtained at various time intervals were further analyzed by GPC for the determination of Mw. The polymerization reactions were performed twice.

Single-crystal X-ray analyses. The crystals were mounted on nylon loops in inert oil. Data for 1 and 2 were collected on a Bruker AXS D8 Kappa diffractometer with APEX2 detector (mono-chromated MoKα radiation, λ = 0.71073 Å) at 100(2)K. The data for 3 were collected on a Bruker AXS D8 Venture diffractometer with Photon II detector (mono-chromated CuKα radiation, λ = 1.54178 Å, micro-focus source) at 100(2)K. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F2 (SHELXL-2014.0). Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). Hydrogen atoms were refined using a riding model or rigid methyl groups. In 1 an ideal disorder over two positions was assumed for the placement of the H-atoms of the methyl group (AFIX 127). In 2 the terminal C of the ethyl group is disordered over two position. The C=C bond lengths were restrained to be equal (SADI). In 3 the CF3 groups show rotational disorder and were modelled with two alternate positions. The anisotropic displacement parameters suggest further disorder however the residual electron density is too featureless to identify and refine further alternate positions. All bond lengths and angles of the CF3 groups were restrained to be equal (SADI) and RIGU restraints were applied to the anisotropic displacement parameters of the fluorine atoms.

CCDC-2076795 (1), -2076796 (2), and -2076797 (3) 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.

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Huang, T.-T. Liao, C.-C. Lin, J. Polym. Sci. Part A 2013, 51, 1185–1196; f) W.-J. Chuang, Y.-T. Huang, Y.-H. Chen, Y.-S. Lin, W.-Y. Lu, Y.-C. Lai, M. Y. Chiang, S. C. N. Hsu, H.-Y. Chen, RSC Adv. 2016, 6, 33014–33021; g) H.-Y. Tang, H.-Y. Chen, J.-H. Huang, C.-C. Lin, Macromolecules 2007, 40, 8855–8860.

[4] a) B. Raghavendra, P. V. S. Shashank, M. K. Pandey, N. D. Reddy, Organometallics 2018, 37, 1656–1664; b) H.-C. Huang, Z.-J. Li, B. Wang, X. Chen, Y.-S. Li, J. Polym. Sci. Part A 2018, 56, 203–212; c) Y. Huang, X. Kou, Y.-L. Duan, F.-F. Ding, Y.-F. Yin, W. Wang, Y. Yang, Dalton Trans. 2018, 47, 8121–8133; d) Y.-H. Chen, Y.-J. Chen, H.-C. Tseng, C.-J. Lian, H.-Y. Tsai, Y.-C. Lai, S. C. N. Hsu, M. Y. Chiang, H.-Y. Chen, RSC Adv. 2015, 5, 100272–100280; e) H.-L. Chen, H.-J. Chuang, B.-H. Huang, C.-C. Lin, Inorg. Chem. Commun. 2013, 35, 247–251; f) M.-W. Hsiao, C.-C. Lin, Dalton Trans. 2013, 42, 2041–2051.

[5] a) P. Steiniger, P. M. Schäfer, C. Wölper, J. Henkel, A. N. Ksiazkiewicz, A. Pich, S. Herres-Pawlis, S. Schulz, Eur. J. Inorg. Chem. 2018, 4014–4021; b) S. Ghosh, P. M. Schäfer, D. Dittrich, C. Scheiper, P. Steiniger, G. Fink, A. N. Ksiazkiewicz, A. Tjaberings, C. Wölper, A. H. Gröschel, A. Pich, S. Herres-Pawlis, S. Schulz, Chem. Open 2019, 8, 951–960; c) C. Di Iulio, M. Middleton, G. Kociok-Köhn, M. D. Jones, A. L. Johnson, Eur. J. Inorg. Chem. 2013, 1541–1554; d) C. Scheiper, D. Dittrich, C. Wölper, D. Bläser, J. Roll, S. Schulz, Eur. J. Inorg. Chem. 2014, 2230–2240.

[6] a) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, J. Am. Chem. Soc. 2001, 123, 3229–3238; b) M. H. Chisholm, J. C. Huffman, K. J. Phomphrai, Dalton Trans. 2001, 222–224; c) M. H. Chisholm, K. Phomphrai, Inorg. Chim. Acta 2003, 350, 121–125; d) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, Dalton Trans. 2004, 570–578; e) L. F. Sanchez-Barba, D. L. Hughes, S. M. Humphrey, M. Bochmann, Organometallics 2006, 25, 1012–1020; f) C. N. Ayala, M. H. Chisholm, J. C. Gallucci, C. Krempner, Dalton Trans. 2009, 9237–9245; g) H.-Y. Chen, B.-H. Huang, C.-C. Lin, Macromolecules 2005, 38, 5400–5405; h) M. H. Chisholm, J. C. Gallucci, K. Phomphrai, Inorg. Chem. 2005, 44, 8004–8010.

[7] N. M. Rezayee, K. A. Gerling, A. L. Rheingold, J. M. Fritsch, Dalton Trans. 2013, 42, 5573–5586.

[8] a) R. M. Slattery, A. E. Stahl, K. R. Berretton, A. L. Rheingold, D. B. Green, J. M. Fritsch, J. Polym. Sci. Part A 2019, 57, 48–59; b) K. A. Gerling, N. M. Rezayee, A. L. Rheingold, D. B. Green, J. M. Fritsch, Dalton Trans. 2014, 43, 16498–16508.

[9] W.-Y. Lu, K.-H. Wu, H.-Y. Chen, C.-C. Lin, Front. Chem. 2019, 7, 189 (1–11).

[10] A. Kronast, M. Reiter, P. T. Altenbuchner, C. Jandl, A. Pöthig, B. Rieger Organometallics 2016, 35, 681–685.

[11] M. Fuchs, S. Schmitz, P. M. Schäfer, T. Secker, A. Metz, A. N. Ksiazkiewicz, A. Pich, P. Kögerler, K. Y. Monakhov, S. Herres-Pawlis, Eur. Polym. J. 2020, 122, 109302–109308.

[12] D. M. González, J. Cisterna, I. Brito, T. Roisnel, J.-R. Hamon, C. Manzur, Polyhedron 2019, 162, 91–99.

[13] a) K. Huse, H. M. Weinert, C. Wölper, S. Schulz, Dalton Trans. 2020, 49, 9773–9780; b) K. Huse, C. Wölper, S. Schulz, Eur. J. Inorg. Chem. 2018, 3472–3478.

[14] K. Huse, B. Li, S. Ghosh, C. Wölper, S. Schulz, Z. Anorg. Allg. Chem. 2021, 647, 430–435.

[15] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, Organometallics 2010, 29, 2176–2179.

[16] E. Durand, M. Clemanecy, A.-A. Quoineaud, J. Verstraete, D. Espinat, J.-M. Lancelin, Energy Fuels 2008, 22, 2604–2610.

[17] M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Keen, M. A. Hillmyer, E. J. Munson, Macromolecules 2002, 35, 7700–7707.

[18] K. Huse, C. Wölper, S. Schulz, Eur. J. Inorg. Chem. 2018, 3472–3478.

[19] G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467–473.

[20] G. M. Sheldrick, Acta Crystallogr. Sect. A 2008, 64, 112–122.

[21] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, J. Appl. Crystallogr. 2011, 44, 1281–1284.

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\[ \text{rac-LA} \rightarrow \text{BnOH, Toluene, 100 °C} \rightarrow \text{Isotactically enrich PLA} \]