UCLA

UCLA Previously Published Works

Title

Highly Active Yttrium Catalysts for the Ring-Opening Polymerization of ϵ -Caprolactone and δ -Valerolactone

Permalink

<https://escholarship.org/uc/item/1cm7724p>

Journal

Organometallics, 34(19)

ISSN

0276-7333

Authors

Wang, X
Brosmer, JL
Thevenon, A
et al.

Publication Date

2015-10-12

DOI

10.1021/acs.organomet.5b00442

Peer reviewed

Highly Active Yttrium Catalysts for the Ring-Opening Polymerization of ϵ -Caprolactone and δ -Valerolactone

Xinke Wang, Jonathan L. Brosmer, Arnaud Thevenon, and Paula L. Diaconescu*

Department of Chemistry and Biochemistry, University of California, Los Angeles, 607 Charles E Young Drive East,
Los Angeles, CA 90095

Supporting Information Placeholder

ABSTRACT: The activity of several yttrium alkoxide and aryloxide complexes supported by a ferrocene-based ligand incorporating two thiol phenolates, thiolfan (1,1'-di(2,4-di-*tert*-butyl-6-thiomethylenephenoxy)ferrocene), was studied. The *t*-butoxide complex could only be isolated in the ate form, while a monophenoxide complex could be obtained for OAr = 2,6-di-*tert*-butylphenolate. The synthetic utility of these yttrium complexes has been demonstrated by the ring-opening polymerization of cyclic esters with a high activity toward ϵ -caprolactone and δ -valerolactone being found for the yttrium phenoxide complex.

INTRODUCTION

Polyesters such as polycaprolactone (PCL) and polyvalerolactone (PVL) are considered “green materials” because they are biocompatible, readily biodegradable, and easily recyclable.¹⁻⁴ The lack of toxicity of PCL makes it attractive as a matrix for drug delivery systems, especially since it is considerably less expensive than other biodegradable polyesters, such as polyglycolide, polylactide, or their copolymers.⁵ Although tin and aluminum compounds have been widely used as catalysts in the ring-opening polymerization of cyclic esters,⁶⁻⁷ rare earth metal complexes represent an attractive choice due to their low toxicity, rich and diverse coordination chemistry, and high reactivity.⁸⁻¹⁷ Among them, yttrium is relatively inexpensive, readily available, and shows promising reactivity. Ligand design is crucial to the activity of the resulting metal complexes. In our group, we have been interested in ferrocene-derived metal complexes because the ferrocene group provides a strong electronic donation and a unique geometry for the resulting metal complexes.¹⁸⁻³¹ Herein, we report the synthesis and characterization of new yttrium complexes supported by ferrocene-based ligands that are extremely active catalysts for the polymerization of ϵ -caprolactone or δ -valerolactone.

RESULTS AND DISCUSSION

Synthesis and characterization of metal complexes. The precursor $H_2(\text{thiolfan})$ (1,1'-di(2,4-di-*tert*-butyl-6-thiomethylenepheno)ferrocene) was previously used by our group as a supporting ligand for zirconium.³² Its sodium salt was obtained by deprotonation with an excess amount of sodium hydride in THF, and then used in situ, after filtration, in a reaction with an equivalent amount of $YCl_3(THF)_3$ at ambient temperature (Eq 1). After removing the volatiles under a reduced pressure, the residue was extracted with toluene, and the filtrate was concentrated and layered with hexanes. Cooling down this solution to -30 °C led to the precipitation of a pale yellow solid in high yield (84%). The product, $(\text{thiolfan})YCl(THF)$, was found to coordinate a THF molecule by NMR spectroscopy, but recrystallization using the procedure described above afforded a THF free compound. The solid state molecular structure

of [(thiolfan)YCl]₂ indicates a dinuclear complex (Figure 1); in solution, the structure has higher symmetry than in the solid state as attested by the presence of only two *t*-butyl peaks found for the four *t*-butyl groups. In addition, in (thiolfan)YCl (Figure 1), the two yttrium thiolfan fragments are held together by bridging chloride ligands in such a way that each metal ion adopts a distorted octahedral geometry with the two chlorides arranged cis to one another.

Figure 1. Solid state molecular structure with thermal ellipsoids represented at 50% probability of one of the two crystallographically independent molecules of [(thiolfan)YCl]₂; hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Y(1)-O(1), 2.072(3); Y(1)-O(2), 2.072(3); Y(1)-Cl*, 2.6882(11); Y(1)-Cl(1), 2.7115(12); Y(1)-S(1), 2.8702(11); Y(1)-S(2), 2.9713(12); O(1)-Y(1)-O(2), 112.32(10); O(1)-Y(1)-Cl*, 97.86(7); O(2)-Y(1)-Cl*, 90.80(7); O(1)-Y(1)-Cl(1), 101.44(7); O(2)-Y(1)-

Cl(1), 145.99(7); Cl*-Y(1)-Cl(1), 80.39(4); O(1)-Y(1)-S(1), 70.61(7); O(2)-Y(1)-S(1), 101.25(7); Cl*-Y(1)-S(1), 165.74(3); Cl(1)-Y(1)-S(1), 93.44(3); O(1)-Y(1)-S(2), 155.77(7); O(2)-Y(1)-S(2), 75.31(7); Cl*-Y(1)-S(2), 105.15(3); Cl(1)-Y(1)-S(2), 75.49(3); S(1)-Y(1)-S(2), 85.47(3).

Scheme 1. Synthesis of yttrium complexes.

The stoichiometric reaction of potassium *t*-butoxide with (thiolfan)YCl(THF) in toluene led to the formation of a yellow compound in 46% yield (Scheme 1): the ¹H NMR spectrum of the isolated product showed two sets of *t*-butoxide peaks; X-ray diffraction analysis confirmed that the product is the ate complex (thiolfan)Y(OrBu)₂K (Figure 2). The solid state molecular structure of (thiolfan)Y(OrBu)₂K (Figure 2) shows a polymeric compound displaying potassium-arene interactions between repeating units, as observed for other ionic complexes by us^{18, 23, 26, 33-35} and others.³⁶⁻⁴² The two *t*-butoxide ligands are equivalent; potassium interacts with both an intramolecular alkoxide oxygen donor and in an η⁶ fashion intermolecularly with a phenyl aryloxide ring to form a one dimensional polymer. The solution structure

of (thiolfan)Y(*O**t*Bu)₂K indicates that the polymer dissociates in solution, as attested by ¹H NMR spectroscopy (Figure S3).

Figure 2. Solid state molecular structure with thermal ellipsoids represented at 50% probability of (thiolfan)Y(*O**t*Bu)₂K; hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Y-O(2), 2.088(7); Y-O(2)#1, 2.088(7); Y-O(1), 2.190(5); Y-O(1)#1, 2.190(5); Y-S, 3.0180(18); Y-S#1, 3.0180(18); O(2)-Y-O(2)#1, 107.7(5); O(2)-Y-O(1), 101.5(3); O(2)#1-Y-O(1), 91.7(3); O(2)-Y-O(1)#1, 91.7(3); O(2)#1-Y-O(1)#1, 101.5(3); O(1)-Y-O(1)#1, 157.6(2); O(2)-Y-S, 165.5(3); O(2)#1-Y-S, 86.5(2); O(1)-Y-S, 74.27(13); O(1)#1-Y-S, 88.46(12); O(2)-Y-S#1, 86.5(2); O(2)#1-Y-S#1, 165.5(3); O(1)-Y-S#1, 88.46(12); O(1)#1-Y-S#1, 74.27(13).

Compound (thiolfan)Y(*O**t*Bu)₂K was synthesized in high yield (94%) by adding two equivalents of potassium *t*-butoxide; the one-pot synthesis from (thiolfan)H₂ also works in high yield (84%). Removal of potassium *t*-butoxide by adding THF or 18-crown-6 was not successful. However, potassium *t*-butoxide likely dissociates by adding THF (Figure S12), since *t*-butyl proton signals are shifted greatly in the corresponding ¹H NMR spectrum and are no longer equivalent in solution. The addition of 18-crown-6

leads to a product in which all *t*-butoxide protons are equivalent in the corresponding ^1H NMR spectrum (Figure S13-14).

We also attempted to generate a salt free *t*-butoxide compound by starting from the corresponding benzyl complex, however, only the formation of (thiolfan)YBn₂K (Scheme 1, 81%) was observed. Interestingly, (thiolfan)YBn₂K crystallized as a cyclic tetramer (Figure 3), an unusual arrangement for ate complexes.⁴³⁻⁴⁵ In (thiolfan)YBn₂K, the potassium ion is bound to two benzyl ligands coordinated to different yttrium centers and to a phenolate ligand to form a bent sandwich diarene potassium fragment.

Figure 3. Solid state molecular structure with thermal ellipsoids represented at 50% probability of (thiolfan)YBn₂K; hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Y-O(1), 2.100(3); Y-O(2), 2.182(3); Y-C(8), 2.471(5); Y-C(1), 2.475(5); Y-S(1), 3.0439(12); Y-S(2), 3.0488(13); O(1)-Y-O(2), 163.17(11); O(1)-Y-C(8), 94.47(14); O(2)-Y-C(8), 101.14(14); O(1)-Y-C(1), 91.34(13); O(2)-Y-C(1), 94.06(14); C(8)-Y-C(1), 93.04(19); O(1)-Y-S(1), 71.40(8); O(2)-Y-S(1), 91.89(8); C(8)-Y-

S(1), 148.61(13); C(1)-Y-S(1), 114.58(13); O(1)-Y-S(2), 104.58(8); O(2)-Y-S(2), 73.70(8); C(8)-Y-S(2), 75.55(14); C(1)-Y-S(2), 160.91(11); S(1)-Y-S(2), 81.04(3).

In order to synthesize a neutral complex, NaOAr (OAr = 2,6-di-*t*-butylphenolate) was used leading to (thiolfan)Y(OAr) (Scheme 1, 93%) as assessed by NMR spectroscopy (Figures S7-8) and X-ray crystallography (Figure 4). Unlike [(thiolfan)YCl]₂, (thiolfan)YOAr is a monomer in the solid state (Figure 4), likely due to the steric hindrance of the OAr ligand. The solid structure of (thiolfan)YOAr shows a distorted trigonal bipyramidal geometry at yttrium, as the bulky OAr ligand occupies almost half of the space around yttrium (Figure 4).

Compound (thiolfan)Y[N(SiMe₃)₂] was prepared by a similar method to that used for the synthesis of (thiolfan)Y(OAr) (Scheme 1, 81%), however, it could not be crystallized under similar conditions (characterization was achieved by ¹H, ¹³C NMR spectroscopy, and elemental analysis). By adding *t*-butanol to (thiolfan)Y[N(SiMe₃)₂], (thiolfan)Y(O*t*Bu) was synthesized in situ as confirmed by ¹H NMR spectroscopy (Figure S15), however, attempts to isolate this product were unsuccessful because it decomposed while being manipulated (Figure S16). Given the instability of (thiolfan)Y(O*t*Bu), we reasoned that smaller alkoxides would be even less stable and did not attempt their synthesis.

Figure 4. Solid state molecular structure with thermal ellipsoids represented at 50% probability of (thiolfan)Y(OAr); hydrogen atoms omitted for clarity. Selected distances (Å) and angles (°): Y-O(3), 2.059(3); Y-O(1), 2.072(3); Y-O(2), 2.079(3); Y-S(2), 2.8733(14); Y-S(1), 2.9605(14); O(3)-Y-O(1), 113.32(11); O(3)-Y-O(2), 103.55(12); O(1)-Y-O(2), 113.25(12); O(3)-Y-S(2), 137.27(8); O(1)-Y-S(2), 107.35(9); O(2)-Y-S(2), 70.59(8); O(3)-Y-S(1), 92.43(8); O(1)-Y-S(1), 74.92(8); O(2)-Y-S(1), 156.25(9); S(2)-Y-S(1), 85.73(3).

Catalytic Behavior toward Ring-Opening Polymerization (ROP) of ϵ -Caprolactone (ϵ -CL) and δ -Valerolactone (δ -VL). The catalytic activity of the newly synthesized yttrium oxide complexes in the polymerization of ϵ -CL, δ -VL, and γ -BL was examined since yttrium compounds are often reported as efficient catalysts for the ring-opening polymerization of cyclic esters.^{9, 12-17, 29, 31, 46-50} Compounds (thiolfan)Y(O*t*Bu)₂K and (thiolfan)Y(OAr) exhibited high activity for the ring-opening polymerization of ϵ -CL and δ -VL, as ¹H NMR spectroscopy showed a near-quantitative monomer conversion within a relatively short time (Table 1). It is important to mention that (thiolfan)Y(OAr) has an extremely high activity toward both monomers (Table 1, entries 2, 4-8, 10, 12) showing near completion within minutes

regardless of whether THF or toluene was used. Unfortunately, the high activity leads to molecular weights higher than expected, indicating that not all catalyst molecules initiate. We attribute these results to the fact that the short reaction times do not allow all catalyst molecules to initiate and also to the fact that the high molecular weight polymers trap the catalyst. This proposal is supported by the fact that polymer molecular weights decrease somewhat with the decrease in reaction temperature (Table 1, entries 5 and 6 versus 2), and with the increase of monomer : catalyst ratios (Table 1, entry 10 versus 2).

The activity of (thiolfan)YOAr, which is capable to polymerize 1000 equivalents in 1 minute, is much higher than that of industrially used $\text{Sn}(\text{oct})_2$ ⁵¹⁻⁵² and similar to that of other highly active yttrium catalysts.⁵³⁻⁵⁶ Although the OAr ligand is rather large and could have obstructed access of the monomer to the metal center, it is likely that the high activity is a consequence of the flexibility of the coordination sphere, in which the yttrium-sulphur distances are long, indicating weak bonds. Under similar conditions, the ate complex (thiolfan) $\text{Y}(\text{OtBu})_2\text{K}$ was less active than (thiolfan)YOAr (Table 1, entries 1, 3, 9, 11). Unfortunately, neither (thiolfan) $\text{Y}(\text{OtBu})_2\text{K}$ nor (thiolfan) $\text{Y}(\text{OAr})$ is active toward $\gamma\text{-BL}$ ⁵⁷⁻⁵⁸ even at elevated temperatures, as expected based on the relative thermodynamic stability of the five-membered ring.⁵⁹

Table 1. Polymerization of cyclic esters by different yttrium catalysts.

entry	Monomer	Catalyst	CL/VL:Y	solvent	temp	time	M_n^a	PDI^b
1	CL	$\text{Y}(\text{OtBu})_2\text{K}$	500:1	toluene	25 °C	5 min	232000	1.23
2	CL	YOAr	500:1	toluene	25 °C	30 sec	224000	1.20
3	VL	$\text{Y}(\text{OtBu})_2\text{K}$	500:1	toluene	25 °C	2 min	195000	1.30
4	VL	YOAr	500:1	toluene	25 °C	1 min	187000	1.29

5	CL	YOAr	500:1	toluene	0 °C	10 min	198000	1.25
6	CL	YOAr	500:1	toluene	-30 °C	30 min	204000	1.26
7	VL	YOAr	500:1	toluene	0 °C	30 min	178000	1.30
8	VL	YOAr	500:1	toluene	-30 °C	90 min	172000	1.33
9	CL	Y(OtBu) ₂ K	1000:1	toluene	25 °C	5 min	122000	1.17
10	CL	YOAr	1000:1	toluene	25 °C	1 min	157000	1.14
11	CL	Y(OtBu) ₂ K	500:1	THF	25 °C	5 min	202000	1.24
12	CL	YOAr	500:1	THF	25 °C	2 min	218000	1.19

Conditions: monomer (2.50 mmol or 5.0 mmol), catalyst (5 μ mol), toluene or THF (5 mL), 25 °C. All reactions were carried out to 99% conversion, which was calculated by integrating representative protons from monomer and polymer. ^a Uncorrected M_n (g/mol) determined by GPC versus polystyrene standards. Samples were run in chloroform with 0.25% triethyl amine. ^b Polydispersity index (M_w/M_n).

The reaction time increases to 30 min (ϵ -CL, Table 1, entry 6) or 90 min (δ -VL, Table 1, entry 8) when the temperature is lowered to -30 °C. A solvent dependence of the polymerization behavior was also observed (Table 1, entries 10 and 11), the reactions in THF being slower for both complexes at 25 °C. All gel permeation chromatography (GPC) curves of the isolated polymers are unimodal (Figures S21-24) with narrow molecular weight distributions (polydispersity index, PDI = 1.1-1.4).

CONCLUSIONS

In conclusion, a series of novel yttrium complexes supported by an OSSO tetradentate dianionic ligand based on ferrocene, (thiolfan)YCl(THF), (thiolfan)Y(OtBu)₂K, (thiolfan)YBn₂K, (thiolfan)Y(OAr), and (thiolfan)Y[N(SiMe₃)₂], was synthesized and characterized. Compounds (thiolfan)Y(OtBu)₂K and (thiolfan)Y(OAr) were found to be extremely active single-component catalysts for the ring-opening polymerization of ϵ -CL and δ -VL, affording high molecular weight polymers with low polydispersity indices.

EXPERIMENTAL SECTION

General Procedures. All experiments were performed under a dry nitrogen atmosphere using standard Schlenk techniques or an MBraun inert-gas glove box. Solvents were purified using a two-column solid-state purification system by the method of Grubbs⁶⁰ and transferred to the glove box without exposure to air. NMR solvents were obtained from Cambridge Isotope Laboratories, degassed, and stored over activated molecular sieves prior to use. Nuclear magnetic resonance spectra were recorded on Bruker AV300 or Bruker AV500 spectrometers at 25 °C in C₆D₆. Chemical shifts are reported with respect to solvent residual peaks, 7.16 ppm (C₆D₆). 2,6-di-*tert*-butylphenol and sodium hydride were purchased from Sigma Aldrich and used as received. Potassium *t*-butoxide was purchased from Strem Chemicals Inc., directly brought into a glovebox without exposure to air or moisture, and used as received. ϵ -Caprolactone, δ -valerolactone, and γ -butyrolactone were dried over CaH₂ overnight and distilled before use. Potassium benzyl,⁶¹ NaOAr(THF),⁶² (thiolfan)H₂,³² and YCl₃(THF)₃³⁴ were prepared according to literature procedures. CHN analyses were performed in house on a CE-440 elemental analyzer manufactured by Exeter Analytical, Inc. Molecular weights of the polymers were determined by GPC-LLS and GPC-MALS. GPC-LLS uses an Agilent liquid chromatograph equipped with an Agilent 2690 series pump and autosampler, two columns, Agilent, PLGEL 5 μ m, MIXED-D, 300x7.5 mm, and two detectors, Waters 2410 Differential Refractometer, Waters 2998 Photodiode Array Detector. GPC-MALS uses Waters Alliance 2695 pump and two MZ-Gel SD columns, a Wyatt DAWN HELEOS-II, a Wyatt Optilab rEX, Waters 2996 Photodiode Array Detector and a Wyatt ViscoStar viscometer. The column temperature was set at 25 °C. A flow rate of 1.0 mL/min was used and samples were dissolved in chloroform with 0.25% of triethylamine. Narrow molecular weight polystyrene standards were used for calibration purposes.

Synthesis of (thiolfan)YCl. To a solution of (thiolfan)H₂ (138 mg, 0.20 mmol) in THF (5 mL), a slurry of sodium hydride (48 mg, 2.0 mmol) in THF (2 mL) was added slowly; the mixture was kept stirring for 2 h at room temperature and filtered through glass fiber. The clear filtrate was then added

slowly to a slurry of $\text{YCl}_3(\text{THF})_3$ (82 mg, 0.20 mmol) in THF (3 mL) at room temperature. The cloudy mixture became clear then cloudy again after stirring at room temperature for 2 h. A clear yellow solution was obtained after filtering through glass fiber and volatiles were removed under reduced pressure. The crude product was redissolved in 2 mL of toluene, 3 mL hexanes was layered, and the mixture was kept at $-30\text{ }^\circ\text{C}$. After one day, the solution was filtered and (thiolfan) $\text{YCl}(\text{THF})$ was collected as a pale yellow powder on a medium frit. Yield: 148 mg, 84%. Single crystals of $[(\text{thiolfan})\text{YCl}]_2$ suitable for X-ray diffraction were grown from a concentrated toluene/hexanes solution. ^1H NMR (500 MHz, C_6D_6) δ , ppm: 7.54, 6.77 (d, 2H, $^4J_{\text{HH}} = 2.4\text{ Hz}$, CH of phenolate), 4.67 (broad, 4H, CpH), 4 protons on Cp are too broad and likely overlap with other protons, 3.86 (broad, 4H, SCH_2), 3.75 (broad, 4H, OCH_2 on THF), 1.74 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.35 (broad, 4H, CH_2 on THF), 1.29 (s, 18H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125 MHz, C_6D_6) δ , ppm: 160.3, 138.6, 136.6, 129.3, 126.0 and 123.8 (C and CH on phenolate), 76.7, 71.6 (CH on Cp rings), 70.2 (CS on Cp rings), 74.2 (OC on THF), 43.7 (SCH_2), 35.6, 34.2 ($\text{C}(\text{CH}_3)_3$), 31.9, 30.8 ($\text{C}(\text{CH}_3)_3$), 25.5 (C on THF). Elemental analysis (%): Calcd for $\text{C}_{40}\text{H}_{52}\text{ClFeO}_2\text{S}_2\text{Y}$: C, 59.37; H, 6.48. Found: C, 58.90; H, 6.67.

Synthesis of (thiolfan) $\text{Y}(\text{OtBu})_2\text{K}$. To a solution of (thiolfan) YCl (120 mg, 0.15 mmol) in toluene (3 mL), a slurry of potassium *t*-butoxide (34 mg, 0.30 mmol) in toluene (2 mL) was added slowly; the mixture was kept stirring for 2 h at room temperature. A clear yellow solution was obtained after filtering through glass fiber and volatiles were removed under reduced pressure. The crude product was redissolved in 2 mL of toluene, 1 mL of hexanes was layered, and the mixture was kept at $-30\text{ }^\circ\text{C}$. After overnight, the solution was filtered and (thiolfan) $\text{Y}(\text{OtBu})_2\text{K}$ was collected as a pale yellow microcrystalline solid on a medium frit. Yield: 133 mg, 94%. Single crystals suitable for X-ray diffraction were grown from a concentrated toluene/hexanes solution. ^1H NMR (500 MHz, C_6D_6) δ , ppm: 7.54 and 6.67 (d, 4H, $^4J_{\text{HH}} = 2.5\text{ Hz}$, CH of phenolate), 4.22, 3.89 (broad, 8H, CH on Cp rings), 3.69 (broad, 4H, SCH_2), 1.91 (s, 18H, $\text{C}(\text{CH}_3)_3$), 1.40 (broad, 18H, $\text{OC}(\text{CH}_3)_3$), 1.28 (s, 18H, $\text{C}(\text{CH}_3)_3$). ^{13}C NMR (125 MHz, C_6D_6) δ , ppm: 162.0, 136.2, 127.4, 124.1 and 123.2 (C and CH on phenolate), 76.4 (broad, CH on Cp rings), 73.8 (CH on Cp rings), 70.7 (broad, $\text{OC}(\text{CH}_3)_3$ or C on Cp rings), 69.9 (SCH_2), 41.3, 35.8, 34.0 ($\text{C}(\text{CH}_3)_3$), 35.4

(OC(CH₃)₃), 32.1, 31.2 (C(CH₃)₃). Elemental analysis (%): Calcd for C₄₈H₇₀FeKO₄S₂Y: C, 60.11; H, 7.36. Found: C, 60.23; H, 7.84.

Synthesis of (thiolfan)YBn₂K. To a solution of (thiolfan)YCl (53 mg, 0.065 mmol) in toluene (5 mL), a slurry of potassium benzyl (17 mg, 0.13 mmol) in toluene (5 mL) was added slowly; the mixture was kept stirring for 1 h at room temperature. A clear yellow solution was obtained after filtering through glass fiber and volatiles were removed under reduced pressure. The crude product was redissolved in 1 mL toluene, 1 mL hexanes was layered, and the mixture was kept at -30 °C. After one day, the solution was filtered and (thiolfan)YBn₂K was collected as a yellow power on a medium frit. Yield: 53 mg, 81%. Single crystals suitable for X-ray diffraction were grown from a concentrated toluene/hexanes solution. ¹H NMR (500 MHz, C₆D₆) δ, ppm: 7.53 and 6.59 (d, 4H, ⁴J_{HH} = 2.5 Hz, CH of phenolate), 7.00-7.07 (m, 4H, CH on benzyls), 6.90 (t, J_{HH} = 3.0 Hz, 4H, CH on benzyls), 6.34 (t, J_{HH} = 1.9 Hz, *p*-PhH), 3.72, 3.66 (broad, 8H, CH on Cp rings), 3.66 (broad, 4H, SCH₂), 2.64 (broad, 4H, PhCH₂), 1.89 (s, 18H, C(CH₃)₃), 1.26 (s, 18H, C(CH₃)₃). The ¹³C NMR spectrum was not recorded because of low solubility. Elemental analysis (%): Calcd for C₅₄H₆₆FeKO₂S₂Y: C, 65.18; H, 6.69. Found: C, 65.80; H, 6.94.

Synthesis of (thiolfan)Y(OAr). To a solution of (thiolfan)YCl (200 mg, 0.247 mmol) in THF (5 mL), a solution of NaOAr(THF) (75 mg, 0.25 mmol) in THF (5 mL) was added slowly; the mixture was kept stirring for 1 h at room temperature. A clear yellow solution was obtained after filtering through glass fiber and volatiles were removed under reduced pressure. The crude product was redissolved in 2 mL hexanes and the mixture was kept at -30 °C. After one day, the solution was filtered and (thiolfan)YOAr was collected as a yellow microcrystalline solid on a medium frit. Yield: 225 mg, 93%. Single crystals suitable for X-ray diffraction were grown from a concentrated hexanes solution. ¹H NMR (300 MHz, C₆D₆) δ, ppm: 7.50 and 6.77 (d, 4H, ⁴J_{HH} = 2.5 Hz, CH of phenolate), 7.38 (d, ³J_{HH} = 1.8 Hz, 2H, *m*-CH on OAr), 6.87-6.93 (m, 1H, *p*-CH on OAr), 4.00 (broad, CH on Cp rings and SCH₂), 1.77 (s, 18H, C(CH₃)₃), 1.69 (s, 18H, C(CH₃)₃ on OAr), 1.26 (s, 18H, C(CH₃)₃). ¹³C NMR (125 MHz, C₆D₆) δ, ppm: 161.9, 160.2, 138.5, 137.7, 137.0, 125.8, 125.2, 124.3, 122.1, 117.5, 75.6, 74.5, 71.8, (CH and C on Cp

rings), 42.8 (SCH₂), 35.6, 34.9, 34.1 (C(CH₃)₃), 32.3, 31.9, 30.6 (C(CH₃)₃). Elemental analysis (%): Calcd for C₅₄H₇₃FeO₃S₂Y: C, 66.25; H, 7.52. Found: C, 65.78; H, 7.67.

Synthesis of (thiolfan)Y[N(SiMe₃)₂]. To a solution of (thiolfan)YCl (150 mg, 0.185 mmol) in toluene (5 mL), a slurry of sodium hexamethyldisilazide (31 mg, 0.19 mmol) in toluene (5 mL) was added slowly; the mixture was kept stirring for 30 min at room temperature. A clear yellow solution was obtained after filtering through glass fiber and volatiles were removed under reduced pressure. The crude product was redissolved in 2 mL hexanes and the mixture was kept at -30 °C. After one day, the solution was filtered and (thiolfan)Y[N(SiMe₃)₂] was collected as a yellow microcrystalline solid on a medium frit. Yield: 140 mg, 81%. ¹H NMR (500 MHz, C₆D₆) δ, ppm: 7.50 and 6.73 (d, 4H, ⁴J_{HH} = 2.5 Hz, CH of phenolate), 3.97 (broad, 8H, CH on Cp rings and SCH₂), 3.71 (s, 4H, CH on Cp rings), 1.73 (s, 18H, C(CH₃)₃), 1.27 (s, 18H, C(CH₃)₃), 0.56 (s, 18H, Si(CH₃)₃). ¹³C NMR (125 MHz, C₆D₆) δ, ppm: 160.2 (CO on phenolate), 138.4, 137.0, 126.0, 124.2 and 122.6 (C on phenolate), 76.2 and 71.7 (CH on Cp rings), 74.6 (SC on Cp rings), 43.4 (SCH₂), 35.6 and 34.2 (C(CH₃)₃), 31.9 and 30.6 (C(CH₃)₃), 4.8 (C on TMS). Elemental analysis (%): Calcd for C₄₆H₇₀FeNO₂S₂Si₂Y: C, 59.15; H, 7.55; N, 1.50. Found: C, 58.77; H, 7.86; N, 1.76.

Typical procedure for polymerization reactions. The procedures for the polymerization of ε-caprolactone, δ-valerolactone, and copolymerization of ε-caprolactone with γ-butyrolactone initiated by (thiolfan)Y(OTBu)₂K and (thiolfan)Y(OAr) were similar; a typical polymerization procedure is given herein. A 20 mL vial equipped with a magnetic stirring bar was charged with the desired amount of monomer and solvent. After the monomer was dissolved, a solution of the catalyst was added to the previous solution by syringe in one portion. The mixture was immediately stirred vigorously for the desired time; an increase in the viscosity of the solution was observed. The reaction mixture was quenched by the addition of wet hexanes and then poured into cold methanol (20 mL) to precipitate the polymer, which was dried under reduced pressure and weighed.

X-ray crystallographic structure determinations. X-ray quality crystals were obtained from various concentrated solutions placed in a -40 °C freezer in the glove box. Inside the glove box, the crystals were coated with oil (STP Oil Treatment) on a microscope slide, which was brought outside the glove box. The X-ray data collections were carried out on a Bruker SMART 1000 single crystal X-ray diffractometer using MoK α 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 structure was solved and refined using SHELXTL (Bruker 1998, SMART, SAINT, XPREP AND SHELXTL, Bruker AXS Inc., Madison, Wisconsin, USA). Tables with atomic coordinates and equivalent isotropic displacement parameters, with all the distances and angles and with anisotropic displacement parameters are listed in the cif.

ASSOCIATED CONTENT

Supporting Information. Synthetic details, ¹H NMR spectra, and data from the computational studies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

Email for P.L.D.: pld@chem.ucla.edu

The authors declare no competing financial interests.

ACKNOWLEDGMENT

This work was supported by the NSF (CAREER Grant 0847735 and 1362999 to PLD and CHE-1048804 for NMR spectroscopy) and ACS PRF. Polymers were characterized by GPC at the MRL Shared Experimental Facilities in UCSB that is supported by the MRSEC Program of the National Science Foundation under award NSF DMR 1121053; a member of the NSF-funded Material Research Facilities Network. We thank Dr. Rachel Behrens at the MRL at UCSB for her help with polymer characterization.

DEDICATION

Dedicated to the memory of Gregory L. Hillhouse, a great inspiration and an amazing scientist.

REFERENCES

1. Woodruff, M. A.; Hutmacher, D. W., *Prog. Polym. Sci.* **2010**, *35* (10), 1217-1256.
2. Arbaoui, A.; Redshaw, C., *Polym. Chem.* **2010**, *1* (6), 801-826.
3. Tian, H.; Tang, Z.; Zhuang, X.; Chen, X.; Jing, X., *Prog. Polym. Sci.* **2012**, *37* (2), 237-280.
4. Auras, R.; Harte, B.; Selke, S., *Macromol. Biosci.* **2004**, *4* (9), 835-864.
5. Sinha, V. R.; Bansal, K.; Kaushik, R.; Kumria, R.; Trehan, A., *Int. J. Pharm.* **2004**, *278* (1), 1-23.
6. Iwasa, N.; Fujiki, M.; Nomura, K., *J. Mol. Catal. Chem.* **2008**, *292* (1-2), 67-75.
7. Dechy-Cabaret, O.; Martin-Vaca, B.; Bourissou, D., *Chem. Rev.* **2004**, *104*, 6147.
8. Dyer, H. E.; Huijser, S.; Susperregui, N.; Bonnet, F.; Schwarz, A. D.; Duchateau, R.; Maron, L.; Mountford, P., *Organometallics* **2010**, *29* (16), 3602-3621.
9. Kramer, J. W.; Treitler, D. S.; Dunn, E. W.; Castro, P. M.; Roisnel, T.; Thomas, C. M.; Coates, G. W., *J. Am. Chem. Soc.* **2009**, *131* (44), 16042-16044.
10. Ma, H.; Spaniol, T. P.; Okuda, J., *Angew. Chem. Int. Ed.* **2006**, *45* (46), 7818-7821.
11. Nakano, K.; Kosaka, N.; Hiyama, T.; Nozaki, K., *Dalton Transactions* **2003**, (21), 4039-4050.
12. Ma, H.; Spaniol, T. P.; Okuda, J., *Dalton Trans.* **2003**, (24), 4770-4780.
13. O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B., *J. Chem. Soc. Dalton Trans.* **2001**, 2215.
14. Chamberlain, B. M.; Jazdzewski, B. A.; Pink, M.; Hillmyer, M. A.; Tolman, W. B., *Macromolecules* **2000**, *33* (11), 3970-3977.
15. Maudoux, N.; Roisnel, T.; Carpentier, J.-F.; Sarazin, Y., *Organometallics* **2014**, *33* (20), 5740-5748.
16. Zhang, W.; Liu, S.; Yang, W.; Hao, X.; Glaser, R.; Sun, W.-H., *Organometallics* **2012**, *31* (23), 8178-8188.
17. Bakewell, C.; Cao, T.-P.-A.; Long, N.; Le Goff, X. F.; Auffrant, A.; Williams, C. K., *J. Am. Chem. Soc.* **2012**, *134* (51), 20577-20580.
18. Huang, W.; Diaconescu, P. L., Rare Earth Arene-bridged Complexes Obtained by Reduction of Organometallic Precursors. In *Handbook on the Physics and Chemistry of Rare Earths*, Bünzli, J.-C.; Pecharsky, V., Eds. Elsevier: Amsterdam, The Netherlands, 2014; Vol. 45, pp 261-329.
19. Diaconescu, P. L., *Comments Inorg. Chem.* **2010**, *31* (5-6), 196-241.
20. Diaconescu, P. L., *Acc. Chem. Res.* **2010**, *43* (10), 1352-1363.
21. Brosmer, J. L.; Diaconescu, P. L., *Organometallics* **2015**, *34* (11), 2567-2572.
22. Quan, S. M.; Diaconescu, P. L., *Chem. Commun.* **2015**, *51*, 9643 - 9646.
23. Huang, W.; Le Roy, J. J.; Khan, S. I.; Ungur, L.; Murugesu, M.; Diaconescu, P. L., *Inorg. Chem.* **2015**, *54* (5), 2374-2382.
24. Abubekrov, M.; Diaconescu, P. L., *Inorg. Chem.* **2015**, *54* (4), 1778-1784.
25. Huang, W.; Dulong, F.; Khan, S. I.; Cantat, T.; Diaconescu, P. L., *J. Am. Chem. Soc.* **2014**, *136* (50), 17410-17413.
26. Huang, W.; Dulong, F.; Wu, T.; Khan, S. I.; Miller, J. T.; Cantat, T.; Diaconescu, P. L., *Nat. Commun.* **2013**, *4*, 1448.
27. Green, A. G.; Kiesz, M. D.; Oria, J. V.; Elliott, A. G.; Buechler, A. K.; Hohenberger, J.; Meyer, K.; Zink, J. I.; Diaconescu, P. L., *Inorg. Chem.* **2013**, *52* (9), 5603-5610.
28. Duhović, S.; Oria, J. V.; Odoh, S. O.; Schreckenbach, G.; Batista, E. R.; Diaconescu, P. L., *Organometallics* **2013**, *32* (20 (SI: Ferrocene: Beauty and Function)), 6012-6021.
29. Broderick, E. M.; Thuy-Boun, P. S.; Guo, N.; Vogel, C. S.; Sutter, J.; Miller, J. T.; Meyer, K.; Diaconescu, P. L., *Inorg. Chem.* **2011**, *50* (7), 2870-2877.
30. Broderick, E. M.; Guo, N.; Wu, T.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Cantat, T.; Diaconescu, P. L., *Chem. Commun.* **2011**, *47*, 9897-9899.
31. Broderick, E. M.; Guo, N.; Vogel, C. S.; Xu, C.; Sutter, J.; Miller, J. T.; Meyer, K.; Mehrkhodavandi, P.; Diaconescu, P. L., *J. Am. Chem. Soc.* **2011**, *133* (24), 9278-9281.
32. Wang, X.; Thevenon, A.; Brosmer, J. L.; Yu, I.; Khan, S. I.; Mehrkhodavandi, P.; Diaconescu, P. L., *J. Am. Chem. Soc.* **2014**, *136* (32), 11264-11267.

33. Huang, W.; Abukhalil, P. M.; Khan, S. I.; Diaconescu, P. L., *Chem. Commun.* **2014**, 50 (40), 5221 - 5223.
34. Huang, W.; Upton, B. M.; Khan, S. I.; Diaconescu, P. L., *Organometallics* **2013**, 32 (5, SI: Recent Advances in Organo-f-Element Chemistry), 1379–1386.
35. Diaconescu, P. L.; Cummins, C. C., *Inorg. Chem.* **2012**, 51 (5), 2902-2916.
36. Watt, M. M.; Collins, M. S.; Johnson, D. W., *Acc. Chem. Res.* **2013**, 46 (4), 955-966.
37. Wheeler, S. E., *Acc. Chem. Res.* **2013**, 46 (4), 1029-1038.
38. Gokel, George W.; De Wall, Stephen L.; Meadows, Eric S., *Eur. J. Org. Chem.* **2000**, 2000 (17), 2967-2978.
39. Ma, J. C.; Dougherty, D. A., *Chem. Rev.* **1997**, 97 (5), 1303-1324.
40. Mahadevi, A. S.; Sastry, G. N., *Chem. Rev.* **2013**, 113 (3), 2100-2138.
41. Nikiforov, G. B.; Crewdson, P.; Gambarotta, S.; Korobkov, I.; Budzelaar, P. H. M., *Organometallics* **2007**, 26 (1), 48-55.
42. Armstrong, D. R.; Brammer, E.; Cadenbach, T.; Hevia, E.; Kennedy, A. R., *Organometallics* **2013**, 32 (2), 480-489.
43. Honeyman, G. W.; Kennedy, A. R.; Mulvey, R. E.; Sherrington, D. C., *Organometallics* **2004**, 23 (6), 1197-1199.
44. Wooles, A. J.; Gregson, M.; Robinson, S.; Cooper, O. J.; Mills, D. P.; Lewis, W.; Blake, A. J.; Liddle, S. T., *Organometallics* **2011**, 30 (20), 5326-5337.
45. Gärtner, M.; Görls, H.; Westerhausen, M., *Inorg. Chem.* **2008**, 47 (4), 1397-1405.
46. Cao, T.-P.-A.; Buchard, A.; Le Goff, X. F.; Auffrant, A.; Williams, C. K., *Inorg. Chem.* **2012**, 51 (4), 2157-2169.
47. Alaaeddine, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J.-F., *Organometallics* **2009**, 28 (5), 1469-1475.
48. Ma, H.; Spaniol, T. P.; Okuda, J., *Inorg. Chem.* **2008**, 47 (8), 3328-3339.
49. Amgoune, A.; Thomas, C. M.; Carpentier, J.-F., *Macromol. Rapid Commun.* **2007**, 28 (6), 693-697.
50. Hitzbleck, J.; Beckerle, K.; Okuda, J.; Halbach, T.; Mülhaupt, R., *Macromol. Symp.* **2006**, 236 (1), 23-29.
51. Stjerndahl, A.; Finne-Wistrand, A.; Albertsson, A. C.; Bäckesjö, C. M.; Lindgren, U., *J. Biomed. Mater. Res. A* **2008**, 87A (4), 1086-1091.
52. Jiang, G.; Jones, I. A.; Rudd, C. D.; Walker, G. S., *J. Appl. Polym. Sci.* **2009**, 114 (1), 658-662.
53. Zheng, Y.; Jiao, R.; Shen, X.-d.; Xue, M.-q.; Yao, Y.-m.; Zhang, Y.; Shen, Q., *Appl. Organomet. Chem.* **2014**, 28 (6), 461-470.
54. Shen, X.; Xue, M.; Jiao, R.; Ma, Y.; Zhang, Y.; Shen, Q., *Organometallics* **2012**, 31 (17), 6222-6230.
55. Sheng, H.-T.; Li, J.-M.; Zhang, Y.; Yao, Y.-M.; Shen, Q., *Polyhedron* **2008**, 27 (6), 1665-1672.
56. Sheng, H.; Xu, F.; Yao, Y.; Zhang, Y.; Shen, Q., *Inorg. Chem.* **2007**, 46 (19), 7722-7724.
57. Moore, T.; Adhikari, R.; Gunatillake, P., *Biomaterials* **2005**, 26 (18), 3771-3782.
58. Nobes, G. A. R.; Kazlauskas, R. J.; Marchessault, R. H., *Macromolecules* **1996**, 29 (14), 4829-4833.
59. Houk, K. N.; Jabbari, A.; Hall, H. K.; Alemán, C., *J. Org. Chem.* **2008**, 73 (7), 2674-2678.
60. Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J., *Organometallics* **1996**, 15 (5), 1518-1520.
61. Bailey, P. J.; Coxall, R. A.; Dick, C. M.; Fabre, S.; Henderson, L. C.; Herber, C.; Liddle, S. T.; Lorono-Gonzalez, D.; Parkin, A.; Parsons, S., *Chem. Eur. J.* **2003**, 9 (19), 4820-4828.
62. Chen, H.-Y.; Mialon, L.; Abboud, K. A.; Miller, S. A., *Organometallics* **2012**, 31 (15), 5252-5261.

A yttrium aryloxide complex supported by an OSSO tetradentate dianionic ligand based on ferrocene, (thiolferrocene)Y(OAr), was found to be an extremely active single-component catalyst for the ring-opening polymerization of ϵ -CL and δ -VL, affording high molecular weight polymers with low polydispersity indices.