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Dinuclear Ce(IV) Aryloxides: Highly Active Catalysts for Anhydride/Epoxide Ring-Opening Copolymerization

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ABSTRACT: A library of new dinuclear Ce^{IV} complexes of the type [NEt₄]₂[Ce₂X₆(TP)(sol)₂] (X = Cl, ODipp, OSiMe₃; sol = py, THF), where TP represents a family of tetraphenolate ligands that control intermetallic distance, are readily made in good yields. The ligands strongly stabilize the cerium +4 oxidation state and allow the incorporation of alkylammonium co-cations in an ‘ate’ complex formulation that enables them to be used as soluble, single-component catalysts for the ring-opening copolymerization (ROCOP) of a variety of anhydrides and epoxides. High turnover frequencies (TOFs) are achieved with high ester linkage selectivity, low dispersities, and rates that are highly tunable by the intermetallic distance enforced by the TP ligand, demonstrating that a closely coupled di-Ce^{IV} unit provides excellent rates of ROCOP catalysis, and that more generally, rare earth complexes deserve further attention as ROCOP initiators.

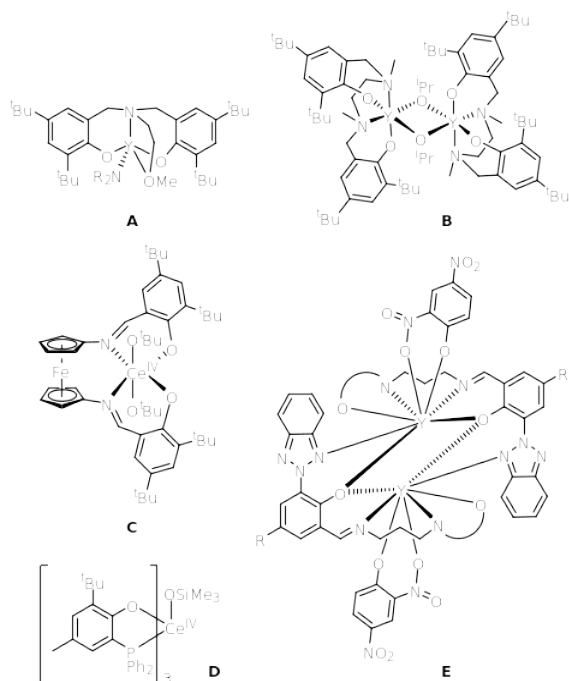
KEYWORDS: cerium, rare-earth elements, dinuclear complexes, bimetallic catalysis, ring-opening copolymerization (ROCOP)

INTRODUCTION

Key factors in realizing a polymer circular economy include the transition from producing polymers from oil-derived sources, to those made from sustainable monomers, using efficient chemical transformations.¹ This demands the development of new catalysts for polymer synthesis, and many of the rare earth elements (RE = Sc, Y, La-Lu) are ideal candidates. Some are more earth-abundant than 3d transition metals such as nickel, copper, and zinc, and their salts are less toxic by ingestion than most d-block salts, for example the LD₅₀ for cerium trichloride is six times higher than that of iron trichloride, and similar to that of sodium chloride.^{2, 3} The rare earth series provides tunability of size and Lewis acidity, and the lack of participation of d-orbitals in the predominantly ionic metal-ligand bonding allows for rapid substrate exchange and reorganization without geometric penalty that is needed for metal cation-controlled product formation and turnover.

A variety of RE complexes have been demonstrated to be active initiators for lactone polymerizations. Much of the initial work in this field was performed using yttrium complexes, which showed excellent activities combined with high levels of stereocontrol.^{4, 5} For example, Guillaume and co-workers have shown that yttrium bisphenolate complexes such as **A**, Chart 1 are active catalysts for the stereocontrolled polymerization of a range of monomers, including β -propiolactones, β -butyrolactone and lactide.⁶⁻⁸ Similarly, Coates and co-workers used a related salan ligand to make the dinuclear yttrium complex **B** (Chart 1) in order to carry out highly syndiospecific polymerizations of enantiopure β -lactones.⁹ Diaconescu and co-workers have conducted thorough investigations with the yttrium analogues of **C** (Chart 1) for the ring-opening polymerization (ROP) of lactide as well as ϵ -caprolactone and δ -valerolactone.^{10, 11}

Chart 1 Examples of RE lactone (co)polymerization catalysts ($R = CH_3; C_8H_{17}$)



A number of catalysts derived from the small, relatively abundant rare earth yttrium have shown great promise in lactone polymerization. However, the larger cerium is the most earth-abundant of the REs (60 ppm in Earth's crust). It is also the only rare earth with a readily accessible, and highly tunable, +4 oxidation state.¹² The increased Lewis acidity of the Ce^{4+} cation compared to Ce^{3+} should be exploitable in polymerization catalysis, particularly in systems that can switch between different types of reactivity.^{13, 14} Despite these attractions, reports of coordination complexes of cerium(IV) remain scarce, and applications – either as stoichiometric or, more importantly, catalytic reagents – beyond the common ceric ammonium nitrate (CAN) are more elusive.^{15, 16} Diaconescu's group demonstrated that cerium(IV) catalysts based on **C**, Chart 1 are active in lactide polymerization and our group extended this demonstration of high catalytic activity to Ce^{IV} -phosphinoaryloxide complexes (**D**, Chart 1) in a recent report.^{10, 17-19}

Some of the key catalyst features in lactone ROP, namely the Lewis acidity of the metal and the nature of the metal-oxygen bond, are also of key importance for the ring-opening copolymerization (ROCOP) of epoxides with CO₂ or anhydrides.²⁰⁻²² In epoxide/CO₂ and epoxide/anhydride ROCOP, dinuclear catalysts generally show improved activities compared to mononuclear analogues when metal cooperativity is possible, and dinuclear pathways are proposed to facilitate epoxide activation and ring-opening.^{23, 24} While highly active dinuclear main group and transition metal initiators have been reported,²⁵⁻³¹ examples of rare earth systems remain limited. The larger, more electropositive metal cations require ligands that are resistant to scrambling, and yet do not block substrate access. Strongly binding, dinucleating ligands are very limited in scope, and almost exclusively limited to Schiff-base derived systems. The rigidity of these has normally not allowed the dinuclear aspect to be probed by anything other than kinetic studies at often unrealistic catalyst concentrations. Moderately active initiators based on various rare earth trications have been reported for CO₂/epoxide ROCOP,³²⁻³⁸ yet in both ROP³⁹ and ROCOP,^{36, 40} larger size and higher Lewis acidity have yielded improved catalytic performance. Cerium complexes in both +3 and +4 oxidation state are also known to catalyze cyclic carbonate formation from CO₂/epoxide reactions.^{41, 42}

Very recently, Ko and co-workers reported the yttrium complex **E**, Chart 1 (R = CH₃; C₈H₁₇), which is a good catalyst for lactide ROP, and ROCOP of cyclohexene oxide and phthalic anhydride – the most commonly studied co-monomers.⁴³ This is the only rare earth catalyst reported so far for the ROCOP of an epoxide with a cyclic anhydride. The pre-catalyst exists as a dimer through X-ligand bridging, but this is unlikely to be retained during the catalytic transformations of oxygenated monomers. The large covalent radius of Ce (2.04 Å) means that

even in the +4 oxidation state, the ionic radius (0.87 Å) is greater than Sc^{III} (0.75 Å) and comparable with Y^{III} (0.90 Å), Dy^{III} (0.91 Å) and Lu^{III} (0.86 Å) yet the more stable Ce^{IV} oxidation state offers greater Lewis acidity which should promote monomer coordination and activation.⁴⁴

⁴⁵ Generally, changing the ionic radii – i.e. the metal – is the most effective way to change the Lewis acidity of a rare-earth complex, as ligand effects are limited due to the predominantly ionic bonding present. Dinuclear Ce^{IV} complexes are therefore interesting targets within epoxide/anhydride ROCOP catalysis.

We have recently shown that a tetraphenolate (TP) ligand platform is capable of stabilizing f-block metal centers in multiple oxidation states, and particularly stabilizes the Ce^{IV} oxidation state relative to Ce^{III}.^{46, 47} Bimetallic complexes of the phenols H₄(*p*TP^t) and H₄(*m*TP^t) have been demonstrated to be active ring-opening polymerization initiators for monomers including lactide (by H₂K₂(*p*TP^t) and H₂K₂(*m*TP^t) adducts),⁴⁸ epoxide (by bis-Al^{III} adducts of *p*TP^t),⁴⁹ and ε-caprolactone (by [MCl₂(OEt)(NCMe)]₂(*p*TP^t) where M = Nb, Ta).⁵⁰

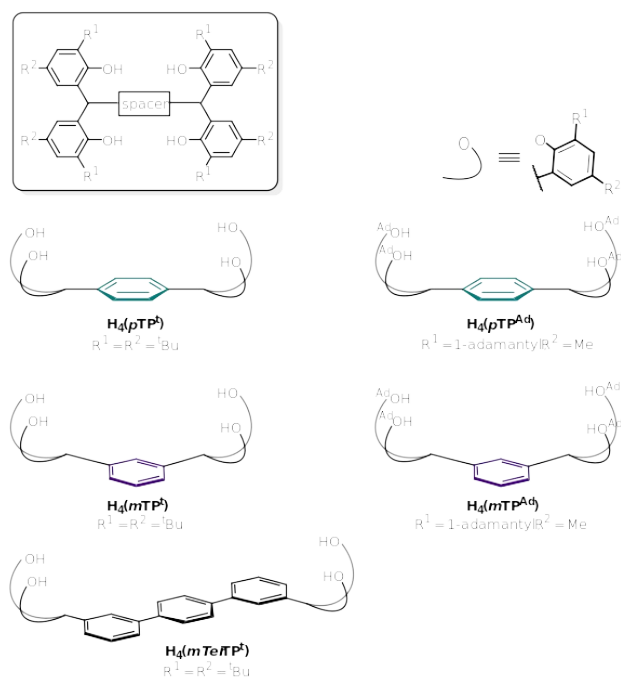
Herein, we report the synthesis of a series of new dinuclear cerium(IV) complexes supported by this TP platform that are even more strongly stabilizing of the Ce^{IV} oxidation state, their performance as rapid, single-component catalysts for the ROCOP of cyclic anhydrides and epoxides, and how the polymerization is fastest when the two metal centers can approach each other closely.

RESULTS AND DISCUSSION

Synthesis of cerium complexes

The pro-ligands $H_4(mTP^i)$ and $H_4(pTP^i)$ (Chart 2) have been reported previously;⁴⁶ the adamantyl derivatives $H_4(mTP^{Ad})$ and $H_4(pTP^{Ad})$ and the terphenyl pro-ligand $H_4(mTerTP^i)$ are new and were synthesized in an analogous manner (see SI section S2.1). We find that “ $Ce(OSiR_3)_4$ ” made *in situ*, as described recently by Anwander and co-workers from $[NH_4]_2[Ce(NO_3)_6]$ or $[NEt_4]_2[CeCl_6]$,⁵¹ provides a clean, one-pot route to the target catalysts, Scheme 1.

Chart 2 Tetraphenol (TP) pro-ligands used in this work. The aromatic link, denoted [spacer] in the box, is varied to provide different lengths of platform to separate the two catalytic metal centers; meta-aryl is colored purple; para-aryl teal; and meta-terphenyl is colored black for clarity.

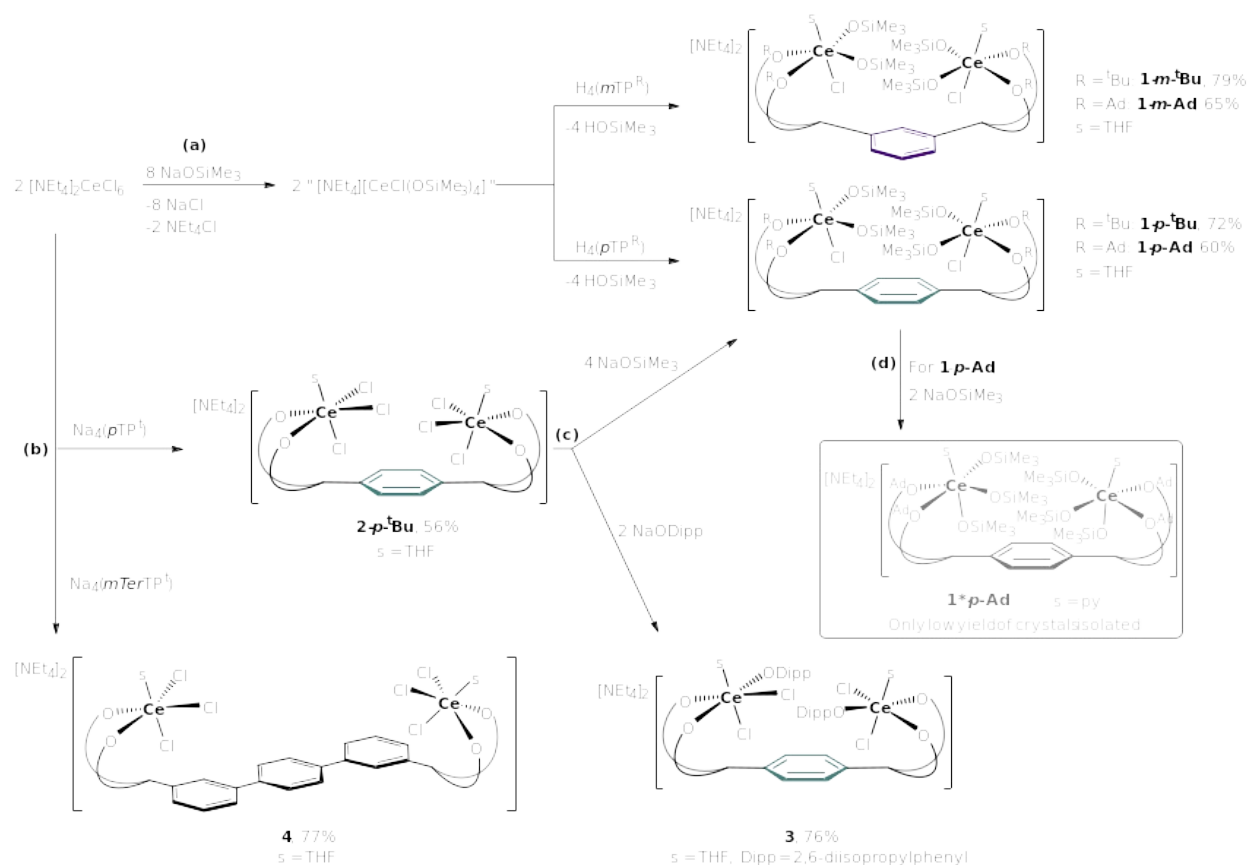


When a cold THF suspension of $[NEt_4]_2[CeCl_6]$ and sodium trimethylsiloxide is treated with $H_4(pTP^i)$ the color immediately changes from bright yellow to bright green. The mixture darkens

to brown-purple with stirring overnight; evaporation of the filtrate to dryness affords $[\text{NEt}_4]_2[\text{Ce}_2\text{Cl}_2(\text{OSiMe}_3)_4(p\text{TP}^t)]$, **1-*p*-^tBu**, in good yield (72%), (a). This synthesis has been generalized to afford a family of four aryloxide-supported, dicerium siloxides, namely **1-*m*-^tBu**, **1-*p*-Ad** and **1-*m*-Ad** using the *mTP*^t, *pTP*^{Ad} and *mTP*^{Ad} ligands respectively. Full details are available in the SI.

The ¹H NMR spectrum of a d₅-pyridine solution of **1-*p*-^tBu** shows only diamagnetic resonances, indicating retention of the desired Ce^{IV} oxidation state (Figure S7). The coordinated *pTP*^t ligand is identified in the ¹H NMR spectrum by two doublets of intensity 4H for the aryloxide protons and two singlets of relative intensity 36H for the *tert*-butyl groups. A singlet at 0.43 ppm is attributed to equivalent OSiMe₃ environments and only one resonance is seen in the ²⁹Si NMR spectrum, at 7.47 ppm. The two tetraethylammonium counter-cations are confirmed as non-interacting via ¹H NMR resonances at 3.21 and 1.17 ppm, and their presence is supported by elemental analysis.

Scheme 1 Synthesis of di-Ce^{IV} complexes supported by tetraphenolate ligands with meta-, para- and terphenyl substituted aryl platforms.



a): The most convenient route to **1** is a THF solution of the appropriate pro-ligand added at 0 °C to the *in situ* generated Ce-siloxide and allowed to warm to RT then stirred for 16 h. b): Syntheses of **2-*p*-ⁱBu** & **4** are from addition of a THF solution of the respective tetrasodium salt (formed *in situ*) to $[\text{NEt}_4]_2[\text{CeCl}_6]$ at RT and stirring for 16 h. c): Reactions from **2-*p*-ⁱBu** to **1-*p*-ⁱBu** and **3** require heating under reflux a THF solution of **2-*p*-ⁱBu** with the required reagent. d): A pyridine solution of **1-*p*-Ad** and NaOSiMe₃ was heated at 100 °C for 16 h. ODipp = OC₆H₃(ⁱPr)₂-2,6 Full experimental details are in the SI.

Alternatively, the salt Na₄(*pTP*^{*i*}) can be generated *in situ* and provides access to di-Ce^{IV} complexes *via* salt-elimination reactions, Scheme 1(b). Addition to a THF solution of Na₄(*pTP*^{*i*}) to a yellow THF suspension of $[\text{NEt}_4]_2[\text{CeCl}_6]$ (2 equiv.) forms a deep purple mixture. $[\text{NEt}_4]_2[\text{Ce}_2\text{Cl}_6(\text{pTP}^i)]$ **2-*p*-ⁱBu** is obtained as a purple microcrystalline powder in 56% yield after work-up from THF.

The high symmetry of the solution spectra means the Ce₂ dianion of **1-*p*-^tBu** could exist in the “*syn*” conformation with both metals on the same face of the phenyl spacer, the “*anti*” with both metals on opposite faces, or there could be free rotation around the platform. The *syn* conformation is drawn for simplicity for each cerium complex in Scheme 1 although both conformers have been observed by us in X-ray diffraction studies of related metal complexes.⁴⁶
^{47, 52} X-ray structural analyses of some of the bimetallic group 1, 5, and 13 complexes of the phenols H₄(*p*TP^t) and H₄(*m*TP^t) also confirm the rotational freedom of the central arene bridge, although to our knowledge, no solution state studies of their behavior has been reported.^{46, 49, 50, 53}
¹H-¹H NOESY NMR spectroscopic experiments were conducted to investigate the ambient solution-state conformation for the siloxide and aryloxide complexes. A *syn* conformation would be expected to show correlation between neighboring –OSiMe₃ protons on the two different cerium centers “pointing” towards each other in the various complexes **1**. Another example would be the protons from two different –ODipp ligands in **3**. No such correlations were observed, consistent with the presence of the *anti*-conformer, or fast free rotation about the platform on the NMR timescale in solution. Variable temperature (VT) NMR experiments on **1-*p*-^tBu** and **1-*p*-Ad** show a dynamic equilibrium process exists in both compounds (SI Figures S8 & S12).

In the ¹H NMR of **1-*p*-Ad**, the most sterically congested pre-catalyst, two –OSiMe₃ ligand environments are visible at 300 K (in a 9:1 ratio) but coalesce by 340 K. This is most reasonably explained, given the lack of geometrical constraints on the metal, by the co-existence of isomers with *syn*- and *anti*- orientation of the metals with respect to rotation around the platform. On steric grounds, we suggest the major (90%) isomer is the *anti*, but free rotation to place the

metals in the desired position for dinuclear catalysis can be achieved at 340 K, well below the temperature at which catalysis occurs.

Treatment of **2-*p*-^tBu** with four equivalents of NaOSiMe₃ in refluxing THF offers an alternative route to **1-*p*-^tBu** (Scheme 1 (c)). Work-up from toluene yields **1-*p*-^tBu** in moderate yield (69%).

Using only two equivalents of NaOSiMe₃ results in a low yield of **1-*p*-^tBu** and unreacted **2-*p*-^tBu**. Reactions designed to target hexakis(siloxide) dicerium complexes gave very poor yields but a small amount of single crystals suitable for an X-ray diffraction study were isolated on one occasion and characterized as [NEt₄]₂[Ce₂(OSiMe₃)₆(*p*TP^{Ad})(py)₂], **1*-*p*-Ad** (Scheme 1 (d) and SI section S2.8)).

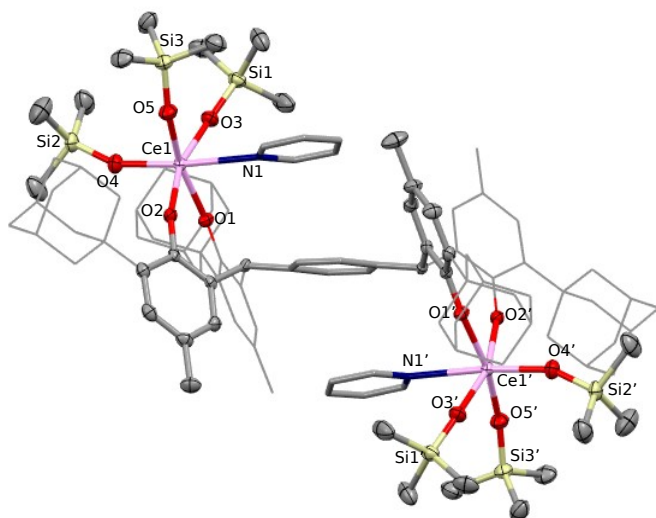


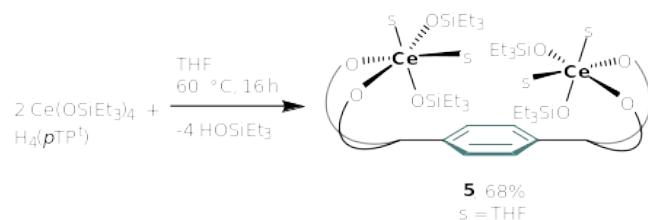
Figure 1. Solid-state structure of the dianion of **1*-*p*-Ad** with displacement ellipsoids (where shown) set at 50% probability, coordinated solvent and selected C atoms drawn capped stick, peripheral C and O atoms drawn wireframe. Tetraethylammonium cations, all H atoms and two pyridine lattice solvent molecules are omitted for clarity. Selected distances (Å) and angles (°) for **1*-*p*-Ad**: Ce1-O1 2.231(2), Ce1-O2 2.209(2), Ce1-O3 2.151(3), Ce1-O4 2.154(3), Ce1-O5 2.168(3), Ce1-N1 2.659(3), O1-Ce1-O2 85.35(9), O1-Ce1-O3 87.96(10), O2-Ce1-O4 98.58(10), O2-Ce1-O5 90.47(10), O3-Ce1-O4 98.45(11), O3-Ce1-N1 79.46(11).

Single crystals of **1*-p-Ad** suitable for an X-ray diffraction study were grown from a concentrated pyridine solution stored at ambient temperature. Exactly half the molecule, one NEt_4 cation and a lattice pyridine make up the asymmetric unit. The solid-state structure (Figure 1) indicates a distorted octahedral geometry around the Ce^{IV} centers – both metals are coordinated by two phenolate oxygens, three trimethylsiloxide ligands and a single pyridine molecule. The average Ce-O phenolate distance (2.220 Å) is slightly longer than the average Ce^{IV} -O siloxide distance (2.158 Å), but both are well within the range of literature Ce^{IV} -O distance reported.^{17, 19, 51, 54-58} Specifically, the subset of average Ce-siloxide distances match very well with comparable 6-coordinate complexes e.g. 2.151 Å in $[\text{Ce}\{\text{OSi}(\text{O}^t\text{Bu})_3\}_4(\text{NH}_3)_2]^{43}$ and 2.143 Å in $[\text{Ce}(\text{OMe})\{\text{OSi}(\text{O}^t\text{Bu})_3\}_3(\text{THF})_2]^{57}$. The chelate angle of the TP ligand (O1-Ce1-O2) is 85.4° in **1*-p-Ad**, which is slightly narrower than in similar TP complexes reported recently by us: the average O-M-O angle is 90.4° in $[\text{Ce}^{\text{IV}}_2(\text{pTP}^t)_2(\text{THF})_4]$, 89.0° in $[\{\text{Ce}^{\text{III}}\text{Cl}(\text{py})_4\}_2(\text{pTP}^t)]$ and 91.3° in $[\{\text{U}^{\text{IV}}\text{I}_2(\text{THF})_2\}(\text{pTP}^t)]^{46, 47}$.

Treatment of **2-p-^tBu** with two equivalents of sodium diisopropylphenoxide replaces two chlorides with ODipp (ODipp = $\text{OC}_6\text{H}_3\text{-}^i\text{Pr}_2\text{-}2,6$), forming $[\text{NEt}_4]_2[\text{Ce}_2\text{Cl}_4(\text{ODipp})_2(\text{pTP}^t)]$ **3** (Scheme 1 (c)). The ^1H NMR spectrum contains four doublets of 2H in the aromatic region and four singlets of 18H in the alkyl region, representing the TP ligand (Figure S17). The ODipp groups are inequivalent on the ^1H NMR timescale with two aromatic doublets (2H each), two aromatic triplets (1H), two septets (2H), whilst the alkyl doublets overlap (2 x 6H). Addition of excess NaODipp (4 equiv.) does not yield any further reaction - only **3** and unreacted NaODipp are observed. The addition of other aryloxide salts (NaOAr; Ar = 2,6-dimethylphenyl and 2,6-*tert*-butylphenyl) with **2-p-^tBu** results in the formation of a few unidentifiable products.

For comparisons in catalysis, the compound with a terphenyl spacer, $[\text{NEt}_4]_2[\text{Ce}_2\text{Cl}_6(m\text{TerTP}^t)]$ **4** was also targeted, and obtained in 77% yield (Scheme 1(b)) from a method analogous to that used to synthesize **2-*p*-^tBu**. Neutral complexes can also be isolated and provide useful comparisons in the catalysis studies. $[\text{Ce}_2(\text{OSiEt}_3)_4(p\text{TP}^t)]$ **5** was synthesized by a protonolysis reaction of $\text{H}_4(p\text{TP}^t)$ and two equivalents of the separately prepared $\text{Ce}(\text{OSiEt}_3)_4$ (Scheme 2).^{51, 59} Heating at 60 °C overnight and a straightforward work-up gives **5** in 68% yield. The ¹H NMR spectrum of **5** shows four aromatic resonances of 2H, a singlet of 4H for the aromatic spacer, two singlets of 36H for the *tert*-butyl groups and a triplet (36H at 1.13 ppm) and quartet (24H at 0.73 ppm) for the triethylsiloxide ligands (Figure S21).

Scheme 2. Synthesis of the neutral dicerium TP analogue **5**.



Relative stability of the cerium +4 formal oxidation state

For a given set of Lewis acidic Ce^{IV} catalysts, the most stabilized Ce^{IV} complex – that with the largest reduction potential – should be the most Lewis acidic and thus the most active catalyst, according to hypothesis. Cyclic voltammetry was used to investigate the electronic influence of the ancillary ligands Cl, OSiMe₃ and ODipp on the $\text{Ce}^{\text{III/IV}}$ redox couple in complexes **1-*p*-^tBu**, **2-*p*-^tBu** and **3**. Measurements were conducted in THF using 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$ as a supporting

electrolyte. Table 1 contains the irreversible reduction waves measured for all three compounds (see SI S2.12 for traces). The most negative reduction potential of $E_{pc} = -2.47$ V vs. Fc/Fc⁺ was observed for **1-*p*-^tBu** which suggests that the siloxide ligands are very effective at stabilizing the +4 oxidation state. Siloxide ligands have precedence in stabilizing Ce^{IV}, as shown in work by the groups of Anwander and Mazzanti.^{51, 58} This also puts **1-*p*-^tBu** amongst the most oxidizing Ce^{IV} complexes yet reported, with a similar reduction potential to CeL(O^tBu)₂ (L = salfen; $E_{pc} = -2.39$ V vs. Fc/Fc⁺ in THF)¹⁰ by Diaconescu and the current record-holding imidophosphorane supported Ce(N=P(piperidine)₃)₄ complexes (reduction range of $-2.30 < E_{pc} < -2.64$ V vs. Fc/Fc⁺ in THF) by La Pierre and co-workers.⁶⁰ Compounds **2-*p*-^tBu** and **3** are also highly oxidizing whilst the voltammogram of **1-*m*-^tBu** is complicated and no clear redox process could be identified. The situation is more complicated for the adamantyl-functionalized complexes. An irreversible oxidation was observed for **1-*p*-Ad** at $E_{pa} = +0.05$ V vs. Fc/Fc⁺ and for **1-*m*-Ad** at $E_{pa} = +0.17$ V vs. Fc/Fc⁺, suggesting that the electron-rich adamantyl groups change the electronic structure of the molecules such that a ligand-based oxidation occurs at lower potential than that of the metal. However, we are still able to suggest from these data, Table 1, that the Cl/OSiMe₃ ligated complexes should be the most active catalysts.

Table 1: Selected reduction potential (E_{pc}) and maximum absorption (λ_{max}) values for Ce-*p*TPⁱ complexes.

Comple x	X ligands	E_{pc} vs. Fc/Fc ⁺ (V)	λ_{max} (nm)
1-<i>p</i>-^tBu	(Cl) ₂ OSiMe ₃	-2.47	406.5
2-<i>p</i>-^tBu	(Cl) ₃	-1.98	505.0
3	(Cl) ₂ ODipp	-1.18	476.5

The compounds have also been characterized by UV-Vis spectroscopy, data can be found in Table 1 and SI Section S2.13. Each complex exhibits a broad absorbance in the region of 450-500 nm in agreement with the expectation of a LMCT band arising from ligand- π to empty Ce-4f orbitals, and the observed dark purple color of the Ce^{IV} complexes.^{54, 61, 62}

Ring-Opening Copolymerization

We tested the cerium complexes synthesized above for their suitability for anhydride/epoxide ROCOP. The monomers phthalic anhydride (PA) and cyclohexene oxide (CHO) are most common and provide a good benchmark for determining the activity of our catalysts, Scheme 3. Standard reaction conditions of 1 mol% catalyst loading with respect to PA in neat CHO solution (800 equiv.) at 100 °C were used, and the polymerizations were monitored by ¹H NMR spectroscopy at various time points to allow for direct comparison of turnover frequencies (TOFs) and any change in the proportion of ester linkages over time.²⁵ Further data including additional time points are available in SI section S3.1.

Scheme 3 ROCOP of phthalic anhydride and cyclohexene oxide using general reaction conditions given.

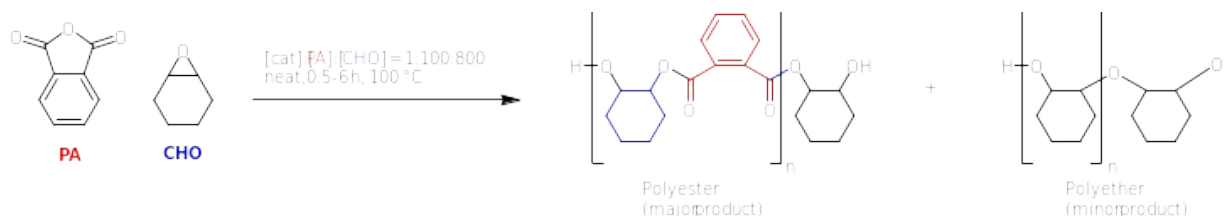


Table 2. Selected polymerization data for PA/CHO with catalysts **1- 5**.^a

Entry	Catalyst	X ligand(s)	Catalyst Loading	Time	% PA conversion ^b	TOF ^c	% Ester ^d	M _n (exp) ^e	M _n (calc) ^f	D ^e
			mol%	h		h ⁻¹		g.mol ⁻¹	g.mol ⁻¹	
1	1-<i>m</i>-^tBu	Cl(OSiMe ₃) ₂	1.0	0.5	49	98	94	4690	6030	1.29
2	1-<i>m</i>-Ad	Cl(OSiMe ₃) ₂	1.0	0.5	99	198	97	4400	12180	1.10
3	1-<i>m</i>-Ad	Cl(OSiMe ₃) ₂	0.5	2.0	99	99	95	14550 (9030)	24350	1.07 (1.29)
								5960		1.08

4	1- <i>p</i> -Bu	Cl(OSiMe ₃) ₂	1.0	0.5	29	58	94	7730 (5180)	3560	1.07 (1.24)
								3420		1.05
5	1- <i>p</i> -Bu	Cl(OSiMe ₃) ₂	0.5	6.0	95	32	85	23910 (9240)	23370	1.08 (1.46)
								5510		1.37
6	1- <i>p</i> -Ad	Cl(OSiMe ₃) ₂	1.0	0.5	51	102	97	3940	6270	1.12
7	2- <i>p</i> -Bu	(Cl) ₃	1.0	0.5	30	60	93	4420	3690	1.05
8	3	(Cl) ₂ ODipp	1.0	0.5	23	46	88	15920 (7720)	2830	1.07 (1.32)
								4530		1.22
9	4 (<i>Ter</i> -TP)	(Cl) ₃	1.0	2.0	97	49	94	10180 (6530)	11930	1.05 (1.23)
								4590		1.06
10	5	(OSiEt ₃) ₂ (neutral)	1.0	2.0	98	49	71	9400	12060	1.38
11	[NEt ₄] ₂ [CeCl ₆]	(Cl) ₆	2.0	2.0	87	22	83	2700	10220	1.23

^aStandard conditions: reactions were run at 100 °C with a molar ratio of catalyst:PA:CHO of 1:100:800 unless otherwise stated. Further runs at various time points to enable more direct catalyst comparisons are included in SI Table S3. ^bDetermined by ¹H NMR spectroscopy (CDCl₃) by integrating the normalized resonances for PA (7.95 ppm) and the phenylene signals in polyester (7.30–7.70 ppm). ^cTurnover frequency (TOF) = (number of moles of anhydride consumed/number of moles of catalyst)/time. ^dDetermined by ¹H NMR spectroscopy (CDCl₃) by integrating the normalized resonances for ester linkages (5.10 ppm) and ether linkages (3.67 ppm). ^eDetermined by SEC in THF with a refractive index detector using narrow-*M_n* polystyrene standards to calibrate the instrument; *M_n* multiplied by a correction factor of 1.85 as reported previously.^{22, 63} Double entries represent bimodal distributions; the numbers in parentheses represent the total *M_n* and Đ values. ^fBased on two polymer chains formed per catalyst molecule, where *M_n* (calc) = (246.5 x %PA conversion)/(catalyst loading x 2).

For the *meta*- and *para*-TP derived complexes **1-2**, reactions carried out for 0.5 h are included in Table 2 to allow direct comparisons with each other. With a catalyst loading of 1 mol%, at least 99% of PA is consumed within 2.5 h for all of the cerium complexes, as determined by the ¹H NMR spectrum of the crude polymer (SI Table 23 and Figure S25). When catalyst loading is decreased (Table 3, Entries 3 & 5), high conversion can still be achieved after a longer reaction time, however the selectivity for ester linkages is compromised. All eight dicerium tetraphenolate complexes investigated generally give excellent catalytic turnover and high ester linkage selectivity.

The kinetics of the PA/CHO ROCOP catalyzed by **1-*p*-^tBu** were investigated by ¹H NMR spectroscopy. The reaction is zero-order with respect to anhydride (See SI S3.3) and first-order with respect to both **1-*p*-^tBu** and CHO. These observations are consistent with other reports and suggest that the anhydride insertion/opening occurs at a much faster rate than the epoxide ring-opening step.^{26, 64} The simple Lewis acidic metal complex tetraethylammonium cerium(IV) chloride show a significant proportion of polyether in the polymer, Entry 11, confirming the controlling role these catalysts play in formation of polyester from the two monomers.

A series of catalytic runs enable us to compare the effect of increasing Lewis acidity of the metal site(s) using X (co-ligand) tuning, increasing the distance between the two metals, and increasing access to the metal(s) for incoming substrates. We hypothesized above that initiation rates would be promoted by increased Lewis acidity of the cerium center, indicated by a more negative Ce^{III/IV} reduction potential. Here we assume that Cl is the most likely initiating group from MALDI-ToF mass spectrometry and NMR spectroscopic data discussed below. This has literature precedent, and the Ce-X BDFE value for Ce-Cl (457 kJ.mol⁻¹) is significantly weaker than Ce-O (790 kJ.mol⁻¹).⁶⁵

For the *p*TP^t complexes, changing the identity of the ancillary X ligands from (Cl/OSiMe₃) to Cl to (Cl/ODipp), i.e. complexes **1-*p*-^tBu** to **2-*p*-^tBu** to **3**, results in a decrease in turnover frequency (see Table 2 and SI Table S3 for more data on reactions with precisely comparable conditions). Thus, increased stabilization of the Ce^{IV} centers results in increased catalytic activity. The siloxide ligands confer a higher degree of selectivity than chloride ligands for ester linkage

formation (compare Entry 4 to 7). With **3**, it may be that the large ODipp ligands hinder monomer association and slow the reaction rate.

A substantial increase in TOF is observed when the *ortho*-aryloxy substituents on the TP, proximal to the Ce center, is changed from *tert*-butyl to 1-adamantyl (compare Entries 1 to 2, and 4 to 6). Whilst there is little difference in the volume occupied by the two groups next to the metal center, the extension beyond the primary coordination sphere of the adamantyl group is significant. The adamantyl substituted complexes may also give polymers with improved (narrower) dispersity than the *tert*-butyl analogues (compare Entries 1 and 2). The adamantyl groups could be providing a hydrocarbon pocket that provides additional dispersion forces to facilitate monomer binding/orientation, or could be distorting the metal complex geometry and destabilizing the initiating group. A significant distortion from an octahedral geometry is visible in siloxide **1*-p-Ad**, and a similar distortion accorded by an adamantyl group was suggested to be responsible for the increased lactone polymerization rate in an Al^{III} catalyst elsewhere.⁶⁶ These two factors (substituent volume and dispersion forces) and taking note that the bulky adamantyl group increases the rate, highlights the sometimes complex, counter-intuitive and ambiguous nature of steric effects upon catalytic systems.

Entries 1 & 2 show that the *meta*-spacer derived complexes are significantly faster than the *para*-spacer analogues (Entries 4 & 6). This suggests that like zinc, two close cerium cations make the best catalytic systems for ROCOP, and cooperative effects are working in the *m*TP but not the *p*TP catalysts. Our recent determinations of solid-state structures of analogous f-block TP systems suggest the M-M distance is significantly shorter in the *meta* complexes compared to the *para* systems. Only a few solid state structures exist of TP complexes in the *syn* conformation,

in the letterbox-shaped di-U^{IV} complex [U₂(*m*TP)₂], the M-M distance is 6.57 Å,⁵² and in the open di-Ce^{III} complex [Ce₂(BH₄)₂(*p*TP^t)], the M-M distance is 10.85 Å.⁴⁷ For example, there is a maximum separation in the *anti*-conformation of 9.32 Å in [U₂I₄(*m*TP^t)(THF)₄] and 10.40 Å in [U₂I₄(*p*TP^t)(THF)₄].^{46, 67}

To further test the effect of metal-metal distance on catalytic activity, we have also made the new terphenyl bridged complex **4** in which the Ce-Ce distance is far too large for cooperativity. The data show that the activity of **4** is actually similar to, or slightly slower than that of **2-*p*-^tBu**, implying considerably weaker cooperative effects in both.

The enhanced catalytic activity and closer M-M distance suggests a strong cooperative effect in the bimetallic *m*TP complexes **1-*m*-^tBu** and **1-*m*-Ad** compared to **1-*p*-^tBu**, **1-*p*-Ad** and **4**. As discussed above, the *syn* and *anti* conformers of all of the TP ligands readily interconvert. It is therefore plausible that the *m*TP complexes convey enough flexibility to bind incoming monomers and polymer, and a distance that enables the two metal cations to work together with a separation that is under 9 Å, making the best catalytic systems for ROCOP. DFT studies to investigate this further are ongoing.

Higher TOFs are reached before complete anhydride conversion is achieved (Table S3). The fastest conversion is observed with **1-*m*-Ad**; Entry 2 (Table 2) shows full conversion within 30 min, and 82% conversion within 20 min with 97% ester selectivity (Table S3, Entry 8). This corresponds to a TOF of 246 h⁻¹, a similar activity to the leading literature catalysts for anhydride/epoxide ROCOP. The heterobimetallic [MgZnBr₂^tBuL] reported by Williams and co-workers (^tBuL = a bis(phenolate) macrocycle), under the same reaction conditions (Table 2), achieves a TOF of approximately 190 h⁻¹ and 99% selectivity in 30 min.²⁵ Comparable TOFs

have been observed by Duchateau and co-workers; a [CrCl(salophen)] complex with the uncommon bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) co-catalyst⁶⁸ reaches a TOF of about 250 h⁻¹ when used in a neat reaction mixture comprising catalyst:PA:CHO:PPNCl of 1:250:250:3 heated at 110 °C for 60 min. To our knowledge, there is only one other report of a rare-earth complex-catalyzed anhydride-epoxide ROCOP – the very recent work by Ko and co-workers using a dinuclear yttrium catalyst.⁴³ They report full conversion after 24 h (TOF ≈ 8 h⁻¹; >99% ester linkages; $M_n = 10400 \text{ g}\cdot\text{mol}^{-1}$) albeit with no intermediate data points, using a catalyst:PA:CHO ratio of 1:200:200, and 0.02 M catalyst concentration in toluene solution at 110 °C.

Tetraalkylammonium salts are common co-catalysts in ROCOP⁶⁹⁻⁷¹ and Coates and co-workers have recently explored incorporation of an aminocyclopropenium group in the catalyst structure to target catalyst longevity and prevent unwanted transesterifications.⁶⁹ We also expect that “ate” complexes will simply have weaker Ce-X bonds (Cl, OSiMe₃), increasing nucleophilicity/reactivity. The neutral analogue **5** yields polymer with good molar mass but relatively poor dispersity and a low proportion of ester linkages (71%), Entry 10. The control [NEt₄]₂[CeCl₆] has better control of monomer incorporation (83% ester links, Entry 11) but only makes oligomers.

MALDI-ToF mass spectrometric studies of the isolated polymer samples suggest the polymerizations catalyzed by **1-*p*-^tBu**, **1-*m*-^tBu**, **1-*p*-Ad**, **2-*p*-^tBu** and **3** are initiated by the Ce-Cl group, in agreement with the significantly weaker Ce-Cl bond, yet individual polymer chains with Cl- and HO- end groups are identifiable. The ¹H NMR spectra of short polymer samples made by **1-*p*-^tBu** from 10 equivalents of PA were analyzed, and show no resonance

corresponding to a $-\text{OSiMe}_3$ terminating group (see Figure S27). Neither are any observed with the standard 100 PA equiv. reactions. However, we note that **5**, which contains only OSiEt_3 initiating groups is a reasonable catalyst, and there is literature precedent for initiation to occur from a metal-bound OSiR_3 group ($\text{R} = \text{alkyl}$).¹⁹

In general, the fastest catalyst, **1-*m*-Ad**, generates the lowest molar mass polymer under the standard catalysis conditions (Entries 2 & 3). The mass spectra for PA/CHO ROCOP contain fragments that can be attributed to Cl-, HO- and Me_3SiO - initiated polymers (Figures S52, S55, S56), so we suggest that the close M-M distance within this catalyst encourages the Cl and OSiMe_3 ligands to bridge both metals, weakening the M-O/Cl bonds such that they can more readily initiate polymerization. Multiple initiations could also explain the rapid turnover for this system, and would correlate with the lower molar masses observed. When lower catalyst loadings of **1-*m*-Ad** or **1-*p*-^tBu**, and extended reaction times are used (Table 2, Entries 3 & 5), high molar mass polymer can be accessed, albeit with some sacrifice in terms of turnover and ester linkage selectivity. The M_n (calc) values in Table 2 are based on two polymer chains per catalyst molecule, i.e. one polymer per metal. MALDI-ToF spectrometry and NMR spectroscopic studies suggest that initiation occurs from the Ce-Cl bonds (vide infra), and all the catalysts **1-*p*-^tBu**, **1-*m*-^tBu**, **1-*p*-Ad** and **1-*m*-Ad** bear one chloro group per metal center. Some runs in Table 2 show an experimental M_n value higher than the theoretical value, for example the Cl/ODipp catalyst **3**, which suggests that the initiation is less efficient and/or that only one polymer chain is initiated per catalyst molecule.

In general, there is better agreement between calculated and measured molar masses for the slower catalysts than for the faster catalysts. In some cases, and especially with *para*-substituted

complexes, bimodal polymer distributions are observed, see pairs of entries for M_n and \bar{D} in Tables 2 and 3 with total M_n and \bar{D} values in parentheses; full data are in the SI (Tables S4 & S5). This observation is relatively common in CO_2 /epoxide and epoxide/anhydride ROCOP and is attributed to epoxide ring-opening by adventitious water to form a diol which can then act as a bifunctional chain transfer agent.⁷² Analysis of the MALDI-ToF mass spectra of the polymers supports this observation, as some OH-terminated polymer, α -hydroxycyclohexyloxy, ω -hydroxy polyester with repeat units of 246 m/z (for PA/CHO) is observed for all complexes (see SI section S3.6 for spectra).

Biorenewable and more challenging monomers

As molecular Ce^{IV} complexes and RE catalysts are rare, we tested our most active catalyst, **1-*m*-Ad**, with a wider range of monomers.⁷³ A broad range of polyesters find widespread application from textiles to electronics to construction, as a result of properties such as high strength and water resistance.⁷⁴

Biorenewable, and more challenging monomers are polymerized by **1-*m*-Ad** (Figure 2 and Table 3). ROCOP of succinic anhydride (SA), propylene oxide (PO) or (+)-limonene oxide (LO) is possible with good turnover and high selectivity. LO is derived from limonene, a waste product found in the peels of citrus fruit, and CHO and SA are also biorenewable.^{73, 75} Good conversion of anhydride is observed with all of the monomer combinations used. This implies a potential benefit from the further exploration of rare-earth catalysts into producing these desirable copolymers. While the molar masses of polymers appear low, the lack of correction factors available for these polymer limits in-depth comparisons of M_n values. However, for some

monomer combinations, particularly for PO/PA, a significant increase in molar mass was achieved by decreasing the catalyst loading to 0.5 mol% (compare Entries 12 & 13).

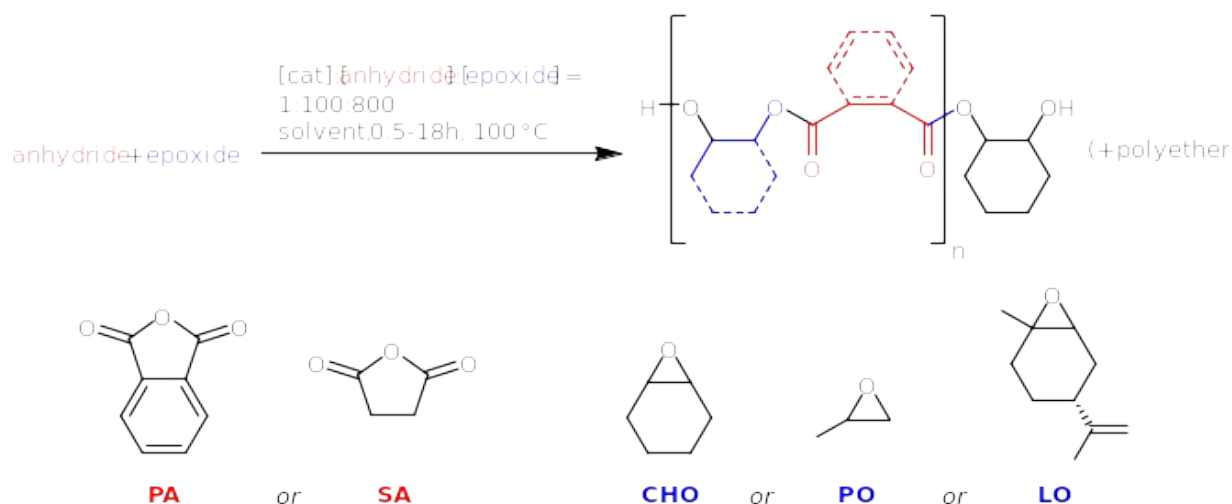


Figure 2. ROCOP with alternative more challenging, and biorenewable monomers; example reaction conditions given.

Table 3. Substrate scope using **1-*m*-Ad** as catalyst.^a

Entry	Monomer Combination	Catalyst Loading	Solvent	% Anhydride Conversion ^b	TOF	% Ester ^b	M_n (exp) ^e	M_n (calc) ^f	\bar{D} ^e
							g.mol ⁻¹	g.mol ⁻¹	
12	PO/PA	1.0	toluene	100	40	96	4990 (3890)	10310	1.07 (1.42)
							1640		1.09
13 ^c	PO/PA	0.5	toluene	99	11	97	19370 (13510)	20410	1.23 (1.53)
							5750		1.09
14 ^c	LO/PA	1.0	neat	82	5	94	7740 (4740)	12320	1.10 (1.34)
							3020		1.09
15 ^d	CHO/SA	1.0	neat	92	184	90	2790	9120	1.46
16 ^c	CHO/SA	0.5	neat	98	11	88	3860	19420	1.35
17	PO/SA	1.0	toluene	98	39	92	3890 (1220)	7750	1.37 (1.28)
							1070		1.02
18 ^c	LO/SA	1.0	neat	89	5	86	1540 (1250)	11230	1.11 (1.51)

							760		1.01
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^aStandard conditions: Reactions were run at 100 °C for 2.5 h with a molar ratio of **1-*m*-Ad**:anhydride:epoxide of 1:100:800. Due to the low boiling point of PO toluene was used as solvent in the indicated reactions. ^bDetermined by ¹H NMR spectroscopy (CDCl₃) by integrating the normalized resonances for anhydride and polyester (conversion); and for ester and ether linkages (selectivity). ^c18 h reaction time. ^d0.5 h reaction time. ^eNo correction factor has been applied for M_n . Double entries represent bimodal distributions, the numbers in parentheses represent the total M_n and \bar{D} values. ^fBased on two polymer chains formed per catalyst molecule, where M_n (calc) = (molar mass of repeat unit x %anhydride conversion)/(catalyst loading x 2). To the best of our knowledge, no correction factors have been reported for these monomer combinations which limits the comparison of the observed and calculated M_n values for these monomer combinations.

Conclusion

Ce^{IV} complexes are highly active catalysts for anhydride/epoxide ROCOP, largely due to the ability to form kinetically labile bonds to oxygenated substrates. Harnessing improved catalyst performance by developing dinuclear complexes is a contemporary interest in polymerization catalysis. The dinucleating ligands show strong binding for large, electropositive metals without blocking substrate access, and are a significant step away from the conventional, widely used dinucleating ligands for this type of catalysis, that are limited almost exclusively to Schiff base ligands. Ligand design and co-ligand electronic/steric tuning profoundly influence the performance of rare earth cation-based ROCOP catalysis. In the absence of a dinucleating ligand system, Ce^{IV} chlorides such as [NEt₄]₂[CeCl₆] can be catalysts for ROCOP. However, chelating phenolate supporting ligands can give higher TOF values (246 h⁻¹ for **1-*m*-Ad** vs 22 h⁻¹ for [NEt₄]₂[CeCl₆], Tables 1 and S3) and narrower dispersities (1.08 vs 1.23, respectively). The high activity of **1-*m*-Ad** can be explained by trends observed across the family of catalysts. The –OSiMe₃ ligands increase the Lewis acidity of the Ce^{IV} cation compared to Cl and ODipp, and the adamantyl substituents in close proximity are superior to *tert*-butyl. Importantly, the *meta*-aryl spaced tetraphenolate ligand brings the two cerium centers closer together than the *para*-spacer,

allowing for cooperative catalysis. Higher molar mass polymer is obtainable when lower catalyst loading is used.

Furthermore, challenging monomers and those relevant to environmental sustainability can also be efficiently copolymerized. This considerably expands the scope for rare-earth based polymerization catalysis, and computational studies to elucidate the mechanism and nature of catalytic intermediates will be reported in due course.

ASSOCIATED CONTENT

Supporting Information. The following files are available free of charge: <https://pubs.acs.org/>

Experimental procedures, cerium complex characterization data, polymer SEC and MALDI-ToF data (PDF). Crystallographic data for the SCXRD study available from the CCDC, code 2032589.

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Notes

The authors declare no competing financial interest.

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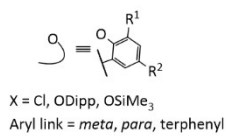
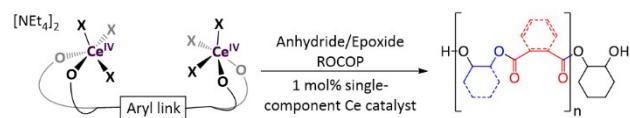
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