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Citation for published version:
https://doi.org/10.1002/anie.200801279

Digital Object Identifier (DOI):
10.1002/anie.200801279

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Peer reviewed version

Published In:
Angewandte Chemie International Edition

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C-3-symmetric lanthanide tris(alkoxide) complexes formed by preferential complexation and their stereoselective polymerization of rac-lactide**

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[**] We thank the Alexander von Humboldt Foundation, the Royal Society, the UK EPSRC and the Universities of Edinburgh and Nottingham for financial support.

Supporting information for this article is available at http://www.angewandte.org or from the author.

Graphical abstract:

Keywords:

homogeneous catalysis, lactides, lanthanides, polymerization, structure elucidation
Abstract

Restoring order: Y\textsuperscript{III}, Eu\textsuperscript{III}, and Er\textsuperscript{III} tris(ligand) complexes of a new chiral alkoxide ligand, tBu\textsubscript{2}P(O)CH\textsubscript{2}CH(tBu)OH (HL), preferentially form as C\textsubscript{3}-symmetric diastereomers. Thus racemic HL affords (RRR)- and (SSS)-[LnL\textsubscript{3}] complexes, which are active catalysts for the stereoselective polymerization of rac-lactide to afford highly isotactic polylactic acid.

Main text

A great number and variety of homogeneous lanthanide catalysts are now used in industry and academia as low cost, low-toxicity, Lewis acidic, and coordination catalysts.\textsuperscript{1} In the search for new asymmetric catalysts, chiral C\textsubscript{3}-symmetric complexes are emerging as interesting competitor systems to the ubiquitous C\textsubscript{2}-symmetric systems.\textsuperscript{2} Trivalent lanthanide cations are obvious candidates for the development of catalysts with three-fold symmetry. However, the lability and the weak coordination geometry preferences of Ln\textsuperscript{III} centers make the synthesis of enantiopure lanthanide coordination compounds a difficult goal. One approach is to use pre-resolved, chiral polydentate ligands such as C\textsubscript{3}-symmetric tris(oxazoline) adducts.\textsuperscript{3} Another involves the coordination of three enantiopure, C\textsubscript{2}-symmetric, biaryl ligands to make a homochiral LnL\textsubscript{3} complex.\textsuperscript{4} The most successful asymmetric and bifunctional lanthanide-based catalysts are based on Li\textsubscript{3}[Ln(L)\textsubscript{3}] (L = chiral enantiopure 1,1'-'-binaphtholate, binolate).\textsuperscript{5} This latter class includes, to our knowledge, the only example of spontaneous resolution of three molecules of a racemic ligand at a lanthanide to date: the reaction of Y(N\{SiMe\textsubscript{3}\}\textsubscript{2})\textsubscript{3} with rac-NaHbinol affords an equal mixture of the heterobimetallic RRR- and SSS-Na\textsubscript{3}[Y(binol)\textsubscript{3}] complexes A (binol=1,1'-bi-2-naphthyl). However, all other lanthanide/alkali metal combinations give different combinations of RRS-/SSR- complexes.\textsuperscript{6} The polymerisation of the biorenewable monomer rac-lactide, B, into the biodegradable polymer polylactide (PLA) provides an interesting challenge for new chiral catalysts,\textsuperscript{7} since the physical properties of the lactide polymers are highly dependent on the polymer stereochemistry. It has been shown that when independently made poly[(R)-(lactic acid)] and poly[(S)-(lactic acid)] are mixed, the chains co-crystallise to form a stereocomplex with a melting point of up to 230 °C, 50 °C higher than simple poly[(S)-(lactic acid)] (PLLA or poly[(L)-(lactic acid)]).\textsuperscript{8} However, the enantiopure R,R-monomer is much more expensive than rac-lactide.

Thus, a one-pot catalytic process in which a racemic mixture of a chiral catalyst polymerises R,R- (D-lactide) and S,S- (L-lactide) monomers separately into two, enantiomerically pure, isotactic polymer chains, which can then mix to form stereocomplex, is an important goal.\textsuperscript{9} Currently, highly selective, single-site catalysts based on the Al-salen framework, C, have been shown to form highly stereoblock
polylactide, in which the long, alternating chains of \((RRRRRR)_n\) and \((SSSSSS)_n\) PLA are formed, which subsequently form stereocomplex polylactide, with melting points up to 196 °C.\(^\text{10}\) Both single site [LLn(OR)] and homoleptic [M(OR)]\(_3\) lanthanide alkoxides have previously been shown to be excellent initiators for the synthesis of PLA, but normally heterotactic.\(^\text{11}\)

Herein we show how a racemic mixture of a bidentate ligand L, which contains a single chiral carbon centre, is resolved into a mixture of two homochiral \(C_3\)-symmetric complexes upon lanthanide complexation, to form \(RRR-LnL_3\) and \(SSS-LnL_3\). The utility of this spontaneous resolution is demonstrated by the use of these chiral complexes as initiators for the formation of high-melting, stereoregular polylactide. HL is a chiral alcohol that derives from a cheap, commercially available chiral (racemic or enantiopure) epoxide.

Treatment of a mixture of racemic 3,3-dimethyl-epoxybutane and lithium n-butyl with di-tert-butylphosphine, followed by oxidation with peroxide, affords colourless \((t-Bu)_2P(O)CH_2CH(t-Bu)OH\), HL 1. Treatment of Ln(N\{SiMe\(_3\}\)\(_2\))\(_3\) (Ln = Y, Eu, Er) with three equivalents of 1 in THF at low temperature affords LnL\(_3\) Ln = Y (2), Eu (3), and Er (4) respectively, in excellent yield, after recrystallization from pentane, eq. 1. Complex 2 is colorless, 3 pale yellow, and 4 is pale pink. Chiral enantiopure 1 (1a) was also made from the \(R\)-epoxide, and used in the synthesis of diastereomerically pure Y(\(R\)-L)\(_3\), \(RRR\)-YL\(_3\), 2a, denoted \(ep\)-YL\(_3\) here for convenience.
The $^1$H and $^{31}$P$^1$H NMR spectra of solutions of 2a show a single ligand environment consistent with a single $C_3$-symmetric $RRR$-YL$_3$ complex, see SI. Spectra of solutions of 2 contain eighty per cent of this homochiral isomer (although now as a mixture of $RRR$- and $SSS$- YL$_3$), and an additional, minor set of resonances which correspond to the diastereomer, $RRS$/SSR-$LnL_3$, present in about 20 % of the total yield. These samples are referred to as rac-YL$_3$ here for convenience. To the best of our knowledge, this is the only configurationally stable, monometallic lanthanide complex to preferentially form a single diastereomer upon complex formation.

**Figure 1.** Displacement ellipsoid drawing of 2 (isostructural with 3 and 4) 50 % probability ellipsoids. P $t$-butyl Me groups, and all hydrogens except chiral CH omitted. Average distances (Å): 2 Y-OR 2.1481, Y-OP2.3749; 3 Eu-OR 2.1981, Eu-OP 2.431; 4 Er-OR 2.1512, Er-OP 2.3675.

The $C_3$-symmetric chirality is confirmed by a single crystal X-ray diffraction study of 2; Figure 1 shows the $RRR$-diastereomer. The complexes of the strongly paramagnetic 3 (Eu) and 4 (Er) are isostructural (crystal structure data are shown in the SI), save for a small degree of disorder in one ligand, arising from a ‘contamination’ by a ligand of the other hand. Modelling of this disorder component shows that 6.6 % of the ligands in the structure of 4 are the wrong hand, and 10 % in the structure of 3. These three metals may all be regarded as small lanthanide cations (six-coordinate $r_{\text{cov.}}$ = 1.040 (Y), 1.087 (Eu), and 1.030 (Er) Å).

The spontaneous formation of this racemic mixture of chiral complexes prompted us to look for asymmetric reactions which this complex might catalyse. The conversion of a racemic mixture of lactide monomer into a racemic mixture of two homochiral lactide polymers presents a suitable
challenge for these complexes. In 2004, Carpentier demonstrated the first example of a group 3 complex which rapidly polymerised rac-lactide into predominantly heterotactic PLA using a single-site Y\textsuperscript{III} initiators with a bulky bisphenolato ancillary ligand\textsuperscript{,14} and more recently up to 71\% iso-tactic enriched PLA from an enantiopure single-site Y\textsuperscript{III} initiator with a bulky C\textsubscript{2}-symmetric diamido ligand.\textsuperscript{15} Thus it is of interest to identify if these rac-LnL\textsubscript{3} complexes can firstly act as stereoselective initiators, and secondly, if a tris-ligand complex can provide a sufficiently controlling environment for tacticity control in the initiation of the polymerisation reaction.

The data from a series of reactions of the racemic YL\textsubscript{3} initiator 2 and rac-lactide are collated in Table 1. Even at –18 °C, the polymerisation is rapid and controlled (also see SI). The polymer weights are high\textsuperscript{16}, and the polydispersities (PDI) of the polymers are narrow. More than half of the monomer is consumed after four minutes, representing a very rapid polymerisation. The melt polymerisation also proceeds smoothly, but with poorer PDI control; this, and full polymerisation data for all of these complexes, is contained in the SI. Mass spectral analysis of the polymer indicates that each chain is terminated by a ligand L molecule (see Supporting Information).

Table 1. Polymerization of rac-lactide using 2.

<table>
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<th>entry</th>
<th>Cat:monomer: solvent ratio\textsuperscript{a}</th>
<th>T /°C</th>
<th>Time /min</th>
<th>Conv.\textsuperscript{b} / %</th>
<th>M\textsubscript{n} g/mol</th>
<th>M\textsubscript{w}/M\textsubscript{n} \textsuperscript{d}</th>
<th>P\textsubscript{i} \textsuperscript{e}</th>
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<tr>
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<td>1 : 100 : 10000</td>
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<td>2</td>
<td>35</td>
<td>47000</td>
<td>1.53</td>
<td></td>
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<tr>
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</tbody>
</table>

\textsuperscript{a}solvent = dichloromethane; \textsuperscript{b}conversion of LA monomer (([LA]₀−[LA])/[LA]₀). \textsuperscript{c}measured by GPC, values based on polystyrene standards, corrected by the Mark-Houwink equation \[M_n(\text{obsd}) = 0.58M_n(\text{GPC})\].\textsuperscript{17} \textsuperscript{d}polydispersity index (M\textsubscript{w}/M\textsubscript{n}), PDI, measured by GPC. \textsuperscript{e}Probability of forming a new i dyad, determined by \textsuperscript{1}H NMR spectroscopy (Coudane, J.; Ustariz-Peyret, C.; Schwach, G.; Vert, M. J. Polym. Sci., Part A: Polym. Chem., 1997, 35, 1651).

The most notable property of these polymers is their very high crystallinity and stereoregularity. The formation of a predominantly isotactic polymer, from rac-2 polymerizing the D- and L-lactide monomers in parallel, is confirmed by \textsuperscript{1}H and \textsuperscript{13}C NMR spectroscopy.\textsuperscript{10b}

The \textsuperscript{1}H NMR spectra of an isotactic polymer chain should look like that of poly-L-lactide, with a single CHMe resonance (if the chains are infinitely long). If the polymerization is less selective, or if transesterification becomes a competing reaction at higher conversions, the original stereochemical
control will be lost and the proton-decoupled spectra will show the different CH environments. Figure 2 shows the proton-decoupled methine region of the $^1$H NMR spectra of three polylactide samples for comparison.\textsuperscript{18}

Sample (a) in Figure 2 shows the dominance of the $iii$ tetrad in the polymer made by $rac$-$YL_3$ from $rac$-lactide at complete conversion, which confirms the stereospecific control of the polymerisation of $D$- and $L$-lactide into separate, isotactic chains. The smaller tetrad resonances are characteristic of the defects in the polymer. Here, the more desirable, isotactic polymer microstructure is present, since the ratio of the defect sizes is 1:2:1:1 corresponding to $iis:iis:iis:iis$. This ratio is only possible for a chain of the stereochemistry $^{RRRRRRSSSSSSSSRRRR}$- (and vice versa) containing single insertion defects. This type of polymer is most able to form stereocomplex upon annealing to mix the chains together so the formation of high – melting polymers may be possible for this system.

![Figure 2](image)

**Figure 2.** Methine region of homonuclear decoupled $^1$H NMR spectra of (a) highly isotactic PLA, table entry 6, with tetrad resonances arising from insertion errors assigned. (b) isotactic PLLA made from $L$-lactide by $ep$-$YL_3$ initiator (0.5 %, CH$_2$Cl$_2$) (c) atactic PLA made from by Y$\{N(SiMe_3)_2\}_3$ (5%, CH$_2$Cl$_2$, 1h).

If the polymer chains were stereoblock, of the form $^{RRRRRRSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSSS
It is interesting to compare the formation of isotactic polymer by complex 2, with the recent results by Davidson's group, who showed that a rac-C₃-symmetric complex of a tetridentate aryloxide, Ge(OPrⁱ){(O-Me₂-2,4-C₆H₂-6-CH₂)₃N}, which interconverts rapidly between P and M isomers, affords highly heterotactic PLA.¹⁹

Analysis of the kinetics of the reaction suggest that only one ligand is displaced upon initiation of the polymerisation, forming an [L₂Ln-O-P-L] propagating species (P = growing polymer chain), so the L₂Ln environment is still sufficiently asymmetric for further stereoselective monomer insertions to take place. This suggests that even the RRS-isomer impurity might give equally good stereocontrol in the polymerisation if the S-ligand was displaced by the initial monomer insertion.

In conclusion, the racemic phosphine oxide-alkoxide ligand HL is very effectively resolved into the diastereomeric RRR- and SSS-LnL₃ complexes of the lanthanide trications, Y^{III}, Eu^{III}, or Er^{III}, to afford a racemic mixture of homochiral, C₃-symmetric LnL₃ complexes. The complexes provide a new class of very active initiators for the polymerization of rac-lactide into highly isotactic polylactic acid which show retention of stereochemical control even at high monomer conversions and high molecular weights. This work also demonstrates that single site catalysts with one monodentate initiating ligand are not necessarily required to achieve good stereochemical control in polymer formation. Work is in hand to optimise the conversion of these polymer mixtures to stereocomplex PLA, and to identify other organic transformations that these C₃-symmetric Lewis acid complexes can catalyse.

**Experimental Section**

**Syntheses:**

HL: modification of R. J. Cross, L. J. Farrugia, P. D. Newman, R. D. Peacock, D. Stirling, *J. Chem. Soc., Dalton Trans.* 1996, 1637. ¹H-NMR δ(C₆D₆): 1.1 (18H, dd, JₚH = 4.5 Hz, P-C(CH₃)₃); 1.15 (9H; s, C-CH₃); 1.7 – 1.9 (2H, m, CH₂); 4.0 – 4.1 (1H, m, CH) [ppm]. ³¹P-NMR δ(C₆D₆): 63.7 ppm δ(C₇D₈): 63.8 ppm. MP: 98 °C. Analysis Found: C 64.25 %, H 11.60; calc. C 64.18 %, H 11.54 %.

YL₃ 2: To a solution of Y[N(SiMe₃)₂]₃ in THF (508 mg, 0.89 mmol, 10 ml) was added a solution of HL in THF (707 mg, 2.7 mmol, 10 ml) at -78 °C, and allowed to warm slowly to RT overnight with stirring. Work up afforded colorless 2. Yield 705 mg (90 %). Integration of the resonances in the spectra of bulk 2 shows the major:minor ratio is 80:20. The pure RRR-diastereomer 2a was made as above, but using enantiopure R-HL instead of racemic HL.
$^1$H-NMR $\delta$(C$_6$D$_6$) major diastereomer (minor diastereomer in brackets): 4.22 (m, 3 H, CH); 1.78 (m, 6H, CH$_2$); 1.24 (1.23) (d, 27H, $^2$J$_{PC} = 11.4$ Hz, P-$^t$Bu); 1.19 (1.20) (s, 27H, C-tBu); 1.14 (1.12) (d, 27H, $^2$J$_{PH} = 11.4$ Hz, P-$^t$Bu). $^{31}$P-NMR $\delta$(C$_6$D$_6$): 68.9 (68.6, 67.6) ppm. Analysis Found: C 57.48 %, H 10.25 %; calc. C 57.78; H 10.39.

EuL$_3$: Yield 440 mg (94 %). $^1$H-NMR $\delta$(C$_6$D$_6$): - 7.6 (3H, CH); - 6.1 (27H, $^t$Bu); - 4.6 (3H, CH$_2$); - 1.4 (3 H, CH$_2$); 0.4 (27 H, $^t$Bu); 9.1 (27 H, $^t$Bu). Analysis Found: C 53.78 %, H 9.48 %; calc. C 53.9 %, H 9.6 %.

ErL$_3$: Yield 720 mg (93 %). $^1$H-NMR $\delta$(C$_6$D$_6$): - 9.15 (6x $^t$Bu H); 24.14 (3 x $^t$Bu H). Analysis Found: C 52.90 %, H 9.61 %; calc. C 53.0 %, H 9.5 %.

**Polymerizations:**

A Schlenk flask was charged with monomer (500 mg, 3.47 mmol), dissolved in the volume of solvent according to the table entry, and the solution stirred at the temperature given in the table. To this was added a solution of initiator (one of 2 to 4): 2.5 mg (0.5 % initiator) or 5 mg (1 % initiator) via cannula, according to table entry. Aliquots were removed via syringe and quenched/precipitated with MeOH after the time stated. The obtained polymer was dissolved in dichloromethane, filtered through silica gel 60 and dried. The yield for each completed polymerization was quantitative.
References and endnotes:


12 Crystallographic data for 2: C43H92Cl2O6P3Y, M = 957.89, crystal dimensions 0.43 × 0.24 × 0.12, orthorhombic, space group *Pca21*, a = 20.186 (3), b = 13.426 (2), c = 20.202 (3) Å, V = 5475.1 (14) Å³, Z = 4, ρ_calcd = 1.162 g cm⁻³, μ = 1.29 mm⁻¹, MoKα radiation (λ = 0.71073 Å), T = 150(2) K. 31313 data (8761 unique, R_int = 0.036, θ < 27.6°) were collected on a Bruker SMART APEX CCD diffractometer using θ scans and solved by heavy-atom and direct methods and were refined by least-squares methods on F² values, with anisotropic displacement parameters for non-H atoms, to give wR2 = 0.055 R = 0.027, S = 0.95 for 523 parameters. Flack parameter = -0.027 (2). Residual electron density extremes were 0.38 and -0.26 e Å⁻³. Crystallographic data (excluding structure factors) for HL, 2, 3, and 4 have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC- Copies of the data can be obtained free of charge from: CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).


16 The Mn are higher than calculated for single-site initiation, indicating that only a proportion of LnL₃ is active as initiator.

