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Low-coordinate rare-earth complexes of the asymmetric 2,4-di-*tert*-butylphenolate ligand prepared by redox transmetallation/protolysis reactions, and their reactivity towards ring-opening polymerisation[†]

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New trivalent lanthanoid aryloxide complexes have been prepared by redox transmetallation/protolysis (rtp) reactions using 2,4-di-*tert*-butylphenol (dbpH). Mononuclear octahedral complexes from tetrahydrofuran (thf) were of the type [Ln(dbp)₃(thf)₃] (Ln = La (1), Pr (2), Nd (3), Gd (4), Er (5)). The lanthanoid contraction results in the rather subtle change in stereochemistry from meridional (La, Pr, Nd, Gd) to facial (Er). An analogous reaction with neodymium in dimethoxyethane (dme), resulted in the isolation of the seven coordinate [Nd(dbp)₃(dme)₂] (6), and this is comparable with the thf complexes in terms of steric crowding. Dinuclear complexes of the type [Ln₂(dbp)₆(thf)₂], (Ln = Nd (7), Er (8)) were obtained when 1 and 5 were recrystallised from toluene. These dimeric complexes contain two bridging and four terminal phenolates, as well as a single coordinated molecule of th at each metal. A similar structural motif was observed for the products when the reaction was performed in diethyl ether, and in the absence of a solvent, yielding [Nd₂(dbp)₆(Et₂O)₂] (9) and [Nd₂(dbp)₆(dbpH)₂] (10) respectively. Complexes of BnOH as a co-initiator they showed features consistent with immortal polymerisation. Use of BnNH₂ led to well-controlled, amine-initiated immortal ROP of *rac*-lactide, only the second report of this type of process for a group 3 or lanthanoid system.

Introduction

Investigations into the structures of lanthanoid aryloxides have given insight into the effect of substituents on coordination number, stereochemistry and nuclearity.¹⁻³ For example, the 2,6-di-*tert*-butyl-4-X-phenolates have had a pivotal role in establishing low coordination numbers (*e.g.* 3) for large lanthanoid ions.^{4,5} By contrast, 3,5-di-*tert*-butylphenolates with distal substituents favours di-nuclear and polynuclear complexes, *e.g.* [Nd₃(OAr)₉(thf)₄],⁶ which have excellent hydrocarbon solubility, which is attractive for sol–gel processes.^{1,7,8}

A recent review by Boyle and Ottley² is dominated by the extensive investigations into symmetrically substituted phenoxides, particularly 2,6-disubstituted derivatives. A recent study of complexes of the asymmetric 2-*tert*-butylphenolate ion⁹ (tbp), and comprehensive reviews/books highlight a distinct lack of data regarding lanthanoid complexes incorporating asymmetrically substituted phenolates.¹⁻³ However, an asymmetric steric bulk may lead to interesting changes in the bonding or bridging ability of the ligand. For this reason, 2,4-di-*tert*-butylphenol was chosen for this investigation. The steric bulk in one *ortho*-position provides the potential for some degree of saturation of the coordination sphere, while the *para-tert*-butyl group should assist hydrocarbon solubility.

Lanthanoid aryloxides are traditionally prepared by protolysis of $Ln(NR_2)_3$ ($R = SiMe_3$) with the phenol or by metathesis reactions. However, the former method requires $Ln(NR_2)_3$ to be highly pure, often requiring multiple crystallisations or sublimations.^{1,3} Metathesis reactions between a lanthanoid halide and an alkali metal phenolate can experience complications arising from halide/alkali halide retention.² Redox transmetallation/protolysis reactions¹⁰⁻¹² are emerging as a versatile alternative to traditional metathesis/protolysis reactions especially for the synthesis of low coordinate rare earth complexes.^{10,13-15}

Such complexes have a number of potential applications, including use of Ln(II) compounds as soluble one-electron reducing agents,¹⁶ routes to lanthanoid doped semiconductors,¹⁷ MOCVD (metal organic chemical vapour deposition) and solgel precursors^{1,7,8} and as catalysts.¹

Polyesters derived from lactic acid are currently a topic of much interest due to their biocompatibility and biodegradability.¹⁸⁻³¹ Derived from 100% renewable resources including corn and sugar beet, these polymers can act as replacements for oil-based materials. These materials are commercially synthesised²⁰ by the metal catalysed ring-opening polymerization (ROP) of the cyclic

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 $[\]dagger$ Electronic supplementary information (ESI) available: Selected bond lengths and angles for $[Nd_2(dbp)_6(dbpH)_2)]$ and $[Er(dbp)_3(thf)_3]$. CCDC reference numbers [CCDC NUMBER(S)]. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0dt00023j

diester lactide (LA) which exists as three stereoisomers, designated *meso*, L and D (the 50:50 mixture of L- and D-lactide is known as *rac*-lactide).



ROP catalysts are generally derived from Lewis acidic metals, feature one or more alkoxide initiating groups, and operate through a coordination-insertion chain growth mechanism.²⁵⁻³⁰ Group 3 and lanthanoid complexes have been at the forefront of ROP catalysis for nearly two decades.28-30 While most of the recent developments in this area have focused on ligand-supported systems,^{27,28,30} homoleptic aryloxides of the type [Ln(OAr)₃] were among the first classes of rare earth lactone or lactide ROP catalyst studied. Feijen et al. reported the ROP of L-LA using the tris(2,6di-*tert*-butylphenoxide) compounds $[Ln(OAr^*)_3]$ (Ar* = O-2,6- $C_6H_3Bu_2^{t}$).^{32,33} When used alone, these are sluggish catalysts for ROP owing to the presence of the two bulky ortho-positioned tert-butyl groups. No specific end groups could be identified in the resultant poly(L-LA) which had broad polydispersity indices (PDIs) and large M_n (number average molecular weight) values compared to those expected for one poly(L-LA) chain forming per initiating Ln-OAr* group. However, in the presence of various alcohols ROH (e.g., R = Bn, Pr^{i} or Bu^{i}), well-controlled ROP was observed giving OR-terminated poly(L-LA) with narrow molecular weight distributions. The M_n values were consistent with one polymer chain forming per ROH added, and it was proposed that [Ln(OAr*)₃] was converted to the less sterically encumbered, but symmetrically substituted [Ln(OR)₃] in situ, this in turn leading to poly(L-LA) by a coordination-insertion mechanism.

Following on from Feijen's seminal work with $[Ln(OAr^*)_3]$, Shen *et al.* recently reported the ROP of *L*-LA and *rac*-LA using less sterically encumbered tris(phenoxide) complexes of the type $[Ln(O-4-C_6H_4Bu')_3]$ and $[Ln(O-2,6-C_6H_3Me_2)_3]$.³⁴ In contrast to Feijen's results for $[Ln(OAr^*)_3]$, these less bulky compounds gave somewhat better controlled ROP, especially for the larger metals. In these cases the reported number average molecular weights were in good agreement with those expected for one poly(LA) chain per Ln–OAr bond, although the PDIs at high conversions were still relatively broad (*ca.* 1.5–1.6).

The new 2,4-di-*tert*-butylphenoxide complexes prepared in this present study provide an opportunity to explore the effect of an unsymmetrical substitution pattern on ring-opening polymerisation by lanthanoid tris(phenolates).

Results and discussion

Reactions were carried out as a one-pot synthesis, in which bis(pentafluorophenyl)mercury¹² and 2,4-di-*tert*-butylphenol (dbpH) were added to an excess of lanthanoid metal (with 1–2 drops of mercury for activation) in a donor solvent, such as the or dme, to give compounds of the type $[Ln(dbp)_3(solv)_x]$ (where x =

3 when in thf, x = 2 when in dme) in moderate to good yields as shown in eqn (1).

$$2Ln(Hg) + 6[dbpH] + 3[Hg(C_6F_5)_2]$$

$$\xrightarrow{solv} 2[Ln(dbp)_3(solv)_x] + 6C_6F_5H + 3Hg$$
solv = thf, x = 3; Ln = La(1), Pr(2), Nd(3), Gd(4), Er(5),
solv = dme, x = 2; Ln = Nd(6)
(1)

A synthesis was also attempted in the absence of bis(pentafluorophenyl)mercury, but no reaction was detected, and only unreacted phenol was recovered, suggesting that this phenol is not sufficiently acidic to undergo a direct reaction with the metal in polar solvents, even after activation with elemental mercury. Accordingly, the reactions plausibly proceed through formation, then protolysis, of pentafluorophenyllanthanoid species, a path for which there is significant evidence.^{10,12} A polar solvent also appears necessary to facilitate redox transmetallation/protolysis, since an attempted synthesis in toluene failed. There is only one example of redox transmetallation/protolysis in toluene,³⁵ namely the generation of the homoleptic [La(Odpp)₃] (Odpp = 2,6-diphenylphenolate) complex, where π -Ph–La interactions detected in the structure may have a role in the success of the synthesis.

In most cases the reaction in thf proceeds quickly, often with a visible colour change occurring within seconds of initiation. Reaction rates appeared to be dependent on the form of the metal, with those that used fresh filings (ytterbium and lanthanum) reacting much more rapidly than those with commercial powders (neodymium, gadolinium, erbium). Praseodymium metal, in the form of chips, resulted in the slowest reaction, presumably due to the smaller surface area of the metal. The progress of the reactions could be monitored by ¹⁹F NMR spectroscopy, since bis(pentafluorophenyl)mercury is converted into pentafluorobenzene, which shows characteristic resonances at -139 ppm, -162 ppm, and -154 ppm.³⁶ In most cases the completion of the reaction can also be seen in the infrared spectrum by the disappearance of the OH stretching absorptions at 3610 cm⁻¹ and 3534 cm⁻¹. However, when Ln = Gd, the X-ray crystal structure showed the presence of 0.5 dbpH of crystallisation per molecule. The IR spectrum showed two v(OH) absorptions (Experimental section), somewhat displaced from the free ligand values, which were regenerated on exposure of the Nujol mull to air. The phenolates could be isolated, in many cases, by simple filtration and subsequent crystallisation. However, in reactions with Sm, Dy, Ho, Y and Yb, although there was evidence of the formation of the appropriate phenolates with some dissolution of metal, observation of appropriately coloured solutions, and formation of pentafluorobenzene, the products could not be crystallised. The IR spectra of the oils showed no OH absorption, consistent with phenolate formation. Overall, the results show that redox transmetallation/protolysis is a suitable synthetic method for phenolates without two ortho substituents to provide steric stabilisation. While the paramagnetic property of most of the lanthanoid complexes makes characterisation by 1H and 13C NMR spectroscopy difficult due to dramatic shifting and broadening of the resonances, assignments have been made for most compounds. Elemental and/or metal analysis results are in agreement with the crystal structure compositions, except for 5 where loosely held solvent of crystallisation observed at 123 K is not detected on analysis of the bulk sample at room temperature.

In the cases of lanthanum to gadolinium, the product is a six coordinate heteroleptic compound with distorted octahedral geometry and a meridional ligand array, as shown in Fig. 1 for Ln = La.



Fig. 1 Molecular structure of $[La(dbp)_3(thf)_3]$ (1). Representative of metals La–Gd. Ligands are arranged meridionally. Hydrogen atoms omitted for clarity.

The structure resembles that of $[Ce(tbp)_3(thf)_3]^9$ (tbp = 2-*tert*butylphenoxide) in terms of coordination number, albeit with the important difference that this cerium complex exhibits facial ligand coordination. Since the only difference in the ligands is the *tert*-butyl group in the *para*-position, the capacity to affect stereochemistry of the complexes in the solid state is not limited to the *ortho*- and *meta*-substituents. A few similar observations exist in the literature,^{15a,37} with some major structural differences between lanthanoid or alkaline earth complexes of 2,6-dimethylphenolates and 2,4,6-trimethylphenolates. Significant differences also exist between structures of $[Yb(OC_6H_2Bu'_2-2,6-X-4)_2(thf)_3]$ complexes from $X = Me^{15b}$ to X = Bu'.^{15c}

Isolation of crystalline products from the reactions of smaller metals (Dy, Ho, Er, Yb) with dbpH proved extremely difficult. Only crystals of $[Er(dbp)_3(thf)_3]$ (5) could be obtained. However, complete solution of the structure was problematic, and so is presented in terms of connectivity only. Numerous attempts to produce more suitable crystals of 5 failed. When a concentrated solution of 5 was layered with dry hexane in an attempt to induce crystallisation, crystals of $[Er_2(dbp)_6(thf)_2]$ (8) were instead obtained. The fact that these complexes lose coordinated thf so readily may be a contributing factor to the difficulty of their crystallisation. It was anticipated that there should be some change as a result of the lanthanoid contraction, perhaps in degree of solvent coordination or nuclearity. However, the observed change from Gd to Er was much more subtle, with the erbium complex showing a switch in ligand arrangement from meridional to facial (Fig. 2). Thus, the smaller lanthanoid has a structure similar to



Fig. 2 Molecular structure of $[Er(dbp)_3(thf)_3]$ (5). Ligands are arranged facially. Hydrogen atoms omitted for clarity.

 $[Ce(tbp)_2(thf)_3]$, again reflecting the influence of the *para-tert*-butyl group on the structural outcome.

As complexes of lanthanoid metals smaller than erbium could not be crystallised, it is not known whether these complexes would preserve the facial conformation, or possibly even adopt a structure with a lower coordination number.

Some comparative bond lengths and angles between $[La(dbp)_3(thf)_3]$ (1), $[Pr(dbp)_3(thf)_3]$ (2), $[Nd(dbp)_3(thf)_3]$ (3), and $[Gd(dbp)_3(thf)_3]$ (4) are given in Table 1. Data for the less precise $[Er(dbp)_3(thf)_3]$ (5) are not included.

Five of the six Ln–O bond lengths contract by more (0.097– 0.13 Å) than the decrease in ionic radius from La³⁺ to Gd³⁺ (0.094 Å),³⁸ but Ln–O(2) contracts only by 0.073 Å, reducing the average contraction to 0.11 Å. The distance from the metal to the quaternary carbon on the ortho-tert-butyl group remains essentially the same, approximately 4.9 Å, and the lanthanoid contraction is off-set by a decrease in the average Ln-O-C angle from lanthanum to gadolinium. Presumably the shortening of the metal-oxygen bond puts a greater steric strain on the system, causing the average Ln-O-C angle to deviate from linearity with each successively smaller metal (see Fig. 3). The change to facstereochemistry places all the aryloxide ligands transoid to thf ligands which have a weak trans influence in contrast to the high *trans* influence of OAr ligands,³⁹ and this arrangement may enhance stabilisation. The clustering of common ligands is a feature of high coordination number lanthanoid complexes.8 Six is a relatively low coordination number for lanthanoid elements and the sum of the steric coordination numbers of the ligands is not excessive at 7.8.40 Comparisons with fac-[Ce(tbp)₃(thf)₃],9 show differences in ligand arrangement. The o-tert-butyl groups of $[Ce(tbp)_3(thf)_3]$ are oriented towards the centre of the molecule to face one another, whereas in [Er(dbp)₃(thf)₃], they are positioned to face away from one another, presumably to reduce repulsion between Bu' groups with a smaller lanthanoid ion in the solid state.

Table 1 Selected bond lengths and angles of [Ln(dbp)₃(thf)₃] (1-4)

	La (1)	Pr (2)	Nd (3)	Gd (4)
Bond lengths/Å				
Ln-O(1)	2.262(3)	2.209(5)	2.207(2)	2.165(4)
Ln-O(2)	2.243(4)	2.212(4)	2.194(2)	2.170(4)
Ln-O(3)	2.283(3)	2.213(4)	2.206(2)	2.162(4)
Ln-O(4) (thf)	2.597(3)	2.552(4)	2.535(2)	2.475(4)
Ln-O(5) (thf)	2.623(3)	2.605(5)	2.580(2)	2.515(4)
Ln-O(6) (thf)	2.570(3)	2.527(5)	2.500(2)	2.444(4)
Ionic radii (metal) ³⁸	1.032	0.990	0.983	0.938
Ln–o-quaternary carbon (average)	4.939	4.916	4.904	4.922
Bond angles/°				
Ln-O(1)-C(1)	153.1(3)	157.8(4)	146.07(19)	161.7(4)
Ln - O(2) - C(15)	156.6(3)	145.2(4)	158.34(19)	144.4(4)
Ln-O(3)-C(29)	157.8(3)	153.6(4)	152.65(19)	142.8(4)
O(1)-Ln-O(2)	130.93(12)	136.04(17)	135.40(8)	140.94(15)
O(2)-Ln-O(3)	110.71(12)	106.27(17)	112.61(8)	100.80(16)
O(3)-Ln- $O(1)$	112.89(13)	112.18(18)	106.35(8)	110.96(15)
O(4)– Ln – $O(5)$ (thf)	68.72(11)	72.50(15)	72.47(7)	76.69(14)
O(5)– Ln – $O(6)$ (thf)	127.57(11)	119.90(16)	120.24(7)	120.60(15)
O(6)-Ln- $O(4)$ (thf)	163.42(11)	166.11(16)	166.01(7)	159.83(14)
O(1)–Ln–O(4)	104.81(11)	106.68(16)	100.72(7)	92.23(15)
O(1)–Ln–O(5)	77.96(12)	78.95(17)	76.72(7)	84.19(14)



Fig. 3 Average Ln-*ortho*-quaternary carbon distance and Ln-O1-C1 angles of 1 and 4.

For comparison, the reaction between neodymium and 2,4-di*tert*-butylphenol was also carried out in 1,2-dimethoxyethane (eqn (1)). The resulting complex was similar to the thf derivative, but contained two molecules of chelating dme, making the metal seven coordinate, rather than six (Fig. 4). The aryloxide ligands are arranged *pseudo*-meridionally with respect to the dme.

Some comparative bond lengths and angles between the thf and dme derivatives are given in Table 2. The dme derivative exhibits a longer average Nd–O(solv.) bond, which is to be expected from the change in coordination number. However, the increase of <Nd–OAr> is less marked. Interestingly, the two longer Nd–OAr bond lengths are transoid to each other reflecting the strong *trans* influence of aryloxide ligands.³⁹

Some structural similarity between the thf and dme derivatives is in accordance with the steric coordination numbers⁴⁰ of 1.21 (thf) and 1.78 (dme), whereby three molecules of thf provide essentially the same steric hindrance as two chelating dme molecules.

Due to the moderate bulkiness of the aryloxide ligand, a point of interest was to determine whether a homoleptic complex was achievable. A number of possible routes were explored. Since the redox transmetallation/protolysis reaction would not proceed in any non-coordinating solvents attempted (hexane, toluene), the



Fig. 4 Molecular structure of $[Nd(dbp)_3(dme)_2]$. The dbp ligands are arranged in a pseudo-meridional manner. Hydrogen atoms are omitted for clarity.

possibility that the thf could be removed by recrystallisation of **3** from toluene was studied. This proved to be partially successful, giving the dinuclear species $[Nd_2(dbp)_6(thf)_2].2C_7H_8$ (**7.2C**₇H₈) (Fig. 5, eqn (2)), and only one molecule of thf per metal centre.

$$2[Ln(dbp)_{3}(thf)_{3}] \xrightarrow{toluene} [Ln_{2}(dbp)_{6}(thf)_{2}] + 4thf$$
(2)

The coordination number of each metal centre was reduced to five. Consequently, <Nd-O> of 7 is shorter than that of 3, and Nd-O(thf) of 7 is shorter (0.1 Å) than <Nd-O(thf)> of 3 despite being transoid to an aryloxide. However, since it is bridging and is 0.2 Å longer than Nd-OAr(terminal) (Table 3), it evidently has little *trans* influence.

Table 2	Selected	bond	lengths	and	angles	of	[Nd(dbp)	$_3(thf)_3]$	(3)	and
[Nd(dbp)	$_{3}(dme)_{2}]$	(6)								

	[Nd(dbp) ₃ (thf) ₃] (3)	$[Nd(dbp)_3(dme)_2]$ (6)
Bond lengths/Å		
Nd–O(1)	2.207(2)	2.243(7)
Nd-O(2)	2.194(2)	2.210(6)
Nd-O(3)	2.206(2)	2.241(6)
Nd-O(solvent) (average)	2.538	2.614
Nd-o-quaternary carbon (average)	4.904	4.881
Bond angles/°		
Nd-O(1)-C(1)	146.07(19)	147.4(6)
Nd-O(2)-C(15)	158.34(19)	162.5(6)
Nd-O(3)-C(29)	152.65(19)	151.5(6)
O(1) - Nd - O(2)	135.40(8)	94.4(2)
O(2) - Nd - O(3)	112.61(8)	103.3(3)
O(3) - Nd - O(1)	106.35(8)	162.1(2)
O(4) - Nd - O(5) (thf)	72.47(7)	63.7(2)
O(5)-Nd-O(6) (thf)	120.24(7)	135.9(2)
O(6)-Nd-O(4) (thf)	166.01(7)	74.4(2)
O(1)-Nd-O(4)	100.72(7)	81.0(2)
O(1)-Nd-O(5)	76.72(7)	104.3(2)

Again the Ln–o-quaternary carbon distance is conserved in the terminal aryloxides, with an average distance of 4.88 Å, similar to those of **1–5** (Table 1). The bridging aryloxides exhibit significantly shorter distances (4.53 Å, Table 3), but this position may be dictated by the bulky o-Bu' group of the nearby terminal aryloxides. Selected bond lengths and angles are given in Table 3. The ¹H NMR spectrum of **7** in C₆D₆ showed two broad aromatic resonances and two broad Bu' resonances, both in a 2 : 1 intensity ratio, attributable to terminal and bridging ligands respectively.

Recrystallisation of $[Er(dbp)_3(thf)_3]$ from toluene (or thf/hexane – above) yielded a structurally similar complex, (8), albeit with no lattice toluene. Table 3 provides bond distance and angle data, and shows similar features to those of 7 with the terminal Er–O distances shortened by the difference between the ionic radii of Nd³⁺ and Er³⁺.³⁸ Surprisingly, Er–OAr(bridging) is shorter than Nd–OAr(bridging) by twice the expected amount.

In a further attempt to obtain a homoleptic complex, the redox transmetallation/protolysis reaction was performed in diethyl ether (eqn (3)), which sometimes does not coordinate¹⁰ to

Table 3	Selected	bond	lengths	and	angles	of	dimeric	complexes	7–9)
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Fig. 5 Molecular structure of $[Nd_2(dbp)_6(thf)_2].2C_7H_8$ (**7.2** C_7H_8). Hydrogen atoms omitted for clarity.

lanthanoid aryloxides owing to its greater steric bulk (compared to thf).⁴⁰ The reaction was successful, and crystals were obtained directly from the reaction flask. They were, however, not the target homoleptic complex, but instead a dinuclear species, $[Nd_2(dbp)_6(Et_2O)_2]$ (9), very similar to 7 (eqn (3), Fig. 6). When compared with 7, Nd–O(ether) increases for 9 due to the greater bulk of diethyl ether compared with thf (steric coordination numbers 1.44 *vs.* 1.21, respectively),⁴⁰ and there is a shortening of the average Nd–*o*-quaternary carbon distance of the terminal aryloxides. This is offset, however, by a lengthening of this same distance of the bridging aryloxides (Table 3).

$$2\text{Ln}(\text{Hg}) + 6[\text{dbpH}] + 3[\text{Hg}(\text{C}_{6}\text{F}_{5})_{2}]$$

$$\xrightarrow{\text{Et}_{2}\text{O}} [\text{Ln}_{2}(\text{dbp})_{6}(\text{Et}_{2}\text{O})_{2}] + 6\text{C}_{6}\text{F}_{5}\text{H} + 3\text{Hg}$$
(3)

An effort was made to synthesise a homoleptic neodymium complex by direct reaction between neodymium and 2,4-di-*tert*-butylphenol, in the absence of any solvent, with a drop of mercury for activation (eqn (4)). When heated to 120 °C for 24 h, a blue deposit was observed on the metal surface, as well as a few single crystals. While the quality of the crystals for X-ray crystallography

	$[Nd_2(dbp)_6(thf)_2](7)$	$[Er_2(dbp)_6(thf)_2]$ (8)	$[Nd_2(dbp)_6(Et_2O)_2](9)$
Bond lengths/Å			
Ln(1)-Ln(1)'	3.933(10)	3.6199(3)	3.9000(4)
Ln(1) - O(1)	2.432(4)	2.243(2)	2.374(2)
Ln(1) - O(2)	2.189(4)	2.084(2)	2.168(2)
Ln(1) - O(3)	2.167(4)	2.064(2)	2.163(3)
Ln(1) - O(4)	2.437(4)	2.342(2)	2.484(2)
Ln(1)-o-quaternary carbon (terminal) (average)	4.881	4.824	4.768
Ln(1)-o-quaternary carbon (bridging)	4.528	4.603	4.583
Bond angles/°			
Ln(1) - O(1) - C(1)	99.3(3)	111.04(17)	91.60(8)
Ln(1)-O(2)-C(15)	157.8(3)	141.8(2)	156.4(2)
Ln(1)–O(3)–C(29)	160.0(4)	153.6(2)	158.8(3)
O(4)-Ln(1)-O(1)'	175.91(14)	169.04(8)	174.44(8)
O(4)-Ln(1)-O(2)	86.74(14)	88.52(8)	87.86(8)
O(4)–Ln(1)–O(3)	84.26(15)	86.28(9)	87.63(9)
O(2)–Ln (1)–O(3)	111.45(15)	120.86(9)	114.56(10)

Table 4 Polymerisation of *rac*-lactide initiated by [Nd(dbp)₃(thf)₃] (3) and [Gd(dbp)₃(thf)₃] (4)^a

Catalyst	Equivs. BnOH	Conversion (%) ^b	$M_{\rm n}$ (calcd)/g mol ⁻¹	$M_{\rm n}({ m GPC})^c/{ m g}~{ m mol}^{-1}$	$M_{\rm w}/M_{\rm n}{}^c$
$[Nd(dbp)_{3}(thf)_{3}](3)$	0	92	4420 ^d	7570	2.7
$[Gd(dbp)_3(thf)_3](4)$	0	91	4370 ^d	10 100	2.2
$[Nd(dbp)_{3}(thf)_{3}](3)$	5	96	2880 ^e	3530	1.5
$[Gd(dbp)_{3}(thf)_{3}](4)$	5	95	2850 ^e	3190	1.6

^{*a*} Conditions: $[rac-LA]_0$: $[Ln]_0 = 100$, 2 mL thf, 293 K, reaction time 30 or 60 mins. ^{*b*} Measured by ¹H NMR in CDCl₃. ^{*c*} Measured by GPC using the appropriate Mark–Houwink corrections for poly(*rac-LA*) in thf. ^{*d*} M_n (calcd) = (conversion × 144.13 × 100)/3. ^{*e*} M_n (calcd) = [(conversion × 144.13 × 100)/5] + 108.1.



Fig. 6 Molecular structure of $[Nd_2(dbp)_6(Et_2O)_2]$ (9). Hydrogen atoms are omitted for clarity.

was relatively poor, the connectivity of the resulting solution and refinement was unambiguous. In the absence of a solvent, unreacted phenol is incorporated to saturate the coordination sphere of the metal, yielding a complex with a structural motif similar to 7, 8 and 9 (Fig. 7).

$$2Nd + 8[dbpH] \xrightarrow{\Lambda}_{Hg} [Nd_2(dbp)_6(dbpH)_2] + 3H_2$$
(4)

Despite the imprecision of the determination, Nd–O(4) is clearly much longer than <Nd–O(2,3)>, which are typical Nd–OAr bond lengths. Hence O(4) is the phenol oxygen. There is also observation of the proton of O4 interacting with the phenyl ring of O1', with a distance of only 2.99 Å between O(3) and the centroid of the O(1)' phenolate ring.

Polymerisation studies

The compounds $[Nd(dbp)_3(thf)_3]$ (3) and $[Gd(dbp)_3(thf)_3]$ (4) were selected as representative examples and their ability to effect the ROP of *rac*-LA in thf at room temperature was assessed. Both compounds gave >90% conversion of monomer to poly(*rac*-LA) within minutes for [rac-LA]₀ : $[Ln]_0 = 100$ as judged by ¹H NMR spectroscopy. The molecular weights and PDIs (M_w/M_n ; Table 4) were determined by gel permeation chromatography (GPC) using the appropriate Mark–Houwink corrections for



Fig. 7 Molecular structure of $[Nd_2(dbp)_6(dbpH)_2]$ (10). Hydrogen atoms are omitted for clarity.

polylactides.⁴¹⁻⁴³ For both **3** and **4** the experimental molecular weights of 7570 and 10 100 g mol⁻¹ were significantly higher than those predicted for one polymer chain growing per Ln–dbp bond. A likely interpretation is that once one or more LA monomers have inserted, the propagation rate for the so-formed Ln-[LA]_x-dbp moiety is significantly larger than that for initiation due to reduced steric hindrance. The very broad PDIs of 2.7 and 2.2 are also consistent with a poorly controlled polymerisation process, with poly(*rac*-LA) chains of considerably different molecular weights forming, perhaps from metal centres with one, two or three propagating chains.

Mindful of Feijen's report^{32,33} that addition of certain alcohols to the very bulky [Ln(OAr*)₃] systems could lead to better-behaved catalyst systems, we carried out further ROP experiments with 3 and 4 in the presence of 5 equivs. BnOH (Table 4). The reduced PDIs of 1.5 and 1.6 are consistent with better controlled systems. Furthermore, in both cases considerably reduced molecular weights of 3530 and 3190 g mol⁻¹ are observed which are close to those expected for one poly(rac-LA) chain forming per added equiv. of BnOH (2880 and 2850 g mol⁻¹). This suggests that, in addition to leading to the exchange of Ln-OAr groups for Ln-OBn counterparts, the excess BnOH (as compared to Ln-OAr bonds) is able to act as a chain transfer agent such that 5 poly(rac-LA) chains form per metal centre. This phenomenon is well-established in alcohol co-initiated ROP and is the basis of so-called immortal polymerisation processes.44 Consistent with the proposed mechanism, the ¹H NMR and MALDI-ToF mass spectra of the resultant poly(rac-LA) featured only HOC(H)Meand BnOC(O)C(H)Me- end groups. Unfortunately, the poly(rac-LA) formed in these and the other ROP experiments described herein exhibited no isotactic or heterotactic bias. The $\Delta(m/z)$ of 72 amu between the adjacent peak envelopes in the MALDI-ToF mass spectra is indicative of extensive transesterification which is typically found for lanthanoid-based ROP catalysts.

While this work was in progress, we reported the well-controlled amine-coinitiated ROP of *rac*-LA in the presence of certain ligand-supported dicationic, zwitterionic and neutral yttrium complexes.⁴⁵ This approach yields amide-terminated poly(*rac*lactide)s of the type RR'N-[poly(*rac*-LA)]-H and so could provide improved routes for the synthesis of dendrimetic, brush and starshaped poly(lactides). We were therefore interested to determine whether complexes of the type Ln(OAr)₃ would also catalyse the amine-coinitiated ROP of *rac*-LA.

Using **3** as a representative example we carried out two series of experiments with BnNH₂ as the co-initiator. The results are summarised in Fig. 8 and 9. For example, ROP of 100 equivs. *rac*-LA in the presence of 5 equivs. BnNH₂ in thf at room temperature gave 94% conversion to benzyl amine-terminated poly(*rac*-LA) within 10 min. The M_n of 3110 g mol⁻¹ measured by GPC was close to that expected (2820 g mol⁻¹) for 5 BnNH-[poly(*rac*-LA)]-H chains forming per metal centre. The PDI of 1.3 for this polymer indicates a much better defined ROP process



Fig. 8 M_n (as measured by GPC) *vs.* $[rac-LA]_t$: $[Nd]_0$ for the ROP of *rac*-LA (between 100 and 500 equivs. at t = 0) using **3** and 5 equivs. BnNH₂ co-initiator. The numbers in parentheses are the PDIs. The gradient of the fitted line ($R^2 = 0.986$) is 35(2) g mol⁻¹ with an intercept of 107.1 g mol⁻¹ (corresponding to the benzylamine-derived end groups).



Fig. 9 M_n (as measured by GPC) *vs.* $[rac-LA]_t:[BnNH_2]_0$ for the ROP of *rac*-LA (200 equivs. at t = 0) using **3** and 3, 5, 7, or 10 equivs. BnNH₂ co-initiator. The numbers in parentheses are the PDIs. The gradient of the fitted line ($R^2 = 0.985$) is 176(5) g mol⁻¹ with an intercept of 107.1 g mol⁻¹ (corresponding to the benzylamine-derived end groups).

compared to the equivalent experiments with 5 equivs. BnOH (PDI = 1.5) or 3 alone without co-initiator (PDI = 2.7). Analogous experiments increasing [*rac*-LA]₀:[3] from 100 to 500 gave the linear relationship with M_n illustrated in Fig. 8. The gradient of the least-squares fit ($R^2 = 0.986$) is 35(2) g mol⁻¹ which compares well with that expected (28.8 g mol⁻¹) for 5 polymer chains growing per metal centre in each case.

Fig. 9 shows a plot of experimental M_n (as measured by GPC) vs. $[rac-LA]_i$: $[BnNH_2]_0$ for the ROP of rac-LA (held constant at 200 equivs. at t = 0) using **3** and 3, 5, 7, or 10 equivs. BnNH₂ co-initiator. The gradient of 176(5) g mol⁻¹ for the fitted line ($R^2 =$ 0.985) is in reasonable agreement with that expected (144.1 g mol⁻¹) for one chain growing per added amine. Finally, the ¹H NMR and MALDI-ToF mass spectra of the poly(rac-LA) formed were consistent with the exclusive formation of BnNH-[poly(rac-LA)]-H, although once again the polymers were atactic and had $\Delta(m/z)$ separations of 72 amu between adjacent peak envelopes in the MALDI-ToF mass spectra.

Since metal alkoxides/aryloxides are not deprotonated by BnNH₂, the data in Fig. 8 and 9 suggest that in the presence of **3**, BnNH₂ rapidly (with respect to propagation) ringopens a molecule of *rac*-LA to form BnNH-C(O)CH(Me)OC-(O)CH(Me)O-H (**11**) *via* an activated monomer mechanism (eqn (5)).⁴⁶ Thereafter, **11** (containing an acidic O–H group) acts in an analogous manner to ROH (*cf.* Table 4 and Feijen's initial reports^{32,33}), forming active species of the type [Nd{-poly(*rac*-LA)-NHBn}₃] under the polymerisation conditions. These would then propagate the ROP through a coordination-insertion mechanism, with the individual BnNH-[*rac*-LA]_n-H chains equilibrating rapidly as proposed in "conventional" immortal polymerisation systems.⁴⁴ An analogous mechanism was proposed previously for the BnNH₂ co-initiated ROP of *rac*-LA in the presence of certain ligand-supported yttrium complexes.⁴⁵

Attempts to extend the amine co-initiated ROP of *rac*-LA to Bu'NH₂ or piperidine as representative bulky primary or secondary amines were unsuccessful. Poly(*rac*-LA)s with broad PDIs between 1.6 and 1.9 and poor agreement between found and predicted molecular weights were obtained. It appears that with these less nucleophilic co-initiators there may be competition between the monomer-activated ROP initiation (*cf*. eqn (5)) and the coordination-insertion initiation inherent in tris(phenolate) complexes in general (*cf*. the first two entries in Table 4).

Conclusion

A number of new mononuclear, heteroleptic lanthanoid aryloxides, $[Ln(dbp)_3(thf)_3]$ (1–5) and $[Nd(dbp)_3(dme)_2]$ (6), with unsymmetrical substitution has been synthesised by redox transmetallation/protolysis and fully characterised, further establishing the generality of this synthetic method. Thf could be removed to an extent by recrystallisation from toluene, resulting in the formation of a five-coordinate dinuclear species, $[Ln_2(dbp)_6(thf)_2]$ (7, 8). Similar species, **9** and **10**, could be obtained when the reaction was performed in diethyl ether, or in the absence of a solvent. The coordination numbers, generally 5 and 6, in the structures of these complexes are low, but higher than for aryloxides with two o-Bu^t substituents.^{4,5,10,15b,15c,47-49}

Complexes 3 and 4 were efficient but poorly-controlled initiators for the ROP of *rac*-lactide, widening the scope of aryloxide initiators to those with bulky unsymmetrical substitution. Improved catalyst systems were obtained using an excess of BnOH as a co-initiator which showed features consistent with immortal polymerisation. Use of BnNH₂ led to well-controlled, amineinitiated immortal ROP of *rac*-lactide, only the second example of this type of process for a group 3 or lanthanoid system.

Experimental

All products were air-sensitive and required the use of Schlenk and vacuum line techniques, and were manipulated under a nitrogen atmosphere. Solvents were dried by distillation over sodium or sodium/benzophenone. Thf used for polymerisation was dried over potassium at reflux and distilled. All solvents were stored in J. Young Teflon valve ampoules. Elemental analyses (C, H) were performed by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Metal analyses were by EDTA titrations with Xylenol Orange indicator, following acid digestion (HCl or H_2SO_4/HNO_3) and buffering with hexamine. Infrared spectra were obtained as Nujol mulls with a Perkin Elmer 1600 FTIR or Perkin Elmer Spectrum RX1 instrument. ¹H and ¹⁹F NMR spectra were recorded on a Bruker AM300MHz spectrometer.

2,4-di-*tert*-Butylphenol (dbpH) was purchased from Sigma-Aldrich, and was not further purified. Bis(pentafluorophenyl)mercury was synthesised according to the published procedure.⁵⁰ Lanthanoid metals were obtained from Rhone Poulenc or Santoku and stored under nitrogen and freshly filed before use (where indicated).

Polymerisation reactions

All manipulations were performed in a glove-box under a dinitrogen atmosphere at ambient temperature. A catalyst solution was prepared by dissolving the metal complex $(1.39 \times 10^{-2} \text{ mmol})$ in thf (0.5 mL). A monomer solution was prepared by dissolving rac-lactide (100 equivs., 0.20 g, 1.39 mmol) in thf (1.5 mL). BnOH (5 equivs., 6.95×10^{-2} mmol) was added to the metal complex solution where indicated. The monomer solution was added to the catalyst solution with rapid stirring. An aliquot of the mixture was taken after 30 min, quenched with a small amount of wet thf, and evaporated to dryness under vacuum. The completeness was monitored by ¹H NMR spectroscopy. A representative procedure for the extended studies involving 3, BnNH₂ and *rac*-lactide is as follows. *Rac*-lactide (200 equivs., 0.40 g, 2.78 mmol) was dissolved in thf (3.5 mL). The monomer solution was added quickly to a mixture of 3 (1 equiv., 1.40×10^{-2} g, 1.39×10^{-2} mmol) and BnNH₂ (3 equivs., 4.5×10^{-3} mL, 4.16×10^{-3} mL, 4.110⁻² mmol) dissolved in thf (0.5 mL) with rapid stirring. After 10 min the reaction was quenched with a small quantity of wet thf. Aliquots were then taken and evaporated to dryness for analysis. In subsequent polymerisation runs, the initial concentration of raclactide was kept constant (0.7 M). The mass of **3** and the volume of BnNH₂ were varied accordingly to observe the relationships between M_n and [rac-lactide]_0 : [BnNH₂]_0 : [**3**]_0. Polymer molecular weights (M_n , M_w) were determined by GPC using a Polymer Laboratories Plgel Mixed-D column (300 mm length, 7.5 mm diameter) and a Polymer Laboratories PLGPC50 Plus instrument equipped with a refractive index detector. Thf (HPLC grade) was used as an eluent at 30 °C with a rate of 1 mL min⁻¹. Linear polystyrenes were used as primary calibration standards, and Mark–Houwink corrections⁴¹⁻⁴³ for poly(*rac*-LA) in thf were applied for the experimental samples.

MALDI-ToF mass spectra were measured using a Waters MALDI micro equipped with a 337 nm nitrogen laser. An accelerating voltage of 25 kV was applied. The polymer samples were dissolved in thf at a concentration of 1 mg mL⁻¹. The cationization agent used was potassium trifluoroacetate (Fluka, > 99%) dissolved in thf at a concentration of 5 mg mL⁻¹. The matrix used was *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2propenylidene]malononitrile (DCTB) (Fluka) and was dissolved in thf at a concentration of 40 mg mL⁻¹. Solutions of matrix, salt and polymer were mixed in a volume ratio of 4:1:4, respectively. The mixed solution was hand-spotted on a stainless steel MALDI target and left to dry. The spectra were recorded in the reflectron mode.

[La(dbp)₃(thf)₃] (1)

Lanthanum metal powder (freshly filed) (0.24 g, 1.7 mmol), bis(pentafluorophenyl)mercury (0.50 g, 0.92 mmol), 2,4-di-tertbutylphenol (0.48 g, 2.3 mmol), and Hg metal (~2 drops), were added to a Schlenk flask along with dry thf (30 ml), and placed in an ultrasound bath for ~144 h. A faint brown coloured solution was observed. The solution was filtered and concentrated under vacuum until a faint pink oil remained. Large clear block crystals grew at -4 °C over a period of 30 days. (0.35 g, 47%); m.p: 108-111 °C; Found: C, 65.92%; H, 8.77%; La, 14.00%. C₅₄H₈₇O₆La (971.2 g mol⁻¹) requires: C, 66.80%; H, 9.03%; La, 14.30%; IR (Nujol mull, cm⁻¹): 1862 w, 1769 w, 1641 w, 1597 s, 1546 w, 1525 m, 1483 s, 1402 s, 1381 s, 1360 s, 1348 m, 1258 s, 1201 s, 1148 m, 1120 m, 1085 s, 1030 s, 907 s, 872 s, 834 s, 736 s, 670 s, 637 m; ¹H NMR (C₆D₆): 7.48 (s, 3H, ArH); 7.25 (d, 3H, ArH); 7.10 (s, 3H, ArH); 3.48 (s, 12H, thf); 1.62 (s, 27H, p-Bu[']); 1.34 (s, 27H, o-Bu[']); 1.26 (s, 12H, thf).

[Pr(dbp)₃(thf)₃] (2)

A similar preparation from praseodymium metal pieces (0.43 g, 3.1 mmol), bis(pentafluorophenyl)mercury (0.53 g, 1.0 mmol), 2,4-di*tert*-butylphenol (0.49 g, 2.4 mmol), and Hg metal (~2 drops), in dry thf (30 ml) with ultrasonication for ~144 h gave a grey coloured solution. After filtration and concentration under vacuum, an oil remained, which gave pale green block crystals in 1 week. (0.40 g, 52%) m.p: 178–182 °C; Found: Pr, 14.21%. $C_{54}H_{87}O_6Pr$ (973.2 g mol⁻¹) requires: Pr, 14.48%; IR (Nujol mull, cm⁻¹): 1862 w, 1769 w, 1641 w, 1597 m, 1525 m, 1402 m, 1360 m, 1348 m, 1257 m, 1202 m, 1147 m, 1120 m, 1085 m, 1030 m, 907 m, 886 m, 834 m, 735 m, 670 m, 637 m; ¹H NMR (C_6D_6): 21.25 (br s, 3H, ArH); 13.71 (br s, 3H, ArH); 12.08 (br s, 3H, ArH); 9.16 (br s, 12H, thf); 3.41 (br s, 27H, *p*-Bu'); -5.60 (br s, 27H, *o*-Bu'); -9.16 (br s, 12H, thf).

[Nd(dbp)₃(thf)₃] (3)

Neodymium metal filings (0.40 g, 2.8 mmol), bis(penta-fluorophenyl)mercury (0.53 g, 0.99 mmol), 2,4-di-*tert*-butylphenol (0.49 g, 2.4 mmol), and Hg metal (~2 drops) in dry thf (30 ml), ultrasonicated for 144 h gave a blue/grey coloured solution. Filtration and concentration under vacuum gave an oil from which large translucent blue block-like crystals (0.42 g, 54%) grew in 2 days; m.p: 110–113 °C; Found: C, 65.89%; H, 9.00%; Nd, 14.20%. $C_{54}H_{87}O_6Nd$ (976.51 g mol⁻¹) requires C, 66.40; H, 8.92%; Nd, 14.77%; IR (Nujol mull, cm⁻¹): 1862 w, 1769 w, 1641 w, 1597 s, 1546 w, 1525 m, 1483 s, 1402 s, 1382 s, 1360 s, 1348 s, 1257 s, 1202 s, 1147 s, 1120 s, 1085 s, 1030 s, 907 s, 871 s, 834 s, 736 s, 670 s, 637 m; ¹H NMR (C_6D_6): 13.59 (br s, 3H, ArH); 13.10 (br s, 3H, ArH); 12.20 (br s, 3H, ArH); 6.34 (br s, 12H, thf); 2.23 (br s, 27H, *p*-Bu'); -1.87 (br s, 27H, *o*-Bu'); -2.39 (br s, 12H, thf).

[Gd(dbp)₃(thf)₃].0.5hdbp (4.0.5hdbp)

Gadolinium metal powder (0.65 g, 4.1 mmol), bis(pentafluorophenyl)mercury (0.67 g, 1.3 mmol), 2,4-di-*tert*-butylphenol (0.61 g, 3.0 mmol), and Hg metal (~2 drops), in dry thf (30 ml), ultrasonicated for 5 days gave a red/brown coloured solution. Filtration and concentration under vacuum yielded an oil from which large irregular orange/brown crystals (0.53 g, 54%) grew in 1 week; m.p: 263–268 °C; Found: C, 66.68%; H, 8.93%; Gd, 14.36%. C₆₁H₉₈O_{6.5}Gd (1092.7 g mol⁻¹) requires: C, 67.05%; H, 9.04%; Gd, 14.39%; IR (Nujol mull, cm⁻¹): 3501 m(br), 3334 m(br), 2555 w, 1863 m, 1817 w, 1771 m, 1643 m, 1600 s, 1455 s, 1402 s, 1359 s, 1259 s, 1201 s, 1150 s, 1122 s, 1085 s, 1026 s, 955 m, 908 s, 887 s, 819 s, 737 s, 671 s, 638 m, 570 m. ¹H NMR spectrum could not be confidently assigned due to paramagnetic broadening.

[Er(dbp)₃(thf)₃] (5)

Erbium metal powder (0.70 g, 3.9 mmol), 2,4-di-tert-butylphenol (0.51 g, 2.47 mmol), bis-pentafluorophenyl mercury (0.64 g, 1.20 mmol), and mercury metal (~2 drops) in dry thf (30 ml), ultrasonicated overnight gave a vellow/brown solution which upon filtration and concentration under vacuum yielded large pink block crystals. (0.34 g, 41%); m.p: 94-100 °C; Found: C, 63.34%; H, 8.63%; Er, 16.59%. C54H87O6Er (999.52 g mol-1) requires: C, 64.89%; H, 8.77%; Er, 16.73%; IR (Nujol mull, cm⁻¹): 1877 w, 1769 w, 1643 w, 1600 s, 1531 s, 1276 s, 1202 m, 1180 m, 1148 m, 1122 w, 1087 m, 1072 m, 1021 m, 956 m, 941 m, 910 m, 870 m, 839 m, 756 w, 739 m, 718 m, 670 m, 639 m, 584 m; ¹H NMR (C₆D₆): 52.09 (br s, 9H, ArH); 25.89 (br s, 24H, thf); -9.31 (s, 27H, p-Bu'); -25.76 (br s, 27H, o-Bu'). Although the single crystal retained 0.5thf of solvation at 123 K for its X-ray structure determination, this was readily lost, e.g. at room temperature before weighing for microanalysis or the metal analysis.

[Nd(dbp)₃(dme)₂] (6)

Neodymium metal filings (0.4 g, 2.4 mmol), bis(penta-fluorophenyl)mercury (0.51 g, 0.95 mmol), 2,4-di-*tert*-butylphenol (0.54 g, 2.6 mmol), and Hg metal (~2 drops), were added to a Schlenk flask along with dry dme (30 ml), and placed in an ultrasound bath for 72 h. A dark blue/green coloured solution was observed. The solution was filtered and concentrated under

vacuum giving pale blue block crystals over 7 days. (0.21 g, 26%); (Found: Nd, 15.51%. $C_{50}H_{83}O_7Nd$ (940.43 g mol⁻¹) requires Nd, 15.34%); IR (Nujol mull, cm⁻¹): 1598 m, 1526 w, 1401 m, 1360 m, 1260 m, 1201 m, 1144 m, 1086 m, 1048 m, 1011 m, 971 m, 906 w, 887 w, 859 m, 820 m, 754 w, 733 m, 669 m, 638 w; ¹H NMR (C_6D_6): 18.98 (br s, 9H, ArH); 15.11 (br s, 20H, dme); 4.95 (br s, 54H, Bu')

[Nd₂(dbp)₆(thf)₂].2C₇H₈ (7.2C₇H₈)

Nd(dbp)₃(thf)₃ was dissolved in toluene (20 ml) and was placed in an ultrasound bath for *ca.* 1 h. The solvent was then slowly evaporated until crystals could be seen to form. Small pale blue rectangular crystals grew over several days at –4 °C in quantitative yield; m.p: 198–202 °C; Found: C, 65.96%; H, 8.67%; Nd, 16.90%. $C_{92}H_{142}O_8Nd_2$ (1664.58 g mol⁻¹) (loss of lattice toluene) requires C, 66.30%; H, 8.65%; Nd, 17.33%; IR (Nujol mull, cm⁻¹): 1602 m, 1529 w, 1486 s, 1402 s, 1361 s, 1260 s, 1226 s, 1202 m, 1177 w, 1151 m, 1124 m, 1085 s, 1018 m, 909 m, 887 m, 837 s, 822 s, 739 m, 727 m, 694 w, 674 m, 642 m; ¹H NMR (C₆D₆): 32.61 (br s, 12H, ArHterminal phenolates); 13.74 (br s, 6H, ArH-bridging phenolates); –2.66 (br s, 72H, Bu'-terminal phenolates); –4.82 (br s, 36H, Bu'bridging phenolates); –8.41 (br s, 16H, thf).

[Er₂(dbp)₆(thf)₂] (8)

Er(dbp)₃(thf)₃ was dissolved in toluene (20 ml) giving a pink/brown solution, and placed in the ultrasound bath for *ca*. 1 h. The solvent was then slowly evaporated until crystals could be seen to be forming. Small pale pink rectangular crystals grew over several days at -4 °C in quantitative yield; m.p: 195–201 °C; (Found: Er, 19.79%. C₉₂H₁₄₂O₈Er₂ (1710.62 g mol⁻¹) requires Er, 19.56%); IR (Nujol mull, cm⁻¹): 2031 w, 1938 w, 1858 w, 1776 w, 1603 m, 1526 m, 1402 m, 1261 m, 1216 m, 1202 m, 1177 w, 1152 m, 1125 m, 1085 m, 1017 m, 911 m, 888 w, 868 w, 840 m, 819 m, 727 s, 694 m, 674 w, 641 m; ¹H NMR spectrum could not be confidently assigned due to paramagnetic broadening.

[Nd₂(dbp)₆(Et₂O)₂] (9)

Similarly, neodymium metal filings (0.50 g, 3.5 mmol), bis(pentafluorophenyl)mercury (0.67 g, 1.3 mmol), 2,4-di-tertbutylphenol (0.51 g, 2.5 mmol), and Hg metal (~2 drops), in dry diethyl ether (30 ml), were stirred at room temperature for 12 h to give a dark blue coloured solution. Small pale blue crystals suitable for X-ray crystallography grew directly from the reaction flask. The solution was filtered and concentrated under vacuum for further characterisation. (0.31 g, 32%); m.p: 192-199 °C; (Found: Nd, 17.23%. C₉₂H₁₄₆O₈Nd₂ (1668.62 g mol⁻¹) requires Nd, 17.29%); IR (Nujol mull, cm⁻¹): 1769 w, 1682 w, 1644 w, 1601 s, 1532 s, 1460 s, 1377 s, 1261 s, 1149 m, 1086 m, 955 m, 909 m, 887 m, 821 s, 727 s, 674 m, 641 m; ¹H NMR spectrum could not be confidently assigned due to broadening. It has been reported that the paramagnetism of Nd³⁺ complexes is often enhanced in dinuclear complexes.^{15a} In other cases, similar complexes exhibit differing degrees of broadening and shifting of resonances.48

[Nd₂(dbp)₆(dbpH)₂] (10)

Neodymium metal powder (0.52 g, 3.64 mmol), 2,4-di-*tert*butylphenol (0.50 g, 2.42 mmol) and mercury (~2 drops) were heated to 130 °C under vacuum in a sealed glass tube for 24 h. Pale blue crystals were obtained directly from the tube. After obtaining the crystal structure, the remaining crystals were separated from excess metal by extracting into hot toluene, filtration, and evaporation to dryness. (0.27 g, 47%); Found: Nd, 13.98%. $C_{112}H_{170}O_8Nd_2$ (1932.96 g mol⁻¹) requires Nd, 14.92%; IR (Nujol mull, cm⁻¹): 3610 s, 3558 s, 3378 m, 1939 m, 1871 m, 1799 m, 1735 w, 1604 s, 1564 s, 1505 s, 1392 s, 1361 s, 1331 m, 1260 s, 1176 s, 1110 s, 1082 s, 1029 s, 920 m, 856 s, 828 s, 728 s, 694 s, 678 s, 644 m; ¹H NMR (C₆D₆): 7.47 (s, 8H, ArH); 7.04 (m, 8H, ArH); 6.06 (s, 8H, ArH); 3.77 (brs, 2H, OH); 1.56 (s, 72H, *p*-Bu'); 1.30 (s, 72H, *o*-Bu').

Additional experimental data

Attempted synthesis of [Nd(dbp)₃(thf)₃] in the absence of Hg(C₆F₅)₂

Neodymium metal filings (0.27 g, 1.87 mmol), 2,4-di-*tert*butylphenol (0.51 g, 2.47 mmol), and Hg metal (~2 drops), were added to a Schlenk flask along with dry thf (30 ml), and placed in an ultrasound bath for 48 h. No colour change was observed in the solution. Filtering and concentration under vacuum yielded only 2,4-di-*tert*-butylphenol.

Attempted synthesis of [Nd(dbp)₃] in toluene

Neodymium metal filings (0.50 g, 3.5 mmol), bis(pentafluorophenyl)mercury (0.67 g, 1.3 mmol), 2,4-di-*tert*-butylphenol (0.51 g, 2.5 mmol), and Hg metal (~2 drops), were added to a Schlenk flask along with dry toluene (30 ml), and placed in an ultrasound bath for 48 h. No colour change was observed. ¹⁹F NMR showed no conversion of bis(pentafluorophenyl)mercury to pentafluorobenzene.

Attempted synthesis of [Ln(dbp)₃(thf)₃]; Ln = Sm, Dy, Ho, Yb, Y

Lanthanoid metal powder (0.70 g), bis(pentafluorophenyl)mercury (0.67 g, 1.25 mmol), 2,4-di-*tert*-butylphenol (0.50 g, 2.42 mmol), and Hg metal (-2 drops), were added to a Schlenk flask along with dry thf (30 ml), and placed in an ultrasound bath for 48 h. The resulting solution (appropriately coloured for Ln = Sm, Ho, Yb) was filtered and concentrated under vacuum, yielding an oil that failed to crystallise; IR (Nujol mull, cm⁻¹): 1729 w, 1602 w, 1488 s, 1362 m, 1287 m, 1262 m, 1202 w, 1177 w, 1151 w, 1120 w, 1087 m, 1021 w, 913 w, 844 w, 821 m, 668 w. ¹⁹F NMR spectra of representative reaction mixtures showed consumption of the mercurial and formation of C_6F_6H .

X-Ray structure determinations[†]

Intensity data were collected using a Bruker X8 Apex II CCD or an Enraf-Nonius KAPPA CCD at 123 K with Mo-K α radiation ($\lambda = 0.71073$ Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fiber which was mounted on the diffractometer. Using psi and omega scans, Nt (total) reflections were measured, which were reduced to No. of unique reflections, with $F_{\circ} > 2\sigma(F_{\circ})$ being considered observed. Data were initially processed and corrected for absorption using the Bruker Apex II program suite,⁵¹ or the programs DENZO⁵² and SORTAV.⁵³ The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2 , with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97⁵⁴ and SHELXL-97⁵⁵ through the graphical interface X-Seed,⁵⁶ which was also used to generate the figures.

General Variata: All compounds exhibit a relatively large ratio of ADP max/min for carbon atoms, due to the contrast between rigid aromatic carbons and the carbons of the Bu' groups which have a greater potential for free rotation. To convey the true nature of the ellipsoids of these atoms they have been refined anisotropically with no restraints. Restraining these atoms would not reflect the variable extremes of the thermal envelopes of all carbon atoms in these compounds. In extreme cases, disorder has been modelled as best as possible. Specific variata for compounds are mentioned below.

Crystal data for [La(dbp)₃(thf)₃]. $C_{54}H_{87}LaO_6$, M = 971.15, $0.28 \times 0.20 \times 0.08 \text{ mm}^3$, monoclinic, space group $P2_1/c$ (No. 14), a = 19.616(4), b = 28.198(6), c = 19.521(4) Å, $\beta = 93.23(3)^\circ$, V = 10780(4) Å³, Z = 8, $D_c = 1.197 \text{ g cm}^{-3}$, $F_{000} = 4128$, Nonius KAPPA CCD, $2\theta_{\text{max}} = 50.0^\circ$, 27 592 reflections collected, 14 832 unique ($R_{\text{int}} = 0.0679$). Final GooF = 1.026, $R_1 = 0.0519$, w $R_2 = 0.1311$, R indices based on 11 587 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1176 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.836 \text{ mm}^{-1}$.

Variata: The crystals were of poor quality, possibly twinned, resulting in a large number of rejected reflections and low completeness (78%). However, this compound is isostructural with compounds 2 and 3.

Crystal data for [Pr(dbp)₃(thf)₃]. $C_{54}H_{87}O_6Pr$, M = 973.15, green block, $0.08 \times 0.05 \times 0.05$ mm³, monoclinic, space group $P2_1/c$ (No. 14), a = 19.575(4), b = 28.185(6), c = 19.489(4) Å, $\beta = 93.19(3)^\circ$, V = 10736(4) Å³, Z = 8, $D_c = 1.204$ g cm⁻³, $F_{000} = 4144$, Nonius KappaCCD, $2\theta_{max} = 55.0^\circ$, 112 224 reflections collected, 24 565 unique ($R_{int} = 0.1339$). Final *GooF* = 1.103, $R_1 = 0.0597$, w $R_2 = 0.1365$, R indices based on 15 392 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1175 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 0.952$ mm⁻¹.

Crystal data for [Nd(dbp)₃(thf)₃]. $C_{54}H_{s7}NdO_6$, M = 976.48, blue block, $0.25 \times 0.20 \times 0.08$ mm³, monoclinic, space group $P2_1/c$ (No. 14), a = 19.5150(4), b = 28.1539(7), c = 19.4626(5) Å, $\beta = 93.238(1)^\circ$, V = 10676.1(4) Å³, Z = 8, $D_c = 1.215$ g cm⁻³, $F_{000} = 4152$, Nonius KappaCCD, $2\theta_{max} = 55.0^\circ$, 117 868 reflections collected, 24 463 unique ($R_{int} = 0.0562$). Final *GooF* = 1.125, $R_1 =$ 0.0447, w $R_2 = 0.0763$, R indices based on 20 451 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1176 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 1.017$ mm⁻¹.

Variata: Elongated thermal ellipsoid of C98 indicates envelope disorder. However, model was unsatisfactory when attempting to model disorder. There is an abnormal thermal ellipsoid of C41, but we deemed it non-sensible to model disorder of a single C atom when Bu' group can freely rotate. Occupancies of C110 and C111 were fixed after trial refinement. **Crystal data for [Gd(dbp)₃(thf)₃].0.5hdbp.** C₆₁H₉₈GdO_{6.5}, M = 1092.64, colourless block, $0.25 \times 0.15 \times 0.04$ mm³, monoclinic, space group $P2_1/n$ (No. 14), a = 24.1258(14), b = 9.3193(6), c = 27.4879(15) Å, $\beta = 105.778(2)^\circ$, V = 5947.4(6) Å³, Z = 4, $D_c = 1.220$ g cm⁻³, $F_{000} = 2320$, Bruker X8 Apex II CCD, $2\theta_{max} = 50.0^\circ$, 72 464 reflections collected, 10 451 unique ($R_{int} = 0.0836$). Final GooF = 1.220, $R_1 = 0.0626$, w $R_2 = 0.1288$, R indices based on 8825 reflections with $I > 2\sigma(I)$ (refinement on F^2), 729 parameters, 36 restraints. Lp and absorption corrections applied, $\mu = 1.162$ mm⁻¹.

Variata: The lattice phenol is disordered over a symmetry site such that the components overlap. Anisotropic refinement of Catoms restrained gave the best solution for modelling disorder.

Crystal data for [Er(dbp)₃(thf)₃].0.5thf. $C_{56}H_{91}ErO_{6.5}$, M = 1035.55, pink block, $0.10 \times 0.07 \times 0.07$ mm³, trigonal, space group *P3c1* (No. 158), a = b = 24.9188(2), c = 16.7294(3) Å, V = 8996.32(19) Å³, Z = 6, $D_c = 1.147$ g cm⁻³, $F_{000} = 3282$, Bruker X8 Apex II CCD, $2\theta_{max} = 50.0^{\circ}$, 81382 reflections collected, 9725 unique ($R_{int} = 0.0453$). Final *GooF* = 1.187, $R_1 = 0.0703$, $wR_2 = 0.1387$, *R* indices based on 8872 reflections with $I > 2\sigma(I)$ (refinement on F^2), 283 parameters, 29 restraints. Lp and absorption corrections applied, $\mu = 1.441$ mm⁻¹. Absolute structure parameter = 0.00(4) (Flack, H. D. *Acta Cryst.* 1983, *A39*, 876–881).

Variata: Attempts to include more atoms in the anisotropic model gave a less satisfactory refinement. Structure is presented for connectivity only, so a full anisotropic refinement was deemed unnecessary. Selected bond lengths and angles are given in supplementary data. Repeated attempts to obtain good quality crystals were unsuccessful. For example use of thf/hexane gave compound $\mathbf{8}$ with loss of thf.

Crystal data for [Nd(dbp)₃(dme)₂]. C₅₀H₈₃NdO₇, M = 940.40, pale blue block, $0.20 \times 0.10 \times 0.10$ mm³, monoclinic, space group $P2_1$ (No. 4), a = 15.866(3), b = 22.379(5), c = 16.364(3) Å, $\beta = 115.92(3)^\circ$, V = 5225.7(18) Å³, Z = 4, $D_c = 1.195$ g cm⁻³, $F_{000} = 1996$, Nonius KappaCCD, $2\theta_{max} = 55.0^\circ$, $55\,029$ reflections collected, 23 311 unique ($R_{int} = 0.1392$). Final *GooF* = 1.032, $R_1 = 0.0726$, w $R_2 = 0.1407$, R indices based on 14 258 reflections with $I > 2\sigma(I)$ (refinement on F^2), 1084 parameters, 1 restraint. Lp and absorption corrections applied, $\mu = 1.038$ mm⁻¹. Absolute structure parameter = -0.001(14) (Flack, H. D. *Acta Cryst.* 1983, A39, 876–881).

Crystal data for [Nd₂(dbp)₆(thf)₂].2C₇H₈. C₁₀₆H₁₅₈Nd₂O₈, M = 1848.80, blue block, 0.20 × 0.07 × 0.06 mm³, triclinic, space group $P\bar{1}$ (No. 2), a = 11.226(2), b = 14.321(3), c = 16.832(3) Å, $\alpha =$ 83.24(3), $\beta = 73.97(3)$, $\gamma = 73.61(3)^{\circ}$, V = 2492.9(9) Å³, Z = 1, $D_c = 1.231$ g cm⁻³, $F_{000} = 978$, Nonius KappaCCD, $2\theta_{max} = 55.0^{\circ}$, 34 572 reflections collected, 11 295 unique ($R_{int} = 0.0844$). Final GooF = 1.172, $R_1 = 0.0630$, w $R_2 = 0.1412$, R indices based on 9523 reflections with $I > 2\sigma(I)$ (refinement on F^2), 542 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.082$ mm⁻¹.

Crystal data for [Er₂(dbp)₆(thf)₂]. $C_{92}H_{142}Er_2O_8, M = 1710.58$, pink block, $0.10 \times 0.07 \times 0.06$ mm³, triclinic, space group $P\overline{1}$ (No. 2), a = 11.6509(2), b = 14.0152(2), c = 14.7135(2) Å, $\alpha = 72.387(1)$, $\beta = 82.619(1), \gamma = 81.695(1)^{\circ}, V = 2256.75(6)$ Å³, $Z = 1, D_c =$ 1.259 g cm⁻³, $F_{000} = 894$, Bruker X8 Apex II CCD, $2\theta_{max} = 55.0^{\circ}$, 29 373 reflections collected, 10 298 unique ($R_{int} = 0.0339$). Final $GooF = 1.066, R_1 = 0.0319, WR_2 = 0.0746, R$ indices based on 9397 reflections with $I > 2\sigma(I)$ (refinement on F^2), 506 parameters, 62 restraints. Lp and absorption corrections applied, $\mu = 1.897 \text{ mm}^{-1}$.

Crystal data for [Nd₂(dbp)₆(Et₂O)₂]. C₉₂H₁₄₆Nd₂O₈, M = 1668.57, blue block, $0.07 \times 0.05 \times 0.05$ mm³, monoclinic, space group $P2_1/c$ (No. 14), a = 14.3151(4), b = 28.3247(7), c = 11.5266(3) Å, $\beta = 105.602(1)^{\circ}$, V = 4501.5(2) Å³, Z = 2, $D_c = 1.231$ g cm⁻³, $F_{000} = 1764$, Bruker X8 Apex II CCD, $2\theta_{max} = 55.0^{\circ}$, 30 589 reflections collected, 10 202 unique ($R_{int} = 0.0492$). Final GooF = 1.207, $R_1 = 0.0501$, w $R_2 = 0.0791$, R indices based on 8730 reflections with $I > 2\sigma(I)$ (refinement on F^2), 480 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.191$ mm⁻¹.

Crystal data for [Nd₂(dbp)₆(dbpH)₂]. $C_{112}H_{170}Nd_2O_8$, M = 1932.96, blue block, $0.07 \times 0.05 \times 0.05$ mm³, triclinic, space group $P\bar{1}$ (No. 2), a = 11.472(2), b = 14.196(3), c = 18.464(4) Å, $\alpha = 73.39(3)$, $\beta = 82.08(3)$, $\gamma = 68.85(3)^\circ$, V = 2685.4(9) Å³, Z = 1, $D_c = 1.195$ g cm⁻³, $F_{000} = 1026$, Nonius KappaCCD, $2\theta_{max} = 50.0^\circ$, 16914 reflections collected, 7603 unique ($R_{int} = 0.2217$). Final GooF = 1.044, $R_1 = 0.1350$, $wR_2 = 0.2212$, R indices based on 3405 reflections with $I > 2\sigma(I)$ (refinement on F^2), 269 parameters, 0 restraints. Lp and absorption corrections applied, $\mu = 1.007$ mm⁻¹.

Variata: The crystals were of poor quality, possibly twinned, resulting in a large number of rejected reflections and low completeness (71%). As such, this compound is presented in terms of connectivity only. The lattice thf was refined with isotropic C and O atoms due to high thermal motion. Selected bond lengths and angles are given in supplementary data.[†]

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