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# PAPER

# Direct reaction of iodine-activated lanthanoid metals with 2,6-di*iso*propylphenol<sup>†</sup>

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Rare earth metals activated with *ca*. 2% iodine react directly with 2,6-di*iso* propylphenol (HOdip) in tetrahydrofuran (thf), 1,2-dimethoxyethane (dme), and dig-dme (dig = di(2-methoxyethyl) ether) to give solvated phenolate complexes  $[Ln(Odip)_3(thf)_n]$  (Ln = La, Nd, n = 3; Ln = Sm, Dy, Y, Yb, n = 2),  $[Eu(Odip)(\mu-Odip)(thf)_2]_2$ ,  $[Ln(Odip)_3(dme)_2]$  (Ln = La, Yb) and  $[La(Odip)_3(dig)]$  in good yield for Ln = La, Nd, Eu but modest yield for smaller Ln metals under comparable conditions. However, increasing the excess of metal greatly increased the yield for Ln = Y. The synthetic method has general potential, at least for lanthanoid phenolates. Comparison redox transmetallation/protolysis (RTP) reactions between Ln metals,  $Hg(C_6F_5)_2$  and the phenol gave higher yields in shorter time and, for Eu, gave [Eu(Odip)<sub>3</sub>(thf)<sub>3</sub>] in contrast to an Eu<sup>II</sup> complex from Eu(I<sub>2</sub>). New [Ln(Odip)<sub>3</sub>(thf)<sub>3</sub>] complexes have *fac*-octahedral structures and [Ln(Odip)<sub>3</sub>(thf)<sub>2</sub>] monomeric five coordinate distorted trigonal bipyramidal structures with apical thf ligands. [Eu(Odip)(µ-Odip)(thf)<sub>2</sub>]<sub>2</sub> is an unsymmetrical dimer with two bridging Odip ligands. One five coordinate Eu atom has distorted trigonal bipyramidal stereochemistry and the other is distorted square pyramidal. Whilst [La(Odip)3(dme)2] has irregular seven coordination with mer-Odip and chelating dme ligands,  $[Ln(Odip)_3(dme)_2]$  (Ln = Dy, Y (prepared by ligand exchange), Yb) are monomeric six coordinate with one chelating and one unidentate dme. A six coordinate fac-octahedral arrangement is observed in [La(Odip)<sub>3</sub>(dig)].

# Introduction

Syntheses of rare earth organometallics, organoamides and aryloxides/alkoxides from the elemental metals provide an alternative strategy to the more commonly used salt metathesis and protolysis reactions.<sup>1–5</sup> Free metal-based preparations include (i) redox transmetallation using diarylmercurials,<sup>6–13</sup> thallium cyclopentadienyls,<sup>4,13</sup> pyrazolates,<sup>14,15</sup> and aryloxides,<sup>16,17</sup> tin(II)<sup>18</sup> and organotin(IV)<sup>19,20</sup> complexes or triphenylbismuth<sup>10–12</sup> (reaction (1)).

$$m\operatorname{Ln} + n\operatorname{MR}_m \to m\left[\operatorname{LnR}_n\right] + n\operatorname{M}$$
 (1)  
 $_{n=2,3}$ 

(ii) redox transmetallation/protolysis (RTP) (reaction (2)).<sup>9,17,21-26</sup>

$$2Ln + nHgR_2 + 2nLH \rightarrow 2[LnL_n] + nHg + 2nRH$$
 (2)

(iii) direct reaction of lanthanoid metals with protic agents, often at elevated temperatures (reaction (3)).<sup>9,27–29</sup>

$$Ln + nLH \rightarrow [Ln(L)_n] + n/2H_2$$
 (3)

(iv) pseudo Grignard formation (reaction (4)).<sup>30–34</sup>

$$Ln + RI \rightarrow "RLnI"$$
 (4)

and (v) metal atom reactions.35-38

Such reactions (excluding (iv) and (v)) often require activation of the metal surface, although in (1) ( $MR_n = HgR_2$ ) and (2), the generated mercury metal performs this role.<sup>21,23</sup> Of the activation methods, addition of mercury either directly or through addition of mercuric chloride<sup>6,7,23,39,40</sup> is the most common, but raises environmental concerns.41-42 Alternative methods include activation by ammonia<sup>18,43-49</sup> (much less adopted than in alkaline earth chemistry),  $^{50-52}$  naphthalene, with ytterbium naphthalenide serving as pseudo-Yb<sup>0</sup>,<sup>11</sup> addition of preformed LnI<sub>2</sub> or LnI<sub>3</sub>,<sup>10,53</sup> and addition of iodine, either stoichiometric, yielding  $[Sm^{III}(\eta^8-C_8H_8)(hmpa)_3]I$  or catalytic, providing  $[Sm(\eta^8-C_8H_8)$  $(hmpa)_3$ [Sm<sup>III</sup>( $\eta^8$ -C<sub>8</sub>H<sub>8</sub>)<sub>2</sub>]<sup>54</sup> (emulating activation of Grignard reagent formation).<sup>55–57</sup> The last method, used for synthesis of lanthanum 3,5-diphenylpyrazolate [La(Ph<sub>2</sub>pz)<sub>3</sub>(dme)<sub>2</sub>] by redox transmetallation from [SnMe<sub>2</sub>(Ph<sub>2</sub>pz)<sub>2</sub>] in 1,2-dimethoxyethane,<sup>19</sup> offers a convenient approach to LnI<sub>3</sub> activation since Ln metal powders react with iodine in tetrahydrofuran (thf) to give  $[LnI_3(thf)_n]$  (n = 3.5, 4).<sup>58</sup> We now report a detailed assessment of the value of activation by iodine in the reaction of rare earth metals with 2,6-diisopropylphenol in tetrahydrofuran,1,2dimethoxyethane and diglyme. In some cases, a comparison has

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been made of the method with redox transmetallation/protolysis (reaction(2)) using the normally highly effective oxidant  $Hg(C_6F_5)_2$ .<sup>17,21–26</sup> The reactant phenol was initially chosen because a range of structurally characterized lanthanoid 2,6-di-*iso* propylphenolate complexes with thf are known.<sup>2,3,59–63</sup> In the event, a number of new complexes have been crystallographically characterized, including a dimeric Eu<sup>II</sup> species and derivatives with a relatively rare unidentate 1,2-dimethoxyethane ligand.<sup>20,25,64–67</sup>

# **Results and discussion**

#### Syntheses

Rare earth metals activated by iodine (1.7–2.5%) were found to react directly with 2,6-di*iso*propylphenyl (HOdip) on ultrasonication in tetrahydrofuran (thf) and 1,2-dimethoxyethane.

$$2 \operatorname{Ln} + 6 \operatorname{HO} \operatorname{dip} \xrightarrow{\operatorname{solv}/I_2}{)} 2 [\operatorname{Ln} (\operatorname{O} \operatorname{dip})_3 (\operatorname{solv})_n] + 3 \operatorname{H}_2$$
  

$$\operatorname{Ln} = \operatorname{La}, \operatorname{Nd}, \operatorname{Sm}, \operatorname{Dy}, \operatorname{Y}, \operatorname{Yb}; \operatorname{solv} = \operatorname{thf}; n = 3(\operatorname{La}, \operatorname{Nd}) \operatorname{or} n = 2$$
  

$$\operatorname{Ln} = \operatorname{La}, \operatorname{Yb}; \operatorname{solv} = \operatorname{dme}; n = 2$$

Hydrogen was detected by <sup>1</sup>H NMR spectroscopy from a representative reaction. A corresponding reaction with europium metal yielded a europium( $\pi$ ) complex [Eu(Odip)( $\mu$ -dip)(thf)<sub>2</sub>]<sub>2</sub>.

$$2\text{Eu} + 4 \text{ HO dip } \stackrel{\text{thf}}{\rightarrow} [\text{Eu}(\text{Odip})(\mu - \text{Odip})(\text{thf})_2]_2 + 2 \text{ H}_2 \quad (6)$$

An analogous synthesis with La metal and HOdip in dme–dig (dig = di(2-methoxyethyl) ether) yielded [La(Odip)<sub>3</sub>(dig)].

For reaction (5) in thf with a twofold excess of Ln metal, yields were over 50% for Ln = La, Nd (and for Ln = Eu in (6)) but ca 25% for Sm-Yb (Y) (Table 1). However, this smaller metal defect can be overcome since a reaction employing a much larger excess of yttrium gave a 75% yield (metal residues can be recycled). A similar pattern of yields was also observed for reactions in dme, viz. high for Ln = La and smaller for Ln =Yb. A contributing factor to lower yields for  $Sm \rightarrow Yb$  may be the need to wash the product with an excess of hexane to remove adhering unreacted 2,6-diisopropylphenol leading to some dissolution in HOdip-hexane. No reaction was observed between Ln metals and HOdip in the absence of activation by I<sub>2</sub>, and the amount used is the minimum required for effective reaction. However, europium has been observed to react slowly with HOdip in the more polar solvents N-methylimidazole and acetonitrile.<sup>68</sup> Using a much larger amount of iodine led to isolation of  $[YbI_2(thf)_4]$ , for Ln = Yb.

From the reaction of ytterbium with HOdip in dme, a crystal of the known  $[Yb(Odip)_2(\mu-OMe)]_2$  was isolated, presumably formed from metal-induced cleavage of dme (reaction (7)),

$$2Yb + 4 \text{ HOdip} + (\text{MeOCH}_2)_2$$
  

$$\rightarrow [Yb(\text{Odip})_2(\text{OMe})]_2 + 2 \text{ H}_2 + C_2\text{H}_4$$
(7)

since a similar cleavage has been observed in the RTP reacion between Yb metal, HgPh<sub>2</sub>, and HOdip in dme.<sup>69</sup> However, in

	Yield (%)			
Compounds	$I_2$ activation method	RTP method		
$[La(Odip)_3(thf)_3](1)$	64			
$[Nd(Odip)_3(thf)_3]$ ·2thf (2)	52			
$[Eu(Odip)_3(thf)_3] \cdot 2thf(3)$		70		
$[Nd(Odip)_3(thf)_2]$ (4)	$60^a$			
$[Sm(Odip)_3(thf)_2]$ (5)	25	72		
$[Dy(Odip)_3(thf)_2]$ (6)	26	59		
$[Y(Odip)_3(thf)_2]$ (7)	$25(75)^{b}$	59		
$[Yb(Odip)_3(thf)_2]$ (8)	26	68		
$[Eu(Odip)(\mu-Odip)(thf)_2]_2$ (9)	62	_		
$[La(Odip)_3(dme)_2]$ (10)	67	_		
$[Dy(Odip)_3(dme)_2]$ (11)	73 <sup>c</sup>	_		
$[Y(Odip)_3(dme)_2]$ (12)	68 <sup>c</sup>	_		
$[Yb(Odip)_3(dme)_2]$ (13)	30	_		
	69 <sup>c</sup>			
$[La(Odip)_{3}(dig)_{2}] \cdot 0.5dme$ (15)	68	82		

<sup>*a*</sup> From recrystallization of **2** from dme. <sup>*b*</sup> Large excess of Y metal used (Experimental) <sup>*c*</sup> From recrystallization of [Ln(Odip)<sub>3</sub>(thf)<sub>2</sub>] **6–8** from dme

the present case, the amount formed was extremely low, since no methanol could be detected by <sup>1</sup>H NMR spectroscopy on hydrolysis of the bulk product. There was no evidence of solvent cleavage in the corresponding reaction with lanthanum. Pure [Yb(Odip)<sub>3</sub>(dme)<sub>2</sub>] was prepared by crystallization of [Yb (Odip)<sub>3</sub>(thf)<sub>2</sub>] from dme, and the Y and Dy analogues were similarly obtained. Surprisingly, crystallization of dried [Nd(Odip)<sub>3</sub> (thf)<sub>3</sub>] from dme yielded [Nd(Odip)<sub>3</sub>(thf)<sub>2</sub>] with a similar outcome from crystallization from toluene, but crystallization of the crude product from another synthesis from toluene gave single crystals of [Nd(Odip)<sub>3</sub>(thf)<sub>3</sub>]·PhMe (**2b**).

For comparison of methods, a number of the  $[Ln(Odip)_3 (thf)_2]$  (Ln = Sm, Dy, Y, Yb) complexes were prepared by the RTP route from Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (reaction (8), n = 2), all of which gave higher yields in shorter times (Table 1).

$$2 \operatorname{Ln} + 3 \operatorname{Hg}(C_6F_5)_2 + 6 \operatorname{HOdip} \rightarrow [\operatorname{Ln}(\operatorname{Odip})_3(\operatorname{thf})_n] + 3 \operatorname{Hg} + 6 \operatorname{C}_6F_5H$$
(8)

The Eu<sup>III</sup> complex [Eu(Odip)<sub>3</sub>(thf)<sub>3</sub>] which was not obtained from reaction (5) (*cf.* reaction (6)) was prepared by this method (reaction (8), Ln = Eu, n = 3). Overall, iodine activation of Ln metals provides a greener metal-based synthesis of Ln(Odip)<sub>3</sub> complexes, but RTP reactions are faster and higher yielding with smaller Ln metals.

#### Characterisation

(5)

In most cases the complexes were initially isolated as single crystals, and were characterised by X-ray crystal structures in the case of new compounds or known compounds<sup>59–63</sup> not hitherto examined crystallographically. Previously reported compounds of known structure<sup>2,3,59–63</sup> were characterised by unit cells, or, where the synchrotron was used, by a structure re-determination. Bulk samples were washed with hexane to remove adhering

unreacted liquid 2,6-diisopropylphenol. This led to loss of crystallinity and characterisation was performed on the resulting bulk powder. Where compounds were of a known stoichiometric/ structural class, bulk characterization was by IR and <sup>1</sup>H NMR spectroscopy (of hydrolysed samples where paramagnetism produced unsatisfactory spectra) and lanthanoid metal analysis (employing a much larger hence more representative sample than microanalysis). For new compound classes, microanalyses were carried out for representative examples. For [Ln(Odip)<sub>3</sub> (thf)<sub>2</sub>]<sub>2</sub>·2thf complexes and [Ln(Odip)<sub>3</sub>(dme)<sub>2</sub>] species with highly disordered dme of solvation in the single crystals (Ln =Dv. Y), no solvent additional to that ligated was detected by  ${}^{1}H$ NMR spectroscopy and analyses were consistent with absence of solvent of crystallization. When bulk [Eu(Odip)<sub>2</sub>(thf)<sub>2</sub>]<sub>2</sub>, was first isolated, the Eu analysis was in agreement with that for single crystal composition. However, a microanalysis following overseas transfer to New Zealand was indicative of loss of virtually all thf, and the <sup>1</sup>H NMR spectrum of a similarly stored sample showed 0.2 thf per dimer unit. There was no evidence of loss of coordinated thf, dme, or dig from trivalent complexes, and in the case of [La(Odip)<sub>3</sub>(dig)]·0.25dme (15), the dme of solvation was retained in the bulk sample.

#### The role of iodine

After treatment of lanthanum with a small amount of iodine in tetrahydrofuran, both the residual metal and the resulting solution were tested for ability to promote reaction with 2.6-diisopropylphenol. When the latter was treated with La metal and HOdip, a good yield of [La(Odip)<sub>3</sub>(thf)<sub>3</sub>] was obtained. In addition, the residual metal, which gave a different SEM image from fresh La filings (Supplementary data<sup>†</sup>), reacted with HOdip in tetrahydrofuran to give a modest yield of [La(Odip)<sub>3</sub>(thf)<sub>3</sub>]. Thus there appears to be a dual activation role. Further experiments to determine the distribution of La and iodine following treatment of the metal with a small amount of I<sub>2</sub> in thf showed that much of the iodine remained in solution though some was retained by the metal, and only a small percentage of La dissolved. Analysis of the solution showed an La: I ratio of 1:3. Although the mechanism of activation is not known, it may involve a reactive and unstable low oxidation state species, e.g. for Ln = La, Nd, Dy (Scheme 1).

In recent years, molecular divalent compounds of Ln elements,  $^{70,73}$  not normally forming Ln^II derivatives, have been characterised,  $^{53,54,70-73}$  greatly expanding the horizons of lanthanoid chemistry, with the high reactivity of DyI<sub>2</sub> and TmI<sub>2</sub> being well established.  $^{54,73-75}$ 



Scheme 1 A possible explanation of activation by iodine for elements not normally forming stable Ln<sup>II</sup> species.

#### Structural determinations

The complexes  $[Ln(Odip)_3(thf)_3]$ ·2thf (Ln = Nd (2), Eu (3)) are isotypic, and have monomeric fac octahedral structures (Fig. 1 (a)), as reported for [Ce(Odip)<sub>3</sub>(thf)<sub>3</sub>]·PhMe.<sup>60</sup> The neodymium complex was also crystallized as [Nd(Odip)<sub>3</sub>(thf)<sub>3</sub>]·PhMe (2a), which is isotypic with the cerium complex.<sup>60</sup> A precise structure could not be obtained for  $[La(Odip)_3(thf)_3]$  (1), but the connectivity is the same and it has similar unit cell dimensions (Experimental section) to 2a and [Ce(Odip)<sub>3</sub>(thf)<sub>3</sub>]·PhMe.<sup>60</sup> Selected bond lengths and angles of 2 and 3 are listed in Table 2 and those of 2a (similar to 2) in the Supplementary Data.<sup>†</sup> Bond lengths are unexceptional compared with literature data for analogous aryloxides<sup>2,3</sup> but two Ln–O(thf) bonds shorten by 0.064-0.070 Å from 2 to 3, nearly twice that expected from ionic radii differences.<sup>76</sup> The isotypic complexes [Ln(Odip)<sub>3</sub>  $(thf)_2$  (Ln = Nd (4), Y (7), Yb (8)) are five coordinate with distorted trigonal bipyramidal stereochemistry, the aryloxide ligands being equatorial and the thf ligands axial (Fig. 1(b)) with O(thf)-Ln-O(thf) angles 156.69(4)-157.5(3)°. Previous isotypic



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Fig. 1 Molecular structures of (a)  $[Eu(Odip)_3(thf)_3]$ ·2thf (3) and (b)  $[Nd(Odip)_3(thf)_2]$  (4). Hydrogen atoms omitted for clarity.

**Table 2** Selected bond lengths (Å) and angles (°) of  $[Ln(Odip) (thf)_n] \cdot xthf$ 

	Nd (2)	Eu( <b>3</b> )	Nd(4)	Y(7)	Yb( <b>8</b> )
Bond lengths	<i>n</i> = 3	<i>n</i> = 3	<i>n</i> = 2	<i>n</i> = 2	<i>n</i> = 2
Ln(1)-O(1)	2.189(3)	2.161(3)	2.170(2)	2.065	2.049(3)
Ln(1)-O(2)	2.183(3)	2.158(3)	2.171(2)	2.068	2.055(3)
Ln(1)-O(3)	2.189(3)	2.157(3)	2.167(2)	(7) 2.086	2.037(3)
Ln(1)-O(4)	2.550(3)	2.515(3)	2.469(3)	(7) 2.321 (8)	2.322(3)
Ln(1)–O(5) (thf)	2.545(3)	2.481(3)	2.457(3)	2.352	2.327(3)
Ln(1)-O(6) (thf)	2.572(3)	2.502(3)	_		—
Bond angles					
O(1)-Ln-O(2)	103.03	102.46	113.21	113.8	113.97
	(11)	(11)	(10)	(3)	(13)
O(2)-Ln- $O(3)$	101.76	102.45	133.87	133.7	133.74
	(12)	(11)	(10)	(3)	(13)
O(1)-Ln- $O(3)$	102.27	103.35	112.83	112.5	112.28
	(12)	(11)	(10)	(3)	(14)
O(4) (thf)–Ln–	77.04	81.15	157.06	157.5	156.69
O(5) (thf)	(12)	(11)	(10)	(3)	(14)
O(5) (thf)–Ln–	80.77	77.14			
O(6) (thf)	(12)	(12)			
O(6) (thf)–Ln–	77.30	77.75			
O(4) (thf)	(10)	(10)			
O(1)-Ln- $O(5)$	161.81	161.73	100.41	101.0	101.93
(thf)	(12)	(12)	(10)	(3)	(12)
O(3)-Ln-O(6)	Ì6Í.51	162.52			
(thf)	(11)	(11)			
O(2)-Ln-O(4)	162.84	161.65	85.73(9)	85.2	85.20
(thf)	(11)	(11)	. ,	(3)	(12)

structures are known for Ln = La,<sup>61</sup> Pr, Gd, Er, Lu,<sup>63</sup> Sm,<sup>62</sup> Dy.<sup>59</sup> Again, the bond lengths (Table 2) show few surprising features, but the decrease in Ln–O(thf) from **4** to **8** (0.13–0.15 Å) exceeds that (0.11 Å)<sup>76</sup> for the difference in ionic radii. For the light lanthanoids La–Eu, the isolation of either a six or five coordinate complex depends on crystallization conditions rather than ion size. Thus, both have been isolated for the largest rare earth, La, and for Nd, whereas so far only a six coordinate for Pr. Furthermore, both five (**4**) and six coordinate (**2a**) Nd complexes have been crystallized from toluene. The sum of the ligand steric coordination numbers<sup>77</sup> for the six coordinate complexes **2** and **3** is very high (8.73) inferring instability whereas, for the five coordinate **4**, **7**, **8**, it is 7.52, in a stable range.

Comparing the bond lengths of the six and five coordinate Nd complexes **2** and **4**, the change in Nd–O(thf) is much larger (0.10 Å) than expected (0.05 Å).<sup>76</sup> In **2**, all the thf ligands are *trans* to aryloxide groups, which exert a strong *trans* influence<sup>78</sup> (for other groups with a strong *trans* influence in Ln compounds<sup>79</sup>), lengthening the Nd–O(thf) bonds of **2**.

The divalent europium complex  $[Eu(Odip)(\mu-Odip)(thf)_2]_2$  (9) is an unsymmetrical aryloxide bridged dimer with one Odip and two *cis* thf terminal ligands on each five coordinate europium atom (Fig. 2). One terminal Odip ligand O(3) is *trans* to a bridging aryloxide O(2) and *cis* to the other O(1), whereas terminal ligand O(4) is *cisoid* to both bridging Odip ligands (Table 3), illustrating the asymmetry. The stereochemistry at Eu(2) is

Table 3 Selected bond lengths [Å] and angles (°) for complex 9

Eu(1)-O(1)2.440(3) $Eu(1)-O(2)$ 2.454(3) $Eu(1)-O(4)$ 2.285(3) $Eu(1)-O(5)$ 2.528(3) $Eu(2)-O(1)$ 2.416(3) $Eu(2)-O(2)$ 2.500(3) $Eu(2)-O(3)$ 2.271(3) $Eu(2)-O(7)$ 2.487(4) $Eu(2)-O(8)$ 2.605(4) $Eu(1)-Eu(2)$ 3.8924(14)	$\begin{array}{c} O(1)-Eu(1)-O(2)\\ O(1)-Eu(2)-O(3)\\ O(1)-Eu(1)-O(4)\\ O(1)-Eu(1)-O(5)\\ O(2)-Eu(1)-O(4)\\ O(1)-Eu(1)-O(6)\\ O(2)-Eu(1)-O(6)\\ O(2)-Eu(1)-O(6)\\ O(1)-Eu(2)-O(2)\\ O(1)-Eu(2)-O(7)\\ O(1)-Eu(2)-O(7)\\ O(1)-Eu(2)-O(3)\\ O(2)-Eu(2)-O(3)\\ O(2)-Eu(2)-O(7)\\ O(7)-Eu(2)-O(8)\\ Eu(1)-O(2)-Eu(2)\\ Eu(1)-O(1)-Eu(2)\\ \end{array}$	$\begin{array}{c} 75.01(10)\\ 111.52(11)\\ 110.53(11)\\ 96.00(11)\\ 121.54(12)\\ 159.23(11)\\ 132.59(11)\\ 88.52(12)\\ 74.59(10)\\ 90.33(13)\\ 163.28(11)\\ 166.44(10)\\ 100.39(12)\\ 84.65(15)\\ 103.56(11)\\ 106.55(11) \end{array}$

distorted square pyramidal with O(7) apical, whereas it is distorted trigonal bipyramidal at Eu(1) with O(1,6) axial. Despite the difference in ionic radii between  $Eu^{2+}$  and  $Ca^{2+}$ , <sup>76</sup> **9** is iso-typic with the corresponding calcium complex.<sup>80</sup> Although dimers bridged by two aryloxide ligands are common in Ln<sup>III</sup> chemistry,<sup>2,3</sup> they are less so for Ln<sup>II</sup> complexes<sup>2,3</sup> and especially Eu<sup>II</sup> derivatives. In [Eu<sub>2</sub>(Odip)<sub>4</sub>)(NCMe)<sub>5</sub>],<sup>68</sup> there is an unusual  $\mu$ - $\kappa^{1}$ : $\kappa^{1}$  bridging acetonitrile in addition to ligands with a connectivity analogous to 9. Europium(II) also forms unsymmetrical dimeric arrays with one terminal and three bridging aryloxides, as seen in *N*-methylimidazole,<sup>68</sup> dme,<sup>47</sup> and unsolvated<sup>81</sup> [Eu<sub>2</sub>  $(OAr)_4(solv)_n$ ] complexes. In the case of Yb<sup>II</sup>, the double OAr bridges are observed in three unsolvated derivatives<sup>81,82</sup> and a dme solvated silvloxide is known.<sup>49</sup> Considerable variation is seen in the Eu–O(thf) bond lengths of 9 from similar to those of **3** to 0.1 Å longer. The two longer bonds, Eu-O(6,8), are *trans* to bridging Odip ligands (Table 3) hence their trans influence is invoked.

In the case of the  $[Ln(Odip)_3(dme)_2]$  complexes, there is a change from seven coordination with two chelating dme ligands for Ln = La (10) to six coordination with one chelating and one unidentate dme for Ln = Dy(11), Y(12) and Yb(13) (Fig. 3(a),



Fig. 2 Molecular structure of  $[Eu(Odip)(\mu-Odip)(thf)_2]_2$  (9). Hydrogen atoms omitted for clarity.



Fig. 3 Molecular structures of (a)  $[La(Odip)_3(dme)_2]$  (10) and (b)  $[Dy(Odip)_3(dme)_2]$  (11). Hydrogen atoms omitted for clarity.

(b), Table 4), a lanthanoid ionic radius<sup>76</sup> effect. Although **10** is seven coordinate compared with six coordination for [Ln  $(Odip)_3(thf)_3$  (1-3), the steric crowding is comparable in both with the sum of the ligand steric coordination numbers<sup>77</sup> being 8.66 for 10 compared with 8.73 for 1-3. As 8.66 represents considerable crowding, a coordination number change occurs with smaller lanthanoids giving a value of *ca*. 7.7.<sup>77</sup> Compound **10** has irregular stereochemistry with the Odip ligands approaching a mer array, whereas 11-13 are fac octahedral (Table 4). The combination of a chelating and an unidentate dme has previously been observed in several nine coordinate lanthanoid 3,5-diphe-nylpyrazolates.<sup>20,65,66</sup> Unidentate dme though quite rare is wellestablished.<sup>64–67</sup> In [Ln(Ph<sub>2</sub>pz)<sub>3</sub>(dme)<sub>2</sub>] complexes, Ln–O ( $\kappa^1$ dme) is either the shortest Ln-O bond length or between the values for chelating dme, whereas Ln–O(4) ( $\kappa^{1}$ -dme) of 11–13 is clearly the longest Ln-O(dme) bond. This can be attributed to the *trans* influence of the O(2) aryloxide ligand, which is *trans* to O(4). In the series (10), (11), (12), (13), the decrease in Ln-O bond length corresponds well with ionic radius expectations.<sup>76</sup>

The complex  $[La(Odip)_3(dig)]$  (15) is six coordinate with distorted octahedral stereochemistry and *fac* dip ligands (Fig. 4). It

Table 4	Selected bond	lengths [Å	] and angles (°	) for complexes	10 - 13
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Bond lengths	La(10)	Dy(11)	Y(12)	Yb(13)
Ln(1)-O(1)	2.2635(17)	2.111(2)	2.106(2)	2.111(6)
Ln(1)-O(2)	2.2924(15)	2.116(2)	2.107(2)	2.063(6)
Ln(1) - O(3)	2.3052(16)	2.123(2)	2.098(2)	2.049(6)
Ln(1) - O(4)	2.656(2)	2.533(2)	2.523(2)	2.447(5)
Ln(1) - O(5)	2.638(2)	4.533 <sup>à</sup>	4.536 <sup><i>à</i></sup>	5.051 <sup>à</sup>
Ln(1) - O(6)	2.660(18)	2.467(2)	2.438(2)	2.401(6)
Ln(1) - O(7)	2.657(18)	2.464(2)	2.445(2)	2.386(6)
Bond angles				
O(1)-Ln(1)-O(2)	108.19(6)	99.01(9)	102.93(8)	104.4(2)
O(1)-Ln(1)-O(3)	105.07(6)	107.86(9)	107.53(8)	109.1(2)
O(2)-Ln(1)-O(3)	146.60(6)	102.63(9)	99.57(8)	101.5(2)
O(2)-Ln(1)-O(4)	75.26(6)	163.00(9)	162.60(8)	162.1(2)

<sup>a</sup> Calculated for bonding distances.



**Fig. 4** Molecular structure of ([La(Odip)<sub>3</sub>(dig)<sub>2</sub>]·0.25dme (**15**). Hydrogen atoms and dme of crystallization omitted for clarity. Selected bond lengths [Å] and angles (°) in compound **15**: La–O(1) 2.234(3), La–O(2) 2.242(3), La–O(3) 2.252(3), La–O(4) 2.627(3), La–O(5) 2.641(3), La–O(6) 2.712(3); O(1)–La–O(2) 114.11(13), O(1)–La–O(3) 98.87(13), O(2)–La–O(3) 86.57(13), O(3)–La–O(6) 174.39(11).

contrasts  $[La(Odpp)_3(dig)]^{83}$  (Odpp = 2,6-diphenylphenolate) which has a *mer* array. Nevertheless the bond lengths in the two complexes are comparable. La–O(6) is clearly the longer La–O(ether) bond length and this can be attributable to the *trans* influence of a *trans* Odip-ligand.

# Conclusions

A small amount of iodine can be used to activate Ln metals to enable direct reaction with 2,6-diisopropylphenol to occur in thf, dme, or dig–dme. Higher yields are obtained for the larger, more electropositive Ln metals under comparable conditions. However, use of a larger excess of Ln metal enables the small metal deficiency to be overcome. This procedure is a greener metal-based synthesis than RTP reactions using  $Hg(C_6F_5)_2$ , which give higher yields in shorter reaction times. A range of new structures have been obtained for  $[Ln(Odip)_3(thf)_n]$  (n = 2,3), [Eu(Odip)( $\mu$ -Odip)(thf)<sub>2</sub>]<sub>2</sub>, [Ln(Odip)<sub>3</sub>(dme)<sub>2</sub>], and [Ln (Odip)<sub>3</sub>(dig)] complexes with the thf and dme series showing a decrease of coordination number in response to the lanthanoid contraction. The iodine activation method has the potential to become a general metal-based synthesis at least for rare earth phenolates, especially since HOdip is a bulky phenol with unfavourable electron donor substituents. There are potential extensions to alkoxides, amides, amidinate, pyrazolates *etc.*, but considerable further development is needed and is in progress. Disappointingly, only a low yield of [Tb(ttfpz)<sub>3</sub>(thf)<sub>3</sub>] (ttfpz = 3-(2'-thieny1)-5-trifluoromethylpyrazolate) has recently been obtained from iodine activated Tb metal and Httfpz.<sup>84</sup>

# **Experimental**

General: All the lanthanoid metals and lanthanoid(II) and (III) products are highly air- and moisture-sensitive, hence operations were carried out under purified nitrogen using standard Schlenk line and glovebox techniques. 2,6-Diisopropylphenol (Aldrich) was degassed before use.  $Hg(C_6F_5)_2$  was prepared by the literature method.<sup>13</sup> All solvents were dried and deoxygenated by refluxing over and distillation from sodium-benzophenone. Elemental analyses (C, H) were performed by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand. Metal analyses were performed by EDTA titrations with Xylenol Orange as the indicator, following acid digestion (HCl or H<sub>2</sub>SO<sub>4</sub>-HNO<sub>3</sub>) and buffering with hexamine. Infrared spectra (4000-650 cm<sup>-1</sup>) were obtained using Nujol mulls between NaCl plates with a Perkin-Elmer 1600 FTIR spectrometer. Room temperature (30 °C) NMR spectra were recorded on a Bruker DPX 300 instrument with dry degassed perdeuterobenzene  $(C_6D_6)$  as the solvent, and resonances were referenced to residual hydrogen from the solvent.

#### **General procedure**

To a slurry of freshly prepared Ln filings (0.26 g-0.52 g, 3.0 mmol) (except for compound 9) in thf (30 mL) was added small amounts of iodine (0.013 g, 0.051 mmol) and the mixture was allowed to stir for an hour. 2,6-Diisopropylphenol (0.84 mL, 4.5 mmol) was added to the mixture and the flask was placed in an ultrasound bath for 2-5 days. After filtering, the volume of filtrate was reduced under vacuum to 5 mL and the flask was cooled at -6 °C. After 5 days the crystals were collected and generally examined by X-ray crystallography. The crystals were then washed with hexane to remove unreacted liquid ligand and left under vacuum for an hour and further characterisation was performed on the resulting bulk powder. Where the redox transmetallation/protolysis (RTP) method was employed Ln filings (2.0 mmol), Hg(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (1.60 g, 3.0 mmol), Hg (2 drops) and 2,6-diisopropylphenol (1.12 mL, 6.0 mmol) in thf (30 mL) were sonicated overnight. The resulting mixture was filtered to remove the precipitated Hg and evaporated under vacuum to 5 mL and the flask was cooled at -6 °C for 5 days. The crystals were washed with hexane to remove the adhering solution giving the pure powder which was dried under vacuum for further characterisation.

#### [La(Odip)<sub>3</sub>(thf)<sub>3</sub>] (1)

The resulting colourless crystals from the standard iodine activation method sonicating for 2 days, gave poor quality X-ray data only providing connectivity information. Bulk dried powder (0.85 g, 64%); dec. temp. 144–146 °C; found: La, 15.97%.  $C_{48}H_{75}O_6La$  (887.01 g mol<sup>-1</sup>) requires: La 15.66%; IR (Nujol, cm<sup>-1</sup>): 1587 m, 1428 s, 1357 m, 1327 s, 1264 s, 1206 s, 1141 w, 1108 m, 1094 m, 1056 m, 1042 s, 1022 s, 953 w, 934 m, 917 w, 886 s, 854 s, 803 m, 797 w, 755 s, 722 w, 685 s, 616 w, 570s; <sup>1</sup>H NMR of dried sample (300 MHz,  $C_6D_6$ ): 7.18 (d, 6H, *m*-H(OAr)), 6.93 (m, 3 H, *p*-H(OAr)), 3.69 (m, 12H, thf), 3.47 (m, 6H, *CHM*e<sub>2</sub>), 1.34 (d, 36H, CH*M*e<sub>2</sub>), 1.18 (m, 12H, thf). (<sup>1</sup>H NMR chemical shifts are similar to those of [La(Odip)<sub>3</sub>(thf)<sub>2</sub>]<sup>62</sup>). Unit cell dimensions isotypic with [Ce(Odip)<sub>3</sub>(thf)<sub>3</sub>], <sup>59</sup> monoclinic, *a* = 11.4044(15) Å, *b* = 35.747(5), *c* = 13.3608(18),Å;  $\beta$  = 97.540(5)°, volume = 5399.8(12) Å<sup>3</sup>.

# [Nd(Odip)<sub>3</sub>(thf)<sub>3</sub>]·2thf (2)

(See crystal data discussion). The standard iodine activation method and sonicating for 4 days gave blue crystals suitable for X-ray crystallography. Bulk dried powder (0.69 g, 52%); dec. temp. 140-142 °C; Found: Nd, 16.31%. C<sub>56</sub>H<sub>91</sub>O<sub>8</sub>Nd  $(1036.56 \text{ g mol}^{-1})$  requires: Nd, 14.48%; C<sub>48</sub>H<sub>75</sub>O<sub>6</sub>Nd (loss of 2 lattice thf, 892.34 g mol<sup>-1</sup>) requires 16.16%; IR (Nujol, cm<sup>-1</sup>): 1587 m, 1428 s, 1356 m, 1328 m, 1265 s, 1204 s, 1109 m, 1096 m, 1053 w, 1042 m, 1020 s, 934 w, 916 w, 885 m, 857 s, 803 s, 796 w, 753 m, 722 w, 687 m, 616 w, 561 m, 547 w; <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ):  $\delta$  17.45 (br, 6H, CHMe<sub>2</sub>), 14.80 (s, 6H, m-H(OAr)), 11.60 (s, 3H, p-H(OAr)), 3.74 (br s, 36H, CHMe<sub>2</sub>), -6.29 (br s, 12 thf), -11.43 (br s, 12 thf). After a similar preparation, the crude product (yield 48%) was not washed with hexane, but was crystallized from toluene, single crystals of [Nd(Odip)<sub>3</sub>(thf)<sub>3</sub>]·PhMe (2b) being deposited on cooling to -4 °C.

# [Nd(Odip)<sub>3</sub>(thf)<sub>2</sub>] (4)

[Nd(Odip<sub>3</sub>)<sub>3</sub>(thf)<sub>3</sub>]·2thf (0.20 g, 0.20 mmol) was placed under vacuum for 3 h and 50 mL dme was added to the compound and stirred for 3 days at room temperature. After evaporating to 5 mL and cooling at -6 °C for 5 days, blue crystals suitable for X-ray crystallography were collected. Bulk dried powder (0.11 g, 60%); <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  17.80 (br, 6H, *CHM*e<sub>2</sub>), 14.51 (s, 6H, *m*-H(OAr)), 11.70 (s, 3H, *p*-H(OAr)), 3.80 (br s, 36H, CH*M*e<sub>2</sub>), -15.36 (br s, 8H, thf), -27.57 (br s, 8H, thf) (concordant with previous literature).<sup>63</sup> Similarly crystallisation of **2** from hot toluene gave compound **4** (IR and <sup>1</sup>H NMR identification).

## [Eu(Odip)<sub>3</sub>(thf)<sub>3</sub>]·2thf (3)

The standard RTP method gave orange crystals suitable for Xray crystallography. Bulk dried powder (0.85 g, 70%); dec. temp. 146–148 °C; Found: Eu, 16.98%.  $C_{56}H_{91}O_8Eu$  (1044.28 g mol<sup>-1</sup>) requires: Eu, 14.55%;  $C_{48}H_{75}O_6Eu$  (loss of 2 lattice thf, 900.07 g mol<sup>-1</sup>) requires 16.88%; IR (Nujol, cm<sup>-1</sup>): 1586 m, 1428 s, 1341 m, 1330 m, 1262 s, 1207 m, 1155w, 1094 m, 1041 m, 1018 s, 934 w, 918 w, 886 m, 860 s, 800 s, 752 m, 722 s, 688 w, 660 w, 616 w, 563 w; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 48.88 (br s, 12H, thf), 23.24 (br s, 12H, thf), 2.88 (t, 3H, *p*-H(OAr)), -2.54 (d, 6H, *m*-H(OAr)), -3.77 (br, 36H, CHMe<sub>2</sub>), -20.44 (br m, 6H, CHMe<sub>2</sub>). <sup>1</sup>H NMR of an hydrolysed sample (400 MHz, C<sub>6</sub>D<sub>6</sub>, CF<sub>3</sub>CO<sub>2</sub>H 1 drop): 7.02 (d, 6H, *m*-H(OAr)), 6.85 (t, 3H, *p*-H(OAr)), 3.50 (t, 12H, thf), 2.09 (m, 6H, CHMe<sub>2</sub>), 1.45 (t, 12H, thf), 1.22 (d, 36H, CHMe<sub>2</sub>). Both <sup>1</sup>H NMR spectra indicated loss of thf of crystallization.

# [Sm(Odip)<sub>3</sub>(thf)<sub>2</sub>] (5)

The standard iodine activation method and sonicating for 4 days gave very small pale yellow crystals suitable for X-ray crystallography. The unit cell of a complete Synchrotron structure determination (monoclinic, space group  $P2_1$ , a = 9.772(2), b = 19.313(3), c = 12.08(2) Å,  $\beta = 109.566(3)^\circ$ ,  $\alpha = \gamma = 90^\circ$ , V = 2148.17 Å<sup>3</sup>) is in reasonable agreement with the literature.<sup>62</sup> Bulk dried powder (0.309 g, 25%); dec. temp.: 144–148 °C; IR (Nujol, cm<sup>-1</sup>): 1586 m, 1430 s, 1357 w, 1329 s, 1262 s, 1208 m, 1157 w, 1095 m, 1041 m, 1019 s, 933 w, 886 m, 860 s, 801 m, 754 m, 721 w, 688 w. (concordant with previous literature.)<sup>62</sup> <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 7.80 (d, 6H, *m*-H(OAr)), 7.56 (t, 3H, *p*-H(OAr)), 5.20 (m, 6H, *CHM*e<sub>2</sub>), 1.69 (br s, 36H, CH*M*e<sub>2</sub>), -0.01(br s, 8H, thf), -0.84 (br s, 8H, thf). The standard RTP method gave yellow powder (0.89 g, 72%); (IR and <sup>1</sup>H NMR identification).

# [Dy(Odip)<sub>3</sub>(thf)<sub>2</sub>] (6)

The standard iodine activation method and sonicating for 4 days gave small pale yellow crystals suitable for X-ray crystallography and the unit cell (monoclinic, a = 9.29(8), b = 18.86(16), c =12.16(12) Å,  $\beta = 111.4(2)^{\circ}$ , V = 1984(8) Å<sup>3</sup>) is in reasonable agreement with the literature.<sup>59</sup> Bulk dried powder (0.327 g, 26%); dec. temp.: 140-145 °C; found: Dy, 18.47%. Calc for  $C_{44}H_{67}O_5Dy$  (838.5 g mol<sup>-1</sup>): Dy 19.38%; IR (Nujol, cm<sup>-1</sup>): 1586 m, 1434 s, 1357 m, 1331 s, 1271 s, 1210 s, 1170 w, 1095 w, 1042 m, 1017 m, 888 s, 863 s, 753 s, 691 m, 564 m in agreement with that expected.<sup>59</sup> The <sup>1</sup>H NMR spectrum could not be confidently assigned due to paramagnetic broadening. <sup>1</sup>H NMR of an hydrolysed sample (400 MHz, C<sub>6</sub>D<sub>6</sub>, CF<sub>3</sub>CO<sub>2</sub>H 1drop): 7.01 (d, 6H, m-H(OAr)), 6.84 (t, 3H, p-H(OAr)), 3.20 (t, 8H, thf), 2.89 (m, 6H, CHMe<sub>2</sub>), 1.30 (t, 8H, thf), 1.08 (d, 36H, CHMe<sub>2</sub>). The standard RTP method gave yellow powder (0.74 g, 59%); (IR and <sup>1</sup>H NMR of an hydrolysed sample identification).

# [Y(Odip)<sub>3</sub>(thf)<sub>2</sub>] (7)

The standard iodine activation method and sonicating for 5 days gave colourless crystals suitable for X-ray crystallography. Bulk dried powder (0.29 g, 25%); dec. temp. 140–143 °C; found: Y, 11.33%.  $C_{44}H_{67}O_5Y$  (764.89 g mol<sup>-1</sup>) requires: Y 11.62%; IR (Nujol, cm<sup>-1</sup>): 1587 m, 1428 s, 1407 s, 1357 m, 1331 s, 1210 m, 1206 s, 1172 w, 1157 w, 1141 w, 1108 m, 1095 m, 1042 s, 1016 s, 953 w, 934 m, 917 w, 887 s, 863 s, 803 m, 797 w, 755 s, 722 w, 691 s, 616 w, 570m; <sup>1</sup>H NMR (300 MHz,

C<sub>6</sub>D<sub>6</sub>): 7.20 (d, 6H, *m*-H(OAr)), 6.92 (3H, *p*-H(OAr)), 3.79 (m, 8H, thf), 3.51 (m, 6H, CHMe<sub>2</sub>), 1.33 (d, 36H, CHMe<sub>2</sub>), 1.10 (m, 8H, thf). The reaction was repeated using a greater excess of Y powder (1.30 g, 15 mmol), iodine (0.060 g, 0.24 mmol) and 2,6-diisopropylphenol (0.84 mL, 4.5 mmol) and gave colourless crystals. Bulk dried powder (0.86 g, 75%); (IR and <sup>1</sup>H NMR identification). The standard RTP method gave colourless powder (0.676 g, 59%); (IR and <sup>1</sup>H NMR identification).

**[Yb(Odip)<sub>3</sub>(thf)<sub>2</sub>] (8).** The standard iodine activation method and sonicating for 5 days gave yellow crystals suitable for X-ray crystallography. Bulk dried powder (0.33 g, 26%); dec. temp. 156–162 °C; found: Yb, 20.31%. Cale for  $C_{44}H_{67}O_5Yb$ (849.04 g mol<sup>-1</sup>): Yb 20.38%; IR (Nujol, cm<sup>-1</sup>): 1587 m, 1433 s, 1357 m, 1332 s, 1274 s, 1209 s, 1172 w, 1157 w, 1109 w, 1095 w, 1041 m, 1016 m, 934 w, 888 s, 863 s, 804 m, 796 w, 756 s, 752 s, 692 m, 572 m; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 152.24 (br m, 8H, thf), 76.23 (br m, 8H, thf), 9.77 (s, 3H, *m*-H(OAr)), -12.65 (s, 6H, *m*-H(OAr)), -14.87 (br s, 36H, CH*Me*<sub>2</sub>), -15.78 (br m, 6H, *CH*Me<sub>2</sub>) (concordant with previous literature <sup>63</sup>). The standard RTP method gave yellow powder (0.86 g, 68%); (IR and <sup>1</sup>H NMR identification).

# [Eu(Odip)(µ-Odip)(thf)<sub>2</sub>]<sub>2</sub> (9)

The standard synthesis from Eu powder (0.32 g, 2.1 mmol) in thf (30 mL), iodine (0.013 g, 0.051 mmol) and addition of 2,6diisopropylphenol (0.065 mL, 3.5 mmol) gave considerable number of orange crystals suitable for X-ray crystallography. Bulk dried powder (0.91 g, 62%); dec. temp. 144 °C; found (freshly isolated): Eu, 23.04%. C<sub>64</sub>H<sub>100</sub>O<sub>8</sub>Eu<sub>2</sub> (1301.40 g mol<sup>-1</sup>) requires Eu, 23.35%. Microanalysis (after transportation) found: C, 56.35%; H, 7.01%. C48.8H69.6O4.2Eu2 (loss of 3.8 thf, 1027.40 g mol<sup>-1</sup>) requires: C, 57.04%; H, 6.82%; IR (Nujol, cm<sup>-1</sup>): 1587 m, 1428 s, 1407 s, 1357 m, 1331 s, 1210 m, 1206 s, 1199 s, 1154 w, 1139 w, 1105 m, 1037 s, 1016 s, 953 w, 934 m, 917 w, 883 s, 852 s, 836 s, 801 m, 797 w, 745 s, 722 w, 680 m, 616 w, 570 m; <sup>1</sup>H NMR spectrum could not be assigned due to paramagnetic broadening. <sup>1</sup>H NMR of a stored hydrolysed sample (300 MHz, CD<sub>3</sub>CN, CF<sub>3</sub>CO<sub>2</sub>H 1drop): 7.02 (d, 8H, m-H(OAr)), 6.82 (t, 4H, p-H(OAr)), 3.60 (t, 0.8H, thf), 3.22 (m, 8H, CHMe<sub>2</sub>), 1.78 (t, 0.8H, thf), 1.18 (d, 48H, CHMe<sub>2</sub>), indicative of 0.2 thf per  $[Eu_2(Odip)_4]$ .

### [La(Odip)<sub>3</sub>(dme)<sub>2</sub>] (10)

La powder (0.42 g, 3.0 mmol), iodine (0.013 g, 0.051 mmol) and 2,6-diisopropylphenol (0.84 mL, 4.5 mmol) in dme (30 mL) ultrasonicated for 2 days gave colourless crystals suitable for X-ray crystallography. Bulk dried powder (0.86 g, 67%); dec. temp. 104–106 °C; found: La, 16.52%.  $C_{44}H_{71}O_7La$  (850.94 g mol<sup>-1</sup>) requires: La, 16.32%; IR (Nujol, cm<sup>-1</sup>): 1586 m, 1431 s, 1358 m, 1326 s, 1272 s, 1259 s, 1200 m, 1156 w, 1141 m, 1111 m, 1088 m, 1066 s, 1045 m, 983 m, 933 w, 881 m, 846 s, 800 m, 762 m, 746 s, 687 m, 570 w, 550m; <sup>1</sup>H NMR (300 MHz,  $C_6D_6$ ): 7.18 (d, 6H, *m*-H(OAr)), 6.91(t, 3H, *p*-H(OAr)), 3.53 (m, 6H, *CH*Me<sub>2</sub>), 3.11 (br, 8H, dme-CH<sub>2</sub>), 3.06 (br, 12H, dme-Me), 1.31 (br, 36H, CHMe<sub>2</sub>).

(11).  $[Dy(Odip)_3(thf)_2]$ [Dv(Odip)<sub>3</sub>(dme)<sub>2</sub>] (0.50)g, 0.59 mmol) was placed under vacuum for 3 h and 50 mL. Dme was added to the compound and yielded colourless crystals suitable for X-ray crystallography after 5 days at -6 °C. Bulk dried powder (0.38 g, 73%); dec. temp. 160-164 °C; Found: Dy, 18.06%. C<sub>44</sub>H<sub>71</sub>O<sub>7</sub>Dy (874.53g mol<sup>-1</sup>) requires: Dy, 18.58%; IR (Nujol, cm<sup>-1</sup>): 1586 m, 1431 m, 1357 m, 1260 s, 1210 m, 1097 s, 1018 s, 935 w, 888 m, 862 s, 803 m, 799 s, 691 m, 567 w, 550 m; <sup>1</sup>H NMR spectrum could not be assigned due to paramagnetic broadening. <sup>1</sup>H NMR of an hydrolysed sample (300 MHz, C<sub>6</sub>D<sub>6</sub>, CF<sub>3</sub>CO<sub>2</sub>H 1 drop): 7.04 (d, 6H, m-H(OAr)), 6.88 (t, 3H, p-H(OAr)), 3.62 (br, 8 H, dme-CH<sub>2</sub>), 3.28 (br, 12 H, dme-Me), 3.08 (m, 6H, CHMe<sub>2</sub>), 1.24 (d, 36H, CHMe<sub>2</sub>).

# [Y(Odip)<sub>3</sub>(dme)<sub>2</sub>] (12)

[Y(Odip)<sub>3</sub>(thf)<sub>2</sub>] (0.50 g, 0.65 mmol) was similarly treated and yielded colourless crystals suitable for X-ray crystallography. Bulk dried powder (0.36 g, 68%); dec. temp. 158–160 °C.; found: C, 65.85%; H, 8.77%; Y, 11.32%.  $C_{44}H_{71}O_7Y$  (800.93 g mol<sup>-1</sup>) requires: C, 65.98%; H, 8.93%; Y, 11.10%; IR (Nujol, cm<sup>-1</sup>): 1588 m, 1431 s, 1357 m, 1338 s, 1272 s, 1262 s, 1210 m, 1189w, 1110 m, 1084 m, 1057 s, 1043 m, 963 w, 888 m, 859 s, 803 m,755 s, 694 m, 570 w, 550 m; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 7.17 (d, 6H, *m*-H(OAr)), 6.91(t, 3H, *p*-H(OAr)), 3.51 (m, 6H, *CHM*e<sub>2</sub>), 3.18 (br, 20H, dme), 1.29 (d, 36H, CH*M*e<sub>2</sub>). <sup>1</sup>H NMR of an hydrolysed sample (300 MHz, C<sub>6</sub>D<sub>6</sub>, CF<sub>3</sub>CO<sub>2</sub>H 1 drop): 7.17 (d, 6H, *m*-H(OAr)), 6.91 (t, 3H, *p*-H(OAr)), 3.96 (br, 8 H, dme–CH<sub>2</sub>), 3.44 (br, 12 H, dme–Me), 3.24 (m, 6H *CHM*e<sub>2</sub>), 1.23 (d, 36H, CH*M*e<sub>2</sub>).

# [Yb(Odip)<sub>3</sub>(dme)<sub>2</sub>] (13)

Yb powder (0.52 g, 3.0 mmol), iodine (0.013 g, 0.051 mmol) and 2,6-diisopropylphenol (0.84 mL, 4.5 mmol) in dme (30 mL) after sonication for 5 days gave yellow crystals of both [Yb (Odip)<sub>3</sub>(dme)<sub>2</sub>] (13) and known [Yb(Odip)<sub>2</sub>(µ-Ome)(dme)]<sub>2</sub>  $(14)^{69}$  identified by hand picking and comparison of the unit cells (13: crystal system: monoclinic, a = 22.10(3), b = 18.98(3), c = 23.42(3) Å,  $\beta = 115(3)^{\circ}$ , V = 8900 Å<sup>3</sup>, in agreement with values from a full structure determination on the product from the 2nd preparation 14: crystal system: monoclinic, a = 11.235(9), b = 12.967(10), c = 20.168(15) Å,  $\beta = 104.462(12)^{\circ}$ , V =2845 Å<sup>3</sup>, concordant with repeated values<sup>69</sup>). The percentage of 14 is very low as methanol was not observed in the <sup>1</sup>H NMR spectrum of an hydrolysed sample. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>CN, CF<sub>3</sub>CO<sub>2</sub>H 1 drop): 7.00 (d, 6H, m-H(OAr)), 6.81 (t, 3H, p-H(OAr)), 3.43 (s br, 8H, dme-CH<sub>2</sub>), 3.25 (s br, 12H, dme-Me), 2.45 (m, 6H, CHMe2), 1.14 (d, 36H, CHMe2). Bulk dried powder (0.40 g, ca. 30%); dec. temp.: 150-158 °C. 2<sup>nd</sup> preparation:  $[Yb(Odip_3)_3(thf)_2]$  (7) (0.50 g, 0.58 mmol) was placed under vacuum for 3 h and dme 50 mL was added. The solution yielded yellow crystals suitable for X-ray crystallography after 5 days at -6 °C. (0.36 g, 69%); dec. temp.: 150-152 °C; found: C, 58.61%; H, 8.00%; Yb, 19.10%. C<sub>44</sub>H<sub>71</sub>O<sub>7</sub>Yb (885.50 g mol<sup>-1</sup>) requires: C, 59.68%; H, 8.08%; Yb, 19.54%; IR (Nujol, cm<sup>-1</sup>): 1588 m, 1431 s, 1331 s, 1267 s, 1210 m, 1171 w, 1096 s, 1042 s, 1018 w, 936 w, 888 m, 863 s, 803 m, 755 s, 694 m,

654 w. The <sup>1</sup>H NMR spectrum could not be assigned due to paramagnetic broadening.

#### [La(Odip)<sub>3</sub>(dig)]·0.25dme (15)

La powder (0.42 g, 3.0 mmol) in a mixture of diglyme and dme (30 mL), iodine (0.013 g, 0.051 mmol) and 2,6-diisopropylphenol (0.84 mL, 4.5 mmol) with a sonication for 2 days gave colourless crystals suitable for X-ray crystallography after 5 days at Bulk dried powder (0.85 g, 68%); dec. -6 °C. temp. 176-178 °C; Found: C, 62.75%; H, 8.33%; La, 16.52%. C43H67.5O6.5La (827.39 g mol<sup>-1</sup>) requires: C, 62.41%; H, 8.22%; La, 16.78%; IR (Nujol, cm<sup>-1</sup>): 1585 m, 1533 m, 1338 m, 1326 s, 1261 s, 1201 m, 1113 s, 1078 m, 1043 m, 1006 m, 937 m, 886 m, 851 s, 804 m, 747 s, 722 w, 687 w; <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): 7.17 (d, 6H, m-H(OAr)), 6.89 (t, 3H, p-H(OAr)), 3.57 (d, 6H, CHMe<sub>2</sub>), 3.33 (s, 1H, dme-CH<sub>2</sub>), 3.13 (s br, 1.5H, dme-Me), 3.11 (s br, 6H, dig-Me), 2.89 (t, 8H, dig-CH<sub>2</sub>), 1.31 (d, 36H, CHMe<sub>2</sub>). The standard RTP method in a mixture of diglyme and dme (30 mL), gave colourless powder (1.02 g, 61%); (IR and <sup>1</sup>H NMR identification).

#### Experiments to establish the need for and the role of I<sub>2</sub>

(i) Yb powder (0.52 g, 3.0 mmol), iodine (0.507 g, 2.0 mmol) and 2,6- diisopropylphenol (0.84 mL, 4.5 mmol) in thf (30 mL) and sonication for 5 days gave a yellow solution. After filtering, the volume of filtrate was reduced under vacuum to 5 mL and the flask was cooled at -6 °C. After 5 days, crystals of [YbI<sub>2</sub>(thf)<sub>4</sub>] were collected and were identified by the crystal structure.

(ii) 2,6-Diisopropylphenol (0.84 mL, 4.5 mmol) was added to La powder (0.041 g, 3.0 mmol) in thf (30 mL) and placed in an ultrasound bath for 3 days. No colour change was observed in the solution. Filtering and evaporating the solvent under vacuum yielded only 2,6-diisopropylphenol. The same process was repeated with Yb (0.521 g, 3.0 mmol) instead of La and the result was similar.

(iii) 2,6-Diisopropylphenol (0.84 mL, 4.5 mmol) was added to Nd powder (0.43 g, 3.0 mmol) in thf (30 mL) and placed in an ultrasound bath for 3 days. No colour change was observed in the solution. However, after addition of iodine (0.013 g, 0.051 mmol) the colourless reaction mixture developed a bright blue colour indicative of Nd<sup>III</sup> after 2 days of ultrasound treatment.

(iv) Evidence for the formation of H<sub>2</sub>: La powder (0.034 g, 0.025 mmol) in d<sub>8</sub>-thf (2 mL), iodine (0.001 g, 0.004 mmol) and 2,6-diisopropylphenol (0.007 mL, 0.037 mmol) were added to an NMR tube and left it in the sonic bath for 2 days. After the precipitate had settled, a clear solution was obtained.<sup>1</sup>H NMR (300 MHz, d<sub>8</sub>-thf) displays a peak at 4.55 ppm which is indicative of dihydrogen.<sup>85</sup>

(v) To a slurry of La powder (0.66 g, 4.75 mmol) in thf (30 mL) was added iodine (0.086 g, 0.338 mmol) and the mixture was allowed to stir for an hour. The total solution was transferred to a second Schlenk flask already charged with La powder (0.66 g, 4.75 mmol). The metal in the first Schlenk flask was washed with thf which was transferred to the second

Schlenk flask. 2,6-Diisopropylphenol (0.84 mL, 4.5 mmol) was added to each Schlenk flask and they were placed in an ultrasound bath for 2 days. In each case, the clear filtrate obtained after filtering was evaporated under vacuum. After washing the residue with hexane, the <sup>1</sup>H NMR of the product in both flasks was the same and concordant with **1** (1st Schlenk flask: 0.45 g, 33%; 2nd Schlenk flask 0.72 g, 54%).

(vi) To a slurry of La powder (0.66 g, 4.75 mmol) in thf (30 mL) was added iodine (0.086 g, 0.336 mmol) and the mixture was allowed to stir for an hour and then filtered into a second Schlenk flask. The metal in the first Schlenk flask was washed with thf then filtered and the thf washings were transferred to the second Schlenk flask. The contents of the first Schlenk flask were dried under vacuum and digested by HCl (2.0 M) and metal residue was dissolved. The solution in the second Schlenk flask was evaporated to dryness under vacuum and the residue digested by HCl (2.0 M). Analysis for metal and iodine by iodometry<sup>86</sup> was performed on both digests and the percentages of initial La and iodine were determined for both solutions (metal residue: La: 88%, I<sub>2</sub> 5%, Decanted solution: La: 5%, I<sub>2</sub> 94%). The composition of the residue from the second Schlenk flask was I : La = 3 : 1.

#### X-Ray structure determinations

Intensity data were collected using a Bruker X8 Apex II CCD (2, 7, 9 and 13), an Enraf-Nonius KAPPA CCD (8) or Oxford Gemini Ultra (3 and 10) at 123 or 173 K with Mo-Ka radiation  $(\lambda = 0.71073 \text{ Å})$ . Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fiber which was mounted on the diffractometer and immediately placed under a cold N<sub>2</sub> vapor stream. Using phi and omega scans, Nt (total) reflections were measured, which were reduced to N unique reflections, with  $I > 2\sigma(I)$  being considered observed. Data were initially processed and corrected for absorption using the Bruker Apex II program suite<sup>87</sup> or the programs DENZO<sup>88</sup> and SORTAV<sup>89</sup> For compounds 4, 11, 12 and 15, the crystals on which data were collected were microcrystalline and insufficient in size to collect data on a conventional CCD X-ray diffractometer. We therefore collected data on samples that were too small to accurately determine the size of the crystals using a Synchrotron source at the Australian Synchrotron, and therefore do not provide sizes of these samples. For these compounds, data were collected using the MX1 beamline at the Australian Synchrotron, Victoria, Australia. A very small crystal was mounted on a cryoloop and then flash cooled to 100 K. The crystal dimensions could not be measured due to the small size. Data were collected using a single wavelength ( $\lambda = 0.712$  Å). The MX1 end station comprised a phi goniostat and ADSC Quantum 210r  $210 \times 210$  mm large area detector. Due to hardware constraints (fixed detector angle), the maximum available data resolution on MX1 was limited to approximately 0.80 Å at the detector edges. For synchrotron structures, data were collected using the Blue Ice<sup>90</sup> GUI and processed with the XDS<sup>91</sup> software package. Structures were solved using direct methods that yielded the heavy atoms, along with a number of the lighter atoms, and subsequent Fourier synthesis yielded the remaining light-atom positions. Final least squares refinement cycles on  $F^2$ , were performed with anisotropic thermal parameters for non-hydrogen atoms with hydrogen atoms constrained in calculated positions with a riding model. Structure solutions and refinements were performed using the programs SHELXS- 97<sup>92a</sup> and SHELXL-97<sup>92b</sup> through the graphical interface X-Seed,<sup>93</sup> which was also used to generate the figures. All CIF files were checked at http://www.iucr.org/.

CCDC 845097–845108 and 853842–853843 contain the supplementary crystallographic data for this paper. These data (excluding structure factors) can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc. cam.ac.uk/data\_request/cif.

#### General variata

Some compounds exhibit a relatively large ratio of ADP max/ min for carbon atoms. Ellipsoids of  $Pr^i$  (Me) C atoms are relatively large and elongated suggesting thermal motion and disorder in contrast to the rigid C atoms of the aromatic rings (compounds 4, 7, 8, 9, 12 and 15). To convey the true nature of the ellipsoids of these atoms they have been refined anisotropically with no restraints. In extreme cases, disorder has been modelled as best as possible. Specific variata for compounds are mentioned below.

# Crystal data for [Nd(Odip)<sub>3</sub>(thf)<sub>3</sub>]·2thf (2)

C<sub>56</sub>H<sub>91</sub>NdO<sub>8</sub>, M = 1036.53, blue block,  $0.14 \times 0.12 \times 0.04 \text{ mm}^3$ , orthorhombic, space group *Pbcn* (No. 60), a = 25.234(2), b = 22.3796(15), c = 20.0280(17) Å, V = 11310.4 (15) Å<sup>3</sup>, Z = 8,  $D_c = 1.217 \text{ g cm}^{-3}$ ,  $F_{000} = 4408$ , T = 123(2)K,  $2\theta_{\text{max}} = 55.0^\circ$ , 171 113 reflections collected, 12 783 unique ( $R_{\text{int}} = 0.0714$ ). Final *GooF* = 1.114, R1 = 0.0568, wR2 = 0.1640, R indices based on 8737 reflections with  $I > 2\sigma(I)$ , 498 parameters, 0 restraints,  $\mu = 0.966 \text{ mm}^{-1}$ . *Variata*: it was necessary to model electron density associated with disordered solvent molecules in the lattice voids using the PLATON program SQUEEZE.<sup>94</sup> A calculated electron count of 135.9 e<sup>-/</sup>asymmetric unit indicates the presence of 3.4 thf molecules per molecule of the complex. However, this compound is isotypic with compound **3** with exactly two thf molecules in the lattice and they were modelled.

#### Crystal data for [Nd(Odip)<sub>3</sub>(thf)<sub>3</sub>]·C<sub>7</sub>H<sub>8</sub> (2b)

C<sub>55</sub>H<sub>83</sub>NdO<sub>6</sub>, *M* = 984.45, 0.15 × 0.10 × 0.05 mm<sup>3</sup>, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14), *a* = 10.9370(4), *b* = 35.5722(15), *c* = 13.3069(6) Å, *β* = 95.671(2)°, *V* = 5151.8(4) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.269 g cm<sup>-3</sup>, *F*<sub>000</sub> = 2084, Bruker X8 Apex II CCD, Mo-Kα radiation,  $\lambda$  = 0.71073 Å, *T* = 123(1)K, 2*θ*<sub>max</sub> = 53.2°, 31755 reflections collected, 10 651 unique (*R*<sub>int</sub> = 0.0753). Final *GooF* = 1.037, *R*1 = 0.0542, *wR*2 = 0.0819, *R* indices based on 7359 reflections with *I* > 2*σ*(*I*) (refinement on *F*<sup>2</sup>), 572 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu$  = 1.054 mm<sup>-1</sup>. *Variata*: Carbon atom 39 has slightly higher thermal motion than its neighbours. This may be expected for a carbon on a THF molecule.

# Crystal data for [Nd(Odip)<sub>3</sub>(thf)<sub>2</sub>] (4)

 $C_{44}H_{67}NdO_5$ , M = 820.22, blue block, monoclinic, space group  $P2_1$  (No. 4), a = 9.790(2), b = 19.391(2), c = 12.139(3) Å,  $\beta = 110.018(11)^\circ$ , V = 2165.2(7) Å<sup>3</sup>, Z = 2,  $D_c = 1.258$  g cm<sup>-3</sup>,  $F_{000} = 862$ ,  $\lambda = 0.712$  Å, T = 100(2)K,  $2\theta_{max} = 54.2^\circ$ , 15584 reflections collected, 8416 unique ( $R_{int} = 0.0367$ ). Final *GooF* = 1.081, R1 = 0.0289, wR2 = 0.0718, R indices based on 8121 reflections with  $I > 2\sigma(I)$ , 468 parameters, 7 restraints,  $\mu = 1.239$  mm<sup>-1</sup>. Absolute structure parameter =  $0.051(11)^{95}$  *Variata*: ISOR restraint was applied on C(38). One thf was modelled as disordered with C atom position C(38) (refined occupancy 0.74 : 0.26).

# Crystal data for [Eu(Odip)<sub>3</sub>(thf)<sub>3</sub>]·2thf (3)

 $C_{56}H_{91}EuO_8$ , M = 1044.25, orange block,  $0.25 \times 0.25 \times 0.25$  mm<sup>3</sup>, orthorhombic, space group *Pbcn* (No. 60), a = 25.0773(4), b = 22.1250(3), c = 19.9043(3) Å, V = 11043.6(3) Å<sup>3</sup>, Z = 8,  $D_c = 1.256$  g cm<sup>-3</sup>,  $F_{000} = 4432$ , T = 123(2)K,  $2\theta_{max} = 55.0^{\circ}$ , 59568 reflections collected, 12690 unique ( $R_{int} = 0.0308$ ). Final *GooF* = 1.146, R1 = 0.0479, wR2 = 0.1138, R indices based on 9806 reflections with  $I > 2\sigma(I)$ , 566 parameters, 15 restraints.  $\mu = 1.185$  mm<sup>-1</sup>. *Variata*: Two thf molecules in the lattice were modelled as disordered with C atom position (C(71), C(77) and C(78)) and O atom O(7). (Refined occupancy 0.55 : 0.45).

### Crystal data for [Y(Odip)<sub>3</sub>(thf)<sub>2</sub>] (7)

 $C_{44}H_{67}O_5Y$ , M = 764.89, colourless block, 0.12  $\times$  0.10  $\times$ 0.03 mm<sup>3</sup>, monoclinic, space group  $P2_1$  (No. 4), a = 9.6897(14), b = 19.343(3), c = 12.182(2) Å,  $\beta = 109.559(9)^{\circ}, V = 2151.4(6)$ Å<sup>3</sup>, Z = 2,  $D_c = 1.181$  g cm<sup>-3</sup>,  $F_{000} = 820$ , T = 123(2)K,  $2\theta_{max} = 123(2)$ K, Z = 123(2)K, Z50.0°, 11351 reflections collected, 6783 unique ( $R_{int} = 0.1898$ ). Final GooF = 0.777, R1 = 0.0775, wR2 = 0.1644, R indices based on 3233 reflections with  $I > 2\sigma(I)$ , 473 parameters, 55 restraints. Lp and absorption corrections applied,  $\mu =$  $1.395 \text{ mm}^{-1}$ . Absolute structure parameter = 0.012(13).<sup>95</sup> Variata: This is isostructural with compound 4 and 8. One thf (O(4)) was modelled as disordered with C atom position C(37) and C(38) (refined occupancy 45:55); SIMU restraints were applied on this molecule on C(29), C(37A), C(38A), C(39) and C(40). ISOR restraints were applied on C(1), C(13), C(17) and C(29). EXYZ and EADP commands were applied on C(37) and C(37A).

# Crystal data for [Yb(Odip)<sub>3</sub>(thf)<sub>2</sub>] (8)

C<sub>44</sub>H<sub>67</sub>O<sub>5</sub>Yb, M = 849.02, yellow block,  $0.12 \times 0.11 \times 0.03 \text{ mm}^3$ , monoclinic, space group  $P2_1$  (No. 4), a = 9.7148(16), b = 19.483(3), c = 12.344(2) Å,  $\beta = 110.053(11)^\circ$ , V = 2194.7(7) Å<sup>3</sup>, Z = 2,  $D_c = 1.285 \text{ g cm}^{-3}$ ,  $F_{000} = 882$ , T = 173(2)K,  $2\theta_{\text{max}} = 50.0^\circ$ , 10375 reflections collected, 6228 unique ( $R_{\text{int}} = 0.0223$ ). Final *GooF* = 0.999, R1 = 0.0219, wR2 = 0.0491, R indices based on 5732 reflections with  $I > 2\sigma(I)$ , 463 parameters, 1 restraint,  $\mu = 2.170 \text{ mm}^{-1}$ . Absolute structure parameter = 0.015 (8).<sup>95</sup>

# Crystal data for [Eu(Odip)(µ-Odip)(thf)2]2 (9)

C<sub>64</sub>H<sub>100</sub>Eu<sub>2</sub>O<sub>8</sub>, M = 1301.36, yellow block, 0.12 × 0.10 × 0.02 mm<sup>3</sup>, monoclinic, space group  $P2_1/c$  (No. 14), a = 20.135 (10), b = 14.588(7), c = 22.125(12) Å,  $\beta = 100.403(11)^\circ$ , V = 6392(5) Å<sup>3</sup>, Z = 4,  $D_c = 1.352$  g cm<sup>-3</sup>,  $F_{000} = 2696$ , T = 123(2) K,  $2\theta_{max} = 55.0^\circ$ , 55115 reflections collected, 14641 unique ( $R_{int} = 0.0666$ ). Final GooF = 0.978, R1 = 0.0462, wR2 = 0.0895, R indices based on 9461 reflections with  $I > 2\sigma(I)$ , 692 parameters, 0 restraints,  $\mu = 1.994$  mm<sup>-1</sup>. Variata: Thermal parameters on a number of carbons (C(43) and C(46)) were large due to high thermal motion. One thf was modelled as disordered with C atom position C(57), C(58), C(59) and C(60) (refined occupancy 0.17:0.83). ISOR restraints applied for C(58) and C(57). EXYZ and EADP commands were applied on C(57) and C(57A) as well as C(60) and C(60A).

# Crystal data [La(Odip)<sub>3</sub>(dme)<sub>2</sub>] (10)

C<sub>44</sub>H<sub>71</sub>LaO<sub>7</sub>, M = 850.92, colourless plate,  $0.20 \times 0.10 \times 0.08 \text{ mm}^3$ , orthorhombic, space group  $P2_{12}1_{21}$  (No. 19), a = 13.1036(2), b = 13.4935(3), c = 25.6718(4) Å, V = 4539.12(14) Å<sup>3</sup>, Z = 4,  $D_c = 1.245$  g cm<sup>-3</sup>,  $F_{000} = 1792$ , T = 123(2)K,  $2\theta_{\text{max}} = 64.6^{\circ}$ , 44155 reflections collected, 10427 unique ( $R_{\text{int}} = 0.0523$ ). Final GooF = 1.004, R1 = 0.0298, wR2 = 0.0571, R indices based on 9653 reflections with with  $I > 2\sigma(I)$ , 485 parameters, 0 restraints. Lp and absorption corrections applied,  $\mu = 0.985$  mm<sup>-1</sup>. Absolute structure parameter =  $0.009(9)^{95}$ 

### Crystal data [Dy(Odip)<sub>3</sub>(dme)<sub>2</sub>] (11)

C<sub>44</sub>H<sub>71</sub>DyO<sub>7</sub>, M = 874.51, colourless block, monoclinic, space group  $P2_1/n$  (No. 14), a = 14.366(3), b = 19.188(1), c = 16.638(2) Å,  $\beta = 90.624(7)^\circ$ , V = 4586.1(11) Å<sup>3</sup>, Z = 4,  $D_c = 1.267$  g cm<sup>-3</sup>,  $F_{000} = 1828$ ,  $\lambda = 0.712$  Å, T = 100(2)K,  $2\theta_{max} = 54.2^\circ$ , 33363 reflections collected, 9554 unique ( $R_{int} = 0.0361$ ). Final GooF = 1.056, R1 = 0.0366, wR2 = 0.0988, R indices based on 8554 reflections with  $I > 2\sigma(I)$ , 485 parameters, 0 restraints,  $\mu =$ 1.673 mm<sup>-1</sup>. Variata: There are voids of 111 Å<sup>3</sup> in the unit cell presumably belonging to disordered dme molecules in the lattice but these molecules could not be modelled.

### Crystal data [Y(Odip)<sub>3</sub>(dme)<sub>2</sub>] (12)

C<sub>44</sub>H<sub>71</sub>O<sub>7</sub>Y, *M* = 800.92, colourless block, monoclinic, space group *P*2<sub>1</sub>/*n* (No. 14), *a* = 14.373(2), *b* = 19.227(2), *c* = 16.652 (2) Å,  $\beta$  = 90.782(9)°, *V* = 4601.3(10) Å<sup>3</sup>, *Z* = 4, *D*<sub>c</sub> = 1.156 g cm<sup>-3</sup>, *F*<sub>000</sub> = 1720,  $\lambda$  = 0.712 Å, *T* = 100(2)K, 2 $\theta$ <sub>max</sub> = 54.2°, 33768 reflections collected, 9679 unique (*R*<sub>int</sub> = 0.0421). Final *GooF* = 1.068, *R*1 = 0.0547, *wR*2 = 0.1405, *R* indices based on 8420 reflections with *I* > 2 $\sigma$ (*I*), 485 parameters, 0 restraints,  $\mu$  = 1.311 mm<sup>-1</sup>. *Variata*: There are voids of 115 Å<sup>3</sup> in the unit cell presumably belonging to disordered dme molecules in the lattice but these molecules could not be modelled.

# Crystal data [Yb(Odip)<sub>3</sub>(dme)<sub>2</sub>] (13)

C<sub>44</sub>H<sub>71</sub>O<sub>7</sub>Yb, M = 885.50, yellow block,  $0.12 \times 0.10 \times 0.03 \text{ mm}^3$ , monoclinic, space group  $P2_1/c$  (No. 14), a = 22.0514 (5), b = 18.9710(4), c = 23.2542(5) Å,  $\beta = 115.2020(10)^\circ$ , V = 8802.1(3) Å<sup>3</sup>, Z = 8,  $D_c = 1.336$  g cm<sup>-3</sup>,  $F_{000} = 3688$ , T = 123 (2)K,  $2\theta_{\text{max}} = 55.0^\circ$ , 74 411 reflections collected, 19 092 unique ( $R_{\text{int}} = 0.2136$ ). Final GooF = 0.948, R1 = 0.0692, wR2 = 0.1224, R indices based on 9137 reflections with  $I > 2\sigma(I)$ , 969 parameters, 42 restraints. Lp and absorption corrections applied,  $\mu = 2.170 \text{ mm}^{-1}$ . Variata: This compound is structurally similar to compound **11** and **12**. Two discrete molecules were observed in the asymmetric unit. ISOR restraints applied for C(1), C(2), C(3), C(4), C(41), C(48) and C(60).

# Crystal data [La(Odip)<sub>3</sub>(dig)]·0.25dme (15)

 $C_{43}H_{67,5}O_{6,5}La$ , M = 827.39, colourless needles, triclinic, space group  $P\overline{1}$  (No. 2), a = 12.133(2), b = 15.232(3), c = 25.884(5)Å,  $\alpha = 89.63(3)$ ,  $\beta = 79.38(3)$ ,  $\gamma = 69.75(3)^{\circ}$ , V = 4402.5(14) Å<sup>3</sup>, Z = 4 (two molecules in asymmetric unit),  $D_c = 1.248$  g cm<sup>-3</sup>,  $F_{000} = 1738$ , T = 100 K,  $2\theta_{max} = 53.4^{\circ}$ , 62811 reflections collected, 16469 unique ( $R_{int} = 0.0283$ ). Final GooF = 1.158, R1 =0.0479, wR2 = 0.1203, R indices based on 15669 reflections with  $I > 2\sigma(I)$ , 955 parameters, 24 restraints. Lp and absorption corrections applied,  $\mu = 1.013 \text{ mm}^{-1}$ . Variata: Two discrete molecules were observed in the asymmetric unit. Three of the 'Pr groups (C(34)-C(36), C(52)-C(54) and C(61)-(63)) were modelled with the Me groups rotationally disordered about the C(H)-C(Ar) bond and were refined with restrained anisotropic thermal parameter forms (ISOR restraints applied for C(25), C(36), C(53), C(54)). Two voids were detected in the crystal structure (void 1 202 Å<sup>3</sup>, at 1 0 0 and void 2 294 Å<sup>3</sup> at -0.0020.500 0.500) which were plausibly attributable to dme of solvation. The <sup>1</sup>H NMR indicated approximately 0.25 dme per [La(Odip)<sub>3</sub>(dig)]. After an unsatisfactory attempt to model the solvent by inclusion of a partially occupied dme molecule as a rigid body, the electron density associated with solvent molecules in the lattice voids were removed by PLATON SQUEEZE<sup>94</sup> (void1. 12 electrons (calc), 30 electrons (calc)) for the final refinement.

# Crystal data [YbI2(thf)4]

C<sub>16</sub>H<sub>32</sub>I<sub>2</sub>O<sub>4</sub>Yb, M = 715.3, yellow prism,  $0.12 \times 0.11 \times 0.03 \text{ mm}^3$ , triclinic, space group  $P\overline{1}$  (No. 2), a = 8.4437(7), b = 9.8103(8), c = 13.6182(12) Å,  $\alpha = 79.672(5)$ ,  $\beta = 87.987(5)$ ,  $\gamma = 87.362(4)^\circ$ , V = 1108.20(16) Å<sup>3</sup>, Z = 2,  $D_c = 2.143$  g cm<sup>-3</sup>,  $F_{000} = 672$ ,  $\lambda = 0.71073$  Å, T = 123(1)K,  $2\theta_{\text{max}} = 50.0^\circ$ , 19 862 reflections collected, 3817 unique ( $R_{\text{int}} = 0.0526$ ). Final GooF = 1.074, R1 = 0.0806, wR2 = 0.2472, R indices based on 9137 reflections with  $I > 2\sigma(I)$ , 211 parameters, 6 restraints. Lp and absorption corrections applied,  $\mu = 7.019 \text{ mm}^{-1}$ . Variata: The data indicates the molecule is either a different polymorph from the known literature structure<sup>45</sup> or twin. The asymmetric unit has two half molecules, with the Yb atoms lying on independent inversion centres.

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