DALTON
FULL PAPER

A simple synthesis and a structural survey of homoleptic rare earth(III) 2,6-diphenylphenolates

Glen B. Deacon,*[a] Tiecheng Feng,[a] Craig M. Forsyth,[a] Alex Gitlits,[a] David C. R. Hockless,[b] Qi Shen,[a,c] Brian W. Skelton[b] and Allan H. White[b]

[a] *Chemistry Department, Monash University, Vic, 3800, Australia.*
E-mail: Glen.Deacon@sci.monash.edu.au
[b] *Department of Chemistry, University of Western Australia, Nedlands 6907 WA, Australia*
[c] *Chemistry Department, Suzhou University, 1 Shizi Street, Suzhou 215006,*
People's Republic of China

Received 21st December 1999, Accepted 27th January 2000

Reactions of 2,6-diphenylphenol (HOdpp) and rare earth metals, in the presence of mercury, at elevated temperatures in sealed tubes followed by extraction with toluene yielded homoleptic tris(aryloxo)lanthanoid(III) complexes, [Ln(Odpp)$_3$] (Ln = Y (**1**), La (**2**), Ce (**3**), Pr (**4**), Nd (**5**), Gd (**6**), Ho (**7**), Er (**8**), Lu (**9**)). Single crystal X-ray diffraction studies of **1**–**4** and **9** established monomeric structures with the coordination sphere comprising a triangular array of Odpp oxygen atoms with capping phenyl groups above and below. In the isomorphous (triclinic $P\bar{1}$) **1**, **3**, **4** and **9**, there are additional intramolecular π-interactions of the phenyl substituents with the metals (η^6-Ph–Ln and η^1-Ph–Ln). The cell parameters for **2**, though similar, suggest a different form, and the structure has additional intramolecular η^6-Ph–La and η^3-Ph–La interactions with the capping phenyl groups near parallel.

Introduction

The direct reaction of activated lanthanoid metals with weak protic acids is a conceptually simple and potentially fruitful route to a wide range of reactive lanthanoid complexes (*e.g.* refs. 1 and 2).

$$\text{Ln} + n\,\text{HL} \longrightarrow \text{LnL}_n + n/2\ \text{H}_2 \qquad (1)$$

Examples include reactions of ytterbium or europium with cyclopentadiene in liquid ammonia,[1a] metal atom reactions with primary acetylenes and pentamethylcyclopentadiene,[1a–c] the direct synthesis of Ln(NH$_2$)$_3$,[2a] reaction of mercury activated lanthanoids with alcohols[1c,2b–e] where formation of oxoalkoxide cages *e.g.* [Ln$_5$O(Pr^{i}O)$_{13}$] is possible,[1c,2b–e] coordination-assisted reactions with alcohols[3a] and reactions of lanthanoids with bulky 2,6-disubstituted phenols, in liquid ammonia,[3b–e] *N*-methylimidazole,[3c] and acetonitrile.[3c] When these reactions are carried out in the absence of donor solvents, they can provide a route to homoleptic complexes, as demonstrated by the recent synthesis of lanthanoid(II, III or II/III) 3,5-di-*tert*-butylpyrazolates.[4] With bulky aryloxides, homoleptic complexes of low coordination number may be prepared,[5] which may achieve coordination saturation by inter- or intra-molecular π-arene–Ln coordination.[5,6] Thus, reactions of mercury-activated ytterbium and europium metals with 2,6-diphenylphenol (HOdpp) give [Yb(Odpp)(μ-Odpp)]$_2$, [Eu$_2$(Odpp)(μ-Odpp)$_3$], and [Yb$_2^{\text{II}}$(μ-Odpp)$_3$][Yb$^{\text{III}}$(Odpp)$_4$], in which the oxygen-donor low coordination numbers are increased by a remarkable range of intramolecular π-Ph–Ln interactions.[5] We now report the successful development of this synthetic method to give homoleptic tris(2,6-diphenylphenolato)lanthanoid(III) complexes [Ln(Odpp)$_3$] in good yield, and the crystal structures for Ln = Y, La, Ce, Pr, and Lu. Structures for Ln = Nd and Yb prepared by other routes have been reported,[7,8] but the current structure determinations probe the effect of lanthanoid ion size to the limits of the series.

Results and discussion

Synthesis and characterisation

The rare earth aryloxides [Ln(Odpp)$_3$] (Ln = Y (**1**), La (**2**), Ce (**3**), Pr (**4**), Nd (**5**), Gd (**6**), Ho (**7**), Er (**8**), Lu (**9**)) were prepared by heating a mixture of the metal with 2,6-diphenylphenol (HOdpp) in the presence of mercury metal at 200 °C in sealed Carius tubes under vacuum (eqn. (2)).

$$\text{Ln(Hg)} + 3\ \text{HOdpp} \longrightarrow [\text{Ln(Odpp)}_3] + 3/2\ \text{H}_2 \qquad (2)$$

A simple extraction with toluene gave the [Ln(Odpp)$_3$] complexes in good yields. Molten HOdpp (mp = 101–102 °C) possibly acts as a solvent at initial stages of the reactions, but the reaction mixtures progressively solidify. Mercury assists by surface amalgamation/cleaning. In the absence of mercury, the reaction between neodymium metal and HOdpp did not proceed to any noticeable extent when the reaction mixture was heated from 200 °C to 300 °C over 2 days. Only after heating at 350 °C for 23 hours was some slight formation of the product observed.

The application of the preparative method to trivalent lanthanoid complexes (reaction (2)) in addition to its previous use for divalent compounds[5] establishes the generality of the synthesis, which has the particular attractions of simplicity and access to homoleptic complexes. However, it cannot be used to give Ln(Odpp)$_3$ (Ln = Yb, Eu) since the elements react to give divalent ([Ln(Odpp)$_2$]) and mixed valence ([Yb$_2$(Odpp)$_3$]-[Yb(Odpp)$_4$])[5] compounds.

Complex **2** was also prepared by a redox transmetallation/ligand exchange reacton in refluxing toluene in the presence of mercury (eqn. (3)).

$$\text{La} + 3/2\ \text{Hg(C}_6\text{F}_5)_2 + 3\ \text{HOdpp} \xrightarrow{\text{C}_6\text{H}_5\text{CH}_3} [\text{La(Odpp)}_3] + 3\ \text{C}_6\text{F}_5\text{H} + 3/2\ \text{Hg} \qquad (3)$$

DOI: 10.1039/a910277i

Table 1 Unit cell dimensions for [Ln(Odpp)$_3$] complexes. Lattice dimensions and angles are in Å and ° respectively while volumes are in Å^3

Ln Compound	*a*	*b*	*c*	*α*	*β*	*γ*	*V*
Y **1**	15.907(3)	13.541(3)	10.966(2)	116.504(4)	92.816(5)	103.092(4)	2028
La **2**	15.703(6)	13.537(5)	10.391(3)	95.79(3)	104.77(3)	102.13(3)	2060
Ce **3**[a]	15.5685(4)	13.3666(3)	10.9262(1)	116.029(1)	92.403(1)	100.750(1)	1987
Ce **3**	15.880(6)	13.526(7)	10.941(4)	116.47(4)	92.66(3)	103.77(4)	2012
Pr **4**	15.827(6)	13.506(5)	11.012(3)	116.39(3)	92.77(3)	101.30(2)	2043
Nd **5**[b]	15.835(5)	13.499(10)	10.955(11)	116.25(7)	92.87(7)	101.66(6)	2031
Yb **10**[c]	15.934(2)	13.563(1)	10.968(2)	116.71(1)	92.90(2)	103.38(1)	2027
Lu **9**	15.888(5)	13.524(3)	10.939(4)	116.49(2)	92.86(3)	103.63(2)	2012

[a] Data measured at 123 K. All other data sets were measured at room temperature, *ca.* 300 K (**1**) or *ca.* 293 K (all others). [b] Ref. 8. [c] Ref. 7.

Table 2 Selected geometries for **1**–**5**, **9** and **10** (distances in Å, angles in °)

Ln Compound	Y **1**	La **2**	Ce **3**	Pr **4**	Nd **5**[a]	Yb **10**[b]	Lu **9**
Ln–O(1)	2.132(9)	2.242(4)	2.232(2)	2.214(4)	2.193(5)	2.104(4)	2.090(7)
Ln–O(2)	2.085(6)	2.234(5)	2.211(2)	2.189(3)	2.174(3)	2.061(4)	2.049(5)
Ln–O(3)	2.053(6)	2.201(5)	2.183(2)	2.150(3)	2.140(3)	2.031(2)	2.017(4)
O(1)–Ln–O(2)	114.8(3)	114.0(2)	110.4(1)	112.9(1)	114.0(2)	115.6(1)	115.4(2)
O(1)–Ln–O(3)	114.2(3)	116.2(2)	111.2(1)	112.6(1)	113.0(2)	114.4(1)	113.9(2)
O(2)–Ln–O(3)	123.0(3)	128.4(2)	130.6(1)	127.7(1)	126.2(2)	122.5(1)	122.0(2)
Σ Ln–O–Ln	352.$_0$	358.$_6$	352.$_2$	353.$_2$	353.$_2$	352.$_5$	351.$_3$
Ln–O(1)–C(11)	137.6(8)	141.8(4)	138.2(2)	138.1(4)	138.8(4)	135.0(3)	134.5(6)
Ln–O(2)–C(21)	149.6(6)	143.6(4)	149.2(2)	149.8(3)	149.6(3)	149.1(2)	149.1(5)
Ln–O(3)–C(31)	167.7(8)	169.0(4)	162.9(2)	165.7(4)	165.9(4)	168.7(3)	167.4(6)

[a] Ref. 8. [b] The numbering of atoms in **10**[7] has been changed to conform with that of **1**–**5**, **9**.

Redox transmetallation/ligand exchange reactions are normally carried out in polar organic solvents, particularly thf, *e.g.* refs. 7–9 and the occurrence of reaction (3) in toluene indicates these syntheses may have greater scope than hitherto realised. Solvent-complexed [Ln(Odpp)$_3$(thf)$_2$][2b,7–9] derivatives have been prepared by reaction (3) in thf and subsequently converted into [Ln(Odpp)$_3$(thf)] by crystallisation from toluene (Ln = Nd)[8] and into [Ln(Odpp)$_3$(dme)] by crystallisation from dme/pentane (Ln = Yb, Nd).[10] Desolvation of the thf complexes has given **5**, **8**, **9** and [Yb(Odpp)$_3$] (**10**), single crystals of **5** and **10** being obtained by sublimation.[7,8]

The composition of the complexes has been established by C, H, Ln analyses for new, and Ln analyses for known compounds. Crystal structures of **1**, **2**, **3**, **4**, and **9** (below) provide unequivocal identification, as did unit cell data for single crystals of the known[8] **5**. All complexes displayed parent ions in their electron impact mass spectra followed by progressive loss of Odpp ligands. UV/VIS/NIR spectra of solutions of **4**, **5**, **7**, **8** in THF exhibited absorptions characteristic of the corresponding Ln(III) ions.[11] ^{1}H NMR spectra of the diamagnetic complexes **1**, **2** and **9** in C_6D_6 displayed a complex series of resonances for the Odpp ligands. A distinct doublet of doublets at $\delta_{av} = 7.35$ which integrated for 12H, can be attributed to the *ortho* protons of substituent phenyl groups. This implies a single Odpp environment in solution, in contrast to the involvement of some phenyl substituents in intramolecular π-interactions in the solid state structures (see crystal structure discussion section). This can be explained by loss of the π-Ph–Ln interactions on dissolution, possibly a consequence of Ln–C_6D_6 interactions.[5]

Crystal structure determinations

Single crystals of **1**, **2**, **4**, **5**, and **9** suitable for structure determination were obtained from toluene solution, those of **1** being uncongenially small. Crystals of the highly air-sensitive [Ce(Odpp)$_3$] (**3**) were obtained directly from the reaction tube. Unit cell data for **1**–**5**, **9**, **10** (Table 1) indicate that **1**, **3**, **4**, **5**, **9**, **10** are isostructural. Thus, the presumption of a common structural type across the series from Ln = Ce to Ln = Lu, inclusive of Y (for which the data are inferior but consistent) is reasonable. Crystals of **5** from toluene had unit cell dimensions similar to those of crystals previously obtained by sublimation.[8] The cell for **2** (Ln = La) though similar, has differences from the others sufficiently pronounced to suggest an independent form. This is confirmed by differences in structural geometries given in the Tables below. Room temperature values for **3** suggested it to be isostructural with the majority, but the instability of the compound raised some uncertainty with the data. Accordingly, the structure of **3** was established by a low temperature determination, and found to be similar to those of **4**, **5**, **9**, and **10**. Thus there is a structural discontinuity between La and Ce, an unusual situation in an isostoichiometric series of rare earth compounds. It has also been observed for single crystals of [LaCl$_3$(thf)$_2$] (eight-coordinate) and [CeCl$_3$(thf)$_2$] (seven-coordinate), though bulk [CeCl$_3$(thf)$_2$] appears to have the lanthanum structure.[12]

All complexes have a near triangular array of oxygen atoms around Ln (O–Ln–O 110.4(1) (**3**)–130.6(1)° (**3**)) (Table 2) with capping phenyl groups above and below. The structural arrangement is distorted toward trigonal pyramidal as in [Ce(OC$_6$H$_3$Bu$^t_2$-2,6)$_3$][13] rather than being triangular planar as in [Y(OC$_6$H$_3$Bu$^t_2$-2,6)$_3$],[14a] or [Sc(OC$_6$H$_2$Bu$^t_2$-2,6-Me-4)$_3$][14b] by virtue of the displacement of Ln from the triangular plane (see below).

Molecular projections of **2** and **3** with similar orientations are shown in Fig. 1, and that of **9** in a projection normal to those of **2** and **3** in Fig. 2. The latter diagram shows a pseudo two-fold axis along the Lu–O(3) bond. The sum of the O–Ln–O angles ranges from 351.$_3$° (**9**) to 358.$_6$ (**2**) with all but **2** ≤ 353.5°. The Ln–O distances show a steady decrease from **2** to **9**, paralleling the reduction in the Ln^{3+}radii in this sequence.[15]

The average of the La–O distances (2.23 Å) is close to that found in five-coordinate [La(Odpp)$_3$(thf)$_2$][9] (⟨La–O(Odpp)⟩ 2.24 Å) whereas a difference of *ca.* 0.1 Å might be expected[15] between three- and five-coordination, suggesting that there are other interactions additional to Ln–O bonding in the [Ln(Odpp)$_3$] series. Analogously, ⟨Ce–O⟩ in **3** (2.21 Å) is very

Table 3 Lanthanoid–carbon distances (in Å) in **1**–**5**, **9** and **10**

Ln · · · C(12*n*, 22*n*)	Y **1**	La **2**	Ce **3**	Pr **4**	Nd **5**[a]	Yb **10**[b]	Lu **9**
121	2.84(1)	3.107(7)	2.975(3)	2.980(5)	2.946(6)	2.814(4)	2.787(8)
2	2.90(1)	3.159(8)	2.995(3)	3.005(5)	2.974(6)	2.874(5)	2.898(8)
3	3.04(1)	3.248(8)	3.098(3)	3.118(6)	3.092(8)	3.038(6)	3.048(10)
4	3.13(2)	3.274(7)	3.167(3)	3.197(8)	3.158(9)	3.148(6)	3.087(12)
5	3.05(2)	3.206(7)	3.135(3)	3.148(7)	3.104(8)	3.085(5)	3.009(11)
6	2.91(1)	3.133(7)	3.043(3)	3.037(6)	3.004(6)	2.912(4)	2.831(9)
221	3.43(1)[c]	3.173(7)	3.480(3)[c]	3.454(6)[c]	3.443(6)[c]	3.392(5)[c]	3.395(8)[c]
2	2.91(1)	3.052(7)	2.989(3)	2.981(6)	2.964(7)	2.882(5)	2.877(9)
3	3.38(2)[c]	3.282(7)	3.390(3)[c]	3.388(7)[c]	3.365(9)[c]	3.390(7)[c]	3.338(6)[c]

[a] Ref. 8. [b] Ref. 7. [c] 'Non-bonding', as are Ln · · · C(224–226), typically > 3.5 Å, *e.g.* 3.618(7), 3.691(9), 3.510(8) Å for La · · · C(224–226) of **2**.

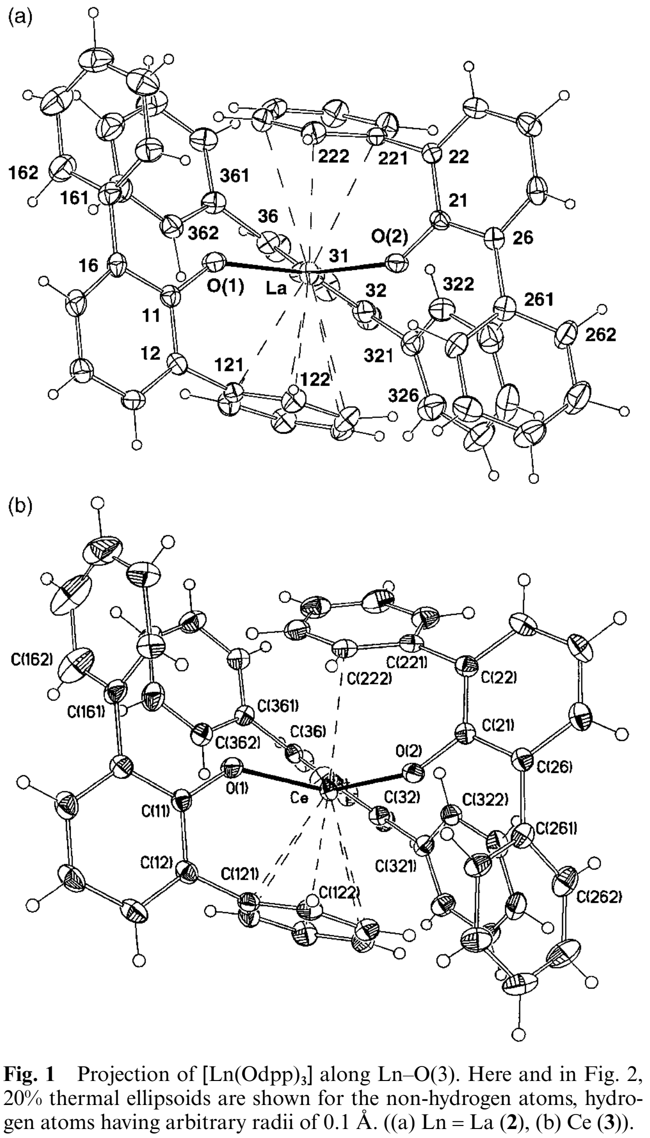

Fig. 1 Projection of [Ln(Odpp)$_3$] along Ln–O(3). Here and in Fig. 2, 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å. ((a) Ln = La (**2**), (b) Ce (**3**)).

similar to ⟨Ce–O⟩ (2.23 Å) for five-coordinate [Ce(OAr)$_3$(Bu^{t}NC)$_2$] (OAr = OC$_6$H$_3$Bu$^t_2$-2,6).[13] Moreover, ⟨Ce–O⟩ in three-coordinate [Ce(OAr)$_3$] (OAr = OC$_6$H$_3$Bu$^t_2$-2,6)[13] (2.14 Å) is considerably shorter than ⟨Ce–O⟩ in **3** reinforcing the evidence for binding additional to Ln–O in the [Ln(Odpp)$_3$] series. In addition, [Lu(Odpp)$_3$] (**9**) has ⟨Lu–O⟩ (2.05 Å) comparable with that (2.07 Å) of five-coordinate [Yb(Odpp)$_3$(thf)$_2$][7] (ionic radius difference between Lu^{3+} and Yb^{3+} ≈0.01 Å for the same coordination number).

Close contacts with some carbon atoms of the capping phenyl groups (Table 3) provide the additional interaction.

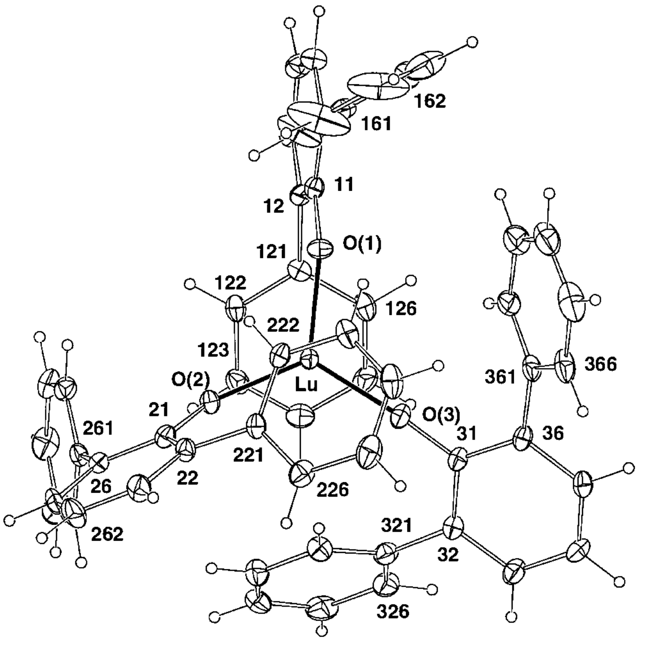

Fig. 2 Projection of [Lu(Odpp)$_3$] normal to the LuO$_3$ array.

Thus, in **2**–**4**, **9**, all carbons of phenyl ring C(121)–C(126) approach the Ln atom closely, giving an intramolecular η^6-Ln interaction. By contrast, *three* carbons of ring C(221)–C(226) of **2** make similar contacts, but only one carbon (C(222)) of this ring for **3**, **4**, and **9** (Table 3). Atoms C(224)–C(226) of **2** are considered non-bonding as they are up to *ca.* 0.4 Å further from lanthanum than C(221)–C(223) (Table 3). Likewise non-interacting C(221) and C(223) of **3**, **4**, **9** are significantly more distant (by up to 0.5 Å) than C(222) (Table 3). These interactions in **2**–**4**, **9** appear comparable with those observed in **5**[8] and **10**[7] taking into account the differences in ionic radius.

The Ln · · · C 'bonding' distances for **2**–**4** and **9** approach the Ln–C bond distances (2.89–2.93 Å)[6] observed in the unequivocally π-arene–lanthanoid complexes [Sm(η^6-C$_6$Me$_6$)(AlCl$_4$)$_3$],[16] [Nd(η^6-C$_6$H$_6$)(AlCl$_4$)$_3$][17] and [Sm(η^6-C$_6$H$_6$)(AlCl$_4$)$_3$].[17] Furthermore, the ⟨La · · · C⟩ interaction in **2** (3.19 Å) may be considered comparable with ⟨La · · · C⟩ (3.06 Å) in η^6-π-arene-bridged [La$_2$(OC$_6$H$_3$Pr$^i_2$-2,6)$_6$],[18] especially given that **2** is formally eight-coordinate whilst [La$_2$(OC$_6$H$_3$Pr$^i_2$-2,6)$_6$] is six-coordinate. However, it is noteworthy that the π-arene–La interactions in [La$_2$(OC$_6$H$_3$Pr$^i_2$-2,6)$_6$] are sufficiently strong so as to be maintained in toluene solution,[18] unlike those of **1**, **2** and **9**. All proposed Ln · · · C bond distances (Table 3) are significantly less than the sum (3.4–3.8 Å) of the Ln metallic radius[19] (pseudo van der Waals radius) and the van der Waals radius of an aromatic ring.[20]

Subtraction of appropriate ionic radii[15] (eight-coordinate for **2** and seven-coordinate for **3**, **4** and **9**) from ⟨Ln · · · C(12*n*)⟩

Table 4 Interplanar dihedral angles (°) of capping phenyl ligands and Ln deviation (δ/Å) from O_3 plane

[Ln(Odpp)$_3$] Angles between	La **2**	Ce **3**	Pr **4**	Lu **9**
η^6-C(12*n*) and O_3	13.4(2)	16.0(2)	15.6(2)	12.6(3)
η^1 or η^3-C(22*n*) and O_3	14.2(2)	28.8(2)	28.3(2)	28.8(3)
η^6-C(12*n*) and η^1 or η^3-C(22*n*)	19.9(3)	42.4(2)	40.6(2)	38.8(3)
C(120)–Ln–C(220)[a]	$176._2$	$175._8$	$177._2$	$173._2$
δ	0.150(1)	0.353(3)	0.330(1)	0.353(1)

[a] C(120) and C(220) are centroids of rings C(12*n*) and C(22*n*) respectively.

gives 2.03, 2.00, 2.02 and 2.02 Å respectively. These values are within the upper limit (2.16 Å) of similarly derived values for complexes with π-arene···Ln coordination,[6] and comparable with 2.03 Å similarly derived from ⟨La···C⟩ of [$La_2(OC_6H_3Pr^i_2$-2,6)$_6$].[18] Analogous subtractions of the appropriate ionic radii[15] from ⟨Ln···C(221–223)⟩ of **2** and from Ln···C(222) of **1**, **3**, **4**, and **9** gives 2.01 and 1.92–1.96 Å respectively, which lie in the bonding range.[6] ⟨La–C(12*n*)⟩ of **2** is longer than ⟨Pr–C(12*n*)⟩ of **4** by *ca.* 0.1 Å (range 0.06–0.15 Å), significantly more than the ionic radius difference[15] between $La^{3+}$and Pr^{3+}, in keeping with a structural difference.

The lanthanoid–π-phenyl interactions in [Ln(Odpp)$_3$] complexes cause localised structural effects as indicated by some trends in the geometrical data in Table 2. Thus, within each complex, the Odpp ligands 1 and 2, which have interacting phenyl substituents (η^6-Ph and η^3/η^1-Ph respectively), consistently have longer Ln–O distances and smaller Ln–O–C angles than those of the Odpp 3 ligand which is solely oxygen bound. Further, these effects correlate with the hapticity of the phenyl interactions. Intramolecular attachment of a phenyl group to the metal closes the Ln–O–C angle, thereby increasing the localised steric repulsion of that particular Odpp ligand, leading to lengthening of the Ln–O bond. A further consequence, observed when the structures are viewed approximately normal to the LnO_3 plane (*e.g.* Fig. 2, for Ln = Lu), is that the phenoxy ring of Odpp 3 (solely oxygen bound) lies almost parallel to the O_3 plane in contrast to the perpendicular nature of the phenoxy rings of the other two ligands.

A very clear indication of the difference in structure between **2** and **3**, **4**, **9** is given by the interplanar angles of the capping phenyl rings, and the displacement of the metal from the O_3 plane (Table 4). For all structures, the η^6-bonded ring is almost parallel to the O_3 plane, but, whilst the η^3-bonded ring of **2** is also nearly parallel (interplanar angle 14.2(2)°), the η^1-bonded rings of **3**, **4**, **9** are tilted considerably to the O_3 plane at 28–29°. In **2** the two capping phenyl rings are near parallel to each other with a 19.9(3)° interplanar angle, but for **3**, **4**, **9**, the rings are substantially inclined (*ca.* 40°). Despite the different binding of the capping ring C(22*n*) from **2** to **3**, **4**, **9**, the centres of the two capping rings are near co-linear with the lanthanoid metal in all structures (Table 4). The deviation of Ln from the O_3 plane is much smaller for **2** than for **3**, **4**, **9**, clearly reflecting the status of **2** as an intramolecular π-sandwich compound whereas **3**, **4**, **9** (and **5**, **10**)[7,8] are only "half" sandwiches. Intramolecular Ph···Ph contacts lie well beyond the sum of two aromatic van der Waals radii[20] and do not appear to be a significant structural influence. The structural discontinuity with **2** appears to be consequent on size and basicity being maximised with lanthanum.

Experimental

The lanthanoid complexes **1**–**9** are highly air- and moisture-sensitive and all preparations were conducted under an inert atmosphere (purified N_2 or Ar) involving conventional glove-box and Schlenk techniques. The cerium complex **3** was extremely air-sensitive, and could only be handled satisfactorily under argon. Toluene was purified, dried, and deoxygenated by refluxing over and distillation from sodium–benzophenone. C_6D_6 (Cambridge Isotopes) was dried over CaH_2. The dried deuterated solvent was then vacuum transferred to a greaseless Schlenk tube and stored under purified argon or nitrogen. Infrared spectra (4000–650 cm^{-1}) were obtained for Nujol mulls sandwiched between NaCl plates with Perkin-Elmer 1600 FTIR spectrometer. Mass spectra were obtained with a VG Trio-1 GC mass spectrometer using a probe for handling air-sensitive solids. Each listed *m*/*z* value for metal containing ions (where the metal has more than one isotope) is the most intense peak of a cluster with an isotope pattern in a good agreement with the calculated pattern. Room temperature (20 °C) NMR spectra were recorded on either a Bruker DPX 300 or a DRX 400 spectrometer. The chemical shift reference was the residual solvent signal C_6D_6 δ_H 7.15. In assignments, primed numbers refer to phenyl protons. Lanthanoid analyses were by the Na_2H_2EDTA titration[21] with xylenol orange indicator of solutions prepared by digestion of accurately weighed samples in concentrated HNO_3/2% concentrated H_2SO_4 followed by dilution with water and buffering with hexamine. Microanalysis samples were sealed in glass ampoules under vacuum and were determined by the Campbell Microanalytical Service, University of Otago, New Zealand. 2,6-Diphenylphenol was from Aldrich, and lanthanoid metals except cerium were obtained from Santoku America, Phoenix. Cerium metal (REACTON Grade) was from Johnson-Matthey Rare Earth Products. Hydrogen gas detection was carried out using an Ai LEAKSEEKER 96.

Preparations of tris(2,6-diphenylphenolato)lanthanoid(III) complexes

General. Lanthanoid metal powder or chunks (0.70–1.40 g; 5.7–8.0 mmol), HOdpp (0.70–1.0 g, 2.8–4.0 mmol) (mole ratio 2 : 1), and 2 drops of mercury were heated under vacuum at 200 °C for 48 h, unless indicated otherwise. Extraction with toluene (2 × 50 ml), filtration, and evaporation gave **1**–**9** (0.55–1.13 g, 59–93%), often suitably crystalline for X-ray structure determination (**1**, **2**, **4**, **5**, **9**). Infrared (ave. $\tilde{\nu}$/cm^{-1} for **1**–**9**; variation ± 3 cm^{-1}): 1594w, 1577w, 1410s, 1306s, 1279m, 1264m, 1169m, 1088w, 1068m, 1011w, 975w, 858m, 761m, 741m, 702m, 666m, 607s. ^{1}H NMR (**1**, **2** and **9** in C_6D_6): δ 6.89–6.96 (m, 21H, H4, H3′, H4′, H5′), 7.23–7.25 (d, J = 7.5 Hz, 6H, H3, H5), 7.34–7.36 (dd, ^3J = 8.1 Hz, ^4J = 1.3 Hz, 12H, H2′, H6′).

[Y($OC_6H_3Ph_2$-2,6)$_3$] 1. Reaction time 24 h. Colourless crystals, yield 70% (Found C, 78.4; H, 4.7; Y, 10.5. $C_{54}H_{39}O_3Y$ requires C, 78.6; H, 4.8; Y, 10.8%). Mass spectrum: *m*/*z* 824 (14%, Y(Odpp)$_3^+$), 579 (81%, Y(Odpp)$_2^+$), 246 (100, HOdpp$^+$), 245 (4%, Odpp$^+$).

[La($OC_6H_3Ph_2$-2,6)$_3$] 2. (i) Colourless crystals (Found La, 15.6. $C_{54}H_{39}LaO_3$ requires La, 15.9%). Mass spectrum: *m*/*z* 874 (15%, ^{139}La(Odpp)$_3^+$), 629 (83%, ^{139}La(Odpp)$_2^+$), 383 (4%, ^{139}LaOdpp − H$^+$) 246 (100%, HOdpp$^+$). (ii) Lanthanum metal powder (0.97 g, 7.0 mmol), bis(pentafluorophenyl)mercury (0.80 g, 1.5 mmol), 2,6-diphenylphenol (0.73 g, 3.0 mmol) and Hg metal (2 drops) were stirred for 18 h in refluxing toluene (50 ml). After filtration of the reaction mixture, the dark brown filtrate was evaporated to *ca*. 10 ml under vacuum and pentane (5 ml) was layered on top to promote crystallisation. Small greenish *crystals* of complex **2** suitable for X-ray structure determination grew over a few days (0.53 g, 61%) (Found: C, 74.0; H, 4.9; La, 15.5. $C_{54}H_{39}LaO_3$ requires C, 74.1; H, 4.5%). The infrared spectrum was in agreement with that of the product from (i).

$[Ce(OC_6H_3Ph_2\text{-}2,6)_3]$ 3. Yellow crystals suitable for X-ray structure determination were obtained directly from the reaction tube. Extraction of the bulk product gave a yellow-greenish microcrystalline solid (yield 71%) (Found C, 73.9; H, 4.8; Ce 15.7. $C_{54}H_{39}CeO_3$ requires C, 74.0; H, 4.5; Ce, 16.0%). Mass spectrum: *m/z* 875 (27%, $^{140}Ce(Odpp)_3{}^+$), 630 (100%, $^{140}Ce(Odpp)_2{}^+$), 246 (67%, $HOdpp^+$), 245 (6%, $Odpp^+$). The filtrate became blue on standing, obviating growth of single crystals from solution. A similar but slower decomposition of the solid was observed on storage under nitrogen in a dry box.

$[Pr(OC_6H_3Ph_2\text{-}2,6)_3]$ 4. Reaction time 96 h. Pale green crystals (yield 66%) (Found C, 74.1; H, 4.7; Pr, 16.3. $C_{54}H_{39}PrO_3$ requires C, 74.0; H, 4.5; Pr, 16.1%). Mass spectrum: *m/z* 876 (18%, $Pr(Odpp)_3{}^+$), 631 (100%, $Pr(Odpp)_2{}^+$), 386 (3%, $PrOdpp^+$), 246 (58, $HOdpp^+$). UV/VIS/NIR spectrum (thf): λ_{max}/nm (ε/l mol^{-1}cm^{-1}) 448 (2), 474 (2), 486 (3), 1146 (sh)(2), 1181 (7), 1396 (sh)(5), 1399 (7).

$[Nd(OC_6H_3Ph_2\text{-}2,6)_3]$ 5. Blue crystals (yield 76%) (Nd, 16.1. Calc. for $C_{54}H_{39}NdO_3$ Nd, 16.4%). Mass spectrum: *m/z* 879 (28%, $Nd(Odpp)_3{}^+$)†, 634 (100%, $Nd(Odpp)_2{}^+$)†, 387 (3%, $^{142}Nd(Odpp)^+$), 246 (5%, $HOdpp^+$), 245 (24%, $Odpp^+$). UV/VIS/NIR spectrum (thf): λ_{max}/nm (ε/l mol^{-1} cm^{-1}) 517 (3), 532 (5), 581 (23), 588 (24), 593 (21), 610 (6), 743 (6), 752 (6), 809 (9), 891 (8). Hydrogen gas was detected as a reaction product. Unit cell data were in agreement with those reported.[8]

$[Gd(OC_6H_3Ph_2\text{-}2,6)_3]$ 6. Colourless crystals (yield 59%) (Found C, 72.8; H, 4.2; Gd, 18.0. $C_{54}H_{39}GdO_3$ requires C, 72.6; H, 4.4; Gd, 17.6%). Mass spectrum: *m/z* 893 (<1%, $^{158}Gd(Odpp)_3{}^+$), 648 (5%, $^{158}Gd(Odpp)_2{}^+$), 246 (5%, $HOdpp^+$), 245 (8%, $Odpp^+$).

$[Ho(OC_6H_3Ph_2\text{-}2,6)_3]$ 7. Pink crystals (yield 63%) (Found C, 71.7; H, 4.6; Ho, 18.1. $C_{54}H_{39}HoO_3$ requires C, 72.0; H, 4.4; Ho, 18.3%). Mass spectrum: *m/z* 900 (7%, $Ho(Odpp)_3{}^+$), 655 (27%, $Ho(Odpp)_2{}^+$), 409 (7%, $HoOdpp - H^+$), 246 (100%, $HOdpp^+$), 245 (4%, $Odpp^+$). UV/VIS/NIR spectrum (thf): λ_{max}/nm (ε/l mol^{-1} cm^{-1}) 424 (2), 451 (51), 462 (25), 472 (3), 500 (2), 541 (3), 648 (3), 1143 (br)(1), 1180 (br)(1).

$[Er(OC_6H_3Ph_2\text{-}2,6)_3]$ 8. Pale pink microcrystalline solid (yield 67%) (Found Er, 18.3. Calc. for $C_{54}H_{39}ErO_3$ Er, 18.5%). Mass spectrum: *m/z* 903 (28%, $Er(Odpp)_3{}^+$)‡, 658 (81%, $Er(Odpp)_2{}^+$)‡, 410 (7%, ($^{166}ErOdpp - H^+$)), 246 (100%, $HOdpp^+$), 245 (6%, $Odpp^+$). UV/VIS/NIR spectrum (thf): λ_{max}/nm (ε/l mol^{-1}cm^{-1}) 378 (50), 408 (1), 490 (2), 521 (44), 656 (4), 1147 (sh)(2), 1183 (3), 1374 (sh)(2), 1398 (3).

$[Lu(OC_6H_3Ph_2\text{-}2,6)_3]$ 9. Reaction conditions: 175 °C for 48 h then 200 °C for 48 h. Colourless crystals (yield 93%) (Found Lu, 19.0. Calc. for $C_{54}H_{39}LuO_3$ Lu, 19.2%). Mass spectrum: *m/z* 910 (19%, $^{175}Lu(Odpp)_3{}^+$), 665 (100%, $^{175}Lu(Odpp)_2{}^+$), 419 (3%, $^{175}LuOdpp - H^+$), 332.5 [2%, ($^{175}Lu(Odpp)_2{}^{2+}$)], 246 (16%, $HOdpp^+$), 245 (3%, $Odpp^+$).

Crystallography

Structure determination. Diffractometer data sets were measured to the level of redundancy described, within the specified $2\theta_{max}$ limit (monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å), yielding N_t total reflections, these being merged after Gaussian absorption correction to yield N_r unique (R_{int} as specified). N_o of these with $I > 3\sigma(I)$ ($I > 2\sigma(I)$ for **3**) were considered 'observed' and used in the full matrix least square refinements after solution of the structures by the heavy atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms (x, y, z, U_{iso})$_H$ being constrained at estimated values (exceptions: Ln = La, Ce where they were refined). Conventional residuals, R, R_w on $|F|$ are quoted, statistical weights being employed. Computation used the SHELXS-97,[22] SHELXL-97[23] and Xtal 3.4[24] program systems.

For Ln = La, Pr, Lu, data were measured on capillary mounted specimens at room temperature (*ca*. 293 K) using an Enraf-Nonius CAD-4 instrument in $2\theta/\theta$ scan mode ($2\theta_{max} = 50°$). Although cell dimensions are similar within the same space group, the Ln = La adduct does not appear to be isomorphous with the Ln = Pr, Nd,[8] Yb,[7] Lu, Y adducts which are isomorphous. In order to encompass the totality of the Ln spectrum, the Ln = Ce compound was also studied; it decayed rapidly in the X-ray beam at room temperature with the data acquisition insufficiently complete to enable satisfactory refinement of the structure. The Ln = Ce cell, moreover, was anomalously small, although seemingly isomorphous with the Ln = Pr, Lu adducts, its volume was appreciably below that for the Ln = Pr complex (Table 1). The reason for the instability is unclear, but it is of interest that for the phenyl ring 16*n*, thermal parameters for that ring alone are very substantially higher than in the Ln = La counterpart, suggesting that some reorientation of the molecule contingent on 'discomfort' in that component may be associated with the phase transition observed between the Ln = La, Pr complexes. The Ln = Ce adduct was successfully reexamined using an Enraf-Nonius CCD instrument operated at 123 K. The resulting data showed that at that temperature the C(16*n*) peripheral thermal parameters remain quite dissimilar to those of the other rings. For Ln = Y, **1**, material was inferior to the other samples. A room-temperature (*ca*. 300 K) study using CCD data is in accord with that of the other samples and fills the extended ionic radius gap between Ln = Nd and Yb.

Crystal/refinement data. $[Ln(Odpp)_3] \equiv C_{54}H_{39}LnO_3$, triclinic, space group $P\bar{1}$ (C^1_i no. 2), $Z = 2$.

(**1**) Ln = Y: $M_r = 824.8$. $D_c = 1.35_0$ g cm^{-3}; $\mu_{Mo} = 14.8$ cm^{-1}; specimen 0.21 × 0.14 × 0.08 mm; $A^*_{min,\ max}$ ('empirical' correction) = 1.11, 2.0. N_t (sphere) = 23503, $N_r = 6958$ ($R_{int} = 0.040$), N_o ($F > 4\sigma(F_o)$) = 4360; $R = 0.076$, $R_w = 0.099$; $n_v = 524$, $|\Delta\rho_{max}| = 1.6$ e Å^{-3}.

(**2**) Ln = La: $M_r = 874.8$. $D_c = 1.41_0$ g cm^{-3}; $\mu_{Mo} = 11.1$ cm^{-1}; specimen 0.2 × 0.2 × 0.4 mm; $A^*_{min,\ max} = 1.19$, 1.27. Unique data, $N_r = 7232$, $N_o = 4192$; $R = 0.044$, $R_w = 0.038$; $n_v = 679$, $|\Delta\rho_{max}| = 0.9$ e Å^{-3}.

(**3**) Ln = Ce: $M_r = 876.0$. ($T = 123$ K) $D_c = 1.46_4$ g cm^{-3}. $\mu_{Mo} = 11.9$ cm^{-1}; specimen 0.18 × 0.20 × 0.25 mm; $A^*_{min,\ max} = 1.17$, 1.49. N_t (sphere; $2\theta_{max} = 60°$) = 17742, $N_r = 10596$; $R = 0.034$, $R_w = 0.082$, ($R = 0.041$, $R_w = 0.089$ all data), $N_o = 9171$; $n_v = 679$, $|\Delta\rho_{max}| = 2.1$ e Å^{-3}.

(**4**) Ln = Pr: M_r 876.8. $D_c = 1.42_5$ g cm^{-3}; $\mu_{Mo} = 12.4$ cm^{-1}; specimen 0.10 × 0.16 × 0.62 mm; $A^*_{min,\ max} = 1.13$, 1.21. N_t (sphere) = 13268, $N_r = 7166$ ($R_{int} = 0.033$), $N_o = 5447$; $R = 0.039$, $R_w = 0.046$; $n_v = 523$, $|\Delta\rho_{max}| = 1.2$ e Å^{-3}.

(**9**) Ln = Lu: $M_r = 910.9$. $D_c = 1.50_4$ g cm^{-3}; $\mu_{Mo} = 25.0$ cm^{-1}; specimen: 0.08 × 0.25 × 0.50 mm; $A^*_{min,\ max} = 1.15$, 1.81. N_t

---

† Owing to the ^{13}C contribution to multicarbon molecules, ions containing ^{144}Nd (and $^{142}Nd^{13}C_2$) are the most intense peaks of some neodymium-containing clusters.

‡ Owing to the ^{13}C contribution to multicarbon molecules, ions formally containing ^{168}Er (and $^{166}Er^{13}C_2$) are the most intense peaks of some erbium-containing clusters.

(combination of 50° and 40° hemispheres) = 11470, $N_r = 7068$ ($R_{int} = 0.048$), $N_o = 4705$; $R = 0.041$, $R_w = 0.048$; $n_v = 523$, $|\Delta\rho_{max}| = 1.2$ e Å^{-3}.

CCDC reference number 186/1830.

See http://www.rsc.org/suppdata/dt/a9/a910277i/ for crystallographic files in .cif format.

Acknowledgements

We are grateful to the Australian Research Council for support, for an Australian Postgraduate Award (to A. G.), and to the Australian Academy of Sciences for an exchange visit by Q. Shen.

References

1 (*a*) F. T. Edelmann, in *Comprehensive Organometallic Chemistry II*, ed. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1995, vol. 4, ch. 2, pp. 11–130; (*b*) H. Schumann, J. A. Meese-Marktscheffel and L. Esser, *Chem. Rev.*, 1995, **95**, 865; (*c*) M. N. Bochkarev, L. N. Zakharov and G. S. Kalinina, *Organoderivatives of the Rare Earth Elements*, Kluwer Academic, Dordrecht, 1995.

2 (*a*) R. Anwander, *Top. Curr. Chem.*, 1998, **179**, 33; (*b*) D. C. Bradley, R. C. Mehrotra and D. P. Gaur, *Metal Alkoxides*, Academic Press, London, 1978, pp. 10–13; (*c*) R. C. Mehrotra, A. Singh and U. M. Tripathi, *Chem. Rev.*, 1991, **91**, 1287; (*d*) L. G. Hubert-Pfalzgraf, *New J. Chem.*, 1995, **19**, 727; (*e*) L. G. Hubert-Pfalzgraf, S. Daniele, A. Bennaceur, J.-C. Daran and J. Vaissermann, *Polyhedron*, 1997, **16**, 1223.

3 (*a*) W. J. Evans, M. A. Greci and J. W. Ziller, *Inorg. Chem.*, 1998, **37**, 5221; (*b*) B. Cetinkaya, P. B. Hitchcock, M. F. Lappert and R. Smith, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 932; (*c*) W. J. Evans, M. A. Greci and J. W. Ziller, *Chem. Commun.*, 1998, 2367; (*d*) W. J. Evans, M. A. Greci and J. W. Ziller, *J. Chem. Soc.*, *Dalton Trans.*, 1997, 3035; (*e*) W. J. Evans, W. G. McClelland, M. A. Greci and J. W. Ziller, *Eur. J. Solid State Inorg. Chem.*, 1996, **33**, 145.

4 G. B. Deacon, A. Gitlits, B. W. Skelton and A. H. White, *Chem. Commun.*, 1999, 1213.

5 G. B. Deacon, C. M. Forsyth, P. C. Junk, B. W. Skelton and A. H. White, *Chem. Eur. J.*, 1999, **5**, 1452.

6 G. B. Deacon and Q. Shen, *J. Organomet. Chem.*, 1996, **511**, 1.

7 G. B. Deacon, S. Nickel, P. MacKinnon and E. R. T. Tiekink, *Aust. J. Chem.*, 1990, **43**, 1245.

8 G. B. Deacon, T. Feng, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1995, **48**, 741.

9 G. B. Deacon, B. M. Gatehouse, Q. Shen, G. N. Ward and E. R. T. Tiekink, *Polyhedron*, 1993, **12**, 1289.

10 G. B. Deacon, T. Feng, P. C. Junk, B. W. Skelton and A. H. White, *Chem. Ber.*, 1997, **130**, 851.

11 W. T. Carnall, in *The Absorption and Fluorescence Spectra of Rare Earth Ions in Solution*, in *Handbook on the Physics and Chemistry of Rare Earths*, ed. K. A. Gschneider and L. Eyring, North-Holland, Amsterdam, 1979, vol. 3, ch. 24, pp. 171–208.

12 G. B. Deacon, T. Feng, P. C. Junk. B. W. Skelton, A. N. Sobolev and A. H. White, *Aust. J. Chem.*, 1998, **51**, 75.

13 H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem.*, 1988, **27**, 1130.

14 (*a*) P. B. Hitchcock, M. F. Lappert and R. G. Smith, *Inorg. Chim. Acta*, 1987, **139**, 183; (*b*) P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc.*, *Chem. Commun.*, 1983, 1499.

15 R. D. Shannon, *Acta Crystallogr.*, *Sect. A*, 1976, **32**, 751.

16 F. A. Cotton and W. Schwotzer, *Organometallics*, 1987, **6**, 1275.

17 B. Fan, Q. Shen and Y. Lin, *J. Organomet. Chem.*, 1989, **377**, 51.

18 R. J. Butcher, D. L. Clark, S. K. Grumbine, R. L. Vincent-Hollis, B. L. Scott and J. G. Watkin, *Inorg. Chem.*, 1995, **34**, 5468.

19 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon, Oxford, 5th edn., 1984, p. 1288.

20 L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, NY, 3rd edn., 1960, p. 261.

21 J. L. Atwood, W. E. Hunter, A. L. Wayda and W. J. Evans, *Inorg. Chem.*, 1981, **20**, 4115.

22 G. M. Sheldrick, Program for Crystal Structure Solution, Universität Göttingen, 1997.

23 G. M. Sheldrick, Program for Crystal Structure Refinement, Universität Göttingen, 1997.

24 S. R. Hall, G. S. D. King and J. M. Stewart (Editors), *Xtal 3.4 User's Manual*, University of Western Australia, Lamb Press, Perth, 1995.

Paper a910277i