

# Diphosphine dioxide complexes of lanthanum and lutetium – The effects of ligand architecture and counter-anion

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## ABSTRACT

The reaction of bis(diphenylphosphino)methane dioxide (dppmO<sub>2</sub>) with LaCl<sub>3</sub>, LaI<sub>3</sub> or LaCl<sub>3</sub>/[NH<sub>4</sub>][PF<sub>6</sub>] produces [La(dppmO<sub>2</sub>)<sub>4</sub>Y<sub>3</sub> (Y = Cl, I, PF<sub>6</sub>) which contain eight-coordinate, distorted square antiprismatic cations. In contrast, LaCl<sub>3</sub> or LaCl<sub>3</sub>/[NH<sub>4</sub>][PF<sub>6</sub>] and 1,2-bis(diphenylphosphino)ethane dioxide (dppeO<sub>2</sub>) produce the polymer [LaCl<sub>3</sub>(dppeO<sub>2</sub>)<sub>1.5</sub>]<sub>n</sub>, which has a six-coordinate La centre with three *mer*-chlorides and three Ph<sub>2</sub>P(O)CH<sub>2</sub>-donors from three different diphosphine dioxide ligands. The bulkier 1,2-bis(diphenylphosphino)benzene dioxide (PPO<sub>2</sub>) forms [LaCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl and [LaCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][PF<sub>6</sub>], which contain eight-coordinate La, and also the seven-coordinate [LaCl(PPO<sub>2</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>. The smaller lutetium ion favours six-coordination in [LuCl<sub>2</sub>(dppmO<sub>2</sub>)<sub>2</sub>]Cl, [LuI<sub>2</sub>(dppmO<sub>2</sub>)<sub>2</sub>]I, [LuCl(dppmO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)][PF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O, [LuCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>]Cl, [LuI<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>]I and [Lu(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub>. All complexes were characterised by microanalysis, IR, <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. X-ray crystal structures are reported for [La(dppmO<sub>2</sub>)<sub>4</sub>Y<sub>3</sub> (Y = I, PF<sub>6</sub>), [LaCl<sub>3</sub>(dppeO<sub>2</sub>)<sub>1.5</sub>]<sub>n</sub>, [LaCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(EtOH)]Cl and [LaCl(PPO<sub>2</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>.

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## 1. Introduction

The coordination chemistries of the lanthanide elements are often viewed as very similar, with the main changes due to the lanthanide contraction, the reduction in the radius of the M<sup>3+</sup> ions between La (1.22 Å) and Lu (0.85 Å), and thus at some point in the series a reduction in coordination number may be driven by steric effects. However, the decrease in radius also results in an increase in the charge/radius ratio along the series and this can have significant effects on the ligand preferences, and depending upon the interplay of steric and electronic effects, discontinuities can occur at different points along the series [1–3]. Phosphine oxides (R<sub>3</sub>PO) have proved popular ligands for lanthanide ions, and examples with a wide variety of R-groups have been reported, the majority of the work using oxygen donor anions, typically nitrate, carboxylate or triflate [4]. The effects of halide counter anions have been less studied. Thus, in acetone or ethanol solutions of LnCl<sub>3</sub> and Ph<sub>3</sub>PO, <sup>31</sup>P{<sup>1</sup>H} NMR spectra show both [Ln(Ph<sub>3</sub>PO)<sub>3</sub>Cl<sub>3</sub>] and [Ln(Ph<sub>3</sub>PO)<sub>4</sub>Cl<sub>2</sub>]Cl are present, the former being the major species for early lanthanides, the latter becoming favoured later in the series [5]. The pure [Ln(Ph<sub>3</sub>PO)<sub>3</sub>Cl<sub>3</sub>] can be isolated from acetone solution and [Ln(Ph<sub>3</sub>PO)<sub>4</sub>Cl<sub>2</sub>]Cl from EtOH (the effect of solvent is often overlooked in lanthanide chemistry [3]). For the

softer bromide or iodide co-ligands the [Ln(Ph<sub>3</sub>PO)<sub>4</sub>X<sub>2</sub>]X (X = Br or I) are usually formed [6,7]. Use of very weakly coordinating anions, such as [PF<sub>6</sub>]<sup>−</sup>, can generate homoleptic cations, such as [Ln(Me<sub>3</sub>PO)<sub>6</sub>][PF<sub>6</sub>]<sub>3</sub> for all the lanthanides [8].

Diphosphine dioxide and higher denticity phosphine oxide complexes are rarer [4], although some examples of the former have received significant study in recent years. Bis(diphenylphosphino)methane dioxide, Ph<sub>2</sub>P(O)CH<sub>2</sub>P(O)Ph<sub>2</sub> (dppmO<sub>2</sub>) typically behaves as a chelate forming six-membered rings in the triflate complexes (8-coordinate) [La(dppmO<sub>2</sub>)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub> and [Dy(dppmO<sub>2</sub>)<sub>4</sub>][CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub> and (7-coordinate) [Lu(dppmO<sub>2</sub>)<sub>3</sub>(H<sub>2</sub>O)][CF<sub>3</sub>SO<sub>3</sub>]<sub>3</sub> [9,10]. The dppmO<sub>2</sub>/Ln(NO<sub>3</sub>)<sub>3</sub> systems are more complicated, with [Ln(dppmO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>][Ln(dppmO<sub>2</sub>)(NO<sub>3</sub>)<sub>4</sub>], [Ln(dppmO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] and [Ln(dppmO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)][NO<sub>3</sub>] isolated depending upon the conditions, the solvent and the specific Ln involved [11]. Increasing the inter-donor linkage, as in Ph<sub>2</sub>P(O)(CH<sub>2</sub>)<sub>n</sub>P(O)Ph<sub>2</sub> (n = 2, 4 or 6) disfavours chelation and di- or polymeric structures are formed with bridging diphosphine dioxides [12–14].

In the present study we have explored the chemistry and structures of complexes formed by lanthanum or lutetium chloride and iodide, with and without added [PF<sub>6</sub>]<sup>−</sup> anions, with three diphosphine dioxides, viz Ph<sub>2</sub>P(O)CH<sub>2</sub>P(O)Ph<sub>2</sub> (dppmO<sub>2</sub>), Ph<sub>2</sub>P(O)CH<sub>2</sub>CH<sub>2</sub>P(O)Ph<sub>2</sub> (dppeO<sub>2</sub>), and *o*-C<sub>6</sub>H<sub>4</sub>(P(O)Ph<sub>2</sub>)<sub>2</sub> (PPO<sub>2</sub>), in order to explore the interplay of anions and ligand architecture upon the complexes formed.

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## 2. Results and discussion

### 2.1. Lanthanum–dppmO<sub>2</sub> complexes

The reaction of LaCl<sub>3</sub>·7H<sub>2</sub>O, LaI<sub>3</sub> and LaCl<sub>3</sub>·7H<sub>2</sub>O + 3 equivalents of [NH<sub>4</sub>][PF<sub>6</sub>], in ethanol with four equivalents of dppmO<sub>2</sub> gave the complexes [La(dppmO<sub>2</sub>)<sub>4</sub>]Cl<sub>3</sub>·4H<sub>2</sub>O, [La(dppmO<sub>2</sub>)<sub>4</sub>]I<sub>3</sub>·2H<sub>2</sub>O, and [La(dppmO<sub>2</sub>)<sub>4</sub>][PF<sub>6</sub>]<sub>3</sub>, respectively. Like other examples, these lanthanide phosphine oxide complexes are prone to retain variable amounts of solvent or water in the lattice, which are not removed by prolonged pumping *in vacuo* [4–6,9], a consequence of the large voids produced by the bulky asymmetric ligands. Although these non-stoichiometric solvate molecules make only small differences to the analytical results, they are evident in the spectroscopic data and in the X-ray crystal structures, where they are often difficult to model. The presence of the same [La(dppmO<sub>2</sub>)<sub>4</sub>]<sup>3+</sup> cation in all three salts is confirmed by the <sup>31</sup>P{<sup>1</sup>H} NMR spectra in CH<sub>2</sub>Cl<sub>2</sub>/CD<sub>2</sub>Cl<sub>2</sub> solution which show a singlet with a near identical chemical shifts. The <sup>1</sup>H NMR spectra are also identical, except for resonances due to some solvate EtOH or water. The solubility in CH<sub>2</sub>Cl<sub>2</sub> is rather poor (but adequate) and the NMR spectra were also recorded in CD<sub>3</sub>OD where solubility was much better, giving very similar chemical shifts. The <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts of dppmO<sub>2</sub> are δP = 25.3 in CH<sub>2</sub>Cl<sub>2</sub> and δP = 29.9 in MeOH and there is no evidence that methanol displaces the dppmO<sub>2</sub> from lanthanum. The residual proton signals in CD<sub>3</sub>OD are near coincident with the δ(CH<sub>2</sub>) resonance in the dppmO<sub>2</sub> in the <sup>1</sup>H NMR spectra, hence measurements were carried out in both solvents. The IR spectra also show two ν(PO) vibrations for each complex, again at identical energies (1160, 1100 cm<sup>−1</sup>) consistent with the same cation, essentially uninfluenced by the anion present. Confirmation of the presence of the [La(dppmO<sub>2</sub>)<sub>4</sub>]<sup>3+</sup> cation was provided by the X-ray crystal structures of [La(dppmO<sub>2</sub>)<sub>4</sub>][PF<sub>6</sub>]<sub>3</sub> and [La(dppmO<sub>2</sub>)<sub>4</sub>][I<sub>3</sub>][I]<sub>2</sub>. The distorted square antiprismatic cations [Ln(dppmO<sub>2</sub>)<sub>4</sub>]<sup>3+</sup>

(Ln = La, Dy) have previously been characterised as triflate salts [9,10]. The core of the [La(dppmO<sub>2</sub>)<sub>4</sub>]<sup>3+</sup> is shown in Fig. 1.

Pale yellow brown crystals grown from ethanolic solutions of [La(dppmO<sub>2</sub>)<sub>4</sub>][I<sub>3</sub>·2H<sub>2</sub>O] were found to contain [La(dppmO<sub>2</sub>)<sub>4</sub>][I<sub>3</sub>][I]<sub>2</sub>. The crystal quality was modest, but the data confirm the presence of the [La(dppmO<sub>2</sub>)<sub>4</sub>]<sup>3+</sup> cation. These data are presented in Table S1 (Appendix A). The formation of the [I<sub>3</sub>]<sup>−</sup> anion is due to oxidation of I<sup>−</sup> by traces of dioxygen, an effect observed in other lanthanide iodide systems [15]. The LaO<sub>8</sub> coordination environment provided by the four chelating dppmO<sub>2</sub> ligands is thus found with Cl, I, PF<sub>6</sub> and CF<sub>3</sub>SO<sub>3</sub> [9] anions, only the strongly coordinating nitrate ions can compete for binding to the lanthanum as in [La(dppmO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] [11].

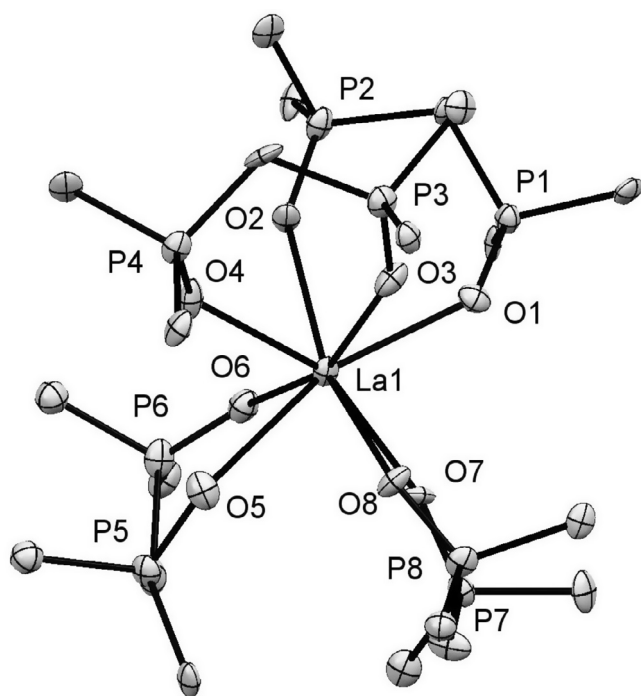
### 2.2. Lanthanum–dppeO<sub>2</sub> complexes

In contrast, reaction of LaCl<sub>3</sub>·7H<sub>2</sub>O with dppeO<sub>2</sub> in EtOH, irrespective of the ratio of reactants, produced the polymer [LaCl<sub>3</sub>(dppeO<sub>2</sub>)<sub>1.5</sub>]<sub>n</sub>·nEtOH. The same complex was obtained even in the presence of excess [NH<sub>4</sub>][PF<sub>6</sub>] and the reaction is clearly driven by precipitation of the polymer. The lanthanum environment is shown in Fig. 2, and part of the extended structure in Fig. S2 (Appendix A).

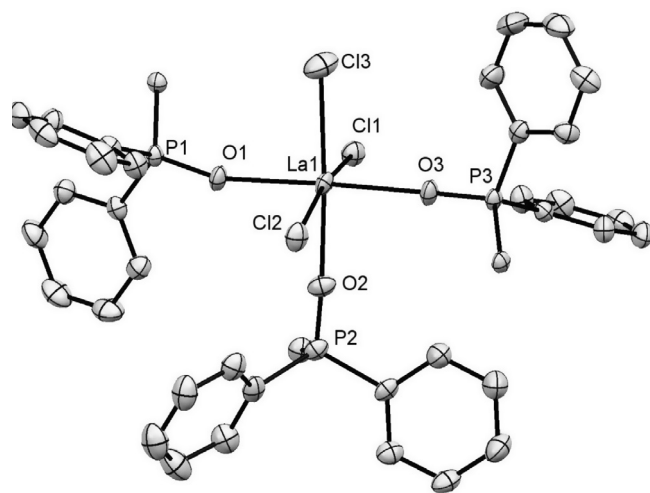
The lanthanum is in a distorted octahedral environment composed of three chlorides and three phosphine oxide groups from three different dppeO<sub>2</sub> ligands, each in a *mer* geometry. The polymer assembles via the bridging dppeO<sub>2</sub> units. Spical et al. [12] reported similar complexes with Nd and Gd and the present complex is isomorphous.

### 2.3. Lanthanum–PPO<sub>2</sub> complexes

The diphosphine dioxides, dppeO<sub>2</sub> and PPO<sub>2</sub>, both produce seven-membered rings upon chelation, but the latter is pre-organised for chelation, as well as being bulkier. These different steric effects would be expected to lead to different geometries or coordination numbers, even on a large metal ion like La<sup>3+</sup>. The reaction of LaCl<sub>3</sub>·7H<sub>2</sub>O with four equivalents of PPO<sub>2</sub> in ethanol



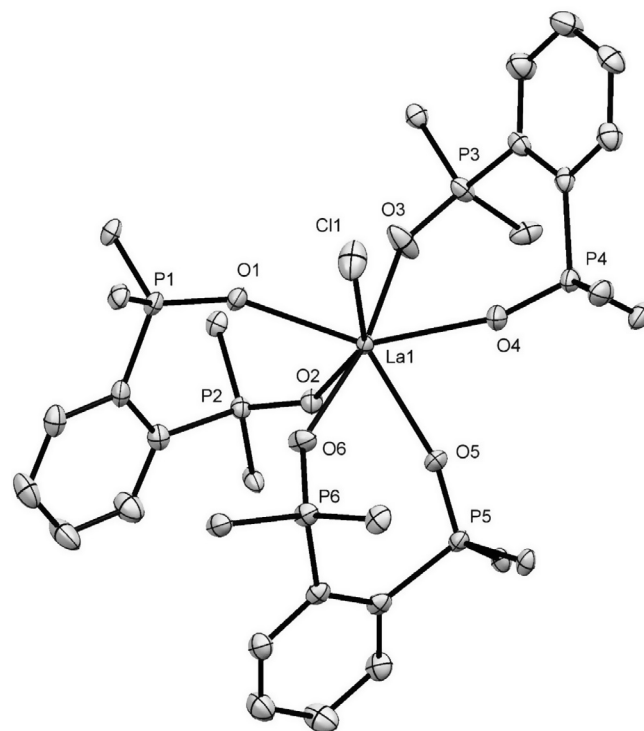
**Fig. 1.** The core geometry of the cation in [La(dppmO<sub>2</sub>)<sub>4</sub>][PF<sub>6</sub>]<sub>3</sub> with atom numbering scheme. H atoms are omitted and only the *ipso* carbons of the phenyl rings are shown for clarity. Selected bond lengths (Å) and angles (°): La–O = 2.471(8)–2.565(7), (*cis*) O–La–O = 70.4(2)–99.3(3).



**Fig. 2.** The lanthanum coordination environment present in the polymer [LaCl<sub>3</sub>(dppeO<sub>2</sub>)<sub>1.5</sub>]<sub>n</sub> with atom numbering scheme. H atoms are omitted for clarity. Only the OPPh<sub>2</sub>CH<sub>2</sub> fragment from each of the distinct ligands is shown. Selected bond lengths (Å) and angles (°) are: La1–O1 = 2.375(3), La1–O3 = 2.382(3), La1–O2 = 2.414(3), La1–Cl3 = 2.7170(16), La1–Cl2 = 2.7892(14), La1–Cl1 = 2.8005(14), O1–La1–O2 = 86.97(11), O3–La1–O2 = 92.12(11), O1–La1–Cl3 = 89.38(8), O3–La1–Cl3 = 91.71(8), O1–La1–Cl2 = 89.59(8), O3–La1–Cl2 = 87.07(8), O2–La1–Cl2 = 85.89(8), Cl3–La1–Cl2 = 97.44(4), O1–La1–Cl1 = 90.78(8), O3–La1–Cl1 = 92.36(8), O2–La1–Cl1 = 82.88(8), Cl3–La1–Cl1 = 93.82(4).

produced a white powder on work-up, with composition  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$ . In the presence of  $[\text{NH}_4][\text{PF}_6]$ , the product was  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2][\text{PF}_6]$ , in both cases the formulation is confirmed by the microanalytical data. The  $[\text{PF}_6]^-$  vibrations apart, the IR spectra of the two complexes also show the presence of the same cation, in particular, the  $\nu(\text{PO})$  were identical. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$  were different in  $\text{CD}_2\text{Cl}_2$  and  $\text{CD}_3\text{OD}$  solutions, with singlets at  $\delta = 40.1$  ( $\text{CD}_3\text{OD}$ ) and  $\delta = 35.5$  ( $\text{CD}_2\text{Cl}_2$ ). The  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances for  $\text{PPO}_2$  are  $\delta\text{P} = 31.4$  in  $\text{CH}_2\text{Cl}_2$  and  $\delta\text{P} = 37.5$  in  $\text{MeOH}$ . A crystal grown from an  $\text{EtOH}$  solution showed the formation of  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})(\text{EtOH})]\text{Cl}$  (Fig. 3), which strongly suggests that the differing  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts can be accounted for by changes in speciation, with  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$  present in the non-coordinating  $\text{CH}_2\text{Cl}_2$  and  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_{2-x}(\text{ROH})_x]\text{Cl}$  in  $\text{CD}_3\text{OD}$  with the alcohol competing with the water for the lanthanum centre. There is no evidence that alcohols displace the  $\text{PPO}_2$  from lanthanum.

In a separate experiment a few crystals were grown from an  $\text{EtOH}$  solution of  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2][\text{PF}_6]$ . These proved, upon structure solution, to be a rearrangement product,  $[\text{LaCl}(\text{PPO}_2)_3][\text{PF}_6]_2$ , with three chelating  $\text{PPO}_2$  ligands on a seven-coordinate, distorted capped octahedral lanthanum centre. The capping chloride ligand was disordered over two sites, but this was satisfactorily modelled (Fig. 4). The crystallisation of different complexes from solution is a common observation in lanthanide coordination chemistry, for example  $[\text{Ln}(\text{Ph}_3\text{PO})_3(\text{NO}_3)_3]$  or  $[\text{Ln}(\text{Ph}_3\text{PO})_2(\text{EtOH})(\text{NO}_3)_3]$  crystallise from ethanol solutions of  $\text{Ln}(\text{NO}_3)_3 + \text{Ph}_3\text{PO}$  under very similar conditions [4,5,16,17]. The formation of a *tris*- $\text{PPO}_2$  complex compared with the *tetrakis*- $\text{dppmO}_2$  cation described above, is probably a consequence of the greater steric demands of  $\text{PPO}_2$ . In the  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2]^+$  and  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})(\text{EtOH})]^+$ , two chelating  $\text{PPO}_2$  ligands are present and the large lanthanum centre achieves eight-coordination by binding four smaller ligands. Seven-coordination with three  $\text{PPO}_2$  ligands and one chloride is also possible, as in  $[\text{LaCl}(\text{PPO}_2)_3][\text{PF}_6]_2$ , but

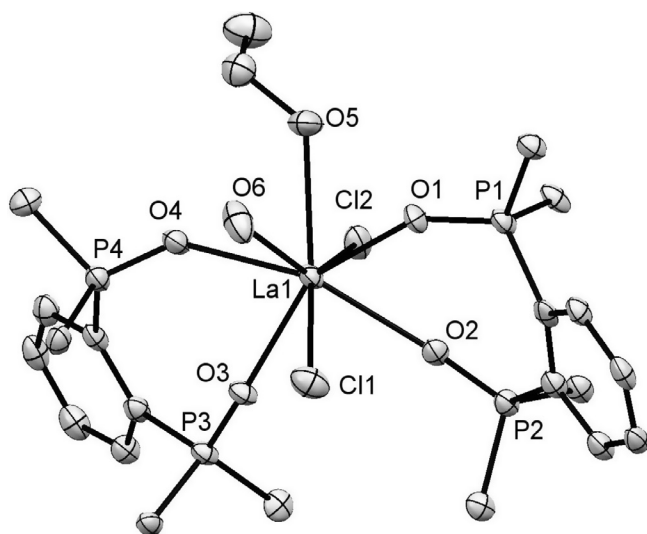


**Fig. 4.** The structure of the cation in  $[\text{LaCl}(\text{PPO}_2)_3][\text{PF}_6]_2$  with atom numbering scheme. H atoms are omitted for clarity. The chloride was disordered over two sites in the ratio 9:1 and only the major form one is shown. Selected bond lengths (Å) and angles ( $^\circ$ ) are: La1–O3 = 2.413(4), La1–O6 = 2.413(4), La1–O4 = 2.436(4), La1–O5 = 2.450(3), La1–O2 = 2.453(3), La1–O1 = 2.454(3), La1–Cl1A = 2.747(15), O3–La1–O4 = 70.52(14), O6–La1–O5 = 70.53(12), O4–La1–O5 = 71.16(12), O3–La1–O2 = 87.22(13), O6–La1–O2 = 86.64(13), O5–La1–O2 = 77.50(12), O3–La1–O1 = 86.09(14), O6–La1–O1 = 82.71(13), O2–La1–O1 = 70.49(11), O3–La1–Cl1A = 61.9(6), O6–La1–Cl1A = 116.3(6), O4–La1–Cl1A = 79.8(5).

eight-coordination with a *tetrakis*- $\text{PPO}_2$  cation is probably ruled out on steric grounds.

#### 2.4. Lutetium-*dppmO*<sub>2</sub> complexes

The reaction of  $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  with three equivalents of *dppmO*<sub>2</sub> in ethanol gave a *bis*-*dppmO*<sub>2</sub> complex on the basis of microanalytical data, which was formulated as  $[\text{LuCl}_2(\text{dppmO}_2)_2]\text{Cl}$ , containing six-coordinate lutetium. Lutetium iodide formed the corresponding  $[\text{LuI}_2(\text{dppmO}_2)_2]\text{I}$ . The IR spectra of each complex showed two  $\nu(\text{PO})$  stretches at slightly different frequencies, reflecting the different halides present. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the  $[\text{LuCl}_2(\text{dppmO}_2)_2]\text{Cl}$  in  $\text{CH}_2\text{Cl}_2$ , in which it was poorly soluble, was a singlet at  $\delta = 36.3$ , whilst in  $\text{MeOH}$  solution the resonance was at  $\delta = 39.1$ . This seems too large a difference to be a solvent shift, probably suggesting that the  $\text{MeOH}$  displaced the coordinated chloride as in some of the lanthanum complexes described above. The reaction of  $\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  with three equivalents of *dppmO*<sub>2</sub> in the presence of  $[\text{NH}_4][\text{PF}_6]$  gave a complex of microanalytical composition  $[\text{LuCl}(\text{dppmO}_2)_2][\text{PF}_6]_2 \cdot 3\text{H}_2\text{O}$ . The presence of a six-coordinate cation,  $[\text{LuCl}(\text{dppmO}_2)_2(\text{H}_2\text{O})]^+$  seems highly probable. There is again a 4 ppm difference between the  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts of the cation in  $\text{CH}_2\text{Cl}_2$  and  $\text{MeOH}$ , probably due to some displacement of the chloride or water ligand in  $\text{MeOH}$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $[\text{LuI}_2(\text{dppmO}_2)_2]\text{I}$  in  $\text{CH}_2\text{Cl}_2$  solution shows four sharp resonances suggesting a mixture of species present in solution which are not undergoing fast exchange on the NMR timescale. None of the resonances corresponded to that of free diphosphine dioxide. Previous studies of  $\text{LnCl}_3/\text{Ph}_3\text{PO}$  system



**Fig. 3.** The structure of the cation in  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})(\text{EtOH})]\text{Cl} \cdot 3.5\text{EtOH}$  with atom numbering scheme. H atoms are omitted for clarity. Selected bond lengths (Å) and angles ( $^\circ$ ) are: La1–O3 = 2.448(3), La1–O1 = 2.458(3), La1–O2 = 2.493(3), La1–O4 = 2.523(4), La1–O5 = 2.607(4), La1–O6 = 2.637(4), La1–Cl2 = 2.8261(14), La1–Cl1 = 2.9073(15), Cl2–La1–Cl1 = 150.01(4), O3–La1–O2 = 86.32(11), O1–La1–O2 = 71.15(11), O3–La1–O4 = 68.65(11), O1–La1–O5 = 68.61(12), O4–La1–O5 = 74.15(11), O1–La1–O6 = 74.85(12), O4–La1–O6 = 76.76(12), O5–La1–O6 = 69.25(13), O3–La1–Cl2 = 87.91(8), O2–La1–Cl2 = 74.67(8), O4–La1–Cl2 = 83.20(8), O5–La1–Cl2 = 77.75(10), O3–La1–Cl1 = 77.15(8), O1–La1–Cl1 = 79.02(9), O2–La1–Cl1 = 78.51(8), O6–La1–Cl1 = 65.05(11).

showed slow exchange between *tris*- and *tetrakis*-LuCl<sub>3</sub>–Ph<sub>3</sub>PO complexes, whereas the lanthanum systems showed only single broad resonances due to fast exchange [5]. Unfortunately, none of the lutetium–dppmO<sub>2</sub> complexes afforded X-ray quality crystals despite numerous attempts, but the presence of six-coordinate lutetium centres appears likely, and in contrast to the higher coordination numbers found in the lanthanum complexes.

### 2.5. Lutetium–PPO<sub>2</sub> complexes

The lutetium–PPO<sub>2</sub> complexes isolated were [LuCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>]Cl, [Lu(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][PF<sub>6</sub>]<sub>3</sub> and [Lu<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>]I, all based upon six-coordinate lutetium. The solution <sup>31</sup>P{<sup>1</sup>H} NMR spectra show a single sharp resonance for each complex, consistent with the presence of one significant species in each with equivalent phosphine oxide groups [5,15].

## 3. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range 4000–200 cm<sup>−1</sup>. <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded using a Bruker AV-II 400 spectrometer and are referenced to the protio resonance of the solvent, and 85% H<sub>3</sub>PO<sub>4</sub>, respectively. Microanalyses were undertaken by London Metropolitan University. Lanthanum and lutetium salts, solvents and other reagents were obtained from Sigma–Aldrich and used as received. The diphosphine dioxides were obtained by air-oxidation of the corresponding diphosphines in anhydrous CH<sub>2</sub>Cl<sub>2</sub> solution catalysed by SnI<sub>4</sub> [18]. Syntheses were routinely carried out under a dinitrogen atmosphere, which is essential in the case of the iodide complexes to prevent polyiodide formation [15].

### 3.1. [La(dppmO<sub>2</sub>)<sub>4</sub>]Cl<sub>3</sub>·4H<sub>2</sub>O

LaCl<sub>3</sub>·7H<sub>2</sub>O (0.025 g, 0.067 mmol) was dissolved in ethanol (10 mL). DppmO<sub>2</sub> (0.11 g, 0.264 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture and stirred for 16 h. The solution was concentrated, cooled at −4 °C overnight and then filtered. The resulting white solid was washed with *n*-hexane (5 mL) then ice-cold ethanol (10 mL) and dried *in vacuo*. Yield: 0.045 g, 34%. Required for C<sub>100</sub>H<sub>96</sub>LaO<sub>12</sub>P<sub>8</sub> (1982.9): C, 60.57; H, 4.88. Found: C, 60.41; H, 4.56%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.56 (s, H<sub>2</sub>O), 3.36 (m, [2H]), 7.15 (br, [8H]), 7.37 (br, [4H]), 7.84 (br, [8H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 33.1 (s). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 3500 vbr, 1623 m (H<sub>2</sub>O), 1159 s, 1100 m (PO).

### 3.2. [La(dppmO<sub>2</sub>)<sub>4</sub>][PF<sub>6</sub>]<sub>3</sub>

LaCl<sub>3</sub>·7H<sub>2</sub>O (0.025 g, 0.067 mmol) and [NH<sub>4</sub>][PF<sub>6</sub>] (0.033 g, 0.202 mmol) were dissolved in ethanol (10 mL). DppmO<sub>2</sub> (0.11 g, 0.264 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture which immediately became cloudy. The resulting mixture was stirred for 16 h. The solvent was removed *in vacuo* and the residual white solid was washed with *n*-hexane (5 mL) then cold ethanol (10 mL), the solid separated and dried *in vacuo*. Yield: 0.097 g, 65%. Required for C<sub>100</sub>H<sub>88</sub>F<sub>18</sub>LaO<sub>8</sub>P<sub>11</sub> (2239.3): C, 53.64; H, 3.96. Found: C, 53.50; H, 3.79%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 3.30 (t, [2H], <sup>2</sup>J<sub>HP</sub> = 12 Hz), 7.13 (m, [8H]), 7.74 (m, [4H]), 7.64 (m, [8H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 33.5 (s, [8P], PO), −143.6 (sept, [3P], PF<sub>6</sub>). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 1157 s, 1098 m (PO), 836 s (PF<sub>6</sub>), 557 s (PF<sub>6</sub>). Crystals were grown by layering a solution of dppmO<sub>2</sub> in ethanol on top of a solution of LaCl<sub>3</sub>·7H<sub>2</sub>O and [NH<sub>4</sub>][PF<sub>6</sub>] (4:1:3 M ratio) in ethanol.

### 3.3. [La(dppmO<sub>2</sub>)<sub>4</sub>]I<sub>3</sub>·2H<sub>2</sub>O

DppmO<sub>2</sub> (0.16 g, 0.385 mmol) was dissolved in dry ethanol (15 mL). LaI<sub>3</sub> (0.05 g, 0.096 mmol) dissolved in dry ethanol (10 mL), under nitrogen, was then added to the ligand solution and stirred for 16 h. The solvent was removed *in vacuo*, and the residual bright yellow solid was washed with dry dichloromethane (5 mL) and dried *in vacuo*. Yield: 0.151 g, 71%. Required for C<sub>100</sub>H<sub>92</sub>I<sub>3</sub>LaO<sub>10</sub>P<sub>8</sub> (2185.2): C, 54.07; H, 4.17. Found: C, 52.20; H, 4.21% -the slightly low values reflect some small amounts of [I<sub>3</sub>]<sup>−</sup> present, see discussion. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.56 (s, H<sub>2</sub>O), 3.47 (br, [2H]), 7.12 (s, [4H]), 7.35 (br, [8H]), 7.71 (br, [4H]), 7.95 (br, [4H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD): δ = 33.8 (s, PO). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 3500 vbr, 1623 m (H<sub>2</sub>O), 1161 s, 1098 s (PO). Crystals were grown by layering a solution of dppmO<sub>2</sub> in ethanol on top of a solution of LaI<sub>3</sub> (4:1 M ratio) in ethanol.

### 3.4. [LaCl<sub>3</sub>(dppeO<sub>2</sub>)<sub>1.5</sub>]<sub>n</sub>

LaCl<sub>3</sub>·7H<sub>2</sub>O (0.05 g, 0.135 mmol) was dissolved in ethanol (10 mL). DppeO<sub>2</sub> (0.09 g, 0.21 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture. Solid immediately precipitated out and the mixture was stirred for 16 h. The mixture was filtered and the white solid was washed with *n*-hexane (5 mL) and dried *in vacuo*. Yield: 0.081 g, 67%. Required for C<sub>78</sub>H<sub>72</sub>Cl<sub>6</sub>La<sub>2</sub>O<sub>6</sub>P<sub>6</sub> (1781.76): C, 52.58; H, 4.07. Found: C, 52.68; H, 3.89%. <sup>1</sup>H NMR (CD<sub>3</sub>OD): δ = 2.80 (m, [4H]), 7.46 (m, [8H]), 7.62 (m, [4H]), 7.79 (m, [8H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD): δ = 43.2 (s). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 1144 s, 1091 s (PO). Crystals were grown by layering a solution of dppeO<sub>2</sub> in ethanol on top of a solution of LaCl<sub>3</sub>·7H<sub>2</sub>O (2:1 M ratio) in ethanol.

### 3.5. [LaCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>]Cl

LaCl<sub>3</sub>·7H<sub>2</sub>O (0.01 g, 0.0269 mmol) was dissolved in ethanol (10 mL). 1,2-Bis(diphenylphosphino)benzene dioxide (0.05 g, 0.11 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture and stirred for 16 h. The solvent was removed *in vacuo*, and the residual white solid was washed with *n*-hexane (5 mL) and ice cold ethanol (10 mL) and dried *in vacuo*. Yield: 0.028 g, 84%. Required for C<sub>60</sub>H<sub>52</sub>Cl<sub>3</sub>LaO<sub>6</sub>P<sub>4</sub> (1238.19): C, 58.20; H, 4.23. Found: C, 57.35; H, 3.98%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.67 (s, H<sub>2</sub>O), 7.15 (m), 7.32 (m), 7.50 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD): δ = 40.1 (s, PO); (CD<sub>2</sub>Cl<sub>2</sub>): δ = 35.5. IR spectrum (Nujol mull)/cm<sup>−1</sup>: 1158 s (PO), 1095 s (PO), 208 m (LaCl). Crystals were grown by dissolving the product in ethanol and cooling the solution in a freezer. These were identified as [LaCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)(EtOH)]Cl by X-ray crystallography.

### 3.6. [LaCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>][PF<sub>6</sub>]

LaCl<sub>3</sub>·7H<sub>2</sub>O (0.01 g, 0.027 mmol) and [NH<sub>4</sub>][PF<sub>6</sub>] (0.012 g, 0.081 mmol) were dissolved in ethanol (10 mL). PPO<sub>2</sub> (0.05 g, 0.11 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture and stirred for 16 h, the solution remained clear in this time. The solvent was removed *in vacuo*, and the residual white solid was washed with hexanes (5 mL) then cold ethanol (10 mL) and dried *in vacuo*. Yield: 0.02 g, 65%. Required for C<sub>60</sub>H<sub>52</sub>Cl<sub>2</sub>F<sub>6</sub>LaO<sub>6</sub>P<sub>5</sub> (1347.05): C, 53.45; H, 3.89. Found: C, 53.36; H, 3.72%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ = 1.56 (s, H<sub>2</sub>O), 7.04 (m), 7.26 (m), 7.41 (m), 7.72 (m). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>OD): 40.0 (s, PO), −143.2 (sept, PF<sub>6</sub>); (CD<sub>2</sub>Cl<sub>2</sub>): δ = 35.4 (PO), −143.2 (sept, PF<sub>6</sub>). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 3200 br, 1620 m (H<sub>2</sub>O), 1156 s, 1095 s (PO), 841 s, 559 m (PF<sub>6</sub>). A small number of crystals grown from this complex in ethanol proved to be [LaCl(PPO<sub>2</sub>)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>.



**Table 1**  
Crystallographic data.<sup>a</sup>

Compound	[La(dppmO <sub>2</sub> ) <sub>4</sub> ][PF <sub>6</sub> ] <sub>3</sub> ·2EtOH	[LaCl <sub>3</sub> (dppeO <sub>2</sub> ) <sub>1.5</sub> ] <sub>n</sub> ·nEtOH	[LaCl(PPo <sub>2</sub> ) <sub>3</sub> ][PF <sub>6</sub> ] <sub>2</sub> ·3.5EtOH·2.8H <sub>2</sub> O
Formula	C <sub>104</sub> H <sub>98</sub> F <sub>18</sub> LaO <sub>10</sub> P <sub>11</sub>	C <sub>41</sub> H <sub>42</sub> Cl <sub>13</sub> LaO <sub>4</sub> P <sub>3</sub>	C <sub>97</sub> H <sub>98.6</sub> ClF <sub>12</sub> LaO <sub>12.3</sub> P <sub>8</sub>
<i>M</i>	2329.40	936.92	2111.28
Crystal system	monoclinic	triclinic	triclinic
Space group (no.)	Cc (9)	<i>P</i> $\bar{1}$ (2)	<i>P</i> $\bar{1}$ (2)
<i>a</i> (Å)	19.551(3)	13.049(5)	13.3783(10)
<i>b</i> (Å)	19.565(4)	13.779(5)	14.6431(10)
<i>c</i> (Å)	28.384(5)	14.880(6)	26.1970(10)
$\alpha$ (°)	90	106.674(4)	91.251(2)
$\beta$ (°)	102.974(5)	97.070(2)	90.9680(10)
$\gamma$ (°)	90	116.987(3)	99.7980(10)
<i>U</i> (Å <sup>3</sup> )	10580(3)	2180.9(14)	5054.8(5)
<i>Z</i>	4	2	2
$\mu$ (Mo K $\alpha$ ) (mm <sup>−1</sup> )	0.659	1.311	0.655
<i>F</i> (000)	4744	946	2162
Total number reflections	29447	18685	82915
<i>R</i> <sub>int</sub>	0.082	0.061	0.055
Unique reflections	16131	8545	19883
No. of parameters, restraints	1191, 187	496, 4	1254, 206
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.078, 0.171	0.044, 0.136	0.063, 0.168
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.115, 0.196	0.050, 0.143	0.083, 0.188
Compound	[LaCl <sub>2</sub> (PPo <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O)(EtOH)]Cl·3.5EtOH		
Formula	C <sub>69</sub> H <sub>77</sub> Cl <sub>3</sub> LaO <sub>9.50</sub> P <sub>4</sub>		
<i>M</i>	1427.45		
Crystal system	triclinic		
Space group (no.)	<i>P</i> $\bar{1}$ (2)		
<i>a</i> (Å)	11.463(3)		
<i>b</i> (Å)	11.583(3)		
<i>c</i> (Å)	26.786(4)		
$\alpha$ (°)	79.027(4)		
$\beta$ (°)	85.736(4)		
$\gamma$ (°)	75.822(5)		
<i>U</i> (Å <sup>3</sup> )	3384.0(13)		
<i>Z</i>	2		
$\mu$ (Mo K $\alpha$ ) (mm <sup>−1</sup> )	0.900		
<i>F</i> (000)	1470		
Total number reflections	54018		
<i>R</i> <sub>int</sub>	0.102		
Unique reflections	13311		
No. of parameters, restraints	836, 35		
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.062, 0.159		
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.079, 0.178		

<sup>a</sup> Common data: *T* = 293 K; wavelength (Mo K $\alpha$ ) = 0.71073 Å;  $\theta$ (max) = 27.5°.

<sup>b</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$ .

### 3.7. [LuCl<sub>2</sub>(dppmO<sub>2</sub>)<sub>2</sub>]Cl

LuCl<sub>3</sub>·6H<sub>2</sub>O (0.05 g, 0.13 mmol) was dissolved in ethanol (10 mL). DppmO<sub>2</sub> (0.16 g, 0.39 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture and stirred for 16 h. The solvent was removed *in vacuo* and the residual fawn solid was washed with cold ethanol (5 mL) and dried *in vacuo*. Yield: 0.08 g, 55%. Required for C<sub>52</sub>H<sub>50</sub>Cl<sub>3</sub>LuO<sub>5</sub>P<sub>4</sub> (1160.16): C, 53.84; H, 4.34. Found: C, 53.55; H, 3.65%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 3.72 (br s, [2H]), 7.25 (br s, [8H]), 7.42 (t, [4H]), 7.91 (br s, [8H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 36.4 (s, PO); (CD<sub>3</sub>OD):  $\delta$  = 40.1. IR spectrum (Nujol mull)/cm<sup>−1</sup>: 1158 s, 1098 s (PO).

### 3.8. [LuCl(dppmO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)][PF<sub>6</sub>]<sub>2</sub>·2H<sub>2</sub>O

LuCl<sub>3</sub>·6H<sub>2</sub>O (0.05 g, 0.13 mmol) and [NH<sub>4</sub>][PF<sub>6</sub>] (0.063 g, 0.39 mmol) were dissolved in ethanol (10 mL). DppmO<sub>2</sub> (0.16 g, 0.38 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture which immediately turned cloudy. The resulting mixture was stirred for 16 h. The solvent was removed *in vacuo* and the residual fawn solid was washed with cold ethanol (5 mL) and dried *in vacuo*. Yield: 0.15 g, 85%. Required for C<sub>50</sub>H<sub>50</sub>ClF<sub>12</sub>LuO<sub>7</sub>P<sub>6</sub> (1386.60): C, 43.27; H, 3.63. Found: C, 43.37; H 3.64%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 2.38 (br, H<sub>2</sub>O), 3.84 (br, [2H]), 7.25 (s, [8H]),

7.46 (m, [4H]), 7.66 (m, [8H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 35.8 (s, PO), −143.2 (sept, PF<sub>6</sub>); (CD<sub>3</sub>OD):  $\delta$  = 40.1 (s, PO), −143.2 (sept, PF<sub>6</sub>). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 3200 br, 1620 m (H<sub>2</sub>O), 1152 s, 1096 s (PO), 839 s, 557 s (PF<sub>6</sub>).

### 3.9. [LuI<sub>2</sub>(dppmO<sub>2</sub>)<sub>2</sub>]I

LuI<sub>3</sub> (0.022 g, 0.04 mmol) was dissolved in dry ethanol (10 mL). DppmO<sub>2</sub> (0.05 g, 0.12 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture, which was stirred for 16 h. The solvent was removed *in vacuo* and the resulting product washed with *n*-pentane (5 mL) and ethanol (5 mL) and dried *in vacuo*. Yield: 0.046 g, 82.5%. Required for C<sub>50</sub>H<sub>44</sub>I<sub>3</sub>LuO<sub>4</sub>P<sub>4</sub> (1387.90): C, 43.25; H, 3.19. Found: C, 43.64; H, 3.09%. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  = 4.49 (br s [2H]), 7.21 (s, [8H]), 7.47 (s, [4H]),  $\delta$  7.94 (m, [8H]). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K):  $\delta$  41.4 (s),  $\delta$  40.6 (s),  $\delta$  39.1 (s),  $\delta$  36.0 (s). IR spectrum (Nujol mull)/cm<sup>−1</sup>: 1147 br s, 1094 s (PO).

### 3.10. [LuCl<sub>2</sub>(PPO<sub>2</sub>)<sub>2</sub>]Cl

LuCl<sub>3</sub>·6H<sub>2</sub>O (0.014 g, 0.035 mmol) was dissolved in ethanol (10 mL). PPO<sub>2</sub> (0.05 g, 0.10 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture, which was then stirred for 16 h. The solvent was removed *in vacuo*, and the residual white

solid was washed with *n*-hexane (5 mL) then cold ethanol (10 mL) and dried *in vacuo*. Yield: 0.022 g, 83%. Required for  $\text{C}_{60}\text{H}_{48}\text{Cl}_3\text{LuO}_4\text{P}_4$  (1238.23): C, 58.20; H, 3.91. Found: C, 57.95; H, 4.08%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.25 (br, [8H]), 7.47 (br [16H]).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 42.1 (s, PO), ( $\text{CD}_3\text{OD}$ ):  $\delta$  = 40.7 (s, PO). IR spectrum (Nujol mull)/ $\text{cm}^{-1}$ : 1156 br s, 1094 s (PO).

### 3.11. $[\text{Lu}(\text{PPO}_2)_2(\text{H}_2\text{O})_2][\text{PF}_6]_3$

$\text{LuCl}_3 \cdot 6\text{H}_2\text{O}$  (0.014 g, 0.035 mmol) and  $[\text{NH}_4][\text{PF}_6]$  (0.017 g, 0.105 mmol) were dissolved in ethanol (10 mL).  $\text{PPO}_2$  (0.05 g, 0.104 mmol) dissolved in ethanol (15 mL) was then added to the reaction mixture, which was then stirred for 16 h. The solvent was removed *in vacuo*, and the residual white solid was washed with *n*-hexane (5 mL), then cold ethanol (10 mL) and dried *in vacuo*. Yield: 0.05 g, 90%. Required for  $\text{C}_{60}\text{H}_{52}\text{F}_{18}\text{LuO}_6\text{P}_7$  (1584.78): C, 44.96; H, 3.27. Found: C, 45.61; H, 3.57%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 1.26 (s,  $\text{H}_2\text{O}$ ), 7.26 (br [8H]),  $\delta$  7.42 (br [16H]).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 41.1 (br, PO),  $-143.2$  (sept,  $\text{PF}_6$ ). IR spectrum (Nujol mull)/ $\text{cm}^{-1}$ : 1155 br, 1094 m (PO) 839 s, 560 s ( $\text{PF}_6$ ).

### 3.12. $[\text{Lu}(\text{PPO}_2)_2\text{I}_2]\text{I}$

$\text{LuI}_3$  (0.05 g, 0.088 mmol) was dissolved in dry ethanol (10 mL).  $\text{PPO}_2$  (0.182 g, 0.38 mmol) dissolved in ethanol (15 mL). The solution was stirred for 20 min and then taken to dryness *in vacuo*. The white product was dissolved in acetonitrile and the solution cooled to  $-4^\circ\text{C}$  overnight, resulting in a white powder. This was filtered off and dried *in vacuo*. The solid was finally recrystallised by layering a solution in dichloromethane with *n*-hexane. Yield: 0.055 g, 41%. Required for  $\text{C}_{60}\text{H}_{48}\text{I}_3\text{LuO}_4\text{P}_4$  (1511.93): C, 47.62; H, 3.20. Found: C, 47.84; H, 3.31%.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.00–7.42 (br m).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 42.5 (br). IR spectrum (Nujol mull)/ $\text{cm}^{-1}$ : 1142 s, 1094 s (PO).

### 3.13. X-ray experimental

Details of the crystallographic data collection and refinement parameters are given in Table 1. Crystals suitable for single crystal X-ray analysis were obtained as described above. Data collections used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector mounted at the window of an FR-E+ SuperBright molybdenum ( $\lambda = 0.71073 \text{ \AA}$ ) rotating anode generator with VHF Varimax optics (70  $\mu\text{m}$  focus) with the crystal held at 100 K ( $\text{N}_2$  cryostream). Structure solution and refinements were performed with either  $\text{SHELX(S/L)97}$  or  $\text{SHELX(S/L)2013}$  [19]. All the structures have disordered co-solvent, either water or ethanol. No attempt was made to locate the protons on the co-solvent. For the compound  $[\text{La}(\text{dppmO}_2)_4]\text{I}_3$ , the structure contains two iodides and one triiodide as the counter ions rather than three iodides, although one iodide and the triiodide are refined in a disordered mode and we could not locate all the iodine atoms with full occupancy due to the disorder. For the compound,  $[\text{LaCl}(\text{PPO}_2)_3][\text{PF}_6]_2$ , the fluorine atoms of one  $\text{PF}_6^-$  were refined in a disorder model as well. H atoms bonded to C were placed in calculated positions using the default C–H distance and refined using a riding model. The crystallographic data in cif format have been deposited as CCDC 1538426 ( $[\text{La}(\text{dppmO}_2)_4][\text{I}_3][\text{I}]_2$ ), 1538427 ( $[\text{La}(\text{dppmO}_2)_4][\text{PF}_6]_3 \cdot 2\text{EtOH}$ ), 1538428 ( $[\text{LaCl}(\text{PPO}_2)_3][\text{PF}_6]_2 \cdot 3.5\text{EtOH} \cdot 2.8\text{H}_2\text{O}$ ),

1538429 ( $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})(\text{EtOH})]\text{Cl} \cdot 3.5\text{EtOH}$ ), 1538430 ( $[\text{LaCl}_3(\text{dppeO}_2)_{1.5}]_n\text{EtOH}$ ).

## 4. Conclusions

The large  $\text{La}^{3+}$  ion ( $r = 1.22 \text{ \AA}$ ) readily achieves eight-coordination with four  $\text{dppmO}_2$  ligands involving six-membered chelate rings even in the presence of the coordinating anions Cl or I. In contrast, the extra  $\text{CH}_2$  unit present in the backbone in the  $\text{dppeO}_2$  ligand leads to only polymeric (six-coordinate) species being formed with La. However, the bulkier and more rigid, pre-organised ( $\text{PPO}_2$ ) also forms eight-coordinate La in  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2]\text{Cl}$  and  $[\text{LaCl}_2(\text{PPO}_2)_2(\text{H}_2\text{O})_2][\text{PF}_6]$ , but the coordination sphere is composed of a mixture of two  $\text{PPO}_2$  ligands and four small monodentate ligands ( $\text{Cl}^-$  and  $\text{H}_2\text{O}$ ). Three  $\text{PPO}_2$  ligands are probably the maximum that can be accommodated even on this large metal ion, as in the seven-coordinate  $[\text{LaCl}(\text{PPO}_2)_3][\text{PF}_6]_2$ . The smaller lutetium ion is six-coordinate in all six complexes reported;  $[\text{LuCl}_2(\text{dppmO}_2)_2]\text{Cl}$ ,  $[\text{Lu}_2(\text{dppmO}_2)_2]\text{I}$ ,  $[\text{LuCl}(\text{dppmO}_2)_2(\text{H}_2\text{O})][\text{PF}_6]_2$ ,  $[\text{LuCl}_2(\text{PPO}_2)_2]\text{Cl}$ ,  $[\text{Lu}_2(\text{PPO}_2)_2]\text{I}$  and  $[\text{Lu}(\text{PPO}_2)_2(\text{H}_2\text{O})_2][\text{PF}_6]_3$ .

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## Appendix A. Supplementary data

CCDC 1538426–1538430 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://dx.doi.org/10.1016/j.poly.2017.04.039>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2017.04.039>.

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