Synthesis and Crystal Structure of a Lanthanum Complex with a Diphenylphosphide Ligand†

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Reaction of a solution of $[LaL_3(Ph_3PO)]$ [L = $N(SiMe_3)_2$] with Ph_2PH followed by Ph_3PO yields $[LaL_2(PPh_2)(Ph_3PO)_2]$, which has been isolated as highly air-sensitive orange crystals and characterised by solution NMR spectroscopy (^{31}P and ^1H) and X-ray crystallography. The structure was refined to a final *R* value of 0.056 and shows the complex to have a terminal PPh_2^- ligand with planar co-ordination at P. Variable-temperature ^{31}P NMR spectroscopy indicates rapid exchange between free and co-ordinated Ph_3PO at room temperature but at 193 K is consistent with the solid-state structure with two Ph_3PO ligands.

Complexes of the lanthanides with 'soft' donor ligands are of considerable interest as the possibility of a covalent contribution to the bonding should be maximised in such complexes. There are, however, few reports of lanthanide complexes with second row donor ligands. A small number of lanthanide (Ln) complexes with phosphido ligands have been reported, *e.g.* $[Ln(\eta\text{-}C_5H_5)_2(PPhBu^t)]$,[1] $[Sm(\eta\text{-}C_5H_4Me)_2(PPh_2)]$[2] and $[Lu(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2\{Li(tmen)\}]$ (tmen = *N,N,N',N'*-tetramethylethylenediamine),[3] but only the last has been characterised by X-ray diffraction. Complexes with tertiary phosphine ligands (usually chelating) are slightly less rare, and a number of these have been characterised by X-ray diffraction, e.g. $[Yb(\eta\text{-}C_5Me_5)_2Cl(dmpe)]$ [dmpe = 1,2-bis(dimethylphosphino)ethane][4] and $[Ln(OCBu^t_2CH_2PMe_2)_3]$ (Ln = Y or Nd).[5]

Our interest in the synthesis of lanthanide complexes with phosphido ligands began some years ago with the preparation of $[LnL_2(PPh_2)]$ [Ln = La or Eu, L = $N(SiMe_3)_2$] and $[LnL_2(PPh_2)(Ph_3PO)]$ (Ln = La, Eu or Y) which were characterised in solution by ^{31}P and ^1H NMR spectroscopy, but were far too oxygen- and moisture-sensitive to be isolated and characterised in the solid state.[6] We now report our results on $[LnL_2(PPh_2)(Ph_3PO)_2]$, which is, to our knowledge, the first isolated lanthanide complex with a terminally bound PPh_2^- ligand, and the only example of this ligand with planar co-ordination at P.

Results and Discussion

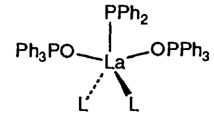
Preparation of $[LaL_2(PPh_2)(Ph_3PO)_2]$.—If a colourless solution of $[LaL_3(Ph_3PO)]$ in toluene is allowed to react at room temperature with 1 equivalent of Ph_2PH, then after several hours an orange solution of $[LaL_2(PPh_2)(Ph_3PO)]$ is produced. Crystals can be isolated from this solution, as already reported,[6] but they are far too oxygen- and moisture-sensitive to be characterised except by solution NMR spectroscopy. We have now found that if this solution is added to a toluene solution of Ph_3PO, then orange crystals, which analyse as $[LaL_2(PPh_2)(Ph_3PO)_2]\cdot nC_7H_8$ $(1 < n < 2)$, are deposited after a period of 2–3 d. It is important that the $[LaL_2(PPh_2)(Ph_3PO)]$ solution is added to the Ph_3PO solution, rather than the reverse, otherwise the reaction takes a different course and deep red crystals containing no La are deposited, and no La containing product can be characterised.

Table 1 Selected bond lengths (Å) and angles (°) for $[LaL_2(PPh_2)(Ph_3PO)_2]$

La–P(1)	3.165(6)	P(2)–O(1)	1.499(8)
La–O(1)	2.472(8)	Si(1)–N(1)	1.71(1)
La–N(1)	2.40(1)	Si(2)–N(1)	1.72(1)
P(1)–C(1)	1.82(2)		
P(1)–La–O(1)	81.4(2)	La–P(1)–C(1)	127.6(6)
P(1)–La–N(1)	123.7(3)	C(1)–P(1)–C(1')	105.0(1)
O(1)–La–O(1')	162.8(4)	La–O(1)–P(2)	162.0(5)
O(1)–La–N(1)	87.1(3)	La–N(1)–Si(1)	117.5(6)
O(1)–La–N(1')	102.5(3)	La–N(1)–Si(2)	121.4(6)
N(1)–La–N(1')	112.7(5)	Si(1)–N(1)–Si(2)	120.9(6)

The crystals of $[LaL_2(PPh_2)(Ph_3PO)_2]$ are highly oxygen- and moisture-sensitive, but, in the absence of air are indefinitely stable at room temperature. After a period of several weeks in solution there is a small amount of decomposition to give Ph_2PPPh_2, identified by ^{31}P NMR spectroscopy as the major phosphorus containing product.

Structure of $[LaL_2(PPh_2)(Ph_3PO)_2]$.—Crystals of $[LaL_2(PPh_2)(Ph_3PO)_2]$ can, with care, be mounted in Lindeman capillaries under an atmosphere of argon, and X-ray crystallography has shown the complex to have the structure shown below, with La being five-co-ordinate. Table 1 gives



selected bond lengths and angles, and Fig. 1 shows a PLUTO plot with the atom numbering scheme. The major feature of interest is the La to PPh_2^- bond. The La–P bond length of 3.165(6) Å can be compared with Lu–P distances of 2.782(1) and 2.813(2) Å in $[Lu(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2\{Li(tmen)\}]$,[3] *i.e.* on average *ca.* 0.37 Å shorter than La–P. Taking account of the decrease in ionic radius on going from La^{3+} to Lu^{3+} (*ca.* 0.17 Å) the Lu–P bonds are shortened further by *ca.* 0.2 Å; this extra shortening of the Lu–P bonds may be due to the greater polarising ability of the smaller Lu^{3+} ion. The La to PPh_2^- bond lies on a crystallographic two-fold axis and therefore the PPh_2^- ligand has unique planar geometry at P, indicating that, as in lanthanide complexes with more conventional 'hard' ligands, the structure is determined by steric factors rather than by maximising interaction with a phosphorus lone pair.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

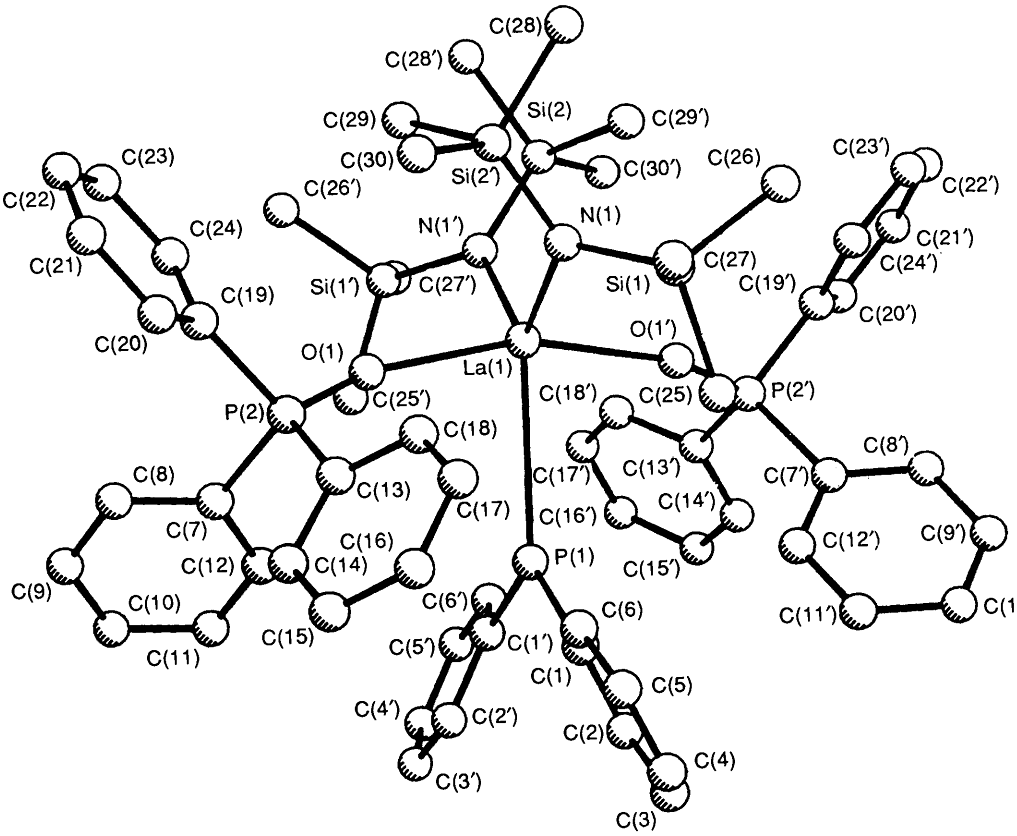

Fig. 1 PLUTO plot of $[LaL_2(PPh_2)(Ph_3PO)_2]$ showing the atom numbering scheme

^{31}P *NMR Studies of* $[LaL_2(PPh_2)(Ph_3PO)_2]$.—At room temperature a broad, unresolved resonance centred at 38 ppm is observed; on lowering the temperature, separate resonances are resolved as shown in Fig. 2. The rather featureless room-temperature spectrum is not too surprising as the ^{31}P spectrum of $[LaL_3(Ph_3PO)]$ is also found to be broad at room temperature due to rapid exchange between free and co-ordinated Ph_3PO, and the quadrupolar ^{139}La nucleus ($I = \frac{7}{2}$) leads to a considerable broadening of the ^{31}P spectrum of $[LaL_2(PPh_2)]$.[6] In the present case it appears that the resonance due to PPh_2^- is so broadened as to be indistinguishable beneath the Ph_3PO resonance. However, on lowering the temperature to 273 K separate resonances due to free (higher field) and co-ordinated (lower field) Ph_3PO are resolved, and at 243 K the PPh_2^- resonance is sufficiently sharp to become visible at *ca.* 25 ppm. At 193 K all the Ph_3PO is co-ordinated, as in the solid-state structure, and the spectrum shows just two resonances: a singlet at 34 ppm due to Ph_3PO and a singlet at 25.2 ppm due to PPh_2^-. As in our studies[6] of $[LnL_2(PPh_2)(Ph_3PO)]$ we have been unable to resolve any $^{31}P-^{31}P$ coupling.

The chemical shift of the PPh_2^- ligand is very similar to that reported for $[LaL_2(PPh_2)]$ (26.5 ppm) but quite different from that reported for $[Lu(\eta\text{-}C_5H_5)_2(\mu\text{-}PPh_2)_2\{Li(tmen)\}]$ (5.68 ppm), and from those found in complexes of the type $[Ln(PPh_2)_3L'_n]$ (Ln = La or Y; L′ = tetrahydrofuran or $MeOCH_2CH_2OMe$) (−16 to −27 ppm),[7] which appears to indicate that there are two distinct modes of bonding of the PPh_2^- ligand to lanthanide centres. As a comparison, the 'ionic' PPh_2^- in $[Li(12\text{-crown-}4)][PPh_2]$ (12-crown-4 = 1,4,7,10-tetraoxacyclododecane) has a chemical shift of −6.9 ppm,[8] and the terminally bound pseudotetrahedral PPh_2^- ligand in $[Li(pmdien)(PPh_2)]$ (pmdien is pentamethyldiethylenetriamine) has a chemical shift of −22.11 ppm at 20 °C.[9] It may be significant that the present case is the only example of a PPh_2^- ligand with planar geometry at P; all other structurally characterised cases have pseudotetrahedral geometry.

Experimental

All manipulations were carried out under an atmosphere of dried and deoxygenated nitrogen using standard Schlenk techniques. Solvents were distilled from sodium benzophenone ketyl and stored over 4 Å molecular sieves under an atmosphere of nitrogen prior to use. Samples for NMR spectroscopy were dissolved in C_6D_6 (^1H) or C_6D_6/C_7H_8 (^{31}P) and sealed under vacuum as previously described.[6] NMR spectra were recorded on a Bruker WM 250 spectrometer; chemical shifts are reported downfield from $SiMe_4$ (^1H) or 85% H_3PO_4 (^{31}P) as external reference. The compound $[LaL_3]$ was prepared by the reported procedure.[10]

Preparation of $[LaL_2(PPh_2)(Ph_3PO)_2]$.—A solution of $[LaL_3]$ (1.22 g, 1.96 mmol) in toluene (15 cm^3) was added to a solution of Ph_3PO (0.54 g, 1 equivalent) in toluene (10 cm^3). Then Ph_2PH (0.34 cm^3, 1 equivalent) was added and the solution left to react at room temperature for 4 h. The resulting deep yellow-orange solution was decanted off from a small amount of fine white precipitate and added to a solution of Ph_3PO (1.09 g, 2 equivalents) in toluene (10 cm^3). After 3 d at room temperature, orange crystals had precipitated. The supernatant was decanted off and the product was recrystallised from toluene to yield orange needles of $[LaL_2(PPh_2)(Ph_3PO)_2]\cdot nC_7H_8$ ($1 < n < 2$). Yield: 0.558 g (22%) (Found: C, 64.05; H, 6.85; N, 2.05. $C_{74}H_{92}LaN_2O_2P_3Si_4$ requires C, 64.40; H, 6.30; N, 2.03; $C_{67}H_{84}LaN_2O_2P_3Si_4$ requires C, 62.20; H, 6.55; N, 2.15%). ^1H NMR (298 K, C_6D_6): δ 0.20 (s, $SiMe_3$), 2.10 (s, Ph*Me*) and 6.5–7.7 (m, aromatics).

Structure Determination of $[LaL_2(PPh_2)(Ph_3PO)_2]$.—*Crystal data.* $C_{67}H_{84}LaN_2O_2P_3Si_4$, $M = 1293.58$, monoclinic, $a = 11.69(2)$, $b = 35.78(1)$, $c = 18.73(2)$ Å, $\beta = 101.2(1)°$, $U = 7684(12)$ Å^3, space group $C2/c$ (no. 15), $Z = 4$, $D_c = 1.118$ g cm^{-3}, $F(000) = 2696$. The cell constants were obtained from 15 carefully centred reflections in the range $6.84 < 2\theta < 10.97°$.

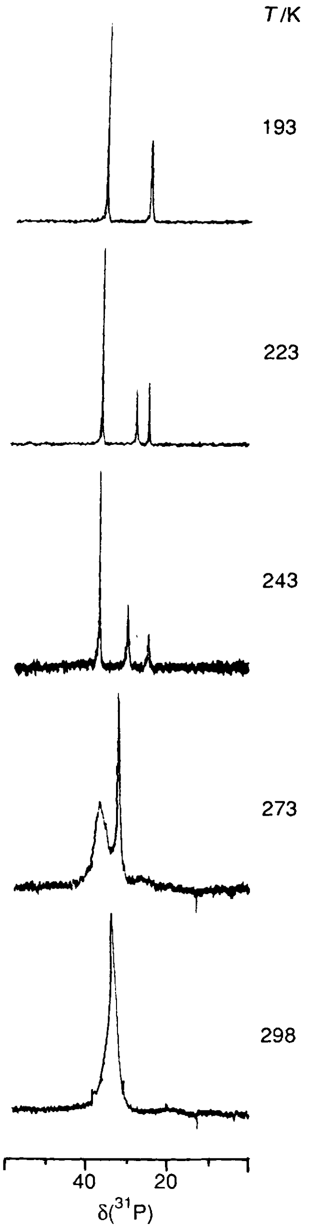

Fig. 2 Variable-temperature ^{31}P NMR spectra of $[LaL_2(PPh_2)(Ph_3PO)_2]$

Orange, air-sensitive plates; crystal dimensions 0.2 × 0.1 × 0.45 mm, μ(Mo-Kα) = 7.16 cm^{-1}. The crystal was sealed under argon in a Lindeman capillary.

Data collection and processing. Rigaku AFC6S diffractometer, ω-2θ mode with ω scan width = 1.10 + 0.30 tanθ, ω scan speed 4.0° min^{-1}, Mo-Kα radiation (λ = 0.710 69 Å); 7316 reflections measured ($1.8 \leqslant \theta \leqslant 25.0°$), of which 6884 were unique. Data were collected at 23 °C; there was no crystal decay during data collection. An empirical absorption correction, based on azimuthal scans of several reflections, was applied which resulted in transmission factors ranging from 0.88 to 1.00. The data were corrected for Lorentz and polarisation effects.

Structure analysis and refinement. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically; hydrogen atom positions were calculated from the riding model; isotropic thermal parameters were refined; positional parameters were not. The final cycle of full-matrix least-squares refinement was based on 2615 observed reflections $[I > 4.00\ \sigma(I)]$ and 352 variable parameters and converged (largest parameter shift was 3.63 times its e.s.d.) with unweighted and weighted agreement factors of $R = 0.056$ and $R' = 0.071$. The maximum and minimum peaks in the final difference Fourier map corresponded to 1.28 and −0.40 e$^-$ Å^{-3}, respectively. The maximum peaks on the final difference map are in the region occupied by one of the toluene solvent molecules. The solvent occupies two sites in the unit cell, with each site having half occupancy (although elemental analysis indicates a non-integral number of solvent molecules per complex in the bulk material). The structure refinement was hampered by disorder in these sites. However as the solvent molecules are well away from the lanthanum complex [nearest C–C distance is C(33)(solvent)–C(22) 4.86 Å] the problems caused by the solvent molecules do not affect the structure of the complex. Neutral atom scattering factors were taken from Cromer and Waber.[11] Anomalous dispersion effects were included in F_{calc};[12] the values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[13] All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation[14] and Fig. 1 drawn using PLUTO.[15] Atomic coordinates are given in Table 2.

Table 2 Fractional atomic coordinates for $[LaL_2(PPh_2)(Ph_3PO)_2]^a$

Atom	*x*	*y*	*z*
La^b	1.000 0	0.134 20(4)	3/4
P(1)^b	1.000 0	0.045 7(2)	3/4
P(2)	1.150 8(3)	0.108 9(1)	0.586 4(2)
Si(1)	0.723 4(4)	0.160 6(1)	0.650 0(2)
Si(2)	0.917 1(4)	0.209 8(1)	0.622 9(3)
O(1)	1.112 5(7)	0.123 9(2)	0.652 8(4)
N(1)	0.869(1)	0.171 4(3)	0.663 9(5)
C(1)	0.892(1)	0.014 8(5)	0.697(1)
C(2)	0.861(2)	−0.019 7(5)	0.722(1)
C(3)	0.772(2)	−0.040 9(5)	0.679(1)
C(4)	0.718(2)	−0.028 1(9)	0.610(1)
C(5)	0.746(2)	0.004 5(7)	0.584(1)
C(6)	0.831(2)	0.024 9(5)	0.626(1)
C(7)	1.268(1)	0.075 1(4)	0.608 6(7)
C(8)	1.362(1)	0.076 6(5)	0.572 8(9)
C(9)	1.451(1)	0.050 6(6)	0.592(1)
C(10)	1.445(2)	0.023 7(6)	0.639(1)
C(11)	1.347(2)	0.022 4(5)	0.673(1)
C(12)	1.263(1)	0.048 1(4)	0.658 2(9)
C(13)	1.032(1)	0.086 4(4)	0.525 9(7)
C(14)	1.051(1)	0.055 4(5)	0.485 0(9)
C(15)	0.957(2)	0.039 6(5)	0.438(1)
C(16)	0.846(2)	0.055 4(6)	0.428(1)
C(17)	0.830(1)	0.086 1(6)	0.469(1)
C(18)	0.921(1)	0.101 6(4)	0.518 1(8)
C(19)	1.204(1)	0.145 5(5)	0.536 5(9)
C(20)	1.177(2)	0.148 4(6)	0.462(1)
C(21)	1.226(3)	0.178(1)	0.429(1)
C(22)	1.300(2)	0.202 7(8)	0.470(2)
C(23)	1.328(2)	0.199 4(7)	0.541(1)
C(24)	1.279(2)	0.170 7(6)	0.574(1)
C(25)	0.704(2)	0.112 3(6)	0.683(1)
C(26)	0.636(1)	0.190 7(6)	0.702(1)
C(27)	0.647(1)	0.162 2(6)	0.554(1)
C(28)	0.828(2)	0.252 8(5)	0.629(1)
C(29)	1.070(1)	0.221 5(5)	0.666(1)
C(30)	0.917(2)	0.204 3(5)	0.524(1)
C(31)^c	1.000 0	0.129(1)	1/4
C(32)^b	1.066(3)	0.191(1)	0.218(2)
C(33)^c	1.000 0	0.198(2)	1/4
C(34)^b	1.048(4)	0.146(1)	0.219(2)
C(35)^c	1/2	0.120(4)	1/4
C(36)^b	0.510(6)	0.152(2)	0.205(4)
C(38)^b	0.494(4)	0.110(2)	0.159(3)
C(39)^b	1.118(4)	0.156(1)	0.194(3)

[a] C(31)–C(29) are solvent. [b] Occupancy 0.5. [c] Occupancy 0.25.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are grateful to the SERC for financial support (Earmarked studentship to S. R. M. and diffractometer), Mr. J. Barkley for assistance with the structure determination, the Nuffield Foundation (Equipment grant to H. C. A.), Johnson Matthey plc for a gift of rare earth oxides and Professor M. B. Hursthouse for carrying out preliminary X-ray studies at Queen Mary College, London.

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Received 8*th July* 1991; *Paper* 1/03431F