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# Pentakis(triphenylphosphine oxide)chlorolanthanide Bis(ferric tetrachloride) Complexes

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## Abstract

Twelve new complexes with the general formula $[(Ph_3P{=}O)_5LnCl][FeCl_4]_2$ where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Y were synthesized. The X-ray diffraction crystal structural analysis of $[(Ph_3P{=}O)_5LaCl][FeCl_4]_2$ showed that the $[(Ph_3P{=}O)_5LaCl]^{2+}$ cation was of six-coordinated distorted octahedral geometry and the $[FeCl_4]^-$ anion was of tetrahedral geometry. The INDO method study revealed that the coordination of P=O groups to the lanthanide made the Ln–Cl bond more reactive than that in $LnCl_3$, so that Lewis acids, such as $FeCl_3$, could abstract chloride to give the title complexes.

## Introduction

Phosphine oxide has a great tendency to coordinate to lanthanide; complexes of formula $(Ph_3P{=}O)_4LnCl_3$ are known [1]. Because the P=O group acts as a Lewis base in the coordination of P=O to lanthanide chloride, the Ln–Cl thus weakens. Under this condition, in the presence of Lewis acids such as $CuCl_2$, the transfer of chloride from lanthanide to copper can happen to give complexes of formula $[(Ph_3P{=}O)_4LnCl_2]^+[CuCl_3]^-$ [2].

It is very interesting that in the presence of stronger Lewis acids, such as $FeCl_3$, the transfer of two chlorides has become possible and a series of new complexes with the general formula $[(Ph_3P{=}O)_5LnCl][FeCl_4]_2$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Y) are prepared and characterized. This is the first observation of the coordination of 5 molecules of phosphine oxide to a lanthanide. Here we report the preparation and structural characterization of these complexes.

## Experimental

### *Synthesis*

Under pure nitrogen 5 mmol of triphenylphosphine oxide, 1.2 mmol of anhydrous lanthanide chloride and 2.4 mmol of ferric chloride were stirred in 20 ml of $CH_2Cl_2$ at room temperature for 6 h. The solution became light yellow. The filtered solution was mixed with 30 ml of petroleum ether (30–60°), a second filtration was carried out for the removal of unreacted $FeCl_3$, and the second portion of petroleum ether (20 ml) was added. The crude product of light yellow solid was collected and recrystallized from $CH_2Cl_2$–petroleum ether. The pure product was dried over $P_2O_5$. The yield was 74–80%, melting point (m.p.) 200 °C. These complexes are stable to heat, insoluble in water, methanol and other nonpolar solvents, but soluble in dichloromethane and chloroform.

Other approaches to the title complexes include the reaction of $[(Ph_3P{=}O)_4LnCl_2][CuCl_3]$ with 2 equivalents of $FeCl_3$, the reaction of $(Ph_3P{=}O)_4LnCl_3$ with 2 equivalents of $FeCl_3$, and the reaction of $(Ph_3P{=}O)_2FeCl_3$ with lanthanide chloride.

Elemental analysis showed the composition of these complexes as $[(Ph_3P{=}O)_5LnCl][FeCl_4]_2$ (see 'Supplementary Material').

### *Characterization and X-ray Diffraction Crystal Structural Analysis*

IR spectra were recorded on a Nicolet FT-IR 5DX spectrometer (400–4600 $cm^{-1}$, KBr disc) and a FT-IR 170 SX spectrometer (100–500 $cm^{-1}$, nujol). $^{31}P$ NMR were obtained on a JEOL NMR FX-90Q spectrometer ($CDCl_3$, 85% $H_3PO_4$ as outer standard).

The single crystal of $[(Ph_3P{=}O)_5LaCl][FeCl_4]_2$ suitable for X-ray diffraction analysis was obtained from a mixed solvent of dichloromethane and petroleum ether on slow evaporation of the solvent. A crystal having approximate dimensions of 0.3 × 0.3 × 0.3 mm was mounted on a glass fiber in a random

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orientation. Preliminary examination and data collection were performed with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. A total of 9421 independent reflections were collected in the range of $2 < \theta < 20°$ by $\omega-2\theta$ scan technique at room temperature, in which 7708 reflections with $I > 3\sigma(I)$ were considered to be observed and used in the succeeding refinement. The corrections for LP factors and for absorption based on a series of scans were applied to the data. The cell parameters and the conditions for data collection are listed in Table 1.

The structure was solved by direct method (MULTAN 82). The La atom was located on an E map. The coordinates of the other non-hydrogen atoms were found in the succeeding difference Fourier syntheses. The hydrogen atoms were not included in the refinement. The final refinement by full matrix least-squares method with isotropic thermal parameters for carbon atoms and anisotropic thermal parameters for the others was converged with unweighted and weighted $R$ factors of 0.062 and 0.069. The highest peak on the final difference Fourier map had a height of 1.08 e/Å$^3$. All calculations were performed on a PDP11/44 computer using the SDP-PLUS program package.

An unrestricted INDO method suitable for lanthanide compounds and the parameters involved were taken from the literature [3, 4]. The structural data of $[(Ph_3P{=}O)_4GdCl_2]^+$ were taken from ref. 2. To simplify the calculations a substitution of phenyl rings by hydrogens was made. This was reasonable because there was no conjugation between the phenyl rings and P=O group and the Gd–O and Gd–Cl bond orders in the simplified model $[(H_3P{=}O)_4GdCl_2]^+$ should be close to the original values.

TABLE 1. Data of X-Ray structure analysis of $[(Ph_3P{=}O)_5LaCl][FeCl_4]_2$

| | |
|---|---|
| Formula | $C_{90}H_{75}Cl_9Fe_2LaO_5P_5$ |
| Molecular weight | 1961 |
| $a$ (Å) | 13.997(3) |
| $b$ (Å) | 15.417(2) |
| $c$ (Å) | 23.329(2) |
| $\alpha$ (°) | 88.49(1) |
| $\beta$ (°) | 76.80(1) |
| $\gamma$ (°) | 87.35(2) |
| $V$ (Å$^3$) | 4895.4 |
| $Z$ | 2 |
| $D_{calc}$ (g cm$^{-3}$) | 1.33 |
| Space group | $P1$, triclinic |
| Space mode | $\omega/2\theta$ |
| Radiation Mo K$\alpha$ | $\lambda$ = 0.71073 |
| $\theta_{max}$ (°) | 20 |
| No. unique reflections | 7708 |
| $R$ | 0.062 |
| $R_w$ | 0.069 |

The four Gd–O bond lengths used were 2.278; 2.280; 2.291; 2.279 Å and the two Gd–Cl bond lengths were 2.646; 2.660 Å. $GdCl_3$ was taken in trigonal planar geometry with a Gd–Cl bond length of 2.496 Å.

## Results and Discussion

### *The Crystal Structure of $[(Ph_3P{=}O)_5LaCl][FeCl_4]_2$ as a Representative of the Title Complexes*

The positional parameters of the non-hydrogen atoms with their estimated standard deviations are given in Table 2. The bond distances and bond angles are given in Tables 3 and 4, respectively.

TABLE 2. Positional parameters and their e.s.d.s

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| La | 0.08750(5) | 0.26061(4) | 0.79627(3) | 2.78(1) |
| O1 | 0.2238(5) | 0.1546(5) | 0.7837(3) | 4.3(2) |
| O2 | 0.1718(5) | 0.3946(5) | 0.7832(3) | 3.9(2) |
| O3 | 0.1247(6) | 0.2526(5) | 0.6913(3) | 4.9(2) |
| O4 | −0.0575(5) | 0.3517(5) | 0.8046(3) | 4.1(2) |
| O5 | −0.0233(6) | 0.1435(5) | 0.8129(4) | 4.5(2) |
| Cl1 | 0.0776(3) | 0.2667(2) | 0.9149(1) | 5.23(8) |
| P1 | 0.2980(2) | 0.0811(2) | 0.7864(2) | 3.93(8) |
| P2 | 0.2282(2) | 0.4643(2) | 0.8029(1) | 3.60(7) |
| P3 | 0.1487(2) | 0.2701(2) | 0.6256(1) | 4.21(8) |
| P4 | −0.1452(2) | 0.4141(2) | 0.8105(1) | 3.61(7) |
| P5 | −0.0928(2) | 0.0716(2) | 0.8318(1) | 3.73(7) |
| C111 | 0.4146(9) | 0.0988(8) | 0.7378(5) | 4.3(3)* |
| C112 | 0.501(1) | 0.0611(9) | 0.7502(6) | 5.6(3)* |
| C113 | 0.590(1) | 0.064(1) | 0.7056(7) | 6.7(4)* |
| C114 | 0.587(1) | 0.105(1) | 0.6539(7) | 7.8(4)* |
| C115 | 0.505(1) | 0.146(1) | 0.6405(8) | 8.8(5)* |
| C116 | 0.413(1) | 0.142(1) | 0.6848(7) | 6.8(4)* |
| C121 | 0.2592(8) | −0.0184(8) | 0.7611(5) | 4.1(3)* |
| C122 | 0.325(1) | −0.092(1) | 0.7527(7) | 6.5(4)* |
| C123 | 0.292(1) | −0.169(1) | 0.7307(8) | 8.0(4)* |
| C124 | 0.201(1) | −0.169(1) | 0.7166(7) | 7.2(4)* |
| C125 | 0.139(1) | −0.095(1) | 0.7246(7) | 6.9(4)* |
| C126 | 0.1682(9) | −0.0187(8) | 0.7476(6) | 5.1(3)* |
| C131 | 0.3183(8) | 0.0679(8) | 0.8594(5) | 4.0(3)* |
| C132 | 0.3086(9) | 0.1426(8) | 0.8930(6) | 5.1(3)* |
| C133 | 0.329(1) | 0.136(1) | 0.9502(7) | 6.4(4)* |
| C134 | 0.357(1) | 0.055(1) | 0.9713(7) | 6.6(4)* |
| C135 | 0.365(1) | −0.018(1) | 0.9379(7) | 7.3(4)* |
| C136 | 0.346(1) | −0.0140(9) | 0.8810(6) | 6.0(3)* |
| C211 | 0.2906(8) | 0.5260(7) | 0.7403(5) | 3.8(2)* |
| C212 | 0.2434(9) | 0.5411(9) | 0.6953(6) | 5.2(3)* |
| C213 | 0.288(1) | 0.593(1) | 0.6461(7) | 7.3(4)* |
| C214 | 0.378(1) | 0.626(1) | 0.6460(7) | 7.4(4)* |
| C215 | 0.425(1) | 0.612(1) | 0.6900(7) | 6.9(4)* |
| C216 | 0.382(1) | 0.5601(9) | 0.7404(6) | 5.5(3)* |
| C221 | 0.3179(9) | 0.4166(8) | 0.8388(5) | 4.3(3)* |
| C222 | 0.393(1) | 0.365(1) | 0.8057(7) | 6.6(4)* |
| C223 | 0.465(1) | 0.323(1) | 0.8331(8) | 7.7(4)* |
| C224 | 0.457(1) | 0.337(1) | 0.8905(8) | 8.2(4)* |
| C225 | 0.380(1) | 0.382(1) | 0.9268(8) | 9.1(5)* |

*(continued)*

TABLE 2. *(continued)*

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| C226 | 0.307(1) | 0.426(1) | 0.8990(7) | 6.8(4)* |
| C231 | 0.1492(8) | 0.5392(7) | 0.8510(5) | 3.7(2)* |
| C232 | 0.0710(9) | 0.5067(9) | 0.8932(6) | 5.2(3)* |
| C233 | 0.007(1) | 0.5655(9) | 0.9320(7) | 6.3(3)* |
| C234 | 0.024(1) | 0.654(1) | 0.9267(7) | 6.4(4)* |
| C235 | 0.101(1) | 0.685(1) | 0.8848(7) | 6.8(4)* |
| C236 | 0.166(1) | 0.6285(9) | 0.8453(6) | 5.5(3)* |
| C311 | 0.0713(8) | 0.3549(8) | 0.6067(5) | 4.1(3)* |
| C312 | 0.108(1) | 0.4347(9) | 0.5820(6) | 5.7(3)* |
| C313 | 0.042(1) | 0.500(1) | 0.5697(7) | 7.4(4)* |
| C314 | −0.059(1) | 0.486(1) | 0.5820(7) | 7.3(4)* |
| C315 | −0.094(1) | 0.4074(9) | 0.6058(7) | 6.3(3)* |
| C316 | −0.0309(9) | 0.3420(9) | 0.6192(6) | 5.1(3)* |
| C321 | 0.1355(9) | 0.1739(8) | 0.5870(6) | 4.6(3)* |
| C322 | 0.091(1) | 0.1794(9) | 0.5385(6) | 5.7(3)* |
| C323 | 0.087(1) | 0.100(1) | 0.5074(7) | 7.0(4)* |
| C324 | 0.125(1) | 0.025(1) | 0.5260(7) | 7.6(4)* |
| C325 | 0.167(1) | 0.018(1) | 0.5740(8) | 8.2(4)* |
| C326 | 0.173(1) | 0.097(1) | 0.6057(7) | 6.5(4)* |
| C331 | 0.2738(9) | 0.3015(8) | 0.6010(6) | 4.7(3)* |
| C332 | 0.316(1) | 0.3457(9) | 0.6383(6) | 5.4(3)* |
| C333 | 0.412(1) | 0.376(1) | 0.6188(7) | 7.5(4)* |
| C334 | 0.460(1) | 0.364(1) | 0.5619(8) | 9.1(5)* |
| C335 | 0.421(2) | 0.318(1) | 0.523(1) | 10.8(6)* |
| C336 | 0.323(1) | 0.283(1) | 0.5423(8) | 8.5(4)* |
| C411 | −0.2239(8) | 0.3819(7) | 0.7647(5) | 3.7(2)* |
| C412 | −0.2236(9) | 0.2935(9) | 0.7538(6) | 5.2(3)* |
| C413 | −0.286(1) | 0.267(1) | 0.7180(7) | 7.1(4)* |
| C414 | −0.344(1) | 0.326(1) | 0.6946(7) | 7.1(4)* |
| C415 | −0.344(1) | 0.413(1) | 0.7056(7) | 6.6(4)* |
| C416 | −0.282(1) | 0.4436(9) | 0.7416(6) | 5.3(3)* |
| C421 | −0.1089(8) | 0.5222(8) | 0.7892(5) | 4.0(3)* |
| C422 | −0.046(1) | 0.5323(9) | 0.7354(6) | 6.1(3)* |
| C423 | −0.013(1) | 0.617(1) | 0.7147(8) | 7.7(4)* |
| C424 | −0.048(1) | 0.685(1) | 0.7517(8) | 7.9(4)* |
| C425 | −0.110(1) | 0.678(1) | 0.8045(8) | 8.6(5)* |
| C426 | −0.145(1) | 0.592(1) | 0.8252(7) | 6.6(4)* |
| C431 | −0.2151(8) | 0.4150(7) | 0.8853(5) | 3.8(2)* |
| C432 | −0.317(1) | 0.4416(9) | 0.8968(6) | 6.0(3)* |
| C433 | −0.369(1) | 0.442(1) | 0.9570(7) | 7.0(4)* |
| C434 | −0.325(1) | 0.4170(9) | 1.0012(6) | 6.1(3)* |
| C435 | −0.226(1) | 0.3909(9) | 0.9896(6) | 6.0(3)* |
| C436 | −0.1700(9) | 0.3897(8) | 0.9299(6) | 4.7(3)* |
| C511 | −0.1068(8) | 0.0159(8) | 0.7680(5) | 4.1(3)* |
| C512 | −0.149(1) | −0.0659(9) | 0.7728(6) | 5.7(3)* |
| C513 | −0.163(1) | −0.103(1) | 0.7211(7) | 6.7(4)* |
| C514 | −0.136(1) | −0.060(1) | 0.6673(7) | 7.3(4)* |
| C515 | −0.094(1) | 0.020(1) | 0.6629(7) | 6.8(4)* |
| C516 | −0.079(1) | 0.0592(9) | 0.7139(6) | 5.3(3)* |
| C521 | −0.2120(8) | 0.1111(7) | 0.8701(5) | 3.9(2)* |
| C522 | −0.2166(9) | 0.1632(9) | 0.9177(6) | 5.3(3)* |
| C523 | −0.311(1) | 0.1907(9) | 0.9535(7) | 6.3(3)* |
| C524 | −0.393(1) | 0.1643(9) | 0.9381(6) | 6.2(3)* |
| C525 | −0.391(1) | 0.112(1) | 0.8915(7) | 7.2(4)* |
| C526 | −0.298(1) | 0.0851(9) | 0.8553(6) | 5.8(3)* |
| C531 | −0.0508(8) | −0.0008(7) | 0.8825(5) | 3.7(2)* |
| C532 | −0.1141(9) | −0.0617(8) | 0.9164(6) | 4.9(3)* |
| C533 | −0.0789(9) | −0.1164(9) | 0.9568(6) | 5.2(3)* |

*(continued)*

TABLE 2. *(continued)*

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| C534 | 0.0159(9) | −0.1120(9) | 0.9637(6) | 5.2(3)* |
| C535 | 0.0778(9) | −0.0508(9) | 0.9314(6) | 5.3(3)* |
| C536 | 0.0445(9) | 0.0041(8) | 0.8904(5) | 4.4(3)* |
| Fe1 | 0.2180(2) | 0.7481(1) | 0.50879(9) | 5.63(5) |
| Cl2 | 0.2661(3) | 0.6128(3) | 0.4884(2) | 7.4(1) |
| Cl3 | 0.1798(3) | 0.8136(3) | 0.4324(2) | 6.8(1) |
| Cl4 | 0.0892(4) | 0.7552(3) | 0.5816(2) | 9.4(1) |
| Cl5 | 0.3374(3) | 0.8132(3) | 0.5321(3) | 10.1(1) |
| Fe2 | 0.4574(2) | 0.2573(2) | 0.1445(1) | 6.84(6) |
| Cl6 | 0.6183(4) | 0.2516(3) | 0.1252(3) | 10.0(2) |
| Cl7 | 0.4080(5) | 0.1326(5) | 0.1744(4) | 22.2(3) |
| Cl8 | 0.4007(5) | 0.3553(5) | 0.2070(3) | 19.6(2) |
| Cl9 | 0.4085(6) | 0.2911(6) | 0.0657(3) | 19.7(3) |
| C1 | 0.277(4) | 0.307(4) | 0.361(2) | 15(2)* |
| Cl11 | 0.307(1) | 0.3970(9) | 0.3962(6) | 12.5(4)* |
| Cl12 | 0.171(1) | 0.2801(9) | 0.3918(6) | 14.8(4)* |
| Cl21 | 0.430(1) | 0.170(1) | 0.3653(9) | 21.0(7)* |
| Cl22 | 0.387(1) | 0.073(1) | 0.4540(9) | 21.8(6)* |
| C2 | 0.478(3) | 0.108(2) | 0.398(2) | 10.9(9)* |

Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^{2*}B(1,1) + b^{2*}B(2,2) + c^{2*}B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B1,3) + bc(\cos\alpha)B(2,3)]$.

TABLE 3. Bond distances (Å)

| Atom 1 | Atom 2 | Distance | Atom 1 | Atom 2 | Distance |
|---|---|---|---|---|---|
| La | O1 | 2.425(4) | P3 | C311 | 1.770(5) |
| La | O2 | 2.403(4) | P3 | C321 | 1.793(7) |
| La | O3 | 2.389(3) | P3 | C331 | 1.799(8) |
| La | O4 | 2.388(4) | P4 | C411 | 1.794(7) |
| La | O5 | 2.400(3) | P4 | C421 | 1.790(7) |
| La | Cl1 | 2.742(1) | P4 | C431 | 1.794(6) |
| O1 | P1 | 1.510(3) | P5 | C511 | 1.790(5) |
| O2 | P2 | 1.504(3) | P5 | C521 | 1.791(6) |
| O3 | P3 | 1.512(4) | P5 | C531 | 1.783(7) |
| O4 | P4 | 1.507(3) | Fe1 | Cl2 | 2.192(2) |
| O5 | P5 | 1.499(3) | Fe1 | Cl3 | 2.184(2) |
| P1 | C111 | 1.790(5) | Fe1 | Cl4 | 2.177(2) |
| P1 | C121 | 1.807(6) | Fe1 | Cl5 | 2.166(2) |
| P1 | C131 | 1.796(7) | Fe2 | Cl6 | 2.192(2) |
| P2 | C211 | 1.795(8) | Fe2 | Cl7 | 2.119(4) |
| P2 | C221 | 1.783(8) | Fe2 | Cl8 | 2.125(3) |
| P2 | C231 | 1.788(7) | Fe2 | Cl9 | 2.147(4) |

Numbers in parentheses are e.s.d.s in the least significant digits.

This compound is an ionic complex consisting of a divalent cation, $[(Ph_3P{=}O)_5LaCl]^{2+}$, and 2 monovalent anions, $[FeCl_4]^-$. The cation possesses a six-coordinated distorted octahedral geometry as shown in Fig. 1. La, O(1), O(2), O(4) and O(5) are located in one plane, Cl(1) and O(3) are located above

TABLE 4. Bond angles (°)

| Atom 1 | Atom 2 | Atom 3 | Angle | Atom 1 | Atom 2 | Atom 3 | Angle |
|---|---|---|---|---|---|---|---|
| O1 | La | O2 | 101.4(1) | C121 | P1 | C131 | 111.2(3) |
| O1 | La | O3 | 81.5(1) | O2 | P2 | C211 | 109.9(3) |
| O1 | La | O4 | 173.1(1) | O2 | P2 | C221 | 110.0(3) |
| O1 | La | O5 | 89.0(1) | O2 | P2 | C231 | 111.9(3) |
| O1 | La | Cl1 | 90.98(9) | C211 | P2 | C221 | 108.2(4) |
| O2 | La | O3 | 86.8(1) | C211 | P2 | C231 | 106.9(3) |
| O2 | La | O4 | 84.8(2) | C221 | P2 | C231 | 109.8(3) |
| O2 | La | O5 | 169.6(1) | O3 | P3 | C311 | 111.1(2) |
| O2 | La | Cl1 | 89.24(9) | O3 | P3 | C321 | 110.4(3) |
| O3 | La | O4 | 95.9(1) | O3 | P3 | C331 | 110.4(3) |
| O3 | La | O5 | 95.4(1) | C311 | P3 | C321 | 109.3(3) |
| O3 | La | Cl1 | 170.55(9) | C311 | P3 | C331 | 108.1(3) |
| O4 | La | O5 | 84.9(2) | C321 | P3 | C331 | 107.6(3) |
| O4 | La | Cl1 | 92.25(9) | O4 | P4 | C411 | 110.4(3) |
| O5 | La | Cl1 | 90.00(9) | O4 | P4 | C421 | 111.4(3) |
| La | O1 | P1 | 169.3(2) | O4 | P4 | C431 | 110.3(2) |
| La | O2 | P2 | 153.4(3) | C411 | P4 | C421 | 107.9(3) |
| La | O3 | P3 | 166.8(2) | C411 | P4 | C431 | 108.1(3) |
| La | O4 | P4 | 176.3(3) | C421 | P4 | C431 | 108.7(4) |
| La | O5 | P5 | 172.4(2) | O5 | P5 | C511 | 109.2(2) |
| O1 | P1 | C111 | 112.4(2) | O5 | P5 | C521 | 112.2(2) |
| O1 | P1 | C121 | 110.6(2) | O5 | P5 | C531 | 111.0(3) |
| O1 | P1 | C131 | 110.8(3) | C511 | P5 | C521 | 107.8(2) |
| C111 | P1 | C121 | 104.3(3) | C511 | P5 | C531 | 111.4(3) |
| C111 | P1 | C131 | 107.2(3) | C521 | P5 | C531 | 105.2(3) |
| Cl2 | Fe1 | Cl3 | 110.36(8) | Cl6 | Fe2 | Cl7 | 108.2(2) |
| Cl2 | Fe1 | Cl4 | 111.01(8) | Cl6 | Fe2 | Cl8 | 110.2(1) |
| Cl2 | Fe1 | Cl5 | 108.33(9) | Cl6 | Fe2 | Cl9 | 109.7(1) |
| Cl3 | Fe1 | Cl4 | 108.07(8) | Cl7 | Fe2 | Cl8 | 112.5(2) |
| Cl3 | Fe1 | Cl5 | 109.42(9) | Cl7 | Fe2 | Cl9 | 109.1(2) |
| Cl4 | Fe1 | Cl5 | 109.7(2) | Cl8 | Fe2 | Cl9 | 107.4(1) |

Numbers in parentheses are e.s.d.s in the least significant digits.

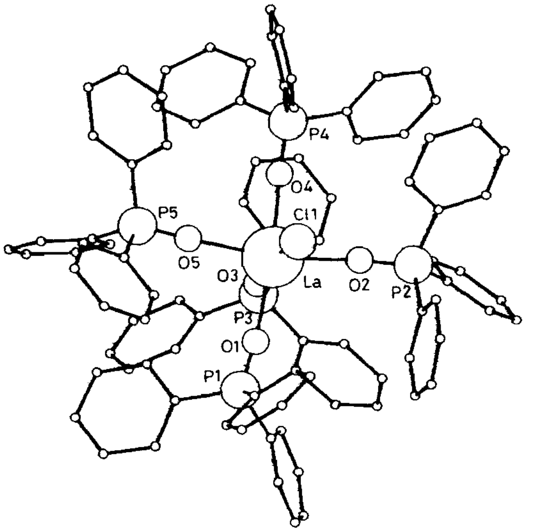

Fig. 1. Molecular structure of $[(Ph_3P{=}O)_5LaCl]^{2+}$.

and beneath this plane. P(1) is *trans* to P(4) and both orient to O(3); the sum of angles La–O(1)–P(1) and La–O(4)–P(4) is 345.5°. P(2) is *trans* to P(4) and both orient to Cl(1); the sum of angles La–O(2)–P(2) and La–O(5)–P(5) is 325.8°. These data show that P(1) and P(4) are remote from O(3) of bulky axial $Ph_3P{=}O$ decreasing the steric hindrance.

The axial P(3) is closer to O(1) than to O(4), so the steric repulsion makes the La–O(1) distance longer than La–O(4) (2.425 *versus* 2.388 Å). La–O(2) and La–O(5) have the average values of 2.403 and 2.400 Å. The P–O distance for free $Ph_3P{=}O$ is 1.46 Å, but in this cation the average P–O distance is 1.506 Å, which indicates a weakening of the P=O bond by coordination to lanthanide.

In $Ph_3P{=}O$ the three dihedral angles between the three C–P–O planes and the three corresponding phenyl ring planes are 24.7°, 59.3°, and 21.1°; there is no conjugation between P=O and the phenyl rings.

In $[(Ph_3P{=}O)_5LaCl]^{2+}$, the dihedral angles between C–P–O and the phenyl ring planes are as follows: C–P(1)–O(1) 31.7°, 6.9°, 30.4°; C–P(2)–O(2) 35.1°, 67.0°, 40.3°; C–P(3)–O(3) 63.4°, 42.7°, 29.3°; C–P(4)–O(4) 29.0°, 51.7°, 23.5°; C–P(5)–O(5) 17.0°, 50.7°, 13.4°. These data show there is also no conjugation between P=O and the phenyl rings.

Both $[FeCl_4]^-$ are of tetrahedral geometry, Cl–Fe–Cl angles are between 107.4° and 112.5° with almost no distortion. As shown in Fig. 2, the $[FeCl_4]^-$ anions are located close to the axial and equatorial $Ph_3P{=}O$ molecules but remote from chloride due to the repulsion between strong polar La–Cl and Fe–Cl bonds.

In the crystal cell the closest distances between metals are: La–La 11.926, La–Fe(2) 10.246, La–Fe(1) 9.108, Fe(1)–Fe(1) 9.711, Fe(1)–Fe(2) 10.139, and Fe(2)–Fe(2) 9.869 Å. There are four molecules of $CH_2Cl_2$ in the cavity of the unit cell.

## *Spectral Properties*

### *IR*

The stretching vibration frequencies for the P=O group in free $Ph_3P{=}O$ are 1190, 1164 $cm^{-1}$. In $[(Ph_3P{=}O)_5LnCl]^{2+}$ $\nu$(P=O) shifts to 1132–1136 $cm^{-1}$ which indicates a weakening of the P=O bond by coordination of the P=O oxygen to lanthanide. $\nu$(Ln–Cl) for seven-coordinated $(Ph_3P{=}O)_4LnCl_3$ are 223–236 (La–Er) and 261 (Y) $cm^{-1}$, but for the title complexes are 233–240 (La–Er) and 264 (Y) $cm^{-1}$. The increase in vibration frequencies is probably due to the decrease of the coordination number, i.e. decreasing of steric repulsion.

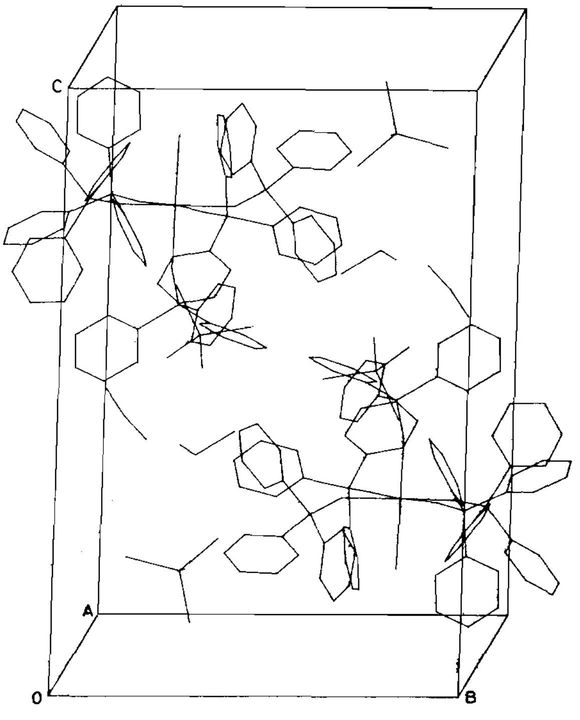

Fig. 2. Packing of $[(Ph_3P{=}O)_5LaCl][FeCl_4]_2$ in a unit cell.

### *$^{31}P$ NMR*

The chemical shift for free $Ph_3P{=}O$ is 23.2 ppm while for $[(Ph_3P{=}O)_5YCl]^{2+}$ two signals of different intensities at 37.7 and 41.7 ppm are recorded. The fact that the chemical shift moves to a lower field is due to a decrease in the shielding of P=O by the coordination of P=O oxygen to lanthanide and the splitting of the signal to a doublet is due to the presence of axial and equatorial $Ph_3P{=}O$.

## *The Formation of $[(Ph_3P{=}O)_5LnCl]^{2+}$*

The energy level, the assignment of the LMOs to chemical bonds, net charge, and Mulliken population of α- and β-spin MOs for $GdCl_3$ and $[(H_3P{=}O)_4GdCl_2]^+$ are obtained from the INDO calculation (see 'Supplementary Material').

In a comparison of the Gd–Cl bond orders of $GdCl_3$ and $[(Ph_3P{=}O)_4GdCl_2]^+$ it can be seen that the Gd–Cl bond for the latter species is much weaker (0.796 versus 0.622), this means coordination of P=O groups to lanthanide weakens the Ln–Cl bond and causes the transfer of chloride from lanthanide to any Lewis acid species in the presence of the $Ph_3P{=}O$ ligand. The comparison of net charges on chlorine for $GdCl_3$ and $[(H_3P{=}O)_4GdCl_2]^+$ (−0.120 versus −0.375) reveals the same result, i.e. the increasing of the chloride basicity facilitates the transfer of chloride to a Lewis acid.

## **Supplementary Material**

Analytical data, energy data, composition and character data are available from the authors on request.

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