



Tertiary phosphine oxide complexes of lanthanide diiodides and dibromides

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ABSTRACT

The reaction of OPR_3 ($R = \text{Me, Ph}$) with YbI_2 , EuI_2 and EuBr_2 in rigorously anhydrous MeCN under N_2 produces the divalent lanthanide complexes $[\text{LnX}_2(\text{OPR}_3)_4]$ ($\text{Ln} = \text{Yb, Eu, X} = \text{I}$; $\text{Ln} = \text{Eu, X} = \text{Br}$) in moderate to good yield, whilst $[\text{SmI}_2(\text{OPR}_3)_4]$ were obtained from SmI_2 and OPR_3 in dry, degassed thf. These are the first examples involving divalent lanthanide ions and the complexes have been characterised by microanalysis, IR, UV–Vis and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. The X-ray crystal structure of $[\text{EuI}_2(\text{OPPh}_3)_4]\cdot\text{MeCN}$ confirmed the six-coordinate Eu(II) species with a *cis*-octahedral geometry, which IR spectroscopy suggests is present in all of the OPPh_3 complexes. In contrast the $[\text{LnX}_2(\text{OPMe}_3)_4]$ complexes appear to be *trans* isomers. The OPPh_3 complexes are readily oxidised by dry O_2 or I_2 , yielding the corresponding trivalent cations, $[\text{LnX}_2(\text{OPPh}_3)_4]^+$; a crystal structure of the product formed by oxidation of $[\text{EuI}_2(\text{OPPh}_3)_4]$ in MeCN solution confirms this to be $[\text{EuI}_2(\text{OPPh}_3)_4]\text{I}_3\cdot 1.5\text{MeCN}$, containing a *trans*-octahedral cation.

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1. Introduction

While the overwhelming majority of lanthanide coordination chemistry involves the Ln(III) state [1–3], the last twenty five years have seen a steady growth of complexes of divalent lanthanides, mostly based upon Eu, Yb and Sm, but with a small number of complexes of Dy, Nd and Tm also characterised [4,5]. In parallel, an organometallic chemistry containing low valent lanthanide centres has been developed, and EuI_2 and SmI_2 are valuable one electron reductants and cross-coupling reagents in organic chemistry [6–8]. Tertiary phosphine oxides (OPR_3) have proved to be popular ligands for trivalent lanthanides, and many examples with a range of R groups are known as oxo-anion salts (nitrate, triflate, etc.), diketonates and halides, as described in a very recent comprehensive review [9]. Taking OPPh_3 (the most thoroughly investigated ligand) as an example, all the LnCl_3 complexes are six-coordinate, with both *mer*- $[\text{LnCl}_3(\text{OPR}_3)_3]$ and *trans*- $[\text{LnCl}_2(\text{OPR}_3)_4]\text{Cl}$ characterised for all (except Pm). The former type is preferred for the early lanthanides, with the cations becoming more favoured later in the series [10], whilst the $[\text{LnX}_2(\text{OPPh}_3)_4]\text{X}$ ($\text{X} = \text{Br, I}$) are favoured for the heavier halides [11,12]. There are also some $[\text{LnCl}(\text{OPPh}_3)_5]^{2+}$ cations formed using halide abstractors and one series of homoleptic cations in the form $[\text{Ln}(\text{OPMe}_3)_6][\text{PF}_6]_3$ [13]. No examples of divalent lanthanide phosphine oxide complexes have been reported [9], although hexamethylphosphoramide

($(\text{Me}_3\text{N})_3\text{PO}$, HMPA) complexes, $[\text{Yb}(\text{HMPA})_4(\text{thf})_2]\text{I}_2$, $[\text{Sm}(\text{HMPA})_6]\text{I}_2$ and $[\text{SmI}_2(\text{HMPA})_4]$ have been isolated from reaction of the appropriate LnI_2 with HMPA in thf solution [14].

Here we report the preparations and properties of complexes of OPPh_3 and OPMe_3 with the divalent LnI_2 ($\text{Ln} = \text{Yb, Eu}$ and Sm) and EuBr_2 .

2. Experimental

Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 spectrometer over the range $4000\text{--}200\text{ cm}^{-1}$. UV–Vis spectra were recorded from sealed PTFE cell with silica window on neat samples, using the diffuse reflectance attachment, in a Perkin Elmer 750S spectrometer. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded using a Bruker AV 400 spectrometer and are referenced to external 85% H_3PO_4 . Microanalyses were undertaken by London Metropolitan University. Lanthanide dihalides, solvents and other reagents were obtained from Sigma–Aldrich and used as received. Trimethylphosphine oxide was dried by sublimation *in vacuo*, and triphenylphosphine oxide melted under vacuum before use. MeCN was dried by distillation from CaH_2 and thf from sodium benzophenone-ketyl. Syntheses were routinely carried out under a dry dinitrogen atmosphere, and all solids and spectroscopic samples were handled in a dry dinitrogen filled glove box. Since the complexes have limited stability in dilute solution, all NMR samples were freshly prepared immediately before recording data.

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2.1. $[\text{YbI}_2(\text{OPPh}_3)_4]$

YbI_2 (0.05 g, 0.12 mmol) was dissolved in anhydrous MeCN (10 mL), a solution of OPPh_3 (0.13 g, 0.47 mmol) in MeCN (5 mL) added, and the mixture stirred from 20 min. during which the orange colour of the solution deepened. The solution was concentrated to a small volume when a bright yellow precipitate formed. This was filtered off, and dried *in vacuo* to yield a bright yellow powder. Yield 0.14 g, 79%. Required for $\text{C}_{72}\text{H}_{60}\text{I}_2\text{O}_4\text{P}_4\text{Yb}$ (1539.2): C, 56.13; H, 3.93. Found: C, 55.89; H, 3.77%. IR spectrum (Nujol mull/cm⁻¹): 1140 br s, 1085 m (PO). UV–Vis (diffuse reflectance/cm⁻¹): 27 320. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = +36.1$.

The MeCN solution of $[\text{YbI}_2(\text{OPPh}_3)_4]$ exposed to air or O_2 resulted in rapid diminution of the $^{31}\text{P}\{^1\text{H}\}$ NMR resonance and development of a new resonance at $\delta = -39.0$, assigned as a Yb (III) species, often with a weak feature at +29.6 ppm (OPPh_3). The same species was generated by addition of I_2 to an MeCN solution of the divalent complex.

2.2. $[\text{YbI}_2(\text{OPMe}_3)_4]$

Was made similarly from YbI_2 (0.05 g, 0.12 mmol) and OPMe_3 (0.043 g, 0.47 mmol) in MeCN. The product was a pale yellow powder. Yield 0.02 g, 21%. Required for $\text{C}_{12}\text{H}_{36}\text{I}_2\text{O}_4\text{P}_4\text{Yb}$ (795.0): C, 18.11; H, 4.56. Found: C, 18.05; H, 4.56%. IR spectrum (Nujol mull/cm⁻¹): 1112 br s (PO). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = +50.9$. Treatment of the CD_3CN solution with I_2 produced an orange-brown solution with $\delta(^{31}\text{P}\{^1\text{H}\}) = -13.9$ and -25.0 .

2.3. $[\text{EuI}_2(\text{OPPh}_3)_4]$

EuI_2 (0.05 g, 0.12 mmol) was dissolved in anhydrous MeCN (10 mL), a solution of OPPh_3 (0.14 g, 0.49 mmol) in MeCN (5 mL) added, and the pale yellow solution stirred from 20 min. The solution was concentrated to small volume when a yellow precipitate formed. This was filtered off and dried *in vacuo* to yield a yellow powder. Yield 0.12 g, 64%. Required for $\text{C}_{72}\text{H}_{60}\text{EuI}_2\text{O}_4\text{P}_4$ (1598.1): C, 56.91; H, 3.98. Found: C, 56.63; H, 4.11%. IR spectrum (Nujol mull/cm⁻¹): 1135 br s, 1082 m (PO). UV–Vis (diffuse reflectance/cm⁻¹): 26 900. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): not observed. An I_2 (or air) oxidised solution had $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = -125.0$. Crystals were obtained from cooling an MeCN solution of the complex.

2.4. $[\text{EuI}_2(\text{OPMe}_3)_4]$

Was made similarly from EuI_2 (0.05 g, 0.12 mmol) and OPMe_3 (0.045 g, 0.49 mmol) in MeCN. The product was a pale yellow powder. Yield 0.06 g, 66%. Required for $\text{C}_{12}\text{H}_{36}\text{EuI}_2\text{O}_4\text{P}_4$ (773.9): C, 18.61; H, 4.69. Found: C, 18.41; H, 4.53%. IR spectrum (Nujol mull/cm⁻¹): 1142 (sh), 1104 br, s, (PO). UV–Vis (diffuse reflectance/cm⁻¹): 27 470(sh), 26 455. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta =$ not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{EuI}_2(\text{OPMe}_3)_4]$ after exposure to air (CD_3CN , 298 K): -8.0 .

2.5. $[\text{EuBr}_2(\text{OPPh}_3)_4]$

EuBr_2 (0.05 g, 0.16 mmol) was dissolved in MeCN (10 mL) and a solution of OPPh_3 (0.18 g, 0.64 mmol) in MeCN (10 mL) added, and the mixture stirred overnight. On standing a yellow precipitate formed, and the solution was concentrated to small volume, and the precipitate filtered off and dried *in vacuo*. Yield 0.14 g, 62%. Required for $\text{C}_{72}\text{H}_{60}\text{Br}_2\text{EuO}_4\text{P}_4$ (1424.1): C, 60.67; H, 4.25. Found: C, 60.55; H, 4.43%. IR spectrum (Nujol mull/cm⁻¹): 1141 br s, 1084 m (PO). UV–Vis (diffuse reflectance/cm⁻¹): 26 040. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): not observed. An air-oxidised solution had $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): $\delta = -97.0$.

2.6. $[\text{EuBr}_2(\text{OPMe}_3)_4]$

Was made similarly from EuBr_2 (0.05 g, 0.16 mmol) and OPMe_3 (0.059 g, 0.64 mmol). The product was a pale yellow powder. Yield 0.07 g, 64%. Required for $\text{C}_{12}\text{H}_{36}\text{Br}_2\text{EuO}_4\text{P}_4$ (680.1): C, 21.19; H, 5.34. Found: C, 21.31; H, 5.45%. IR spectrum (Nujol mull/cm⁻¹): 1108 br s (PO). UV–Vis (diffuse reflectance/cm⁻¹): 25 840. $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_3CN): not observed. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{EuBr}_2(\text{OPMe}_3)_4]$ after addition of Br_2 (CD_3CN , 298 K): -7.7 .

2.7. $[\text{SmI}_2(\text{OPPh}_3)_4]$

SmI_2 (0.05 g, 0.12 mmol) was dissolved in thf (10 mL) to form a dark blue solution. A solution of OPPh_3 (0.14 g, 0.49 mmol) in thf (5 mL) was then added. On stirring, the solution became dark purple and on concentration a dark blue solid was deposited, which was filtered off and dried *in vacuo*. Yield: 0.13 g, 71%. Required for $\text{C}_{72}\text{H}_{60}\text{I}_2\text{O}_4\text{P}_4\text{Sm}$ (1516.5): C, 56.97; H, 3.99. Found: C, 56.59; H, 4.24%. IR spectrum (Nujol mull/cm⁻¹): 1167 br s, 1071 s (PO). UV–Vis (diffuse reflectance/cm⁻¹): 26 730, 17 300. $^{31}\text{P}\{^1\text{H}\}$ NMR (d_8 -thf): $\delta = +18.5$. Treatment of the d_8 -thf solution with I_2 produced a red brown solution with new resonances at $\delta = +35.6$, $+25.7$ (Ph_3PO), together with a red-brown precipitate.

2.8. $[\text{SmI}_2(\text{OPMe}_3)_4]$

Was made similarly from SmI_2 (0.05 g, 0.12 mmol) and OPMe_3 (0.046 g, 0.49 mmol) in thf. The product was a pale blue powder. Yield 0.08 g, 84%. Required for $\text{C}_{12}\text{H}_{36}\text{I}_2\text{O}_4\text{P}_4\text{Sm}$ (772.3): C, 18.64; H, 4.70. Found: C, 18.53; H, 4.70%. IR spectrum (Nujol mull/cm⁻¹): 1103 br s, (PO). $^{31}\text{P}\{^1\text{H}\}$ NMR: insoluble in d_8 -thf and CD_2Cl_2 , decomposed by CD_3CN .

2.9. 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

Table 1
Crystallographic data.^a

Compound	$[\text{EuI}_2(\text{OPPh}_3)_4] \cdot \text{MeCN}$	$[\text{EuI}_2(\text{OPPh}_3)_4] \text{I}_3 \cdot 1.5\text{MeCN}$
Formula	$\text{C}_{74}\text{H}_{63}\text{EuI}_2\text{NO}_4\text{P}_4$	$\text{C}_{150}\text{H}_{129}\text{Eu}_2\text{I}_{10}\text{N}_3\text{O}_8\text{P}_8$
<i>M</i>	2329.40	3922.23
Crystal system	monoclinic	triclinic
Space group (no.)	$\text{Pn} (7)$	$\text{P} \bar{1} (2)$
<i>a</i> (Å)	13.6401(4)	13.6846(3)
<i>b</i> (Å)	17.5450(4)	20.1433(4)
<i>c</i> (Å)	14.0307(4)	28.4990(4)
α (°)	90	91.6050(10)
β (°)	95.185(3)	91.558(2)
γ (°)	90	109.605(2)
<i>U</i> (Å ³)	3344.03(16)	7391.9(3)
<i>Z</i>	2	2
$\mu(\text{Mo K}\alpha)$ (mm ⁻¹)	2.006	3.071
<i>F</i> (0 0 0)	1550	3780
Total number reflections	63 559	94 005
<i>R</i> _{int}	0.125	0.040
Unique reflections	13 995	28 933
No. of parameters, restraints	776, 710	1609, 0
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)] ^b	0.045, 0.100	0.050, 0.112
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.053, 0.103	0.063, 0.116

^a Common data: *T* = 293 K; wavelength (Mo Kα) = 0.71073 Å; θ(max) = 27.5°.

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

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