Use of a Highly Hindered Phosphino-alkoxide Ligand in the Formation of Monomeric Homoleptic Lanthanoid Metal Complexes: *X*-Ray Structures of $[\overline{\mathrm{Ln(OCBu^t_2CH_2P}}\mathrm{Me_2)_3}]$ (Ln = Y or Nd)†

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Complexes $[\overline{\mathrm{Ln(OCBu^t_2CH_2P}}\mathrm{Me_2)_3}]$ [Ln = Y (**1**) or Nd (**2**)] are crystalline and hydrocarbon-soluble; they are the first examples of monomeric, homoleptic Group 3 or lanthanoid metal alkoxides and also the first crystallographically authenticated Group 3 or early (f^0–f^3) lanthanoid metal tertiary phosphine complexes [$^1J(^{31}\mathrm{P}-^{89}\mathrm{Y})$ = 59 Hz], with the following geometric parameters for (**1**) [or (**2**) in square brackets]: <Ln–O> 2.090(4) [2.174(2)], <Ln–P> 3.045(2) [3.154(2)] Å, and <O–Ln–O′> 110.5(2) [114.5(1)]°.

Simple lanthanoid metal (here taken to include Sc, Y, and La; and collectively abbreviated as Ln) alkoxides and aryloxides have been much studied.[1] The simple aryloxides are organic solvent-insoluble polymers. Monomeric, homoleptic, hydrocarbon-soluble lanthanoid metal aryloxides have been prepared at Sussex; they were derived from the bulky phenols $\mathrm{HOAr^R}$ ($\mathrm{Ar^R = C_6H_2Bu^t_2}$-2,6-R-4; R = H, Me, or $\mathrm{Bu^t}$), *e.g.*, the *X*-ray-characterised $[\mathrm{Sc(OAr^{Me})_3}]$,[2] $[\mathrm{Y(OAr^H)_3}]$,[3a] and $[\mathrm{Ce(OAr^H)_3}]$.[3b] In contrast, many known lanthanoid metal alkoxides appear to be relatively low molecular weight oligomers of somewhat uncertain composition.[1,4] Single crystal *X*-ray analyses of (i) a chloride contaminated $\mathrm{Nd^{III}}$ isopropoxide $[\mathrm{Nd_6Cl(OPr^i)_{17}}]$ (**I**) showed it to have an essentially hexameric structure with a $\mathrm{Cl^-}$ replacing one of the eighteen $^-\mathrm{OPr^i}$ ligands;[5] and (ii) $[\mathrm{Y_3(\mu_3\text{-}OBu^t)(\mu_3\text{-}Cl)(\mu_2\text{-}OBu^t)_3(OBu^t)_4(thf)_2}]$ (**II**) (thf = tetrahydrofuran) and $[\{\mathrm{Y_4(\mu_3\text{-}OBu^t)_2(\mu_2\text{-}OBu^t)_4(OBu^t)_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_2Li_4(\mu_2\text{-}OBu^t)_2}\}_2]$ were taken as examples of structures containing $\mathrm{Ln_3(\mu_3\text{-}OR)(\mu_3\text{-}X)(\mu_2\text{-}OR)_3}$ building blocks.[4] We now report the first monomeric homoleptic lanthanoid metal alkoxides (**1**) and (**2**), albeit containing β-functionality.

The $\mathrm{Ln^{3+}}$ ions, being hard Lewis acids, have a very extensive co-ordination chemistry involving oxygen- and nitrogen-centred ligands. Conversely, very few tertiary phosphine–lanthanoid metal complexes are known, and *X*-ray data exist for only two: $[\mathrm{Yb\{N(SiMe_3)_2\}_2(dmpe)}]$[6] and $[\mathrm{Yb(\eta\text{-}C_5Me_5)_2(Cl)(dmpm)}]$[7] (dmpe = $\mathrm{Me_2PCH_2CH_2PMe_2}$, dmpm = $\mathrm{Me_2PCH_2PMe_2}$).

We have previously reported the synthesis and structures of the lithium derivatives of two novel, highly hindered, phosphine-functionalised alkoxide ligands, $[\overline{\mathrm{Li(\mu\text{-}OCBu^t_2CH_2P}}\mathrm{R_2)}]_2$ (R = Me or Ph).[8] We now show that they may be used to prepare [equation (1)] the homoleptic lanthanoid metal alkoxides (**1**) and (**2**), which incidentally provide the first examples of a Group 3 or early (pre-Sm) lanthanoid metal tertiary phosphine complex.

$$\mathrm{LnCl_3} + 3/2[\overline{\mathrm{Li(\mu\text{-}OCBu^t_2CH_2P}}\mathrm{Me_2)}]_2 \longrightarrow \underset{(\mathbf{1}),\,(\mathbf{2})}{[\overline{\mathrm{Ln(OCBu^t_2CH_2P}}\mathrm{Me_2)_3}]} + 3\mathrm{LiCl} \qquad (1)$$

(**1**) Ln = Y, 45%, colourless, m.p. *ca.* 260 °C (decomp.)
(**2**) Ln = Nd, 50%, pale blue, m.p. 240—242 °C

Compounds (**1**) and (**2**) gave satisfactory microanalyses, and were further identified by n.m.r. spectroscopy.‡ It is noteworthy that ^{89}Y is an n.m.r. active nucleus ($I = \frac{1}{2}$, 100% abundance) and that $\mathrm{Nd^{3+}}$ is paramagnetic and has the electronic ground state $[\mathrm{Xe}]4f^3$. The ^{1}H n.m.r. spectrum of the yttrium alkoxide (**1**) revealed the $\mathrm{C}H_2$ resonance as a complex multiplet which was unresolved, rather than a doublet {*cf.*,[8] the ^{1}H n.m.r. spectrum of $[\overline{\mathrm{Li(OCBu^t_2CH_2P}}\mathrm{Me_2)}]_2$, which showed only ^{31}P–^{1}H coupling}. The ^{1}H n.m.r. spectrum of the neodymium analogue (**2**) had each signal (i) considerably shifted from that observed for (**1**), and (ii) severely broadened. The ambient temperature $^{31}\mathrm{P}\{^1\mathrm{H}\}$ n.m.r. spectrum of (**1**) exhibted a doublet; the splitting arises from coupling between ^{31}P and ^{89}Y, $^1J(^{31}\mathrm{P}-^{89}\mathrm{Y})$ = 59 Hz, and this is one of the first recorded examples of such coupling. The ^{31}P resonance of (**2**) was not observed.

The structures of crystalline $[\overline{\mathrm{Ln(OCBu^t_2CH_2P}}\mathrm{Me_2)_3}]$ [Ln = Y (**1**) or Nd (**2**)] were determined by single crystal *X*-ray diffraction and are depicted in Figure 1.§ Each of these molecules is a monomer in the facial configuration, and lies on a threefold crystallographic axis. The $\mathrm{LnO_3}$ skeletal geometry is intermediate between pyramidal and planar, with Ln lying out of the $\mathrm{O_3}$ plane in the direction of the $\mathrm{P_3}$ atoms. By contrast, in $[\mathrm{Y(OAr^H)_3}]$ the $\mathrm{YO_3}$ geometry is almost exactly planar [OYO′ = 119.8(6)° (mean)];[3a] although the Sc and Ce analogues are more nearly pyramidal, with the Ln atom in $[\mathrm{Ln(OAr^R)_3}]$ out of the plane of the three ligating oxygen atoms by 0.13 Å (Sc),[2] 0.09 Å (Y),[3a] or 0.54 Å (Ce).[3b]

The Y–O distance in (**1**) of 2.090(4) Å, with the exception of <Y–O> of 2.00(1) Å in $[\mathrm{Y(OAr^H)_3}]$,[3a] and the terminal <Y–O> of 2.05(4) Å in (**II**),[4] is shorter than most of the others previously observed.[9] Somewhat surprisingly, the Nd–O bond distance in (**2**) [2.174(2) Å] is longer than the terminal <Nd–O> [2.05(2) Å] recorded for $[\mathrm{Nd_6Cl(OPr^i)_{17}}]$ (**I**).[5] This is a possible consequence of interligand repulsion in (**2**).

The observed <Y–P> and <Nd–P> distances, 3.045(2) and 3.154(1) Å for (**1**) and (**2**) respectively, are somewhat

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† No reprints available.

‡ *Selected n.m.r. data* [^{31}P at 32.4 MHz (δ in p.p.m. rel. to 85% aq. $\mathrm{H_3PO_4}$), ^{1}H at 80 or 360 MHz (δ in p.p.m. rel. to ext. $\mathrm{SiMe_4}$); in $\mathrm{C_6D_6}$ at 305 K] (**1**): $^{31}\mathrm{P}\{^1\mathrm{H}\}$ δ −45 [d, J_{PY} 59 Hz]: ^{1}H δ 2.14 (2H, m, $\mathrm{CH_2}$), 0.96 (6H, s, $\mathrm{PMe_2}$), and 1.29 (18H, s, $\mathrm{Bu^t}$). (**2**): ^{31}P not observed; ^{1}H δ 18.48 (2H, br. s, $\mathrm{CH_2}$, $w_{\frac{1}{2}}$ 65 Hz), −13.73 (6H, br. s, $\mathrm{PMe_2}$, $w_{\frac{1}{2}}$ 85 Hz), and 11.29 (18H, br. s, $\mathrm{Bu^t}$, $w_{\frac{1}{2}}$ 210 Hz).

§ *Crystal data*: for (**1**): $\mathrm{C_{36}H_{78}O_3P_3Y}$, M = 740.9, cubic, space group *Pa*3, crystal size 0.2 × 0.2 × 0.15 mm, a = 20.521(2) Å, Z = 8, D_c = 1.14 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 14.9 cm^{-1}, 801 reflections $|F^2| > \sigma(F^2)$, $2 < \theta < 22°$, R = 0.049, R' = 0.040. For (**2**): $\mathrm{C_{36}H_{78}NdO_3P_3}$, M = 796.2, rhombohedral, space group $R\bar{3}c$, crystal size 0.5 × 0.3 × 0.2 mm, a = 16.857(3) Å, α = 72.90(1)°, Z = 4, D_c = 1.24 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 13.6 cm^{-1}, 1960 reflections $|F^2| > \sigma(F^2)$, $2 < \theta < 25°$, R = 0.033, R' = 0.040. For both structures data were collected on an Enraf-Nonius CAD4 diffractometer. The structures were solved by routine heavy atom methods and refined by full matrix least squares with all non-hydrogen atoms anisotropic. Hydrogen atoms were located in a difference map and refined isotropically for (**2**), and placed in calculated positions (C–H 1.08 Å) for (**1**). Absorption corrections were not applied for either structure. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue 1.

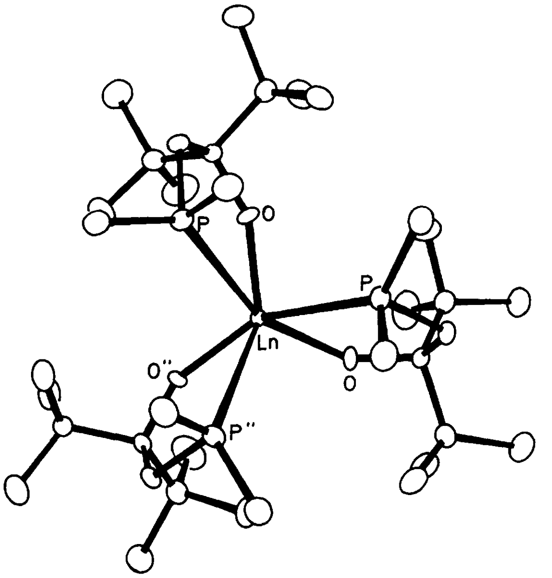

Figure 1. The *X*-ray structure and atom labelling scheme for [$Ln(OCBu^t{}_2CH_2PMe_2)_3$]. Relevant dimensions for the yttrium compound (data for the Nd analogue in square brackets) are: <Y–O> 2.090(4) [2.174(2)], <Y–P> 3.045(2) [3.154(2)], <P–C> 1.834(13) [1.830(15)], <O–C> 1.411(8) [1.407(3)] Å, <P–Y–O> 63.3(1) [60.2(1)], <O–Y–O'> 110.5(2) [114.5(1)], <P–Y–P'> 87.65(6) [88.6(1)]°.

long, perhaps indicative of (i) a somewhat weak interaction, and (ii) the low affinity lanthanoid metals have for soft ligands, such as phosphines. From <Yb–P> in [Yb(η-$C_5Me_5)_2Cl$(dmpm)] (**III**)[7] and Ln^{3+} radii (Y^{3+}, 0.88; Nd^{3+}, 0.995; Yb^{3+}, 0.858 Å), values of *ca.* 2.96 Å for <Y–P> and *ca.* 3.08 Å for <Nd–P> are predicted for the Y and Nd analogues of (**III**), respectively; these are *ca.* 3% shorter than observed in (**1**) or (**2**).

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