

Four- and Five-co-ordinate Lanthanide(II) Aryloxides: X-Ray Structures of the Bis(2,6-di-*t*-butyl-4-methylphenoxo)ytterbium(II) Complexes [Yb(OAr)₂(L)₂] and [Yb(OAr)₂(L')₃] [Ar = C₆H₂Bu^t₂-2,6-Me-4, L = tetrahydrofuran (thf) or OEt₂, L' = thf]

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General methods for the preparation of hydrocarbon-soluble, monomeric ytterbium(II) aryloxides are described {Yb + 2TiOAr, or [Yb(NR₂)₂(OEt₂)₂] + 2ArOH; R = SiMe₃, Ar = C₆H₂Bu^t₂-2,6-Me-4; crystalline [Yb(OAr)₂(thf)₃] (thf = tetrahydrofuran) (**1**) has the unprecedented square-pyramidal Yb^{II} stereochemistry (one thf apical), whereas the complexes [Yb(OAr)₂(L)₂] [L = thf (**2**) or OEt₂ (**3**)] are tetrahedral, with <Yb-OAr> 2.207(12) (**1**), 2.137(10) (**2**), or 2.154(28) Å (**3**); complex (**3**) with thf readily yields (**1**) or (**2**).

There is much current interest in complexes of the lanthanide metals in the +2 oxidation state, LnX₂(L)_n. This is due, in part, to their role as one-electron reductants of considerable selectivity, depending upon the nature of: (i) Ln^{II} [Sm^{II} (f⁶), Eu^{II} (f⁷), or Yb^{II} (f¹⁴)], (ii) X⁻ (I⁻, NR₂⁻, η-C₅Me₅⁻, or η-C₅H₄R⁻; R = H or SiMe₃), (iii) the absence or presence of *n* moles of a neutral coligand L, and (iv) the solvent-solubility of

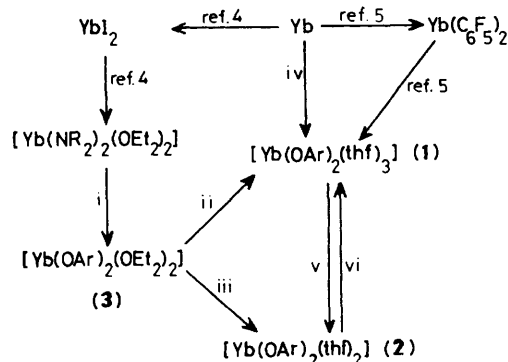
LnX₂(L)_n.¹ The electron-richness of LnX₂ is also manifested in the formation of unusual compounds such as [Yb(NR₂)(μ-NR₂)₂Na]₂ or [{Sm(η-C₅Me₅)₂}(μ-N₂)].³ Well defined hydrocarbon-soluble Ln^{II} complexes are at present restricted to bis(trimethylsilyl)amides and substituted cyclopentadienyls, and extensions to a wider series of ligands are timely.

Scheme 1 summarises routes to monomeric, lipophilic, bulky aryloxides of ytterbium(II), illustrated for the crystallographically characterised complexes $[\text{Yb}(\text{OAr})_2(\text{thf})_3]$ (1), $[\text{Yb}(\text{OAr})_2(\text{thf})_2]$ (2), and $[\text{Yb}(\text{OAr})_2(\text{OEt}_2)_2]$ (3) (Ar = $\text{C}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4}$, thf = tetrahydrofuran), Figures 1 and 2. Starting from ytterbium metal, there are three pathways. That involving YbI_2 and $[\text{Yb}(\text{NR}_2)_2(\text{OEt}_2)_2]$ ⁴ as successive intermediates gives the highest overall yield (72% based on Yb); the conversions of (3) \rightarrow (1) or (3) \rightarrow (2) are quantitative. The redox transmetalation (iv, in Scheme 1) provides (1) in 24% yield.

Compounds (1)–(3) have been characterised by microanalytical and ^1H and ^{13}C n.m.r. spectral data, as well as, most interestingly, by their ^{171}Yb n.m.r. spectra (see legend to Scheme 1). The last technique⁶ was particularly useful to monitor the course of the homogeneous reactions i–iv. As previously noted,⁶ ^{171}Yb signals are often broad, especially when neutral ligand exchange reactions are fast. In the present instance, such processes in $[\text{Yb}(\text{OAr})_2(\text{OEt}_2)_2]$ (3) are much more facile than in $[\text{Yb}(\text{OAr})_2(\text{thf})_3]$ (1) (cf. band-widths at half-height, $w_{1/2}$). This accounts for the instant displacement of OEt_2 from (3) by thf.

A structural feature in lanthanide metal chemistry is the prevalence of high Ln co-ordination numbers, due no doubt to the large Ln^{2+} or Ln^{3+} radii. X-Ray crystallographic data on monohapto complexes of the ubiquitous Ln^{3+} having low (≤ 5) co-ordination numbers are still scant and inevitably involve bulky ligands: $[\text{Lu}(\text{C}_6\text{H}_3\text{-Me}_2\text{-2,6})_4]^-$,⁷ $[\text{Ln}(\text{CHR}_2)_3]$ (Ln = La or Sm),⁸ $[\text{La}(\text{CHR}_2)_3(\mu\text{-Cl})\text{Li}(\text{pmdeta})]$ [pmdeta = $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$],⁹ $[\text{La}(\text{CHR}_2)_3(\mu\text{-Me})\text{Li}(\text{pmdeta})]$,¹⁰ $[\text{LnBu}_4]^-$,¹¹ $[\text{Yb}(\text{CHR}_2)_3\text{Cl}]^-$,¹² $[\text{Ln}(\text{NR}_2)_3]$ (Ln = Sc or Eu),¹³ $[\text{La}(\text{NR}_2)_3(\text{OPPh}_3)]$,¹³ $[\text{La}_2(\text{NR}_2)_4(\text{O}_2)(\text{OPPh}_3)_2]$,¹³ $[\text{Gd}(\text{NR}_2)_2(\mu\text{-SBU}^t)_2]$,¹⁴ $[\text{Sc}(\text{OAr}')_3]$,¹⁵ $[\text{Y}(\text{OAr}')_3]$ (Ar' = $\text{C}_6\text{H}_3\text{Bu}^t\text{-2,6}$),¹⁶ $[\text{Ce}(\text{OAr}')_3]$,¹⁷ and $[\text{Ce}(\text{OAr}')_3(\text{CNBu}^t)_2]$.¹⁷ For related Ln^{2+} complexes X-ray results are available on $[\text{Ln}(\text{NR}_2)(\mu\text{-NR}_2)_2\text{Na}]$ (Ln = Eu or Yb)² and $[\text{Yb}(\text{NR}_2)_2(\text{dmpe})]$ [dmpe = $(\text{Me}_2\text{PCH}_2)_2$].¹⁸

The X-ray structures† of $[\text{Yb}(\text{OAr})_2(\text{L})_2]$ [L = thf (2) or



Scheme 1. Routes to ytterbium(II) 2,6-di-*t*-butyl-4-methylphenoxides. Ar = $\text{C}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4}$, R = SiMe₃. Reagents and conditions: i, 2ArOH, OEt₂, 0 °C, 1 h (then 1 h at 25 °C); ii, thf, 25 °C; iii, 2thf, PhMe, 25 °C; iv, 1.3Yb powder, 1TiOAr, thf, 25 °C, 67 h (then reflux, 5 h); v, saturated solution (at 90 °C) in PhMe, 25 °C, 1 day; vi, thf, 25 °C. Identification procedures: the Yb^{II} aryloxides were obtained by low temperature (−30 °C) crystallisation from thf [yellow (1)], PhMe [ruby (2)], or OEt₂ [orange (3)], and were characterised by microanalysis, ^1H and ^{13}C n.m.r. spectroscopy, and X-ray crystallography (Figures 1 and 2). The ^{171}Yb chemical shifts (with band widths at half height in brackets), relative to $[\text{Yb}(\eta\text{-C}_5\text{Me}_5)_2(\text{thf})_2]$ at 297 K:⁶ for (1) at 233 K 285.5 p.p.m. ($w_{1/2}$ 42 Hz) and for (3) at 193 K 238 p.p.m. ($w_{1/2}$ 240 Hz).

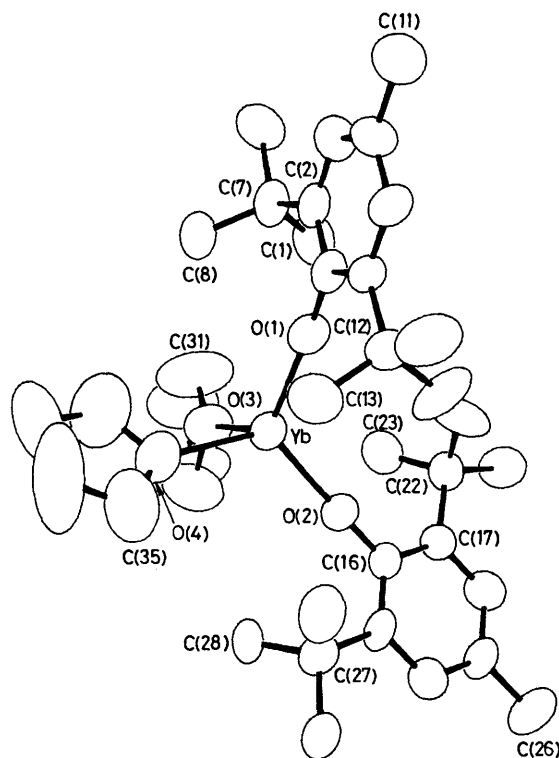


Figure 1. The X-ray structure and atom labelling scheme for $[\text{Yb}(\text{OC}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4})_2(\text{thf})_2]$ (2). Selected bond lengths (Å) and angles (°) {with data for $[\text{Yb}(\text{OC}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4})_2(\text{OEt}_2)_2]$ (3) in parentheses} are: Yb–O(1) 2.139(10) [2.126(9)], Yb–O(2) 2.135(9) [2.182(8)], Yb–O(3) 2.369(10) [2.443(10)], Yb–O(4) 2.382(10) [2.413(12)], O(1)–Yb–O(2) 118.7(3) [119.8(3)], O(1)–Yb–O(3) 119.9(4) [124.1(4)], O(1)–Yb–O(4) 105.5(4) [103.9(4)], O(2)–Yb–O(3) 98.9(4) [100.8(4)], O(2)–Yb–O(4) 121.1(4) [115.2(3)], and O(3)–Yb–O(4) 89.9(4) [89.7(4)].

† Crystal data for (1): $\text{C}_{42}\text{H}_{70}\text{O}_5\text{Yb}\cdot\text{OC}_4\text{H}_8$, $M = 900.11$, monoclinic, space group $P2_1$, $a = 15.393(4)$, $b = 15.619(5)$, $c = 9.859(2)$ Å, $\beta = 95.62(2)^\circ$, $U = 2359$ Å³, $Z = 2$, $D_c = 1.27$ g cm^{−3}, $\mu = 19.2$ cm^{−1}, $F(000) = 944$. 7441 Unique reflections were collected ($0 < 2\theta < 60^\circ$) and corrected for linear decay; 2764 [$I > 2.0\sigma(I)$] were considered observed.

For (2): $\text{C}_{38}\text{H}_{62}\text{O}_4\text{Yb}$, $M = 755.91$, monoclinic, space group $P2_1/n$, $a = 16.227(7)$, $b = 16.271(4)$, $c = 15.262(6)$ Å, $\beta = 105.95(1)^\circ$, $U = 3875$ Å³, $z = 4$, $D_c = 1.30$ g cm^{−3}, $\mu = 23.2$ cm^{−1}, $F(000) = 1568$. 12038 Unique reflections were collected ($0 < 2\theta < 60^\circ$) and corrected for non-linear decay; 3504 [$I > 2.0\sigma(I)$] were considered observed.

For (3): $\text{C}_{38}\text{H}_{66}\text{O}_4\text{Yb}\cdot 0.5\text{C}_4\text{H}_{10}\text{O}$, $M = 797.1$, monoclinic, space group $P2_1/n$, $a = 9.966(10)$, $b = 17.472(2)$, $c = 24.872(7)$ Å, $\beta = 93.95(5)^\circ$, $U = 4321$ Å³, $Z = 4$, $D_c = 1.23$ g cm^{−3}, $F(000) = 1668$, $\mu = 21.9$ cm^{−1}. 7561 Unique reflections were measured to $2 < 2\theta < 50^\circ$; 4537 [$I > \sigma(I)$] were considered observed.

The data sets were obtained with a Philips PW1100 [(1) and (2)] or an Enraf-Nonius CAD4 (3) diffractometer with graphite monochromated Mo- K_α radiation ($\lambda = 0.71069$ Å) and corrected for absorption empirically;¹⁹ there was no crystal decay for (3) during data collection. In each case the structure was solved by heavy atom methods and refined by full-matrix least-squares. For (1) and (2), the phenyl rings were refined as rigid hexagons (C–C, 1.395 Å) and hydrogen atoms were fixed at calculated positions (C–H, 0.97 Å). For (3), hydrogen atoms were omitted. The final discrepancy indices are $R = 0.0731$, $R_w = 0.0642$ for (2), $R = 0.0921$, $R_w = 0.0778$ for (1), and $R = 0.068$, $R_w = 0.108$ for (3). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

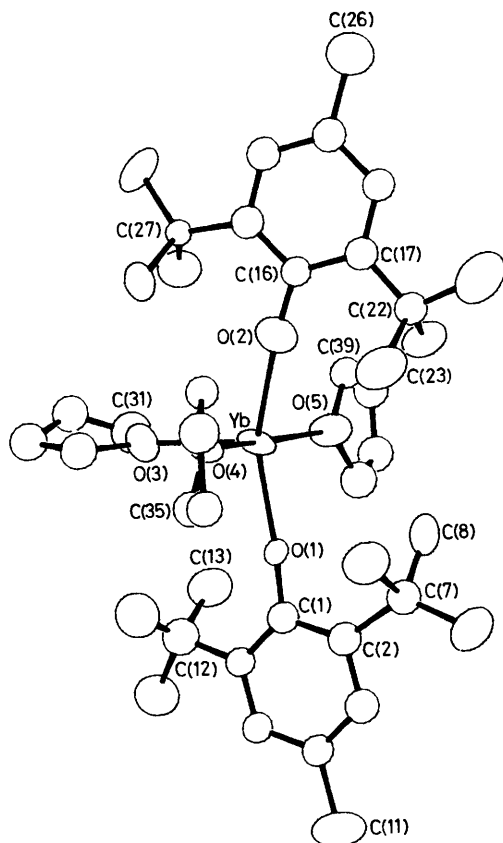


Figure 2. The X-ray structure and atom labelling scheme for $[\text{Yb}(\text{OC}_6\text{H}_2\text{Bu}^t\text{-2,6-Me-4})_2(\text{thf})_3]$ (1). Selected bond lengths (\AA) and angles ($^\circ$) are: Yb–O(1) 2.217(12), Yb–O(2) 2.196(18), Yb–O(3) 2.509(23), Yb–O(4) 2.471(14), Yb–O(5) 2.457(14), O(1)–Yb–O(2) 154.8(10), O(1)–Yb–O(3) 102.5(10), O(1)–Yb–O(4) 89.8(5), O(1)–Yb–O(5) 90.2(5), O(2)–Yb–O(3) 102.6(7), O(2)–Yb–O(4) 89.5(6), O(2)–Yb–O(5) 83.7(7), O(3)–Yb–O(4) 86.4(7), O(3)–Yb–O(5) 109.4(7), and O(4)–Yb–O(5) 163.8(7).

OEt_2 (3)] (Figure 1) establishes them to be monomeric with a distorted tetrahedral geometry at Yb. The average Yb–OAr distances are *ca.* 0.15 \AA shorter than Yb–O(L). The ArO–Yb–OAr angles are much greater (*ca.* 119 $^\circ$) than (L)O–Yb–O(L) (*ca.* 90 $^\circ$). Notable is the deviation of the two planes Yb,O(1),O(2), and Yb,O(3),O(4), from orthogonal [dihedral angle, 75.7 $^\circ$ for (2) and 77.1 $^\circ$ for (3)], resulting in an opening of the O(1)–Yb–O(3) and O(2)–Yb–O(4) angles to *ca.* 120 $^\circ$. Presumably, repulsion between the Bu^t groups and the neutral ligands L is lessened in this manner.

The X-ray structure of $[\text{Yb}(\text{OAr})_2(\text{thf})_3]$ (1) (Figure 2) is distorted square-pyramidal (spy), a unique arrangement in lanthanide chemistry. The basal plane is defined by the two aryloxy oxygens, O(1) and O(2), and two thf oxygens, O(4) and O(5). These atoms are all planar to within 0.07 \AA , while the Yb atom is placed 0.41 \AA above the basal plane. The thf oxygen O(3) occupies the apical site, with the Yb–O(3) vector making an angle of 78.3 $^\circ$ with the base. The average Yb–OAr distance is *ca.* 0.26 or 0.30 \AA shorter than the basal or apical Yb–O(thf) distance, respectively.

In the only other crystallographically characterised five-coordinate Ln complex, $[\text{Ce}(\text{OAr})_3(\text{CNBu}^t)_2]$,¹⁷ the ligands are arranged in a trigonal bipyramidal fashion about Ce³⁺. The spy structure of complex (1) may, in part, be due to a weak Yb \cdots Me interaction [Yb \cdots C(23), 3.424 \AA]. The Yb,O(3),C(23) plane is at an angle of 99.6 $^\circ$ to the basal plane, and the O(3)–Yb \cdots C(23) angle is 149.4 $^\circ$, imparting pseudo-octahedral geometry on the complex.

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