Synthesis and characterisation of iodo functionalised ytterbium(II) and ytterbium(III) alkoxides

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The reaction of YbI_2 in thf with an equimolar quantity of $K(OCPh_3)$ affords $[\{YbI(\mu\text{-}OCPh_3)(\eta^2\text{-dme})\}_2]$ 1; upon photolysis, YbI_2 reacts with dme and yields $[\{YbI_2(\mu OMe)(\eta^2\text{-dme})\}_2]$ 2; the solid-state structures of 1 and 2 are determined.

The chemistry of the II oxidation state derivatives of the lanthanides Sm, Eu and Yb is of considerable interest due to their unique reactivity especially as selective reducing agents and in the activation of small molecules.[1] With respect to synthetic studies of Yb^{II} the availability of YbI_2 has led to a wide range of bis-ligated complexes, including, for example, alkoxides and aryloxides,[2–7] alkyls,[8,9] amides,[10] cyclopentadienyls,[10] chalcogenides,[11,12] phospholes,[13] pyrazolylborates,[14–16] silyls,[17] germyls[17,18] and stannyls[4,19] and thiolates.[20] Few heteroleptic ytterbium(II) complexes have been reported. For aryloxide derivatives we and our colleagues have reported routes to such heteroleptic complexes as $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-Me-}4)\{Sn(CH_2Bu^t)_3\}(thf)_2]$[4] and $[\{Yb[N(SiMe_3)_2](\mu\text{-}OC_6H_2Bu^t{}_2\text{-}2,6\text{-Me-}4)\}_2]$[7] by the direct reaction of the homoleptic bis-stannyl or -amido precursors with 1 equiv. of phenol. Both these compounds react with a further equiv. of phenol to afford the homoleptic $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-Me-}4)_2(thf)_3]$. Two ytterbium(II) heteroleptic alkoxides have recently been reported. The first, an amido derivative $[\{Yb[N(SiMe_3)_2](\mu\text{-}OCBu^t)_2\}_2]$,[21] the second, independently by two of our colleagues, an alkyl, $[\{Yb[C(SiMe_3)_3](\mu\text{-OEt})(OEt_2)\}_2]$.[8,9] As yet however no successful routes to the simple heteroleptic iodo-alkoxide derivatives, '$YbI_n(OR)$' (n = 1 or 2) have been reported.† We now describe a route to both ytterbium-(II) and -(III) iodo-functionalised alkoxide complexes.

The reaction of YbI_2 with 1 equiv. of $K(OCPh_3)$ in thf, followed by crystallisation from a solution of 20% benzene in dme affords as dark brown air-, moisture- and light-sensitive needles $[\{YbI(\mu\text{-}OCPh_3)(\eta^2\text{-dme})\}_2]\cdot C_6H_6$ **1**. Analysis of **1** was considerably facilitated by ^{171}Yb NMR spectroscopy[22] which revealed a single sharp resonance at δ 375 (20% C_6D_6 in dme) ($\omega_{1/2}$ = 50 Hz). It is noteworthy that no other Yb resonances were observed in this spectrum nor was any unusual temperature dependence observed.‡

The X-ray crystal structure of **1** was determined and confirmed it to be dimeric (Fig. 1), with a distorted square-based pyramidal geometry around each ytterbium atom.§ The terminal iodide ligands occupy a basal position about each Yb centre. The Yb–I bond length, 3.090(2) Å, is similar to the Yb–I bond lengths in $[YbI_2(NC_5H_3Me_2\text{-}3,5)_4]$,[23] 3.130(1) Å; $[YbI_2(thf)_4]$,[6] 3.103(1) Å and [YbLI(thf)], 3.065(1) Å [L = tris(3-*tert*-butyl-5-methylpyrazolyl)borate].[24,25] The coordinating oxygens in each of the two dme molecules occupy basal sites with two Yb–O bond lengths of 2.443(12) and 2.573(12) Å. These lengths are comparable with other Yb–dme bond lengths $\{[Yb(\eta\text{-}C_5H_5)_2(dme)]$, av. Yb–O 2.50(3)[26] or 2.466(9) Å[27] and $[Yb(\eta\text{-}C_5Me_5)_2(dme)]$, av. Yb–O 2.45 Å$\}$.[28] The bridging $OCPh_3$ groups are essentially symmetric with bond lengths of 2.302(10) and 2.299(13) Å for Yb–O(1) and Yb–O(1′) respectively. These bond lengths are comparable with the bridging Yb–O bond lengths found in the only other known divalent heteroleptic ytterbium alkoxide, $[\{Yb(\mu\text{-}OCBu^t{}_3)[N(SiMe_3)_2]\}_2]$, [2.297(4) and 2.232(5) Å] and with those found in the homoleptic alkoxide, $[\{Yb(\mu\text{-}OCBu^t{}_3)(\mu\text{-}OCBu^t{}_3)\}_2]$, [2.25(2) and 2.37(2) Å].[21] There is one molecule of solvated benzene for each molecule of **1**, (not shown in Fig. 1). The structure of **1** lies on a crystallographic inversion centre, as does the benzene solvate molecule. Hence the four-membered Yb_2O_2 ring is planar.

Remarkably $[\{YbI_2(\mu\text{-OMe})(\eta^2\text{-dme})\}_2]$ **2** was prepared by photolysis of a slurry of YbI_2 in dme. Photolysis was achieved either by employing a UV lamp¶ or more conveniently by placing a Pyrex Schlenk in direct sunlight. Ethene was observed (^1H NMR) during the reaction, which was complete after *ca.* 150 h. The product gradually crystallised from the reaction and generally formed as large (≈ 1.5 mm) light green cubes on the walls of the reaction vessel. No reaction was observed if the reaction was conducted in the absence of light, even after prolonged periods of several weeks or more. The thermolytic

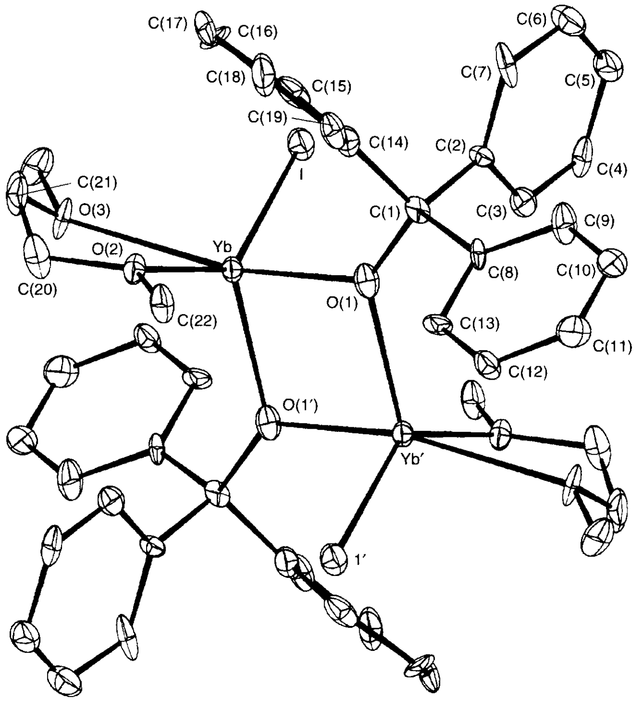

Fig. 1 The molecular structure of $[\{YbI(\mu\text{-}OCPh_3)(\eta^2\text{-}dme)\}_2]\cdot C_6H_6$ **1** and atom numbering scheme. Selected bond lengths (Å) and angles (°): Yb–I 3.090(2), Yb–O(1′) 2.302(10), Yb– O(1) 2.299(13), Yb–O(2) 2.443(12), O(1)–C(1) 1.42(2), O(2)–C(20) 1.41(2), O(2)–C(22) 1.45(2), O(3)–C(21), 1.35(2), O(3)–C(23) 1.47(2), I–Yb–O(1) 99.9(3), I–Yb–O(1′) 114.7(3), I–Yb–O(2) 92.5(4), O(1)–Yb–O(1′) 78.6(4), O(1)–Yb–O(2) 92.5(4), O(1′)–Yb–O(2) 102.6(4), Yb–O(1)–Yb′ 101.4(4), Yb–O(1)–C(1) 129.0(1), Yb′–O(1)–C(1) 129.5(9), Yb–O(2)–C(20) 120.0(1), Yb–O(2)–C(22) 125.4(8), C(20)–O(2)–C(22) 113.0(1), C(21)–O(3)–C(23) 116.0(1), O(1)–C(1)–C(2) 113.0(1), O(1)–C(1)–C(8) 109.0(1), O(1)–C(1)–C(14) 108.0(1).

cleavage of dialkyl ethers by low valent lanthanides has been reported.[8,9]

The analysis of **2** by NMR spectroscopy was somewhat disadvantaged by the paramagnetism of Yb^{III}.[||] The X-ray crystal structure of **2** was determined, confirming that like **1**, it too is dimeric (Fig. 2).[**] The geometry around each ytterbium atom is that of a distorted octahedron, with the oxygen atoms of the coordinating dme occupying both axial and equatorial sites about each ytterbium atom. In contrast to **1**, however, the bridging methoxide groups are asymmetric. The Yb–O(3) bond length, 2.152(4) Å, is shorter than the corresponding Yb-O(3′) length of 2.210(6) Å. The lengthening of the latter may be explained by its *trans* geometry with respect to I(1) for which the Yb–I distance is also lengthened with respect to the Yb–I(2) distance. The Yb–O bond length values are similar to the bridging Yb–O lengths found in $[Yb_5O(OPr^i)_{13}]$, 2.171(28)–2.229(34) Å,[29] $[\{Yb(\eta\text{-}C_5H_5)_2(\mu\text{-}OCH_2CH{=}CHMe)\}_2]$, 2.220(11) and 2.197(11) Å,[30] and $[\{Yb(\eta\text{-}C_5H_5)_2(\mu\text{-}OPr^n)\}_2]$, 2.190(5) and 2.207(6) Å.[31] In addition each ytterbium atom possesses two terminal iodide ligands. The Yb–I bond lengths of 2.941(1) and 2.923(1) Å are similar to the terminal Yb–I bond lengths found in $[Yb(\eta\text{-}C_5Me_5)_2I(thf)]$, 2.959(1) and 2.937(1) Å but significantly shorter than that found in the coordinatively saturated $[Li(OEt_2)_2][Yb(\eta\text{-}C_5Me_5)_2I_2]$, 3.027(1) Å. As for **1**, the molecule lies on a crystallographic inversion centre, and thus, as in **1**, the four-membered Yb_2O_2 ring is planar.

The following features of **1** and **2** are noteworthy. (*i*) **1** is the first example of an iodo functionalised lanthanide(II) alkoxide or aryloxide to be structurally characterised. (*ii*) Similarly **2** is the first example of a structurally authenticated, iodo functionalised lanthanide(III) alkoxide. (*iii*) Both **1** and **2** are structurally unique examples of dimeric species of Ln^{II} and Ln^{III} containing terminal iodide and bridging methoxide ligands. (*iv*) The iodo functionality associated with **1** and **2** should prove an ideal precursor for mixed $Yb(OCPh_3)L$ or $Yb(OMe)L(L')$ complexes respectively. (*v*) Though ytterbium and samarium(III) alkoxides, '$Ln(OR)I_2$' have been proposed as catalysts in Meerwein–Verley–Ponndorf–Oppenauer, MVPO,[35] reactions none have been isolated or structurally characterised. Compound **2** is active as a catalyst in MVPO reactions and suggests a similar nuclearity for such catalysts.[33]

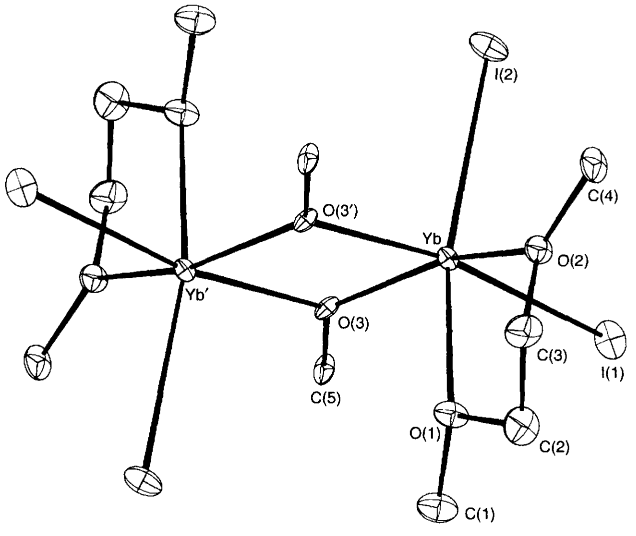

Fig. 2 The molecular structure of $[\{Yb(I)_2(\mu\text{-}OMe)(\eta_2\text{-}dme)\}_2]\cdot C_6H_6$ **2** and atom numbering scheme. Selected bond lengths (Å) and angles (°): Yb–I(1) 2.941(1), Yb–I(2) 2.923(1), Yb–O(1) 2.317(6), Yb–O(2) 2.308(5), Yb–O(3) 2.152(4), Yb–O(3′) 2.210(6), I(1)–Yb–I(2) 94.41(2), I(1)–Yb–O(1) 85.4(2), I(1)–Yb–O(2) 97.2(2), I(1)–Yb–O(3) 95.1(1), I(1)–Yb–O(3′) 168.1(1), I(2)–Yb–O(1) 162.3(1), I(2)–Yb–O(2) 93.3(2), I(2)–Yb–O(3) 106.5(2), I(2)–Yb–O(3′) 93.1(1), O(1)–Yb–O(2) 69.2(2), O(1)–Yb–O(3) 91.2(2), O(1)–Yb–O(3′) 90.3(2), O(2)–Yb–O(3) 155.7(2), O(2)–Yb–O(3′) 91.6(2), O(3)–Yb–O(3′) 73.8(2), Yb(1)–O(1)–C(1) 122.3(5), Yb–O(1)–C(2) 116.9(5), C(1)–O(1)–C(2) 111.4(7), Yb–O(2)–C(3) 116.7(4), Yb–O(2)–C(4) 130.5(5), C(3)–O(2)–C(4) 111.6(6), Yb–O(3)–Yb′ 106.2(2).

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Footnotes

† $YbI(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$, has been observed in solution from the reaction between YbI_2 and $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ though the isolated products were $YbI_2(thf)_4$ and an inseparable mixture of $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2)(thf)_3]$ and $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2)I(thf)_x]$.[17]

‡ *Synthesis and characterising data for* **1**: To a slurry of 2.79 g (6.5 mmol) YbI_2 in *ca.* 30 cm^3 thf was added a solution, in 30 ml thf, of 2.0 g (6.7 mmol) $K(OCPh_3)$. The addition of $K(OCPh_3)$ caused an immediate change of the solution from colourless to orange, stirring for *ca.* 20 h resulted in the formation of a dark brown solution and grey precipitate (KI). Filtration of the solution followed by removal of solvent *in vacuo* and slow cooling to −30 °C, of a dme solution of the residue, led to the formation of small brown needle like crystals. ^{13}C NMR (100.6 MHz, 20% C_6D_6 in dme) δ 101 ($OCPh_3$), phenyl region obscured by solvent. ^{171}Yb NMR (70.02 MHz, 20% C_6D_6 in dme) δ 375. Elemental analysis for $C_{46}H_{50}I_2O_6Yb_2$: C 45.55 (45.36), H, 4.13 (4.10%).

§ *Crystal data for* **1**: $C_{52}H_{56}I_2O_6Yb_2$, M = 1376.9, triclinic, space group $P\bar{1}$ (no. 2), a = 9.784, b = 11.025, c = 12.098 Å, α = 76.36, β = 87.61, γ = 73.45°, U = 1215 Å^3, Z = 1, D_c = 1.88 g cm^{-3}, $F(000)$ = 662, μ(Mo-Kα) = 51.2 cm^{-1}, λ = 0.71073 Å. T = 173 K. Specimen 0.2 x 0.15 x 0.05 mm, unique reflections 4261, significant reflections 3037, empirical correction (T_{max}, T_{min}) 0.97, 0.43, final residuals R = 0.071, R' = 0.074.

¶ Though this method employing a low-pressure 400 W mercury lamp with 5 cm water filter reduced the overall reaction time by almost a factor of four the isolated product was a grey powder and more difficult to manipulate than the crystalline product obtained by the slower photolysis in sunlight.

|| *Synthesis and characterising data for* **2**: 0.5 g of YbI_2 was added to 30 cm^3 of dme and the mixture shaken for a few seconds. The mixture was then left to stand for *ca.* 100 h. Then the solvent and a grey precipitate were removed by cannula and the residual crystals washed with pentane and scraped off the sides of the vessel. Yield 50% . A ^1H NMR (C_6D_6, 298 K) spectrum was obtained for **2** and revealed a broad ($\omega_{1/2}$ = 110 Hz) resonance at δ 1.50 (s, 3 H, OCH_3), a further unresolved broad peak ($\omega_{1/2}$ = 130 Hz) at 3.54 (br, 10 H, coordinated dme), and two, sharper peaks at δ 3.32 and 3.13 were assigned to free dme. Elemental analysis for $C_{10}H_{26}I_4O_6Yb_2$: C 10.98(10.96), H, 2.39(2.47)%.

** *Crystal data for* **2**: $C_{10}H_{26}I_4O_6Yb_2$, M = 1096, monoclinic, space group $P2_1/n$ (non standard no. 14), a = 8.318(4), b = 11.510(6), c = 13.404(10) Å, β = 107.28°, U = 1225.5 Å^3, Z = 2, D_c = 2.97 g cm^{-3}, $F(000)$ = 972, μ(Mo-Kα) = 125.7 cm^{-1}, λ = 0.71069 Å, T 173 K. Specimen 0.4 x 0.4 x 0.3 mm, unique reflections = 2263, total significant reflections = 1946, absorption correction (max, min) = 1.42, 0.77 (by DIFABS). S = 1.4, final residuals, R = 0.031 and R' = 0.039. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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