Three-coordinate Neutral Ligand-free Ytterbium(II) Complexes $[\{YbX(\mu\text{-}X)\}_2]$ (X = OAr 1 or $OCBu^t_3$ 3) or $[\{Yb(NR_2)(\mu\text{-}X)\}_2]$ (X = $OCBu^t_3$ 2 or OAr 4) (Ar = $C_6H_2Bu^t_2$-2,6-Me-4, R = $SiMe_3$); the X-Ray Structures of 1 and 2†

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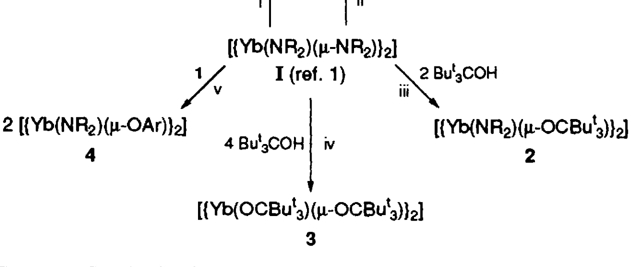
The red, crystalline, benzene-soluble ytterbium(II) and amido-ytterbium(II) alkoxides and aryloxides $[\{YbX(\mu\text{-}X)\}_2]$ (X = OAr **1** or $OCBu^t_3$ **3**) or $[\{Yb(NR_2)(\mu\text{-}X)\}_2]$ (X = $OCBu^t_3$ **2** or OAr **4**) (Ar = $C_6H_2Bu^t_2$-2,6-Me-4, R = $SiMe_3$) have been prepared and NMR-characterised: **1** and **3** from $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I** + 4(or 2)ArOH or $4Bu^t_3COH$, and **2** and **4** from **I** + $2Bu^t_3COH$ or **1**; X-ray diffraction data are provided for **1** and **2**.

There is considerable current interest in the chemistry of organic compounds of the lanthanides (Ln) in the +2 oxidation state, effectively of Sm^{2+} (f^6), Eu^{2+} (f^7) and Yb^{2+} (f^{14}).

We now report the synthesis (Scheme 1), NMR solution spectra‡ and X-ray structures§ of the lipophilic, crystalline complexes $[\{Yb(OAr)(\mu\text{-}OAr)\}_2]$ **1** and $[\{Yb(NR_2)(\mu\text{-}OCBu^t_3)\}_2]$ **2**, which are notable examples of respectively homoleptic (LnX_2) and heteroleptic ($LnXX'$) Ln^{2+} complexes free from stabilising neutral coligands (Ar = $C_6H_2Bu^t_2$-2,6-Me-4, R = $SiMe_3$; $X^- \neq X'^-$ and each a monohapto ligand). Apart from a crystal structure, similar data are also provided for $[\{Yb(OCBu^t_3)(\mu\text{-}OCBu^t_3)\}_2]$ **3** and $[\{Yb(NR_2)(\mu\text{-}OAr)\}_2]$ **4**.

Treatment of $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I**[1] with 2ArOH (i in Scheme 1), followed by crystallisation from hexane gave **1** rather than **4** (a contrast with the Bu^t_3COH reaction, iii in Scheme 1, yielding the heteroleptic complex **2**). NMR spectroscopic solution data on the reaction between **I** and **1** (v in Scheme 1) established that **4** can be formed, but attempts to obtain pure solid **4** have thus far been unsuccessful.

Compounds **1–3** gave satisfactory microanalytical (C, H, N) results. The benzene (or toluene for **1**) solution $^{171}Yb\{^1H\}$ NMR spectral chemical shifts (at 304 K) were of particular diagnostic value, being widely separated for each complex and therefore providing a check on purity with respect to possible ytterbium(II) contaminants: **1** at δ 314 ($w_{\frac{1}{2}}$ = 50 Hz), **2** at δ 758 (80 Hz), **3** at δ 705 (200 Hz), **4** at δ 536 (150 Hz); these δ values may be compared with those for $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **I** 796,[2] $[Yb(NR_2)_2(OEt_2)_2]$ **II** 614,[2] $[Yb(OAr)_2(OEt_2)_2]$ **III** 238,[3a] $[Yb(OAr)_2(thf)_2]$ **IV** 345,[4] and $[Yb(OAr)_2(thf)_3]$ **V** 286[3a] {δ values relative to $[Yb(\eta\text{-}C_5Me_5)_2(thf)_2]$[2]}. The ^1H and ^{13}C NMR spectral data for **1** in benzene at ambient temperature showed that the terminal and bridging ^-OAr ligands gave distinct and separate signals,‡ exchange of ^-OAr ligands occurred upon heating, coalescence temperatures being 358 K for ^1H (of both Me or Bu^t groups) at 360.134 MHz and 338 K for ^{13}C [of $C(CH_3)$] at 125.76 MHz. For **3**, the $^-OCBu^t_3$ ligands were equivalent at ambient temperature;‡ variable-temperature data for **3** are not yet available.



Scheme 1 Synthesis of the red, crystalline ytterbium(II) complexes **1–4** (R = $SiMe_3$, Ar = $C_6H_2Bu^t_2$-2,6-Me-4). *Reaction conditions and solvents* (at 20 °C; for i–iv: volatiles removed at 20 °C/10^{-2} Torr at end of reaction): i, *n*-hexane, 16 h, residue extracted into *n*-hexane, and extract placed at −30 °C; ii, *n*-pentane, 16 h, residue extracted into toluene, and extract placed at −30 °C; iii, *n*-hexane, 2 h, residue extracted into *n*-hexane, and extract placed at 20 °C (overnight); iv, thf–C_6H_6, 3 h; v, NMR spectroscopic experiment in C_6H_6–C_6D_6.

The X-ray structures of **1** and **2** (Figs. 1 and 2) establish them to be dimeric with asymmetrically bridging ^-OAr or $^-OCBu^t_3$ ligands. The Yb(1)–O(1) and Yb(2)–O(2) bond lengths [**1** 2.25(2) and 2.30(2) Å, **2** 2.297(4) and 2.294(5) Å] are shorter than the Yb(2)–O(1) and Yb(1)–O(2) bond lengths [**1** 2.37(2) and 2.31(2) Å, **2** 2.319(5) and 2.320(5) Å]. The asymmetry in the angles at O(1) and O(2) is less marked in **2** [Yb–O(1)–C 136.2(4) and 129.6(4)°, Yb–O(2)–C 135.3(4) and 130.8(4)°] than in **1** [Yb–O(1)–C 153(2) and 104(1), Yb–O(2)–C 146(2) and 114(2)°], perhaps as a consequence of the more spherical nature of the $^-OCBu^t_3$ compared to the ^-OAr ligand.

The terminal Yb–OAr bond lengths [2.10(2) and 2.08(2) Å] are shorter than those of their bridging counterparts, and are similar to those in **III** [av. 2.15(1) Å] and **IV** [av. 2.14(1) Å].[3a] The Yb_2O_2 ring in **1** is planar within 0.03 Å, while the Yb_2O_2 ring in **2** has a fold angle of 24° about the O(1)–O(2) direction. The Yb–N bond lengths in **2** [2.332(6) and 2.327(6) Å] are similar to those in $[Yb(NR_2)_2(dmpe)]$ [dmpe = 1,2-bis(dimethylphosphino)ethane] **VI** [2.331(13) Å][5] and to the terminal Yb–N bond in $[Yb(NR_2)(\mu\text{-}NR_2)_2Na]$ **VII** [2.38(2) Å].[6]

The following additional features are noteworthy. (*i*) Complexes **1–4** have a single LnX_2 precedent, the amide **I**.[1]

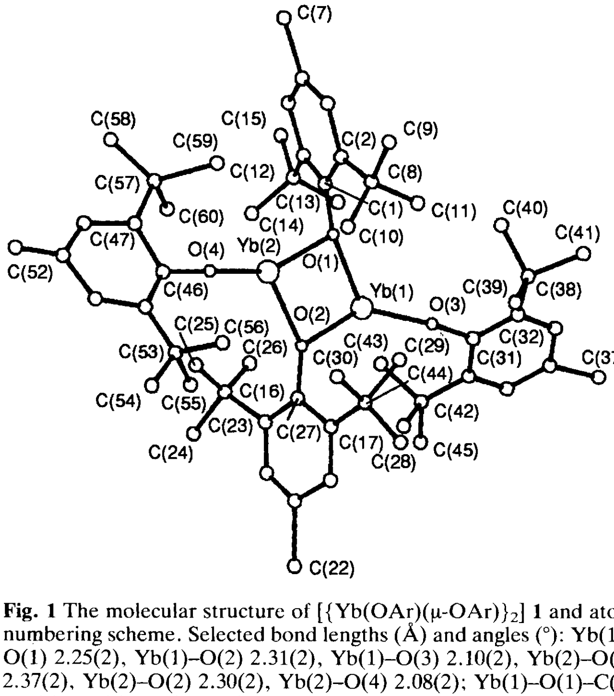


Fig. 1 The molecular structure of $[\{Yb(OAr)(\mu\text{-}OAr)\}_2]$ **1** and atom numbering scheme. Selected bond lengths (Å) and angles (°): Yb(1)–O(1) 2.25(2), Yb(1)–O(2) 2.31(2), Yb(1)–O(3) 2.10(2), Yb(2)–O(1) 2.37(2), Yb(2)–O(2) 2.30(2), Yb(2)–O(4) 2.08(2); Yb(1)–O(1)–C(1) 153(2), Yb(1)–O(2)–C(16) 114(2), Yb(2)–O(2)–C(16) 146(2), Yb(2)–O(1)–C(1) 104(1), O(1)–Yb(1)–O(3) 130.1(6), O(1)–Yb(2)–O(4) 155.4(7), O(2)–Yb(1)–O(3) 141.3(6), O(2)–Yb(2)–O(4) 125.9(7).

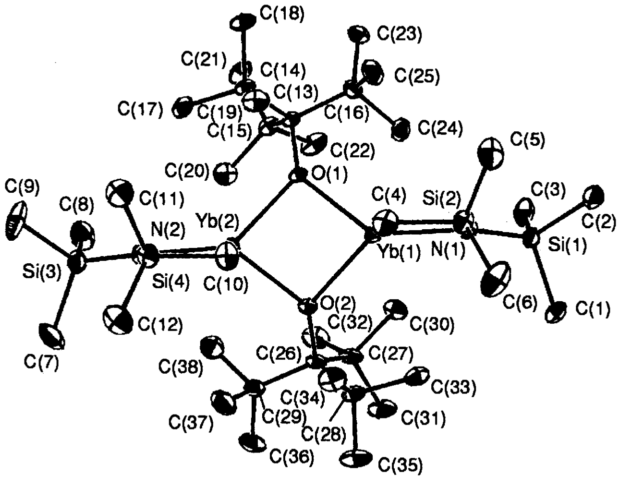


Fig. 2 The molecular structure of $[\{Yb(NR_2)(\mu\text{-}OCBu^t_3)\}_2]$ **2** and atom numbering scheme. Selected bond lengths (Å) and angles (°): Yb(1)–O(1) 2.297(4), Yb(1)–O(2) 2.320(5), Yb(2)–O(1) 2.319(5), Yb(2)–O(2) 2.294(5), Yb(1)–N(1) 2.332(6), Yb(2)–N(2) 2.327(6); Yb(1)–O(1)–C(13) 136.2(4), Yb(1)–O(2)–C(26) 130.8(4), Yb(2)–O(2)–C(26) 135.3(4), Yb(2)–O(1)–C(13) 129.6(4), O(1)–Yb(1)–N(1) 139.5(2), O(1)–Yb(2)–N(2) 135.7(2), O(2)–Yb(1)–N(1) 136.3(2), O(2)–Yb(2)–N(2) 135.7(2).

(*ii*) Complexes **2** and **4** are the first LnXX′ analogues. (*iii*) Three-coordination for a lanthanide metal complex is relatively rare, being restricted to several $[LnX_3]$ complexes with X = CHR_2,[7] NR_2,[8] OAr[9] and $OCBu^t_3$;[10] for Ln^{2+} complexes, the sole examples were **VII** and its europium analogue.[6] (*iv*) Complexes having bridging ^-OAr or $^-OCBu^t_3$ ligands (*cf.* **1–4**) are rare; earlier examples include $[Li(\mu\text{-}OAr)(OEt_2)]_2$[11a] and $[Li(\mu\text{-}OCBu^t_3)]_2$.[11b] (*v*) In **2**, the bridging ligand is $^-OCBu^t_3$ rather than $^-NR_2$, although the latter is known to have this potential as in $[Li(NR_2)(OEt_2)]_2$.[11c] (*vi*) Alkoxides of Ln^{2+} (*cf.* **2** and **3**) were previously unknown, although aryloxides stabilised by having neutral coligands are established, including **III**,[3a] **IV**,[3a] **V**,[3a] $[Yb(OAr)_2(hmpa)_2]$ (hmpa = hexamethylphosphoramide),[12] and $[Yb(OC_6H_2\text{-}Bu^t_3\text{-}2,4,6)_2(thf)_3]\cdot thf$.[3b]

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Footnotes

† No reprints available.

‡ *NMR spectroscopic data*: **1** ^1H (C_6D_6, 250.133 MHz, 298 K), δ 1.37 (s, 36H, Bu^t), 1.57 (s, 36 H, Bu^t), 2.18 (s, 6H, Me), 2.39 (s, 6H, Me), 7.04 (s, 8H, Ar); ^{13}C (C_6H_6–C_6D_6, 125.76 MHz, 303 K), δ 21.26 (q, Me), 21.68 (q, Me), 30.88 [q, $C(CH_3)_3$], 32.87 [q, $C(CH_3)_3$], 34.41 [s, $C(CH_3)_3$], 35.02 [s, $C(CH_3)_3$], 121.33 (s, *C*Me), 125.40 (d, CH), 127.49 (d, CH), 136.32 [s, $C(Bu^t)$], 137.74 [s, $C(Bu^t)$], 155.93 (s, CO), 162.79 (s, CO); **2**: ^1H (C_6D_6, 360.134 MHz, 298 K), δ 0.36 (s, 36H, $SiMe_3$), 1.31 (s, 54H, Bu^t); ^{13}C (C_6D_6, 62.896 MHz, 298 K), δ 6.00 (q, $SiMe_3$), 34.41 [q, $C(CH_3)_3$], 46.12 [s, $C(CH_3)_3$], 92.07 [s, $OC(Bu^t)_3$]; ^{29}Si (C_6D_6, 49.70 MHz, 298 K), δ −15.49; **3**: ^1H (C_6D_6, 250.133 MHz, 298 K), δ 1.54 (s); ^{13}C (C_6H_6–C_6D_6, 62.896 MHz, 304 K), δ 33.54 [q, $C(CH_3)_3$], 46.13 [s, $C(CH_3)_3$], 89.67 [s, $OC(Bu^t)_3$]; **4**: ^1H (C_6D_6, 360.134 MHz, 293 K), δ 0.08 (s, 36H, $SiMe_3$), 1.50 (s, 36H, Bu^t), 2.21 (s, 6H, Me), 7.05 (s, 4H, Ar); ^{13}C (C_6D_6, 125.76 MHz, 293 K), δ 5.00 (q, $SiMe_3$), 20.88 (q, Me), 31.92 [q, $C(CH_3)_3$], 34.74 [s, $C(CH_3)_3$], 126.71 (s, *C*Me), 128.02 (d, CH), 137.06 [s, $C(Bu^t)$], 156.96 (s, CO); ^{29}Si (C_6D_6, 99.36 MHz, 293 K), δ −15.44.

§ *Crystal data*: **1**: $C_{60}H_{92}O_4Yb_2$, M = 1223.5, orthorhombic, space group $P2_12_12_1$, a = 13.240(2), b = 15.520(8), c = 32.091(6) Å, V = 6594 Å^3, $Z = 4$, D_c = 1.23 g cm^{-3}, $F(000) = 2496$, μ = 28.5 cm^{-1}. 6410 unique reflections, 3365 with $I > 2\sigma(I)$, $R = 0.073$, $R_w = 0.090$, S = 2.77. Yb anisotropic, O and C isotropic.

2: $C_{38}H_{90}N_2O_2Si_4Yb_2$, M = 1065.6, monoclinic, space group $P2_1/n$, a = 12.987(2), b = 16.179(4), c = 23.621(4) Å, β = 91.03(1)°, V = 4962 Å^3, $Z = 4$, D_c = 1.43 g cm^{-3}, $F(000) = 2176$, μ = 38.6 cm^{-1}. 9467 total reflections, 5731 unique with $I > 2\,\sigma(I)$, $R = 0.042$, $R_w = 0.043$, S = 1.2. All non-H atoms anisotropic.

Intensities were measured to θ_{max} = 25° on an Enraf-Nonius CAD4 diffractometer using monochromated Mo-Kα radiation (λ = 0.71069 Å), and corrected for absorption. Structure solution was by routine heavy atom methods and refinement by full-matrix least squares with H atoms at fixed positions. 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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