Synthesis and Characterisation of Lanthanide(II) Aryloxides including the First Structurally Characterised Europium(II) Compound $[Eu(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ (thf = tetrahydrofuran)†

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The lanthanide(II) aryloxide complexes $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(OEt_2)_2]$ **1**, $[Yb(OC_6H_3Bu^t{}_2\text{-}2,6)_2(thf)_3]$ **2**, $[Yb(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2(thf)_3]$ **3**, $[Sm(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]$ **4**, $[Eu(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5**, $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]$ **6** and $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)I(thf)_x]$ **7** (thf = tetrahydrofuran) have been synthesized. Each of the complexes **1**–**3** was prepared by the reaction of 2 equivalents of the appropriate potassium aryloxide with YbI_2 in diethyl ether (**1**) or thf (**2** or **3**). Complexes **4**–**6** were prepared by the reaction of 2 equivalents of $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ with $LnI_2(thf)_2$ (Ln = Sm, Eu or Yb) in thf. Reacting YbI_2 with 1 equivalent of $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ in thf yielded complex **7** as the main product, but $^{171}Yb\text{-}\{^1H\}$ NMR spectroscopy showed that **6** and $[YbI_2(thf)_4]$ **8** were also formed. The crystal structure of complex **5** reveals that it adopts a distorted trigonal-bipyramidal conformation with (*i*) apical thf oxygens [O(4)–Eu–O(5) 178.6(2)°, Eu–O(4) 2.590(5) and Eu–O(5) 2.573(5) Å]; (*ii*) the equatorial O(1), O(2) and O(3) thf coplanar; and (*iii*) Eu–O(1) 2.321(5), Eu–O(2) 2.337(5) and Eu–O(3) 2.515(6) Å. The crystal structure of complex **8** showed there to be an octahedral arrangement around the metal, the molecule lying on a crystallographic inversion centre, with angles I–Yb–O(1) 90.1(2), I–Yb–O(2) 91.4(2) and O(1)–Yb–O(2) 88.9(3)°, and bond lengths Yb–I 3.103(1), Yb–O(1) 2.399(9) and Yb–O(2) 2.373(8) Å.

The majority of hydrocarbon-soluble complexes of the lanthanide elements have the metal in the +3 oxidation state, in high co-ordination numbers and often contain one or more π-bonded ligands.[1] However the use of bulky σ ligands such as alkyls,[1c,2] amides,[1c,3] aryloxides[1c,4] and alkoxides[1c,4a,5] has provided access to low co-ordinate lanthanide(III) complexes without π-bonded ligands.

The +2 oxidation state is accessible for samarium ($4f^6$), europium ($4f^7$) and ytterbium ($4f^{14}$) [there is also evidence for organo-cerium(II)[6] and -neodymium(II)[7] complexes]. There has been notable expansion into the area of organolanthanide(II) complexes,[8] including their application to catalysis and synthesis.[9] These complexes act as one-electron reductants with considerable selectivity depending on the nature of (*i*) the lanthanide metal, (*ii*) the anionic ligand, (*iii*) the absence or presence of neutral coligand and (*iv*) the solvent solubility of the complex. The unique reactivity of this class of compound is illustrated amongst other things by formation of the unusual complexes $[\{Sm[\eta\text{-}C_5H_3(SiMe_3)_2\text{-}1,3]_2(\mu\text{-}OH)\}_2]$[10] and $[\{Sm(\eta\text{-}C_5Me_5)_2\}_2(\mu\text{-}\eta^2,\eta^2\text{-}N_2)]$[11] from lanthanide(II) precursors.

Nearly all the reported lanthanide(II) compounds contain a π-bonded ligand, normally a cyclopentadienyl or a close equivalent. However, some complexes featuring solely σ-bonded ligands have been synthesized.[1c,12–14]

Homoleptic lanthanide(II) aryloxide complexes have recently been reported for ytterbium and europium with various aryloxide ligands.[12f,13b,c,f,14] The latter [aryloxide = $OC_6H_2\text{-}Bu^t{}_2\text{-}2,6\text{-}R\text{-}4$ (R = H, Me or Bu^t)] are sterically demanding and thus help stabilise the low metal co-ordination numbers that these complexes adopt.

The methods of preparation of lanthanide(II) aryloxides involved (*i*) protolytic exchange [equations (1),[12f,14] (2),[14a] (3),[12b] (4)[13b] and (5)[13b]], (*ii*) redox transmetallation [equation (6)[14b]], (*iii*) redox transmetallation [equation (7)[14]] or (*iv*) direct reaction of metal and ligand in benzophenone [equation (8)[13c]] or liquid ammonia [equation (9)[13d]] ($OR' = OC_6H_2\text{-}Bu^t{}_2\text{-}2,6\text{-}R\text{-}4$). These data, together with present contributions, are summarised in Table 1 [$(L)_n$ are not included in equations (1)–(9)].

$$[Ln(C_6F_5)_2] + 2HOR' \longrightarrow Ln(OR')_2 + 2C_6F_5H \quad (1)$$

$$[Ln\{N(SiMe_3)_2\}_2] + 2HOR' \longrightarrow Ln(OR')_2 + 2NH(SiMe_3)_2 \quad (2)$$

$$[Ln(C_5Me_5)_2] + 2HOR' \longrightarrow Ln(OR')_2 + 2C_5Me_5H \quad (3)$$

$$[Ln\{Sn(CH_2Bu^t)_3\}_2] + 2HOR' \longrightarrow Ln(OR')_2 + 2SnH(CH_2Bu^t)_3 \quad (4)$$

$$[Ln\{Sn(CH_2Bu^t)_3\}_2] + HOR' \longrightarrow [Ln(OR')\{Sn(CH_2Bu^t)_3\}] + SnH(CH_2Bu^t)_3 \quad (5)$$

$$Ln + Hg(C_6F_5)_2 + 2HOR' \longrightarrow Ln(OR')_2 + 2C_6F_5H + Hg \quad (6)$$

$$Ln + 2Tl(OR') \longrightarrow Ln(OR')_2 + 2Tl \quad (7)$$

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† Lanthanide(II) Alkyls, Amides, Alkoxides and Aryloxides. Part 1.
No reprints available.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: Torr ≈ 133 Pa.

$$Ln(OCPh_2)_2 + 2HOR' \longrightarrow Ln(OR')_2 + H_2 + 2Ph_2CO \quad (8)$$

$$Ln + 2HOR' \xrightarrow{\text{liquid } NH_3} Ln(OR')_2 + H_2 \quad (9)$$

Results and Discussion

Synthesis.—Compound $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(OEt_2)_2]$ **1** was previously synthesized by the reaction of $HOC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4$ with $[Yb\{N(SiMe_3)_2\}_2(OEt_2)_2]$[14a] and structurally characterised. We now report that complex **1** can also be prepared readily from YbI_2 and $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ [equation (10)]; recrystallisation from OEt_2 gave **1** as orange-red needles. Both YbI_2[12h] and $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ are easily synthesized and safely stored under argon.

$$YbI_2 + 2K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4) \xrightarrow{OEt_2} \underset{\mathbf{1}}{[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(OEt_2)_2]} \quad (10)$$

Complexes $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4)_2(thf)_3]$ (R = H **2** or Bu^t **3**; thf = tetrahydrofuran) were previously prepared by protolytic exchange [equation (1)][14b] or redox transmetallation [equation (7) or (8)].[14b] It is now shown that the reaction of YbI_2 with a stoichiometric amount of $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4)$ (R = H or Bu^t)[15] in thf at 0 °C [equation (11)] yielded from thf yellow cubic crystals of **2** or **3**.

$$YbI_2 + 2K(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4) \xrightarrow{thf} [Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4)_2(thf)_3] \quad (11)$$
$$R = H\ \mathbf{2}\ \text{or}\ Bu^t\ \mathbf{3}$$

The europium(II) aryloxide $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5** was previously prepared according to equation (1)[12f,14b] or (3) (Ln = Eu, OR′ = $OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4$)[12b] and complex $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]$ **6** according to equation (1),[14b] (7),[14b] (8)[14] or (9).[13d] Complex $[Sm(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]$ **4** has not previously been reported.

A convenient route to complexes **4**–**6** has now been obtained [equation (12)] using the readily synthesized $LnI_2(thf)_2$[16]

$$LnI_2(thf)_2 + 2K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4) \xrightarrow{thf} [Ln(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3] \quad (12)$$
$$Ln = Sm\ \mathbf{4},\ Eu\ \mathbf{5}\ \text{or}\ Yb\ \mathbf{6}$$

(Ln = Sm, Eu or Yb) and $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ as the starting materials. Recrystallisation of the solids from thf afforded complex **4** as dark red, cubic crystals, or yellow crystals for **5** and **6**.

Table 1 Synthetic routes to lanthanide(II) aryloxide complexes $[Ln(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4)_2(L)_n]$

Ln	R	L	*n*	Synthetic route	Crystal structure	Ref.
Yb	H	thf	3	(*i*), (*ii*), (*iii*), (*vi*)	—	12(*f*), 14(*b*), This work
Yb	H	thf	2	(*v*)	—	14(*b*)
Yb	Me	thf	3	(*i*), (*ii*), (*iii*), (*iv*), (*vi*)	√	12(*f*), 13(*d*), 14, This work
Yb	Me	thf	2	(*i*),[a] (*v*)	√	13(*b*), 14
Yb	Me	OEt_2	2	(*i*),[b] (*vi*)	√	14(*a*), This work
Yb	Me	hmpa	2	(*iv*)[c]	√	13(*c*)
Yb	Bu^t	thf	3	(*i*), (*ii*), (*iii*), (*vi*)	√	12(*f*), 14(*b*), This work
Eu	H	thf	3	(*ii*)	—	14(*b*)
Eu	Me	thf	3	(*i*), (*i*),[d] (*vi*)	√	12(*b*)–(*f*), 14(*b*), This work
Eu	Bu^t	thf	3	(*ii*)	—	14(*b*)
Sm	Me	thf	3	(*vi*)	—	This work

(*i*) Protolytic exchange: [a] from the lanthanide(II) stannyl, [b] from the lanthanide(II) amide, [d] from the decamethyllanthanocene(II); (*ii*) redox transmetallation involving ligand exchange; (*iii*) redox transmetallation from thallium(I) phenolates; (*iv*) direct reaction of metal and ligand in liquid ammonia: [c] direct reaction of metal and ligand in benzophenone (hmpa = hexamethylphosphoramide); (*v*) desolvation in hot toluene; (*vi*) anionic ligand exchange.

Only a few heteroleptic lanthanide(II) complexes have been reported and only four structurally characterised: $[\{Sm(NR_2)(thf)(dme)(\mu\text{-}I)\}_2]$,[12g] $[\{Sm(\eta\text{-}C_5Me_5)(thf)_2(\mu\text{-}I)\}_2]$,[17a] $[\{Eu(\eta\text{-}C_5Me_5)(thf)_2(\mu\text{-}C{\equiv}CPh)\}_2]$[17b] and $[\{Yb(NR_2)(\mu\text{-}OCBu^t_3)\}_2]$[13f] (R = $SiMe_3$, dme = 1,2-dimethoxyethane). The dearth of complexes of this class may be attributed to the facile equilibrium which may exist between the homoleptic and heteroleptic complexes, favouring the former.

The methods of synthesis of heteroleptic lanthanide(II) complexes in principle involve: (*i*) substitution of only one anionic ligand of the homoleptic complex by a differing singly negatively charged ligand, (*ii*) ligand redistribution between two different homoleptic lanthanide(II) species and (*iii*) protolytic exchange of one of the ligands.

The heteroleptic ytterbium aryloxide complex **7** has now been formed by reacting YbI_2 with 1 equivalent of $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ [equation (13)]. The use of $^{171}Yb\text{-}\{^1H\}$ NMR spectroscopy[18] (in thf–C_6D_6 at 304 K) showed that $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)I(thf)_x]$ **7** [δ 353 ($w_{\frac{1}{2}}$ = 30 Hz)] was the main product, but **6** [δ 234 (20 Hz)] and $[YbI_2(thf)_4]$ **8** [δ 456 (20 Hz)] were also present. Crystallisation from thf afforded complex **8** as pale yellow cubes; complexes **6** and **7** were not separated.

$$YbI_2 + K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4) \xrightarrow{thf} \underset{\mathbf{6}}{[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]} +$$
$$\underset{\mathbf{7}}{[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)I(thf)_x]} + \underset{\mathbf{8}}{[YbI_2(thf)_4]} \quad (13)$$

The use of such simple anionic ligand exchange has been widely used for the preparation of lanthanide(II) cyclopentadienyls[1,8,10,19] or amides,[1c,12] but not hitherto for aryloxides.

Crystal Structure of $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5**.—The molecular structure and atom numbering scheme for complex **5** are shown in Fig. 1; bond lengths and angles are in Table 2, fractional atomic coordinates in Table 3.

Only a few organic complexes of europium(II) have been structurally characterised,[12a–d,13e,17b,19,20] with complex **5** being the only example of an europium aryloxide in either the +2 or +3 oxidation state. The structures of several ytterbium(II) aryloxides have been reported including the isoleptic $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$;[14] a comparison of selected bond lengths and angles is given in Table 4.

The structure of crystalline **5** shows it to have five-co-ordinate Eu with a similar conformation to that reported for the ytterbium(II) analogue[14] or $[Yb(OC_6H_2Bu^t_3\text{-}2,4,6)_2(thf)_3]\cdot thf$.[14b]

The structure of **5** may be described as having a distorted trigonal-bipyramidal skeleton with two thf oxygens [O(4) and O(5)] in the axial positions with a near linear OEuO angle, O(4)–Eu–O(5) 178.6(2)°. The two aryloxide oxygens [O(1) and O(2)] and the remaining thf oxygen [O(3)] occupy positions in the distorted trigonal plane with angles O(1)–Eu–O(2) 150.3(2), O(1)–Eu–O(3) 104.2(2) and O(2)–Eu–O(3) 105.5(2)°.

An alternative description for **5** would refer to a distorted square-pyramidal skeleton, there being two O–M–O angles greater than 150°. One thf oxygen [O(3)] would then be said to occupy an apical position with Eu–O(3) 2.515(6) Å and angles

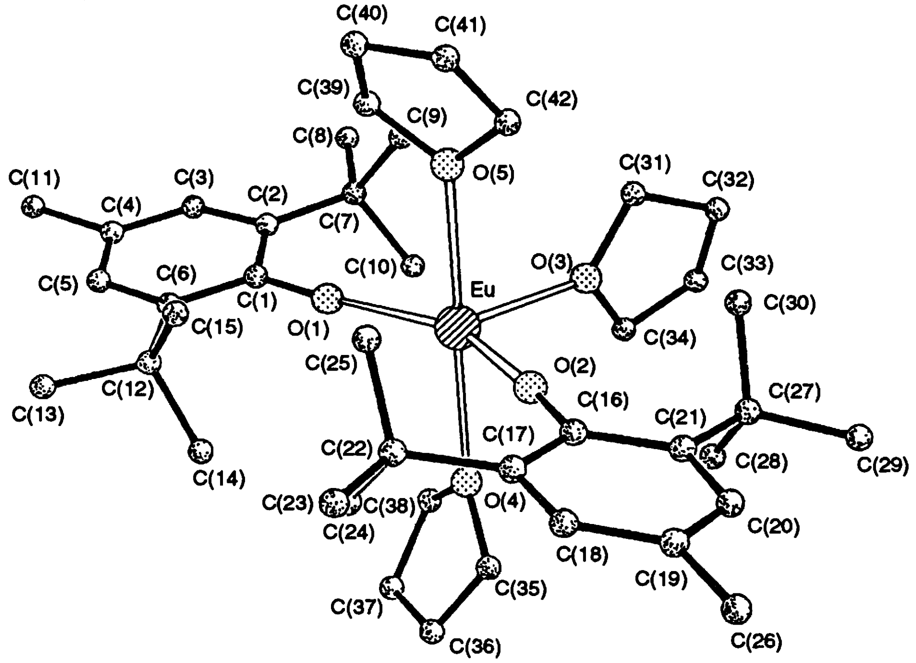

Fig. 1 The molecular structure of $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5** and atom numbering scheme

Table 2 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5**

Eu–O(1)	2.321(5)	Eu–O(2)	2.337(5)
Eu–O(3)	2.515(6)	Eu–O(4)	2.590(5)
Eu–O(5)	2.573(5)		
O(1)–Eu–O(2)	150.3(2)	O(1)–Eu–O(3)	104.2(2)
O(2)–Eu–O(3)	105.5(2)	O(1)–Eu–O(4)	89.0(2)
O(2)–Eu–O(4)	90.2(2)	O(3)–Eu–O(4)	89.2(2)
O(1)–Eu–O(5)	91.6(2)	O(2)–Eu–O(5)	88.7(2)
O(3)–Eu–O(5)	91.9(2)	O(4)–Eu–O(5)	178.6(2)
Eu–O(1)–C(1)	174.1(4)	Eu–O(2)–C(16)	175.2(4)
Eu–O(3)–C(31)	125.8(5)	Eu–O(3)–C(34)	126.0(5)
Eu–O(4)–C(38)	125.7(5)	Eu–O(4)–C(35)	126.4(5)
Eu–O(5)–C(39)	124.6(5)	Eu–O(5)–C(42)	127.8(5)

O(1)–Eu–O(3) 104.2(2), O(2)–Eu–O(3) 105.5(2), O(3)–Eu–O(4) 89.2(2) and O(3)–Eu–O(5) 91.9(2)°. Perpendicular to the O(3)–Eu vector there would then be two thf oxygen atoms [O(4) and O(5)] coplanar with Eu, with the aryloxide oxygen atoms [O(1) and O(2)] deviating from the quasi-equatorial plane. The four Eu–O bond lengths in the latter range from Eu–O(1) 2.321(5), Eu–O(2) 2.337(5), Eu–O(4) 2.590(5) to Eu–O(5) 2.573(5) Å. This shows a shorter $Eu\text{–}OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4$ than $Eu\text{–}OC_4H_8$ bond, the latter being somewhat longer than the 'apical' Eu–O bond.

Using the square-plane description, the '*trans*' (thf) oxygen atoms in the 'equatorial' plane are almost linear, O(4)–Eu–O(5) 178.6(2)°, whereas the '*trans*' $(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ oxygens show a significant bend, O(1)–Eu–O(2) 150.3(2)°. The 'equatorial *cis*' O–Eu–O angles are close to 90°: O(1)–Eu–O(4) 89.0(2), O(1)–Eu–O(5) 91.6(2), O(2)–Eu–O(4) 90.2(2) and O(2)–Eu–O(5) 88.7(2)°.

Crystal Structure of $[YbI_2(thf)_4]$ **8**.—The molecular structure and atom numbering scheme for complex **8** are shown in Fig. 2; bond lengths and angles are in Table 5, fractional atomic coordinates in Table 6.

The structure of **8** shows an octahedral arrangement around the metal, the molecule lying on a crystallographic inversion centre, with angles I–Yb–O(1) 90.1(2), I–Yb–O(2) 91.4(2) and O(1)–Yb–O(2) 88.9(3)°, and bond lengths Yb–I 3.103(1), Yb–O(1) 2.399(9) and Yb–O(2) 2.373(8) Å.

Previously structurally characterised LnI_2 complexes included the samarium and europium iodides $[SmI_2(thf)_5][Co(CO)_4]$,[21] *cis*- and *trans*-$[SmI_2\{O(CH_2CH_2OMe)_2\}_2]$,[22,23] $[\{Sm(\mu\text{-}I)_2(NCBu^t)_2\}_\infty]$ **I**[23] and $[LnI(\mu\text{-}I)(mim)_3]_2$ (Ln = Sm **II** or Eu **III**; mim = *N*-methylimidazole).[24] Complex **8** is structurally most similar to **I**–**III** in that all four complexes are diiodides with the lanthanide centre in a six-co-ordinate octahedral arrangement. The main difference is that in monomeric **8** the iodides are terminal, whereas in **II** and **III** half of the iodides bridge to generate a dimer and in **I** all the iodides are bridging to give a polymer.

The molecular structure of **8** is similar to those observed for $[Yb(EPh_3)_2(thf)_4]$ (E = Si **IVa**, Ge **IVb** or Sn **IVc**)[25,26] and $[Yb\{Sn(SnMe_3)_3\}_2(thf)_4]$ **IVd**.[27] The Yb–O bond lengths in these complexes range from 2.35 Å in **IVd** to 2.48 Å in **IVa**.

Experimental

General.—All manipulations were carried out under vacuum or in a stream of argon by Schlenk techniques. Solvents were dried and distilled over potassium–sodium alloy under argon prior to use. The following compounds were prepared by published procedures: $SmI_2(thf)_2$,[16] $EuI_2(thf)_2$,[16] YbI_2,[12h] $YbI_2(thf)_2$[16] and $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4)$ (R = H or Bu^t).[15] 2,6-Di-*tert*-butyl-4-methylphenol and potassium hydride were purchased from Aldrich. Microanalyses were carried out in the microanalytical department of this School. The NMR spectra were recorded using Bruker WP80, WM250, WM360 or WM500 spectrometers.

Preparation of $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$.—A solution of $HOC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4$ (125.3 g, 0.57 mmol) in thf (500 cm^3) was added to a suspension of KH (20.5 g, 0.51 mol) in thf (150 cm^3) at −78 °C. The white suspension was allowed to warm to room temperature and stirred for 18 h. The volatiles were removed *in vacuo*, the residue was washed with pentane (200 cm^3) and dried for 5 h at 20 °C (10^{-2} Torr) to afford $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ (121.0 g, 0.47 mmol, 82%), as a white powder. NMR: ^1H (C_5D_5N, 360.13 MHz, 20 °C), δ 1.73 (s, 18 H, Bu^t), 2.45 (s, 3 H, Me), 7.22 (s, 2 H, CH).

Table 3 Fractional atomic coordinates (× 10^5 for Eu; × 10^4 for others) with e.s.d.s in parentheses for $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Eu	50 796(3)	23 627(2)	13 943(1)	C(22)	7 148(9)	4 802(5)	1 811(3)
O(1)	3 522(5)	2 481(3)	789(2)	C(23)	7 569(11)	5 731(6)	1 857(4)
C(1)	2 738(6)	2 557(5)	419(2)	C(24)	5 601(8)	4 789(6)	1 761(3)
C(2)	2 271(8)	1 809(6)	184(3)	C(25)	7 681(9)	4 448(6)	1 401(3)
C(3)	1 418(8)	1 937(8)	−203(3)	C(26)	9 863(9)	4 648(6)	3 279(3)
C(4)	1 037(9)	2 718(9)	−366(3)	C(27)	7 659(9)	1 937(6)	2 666(3)
C(5)	1 526(9)	3 433(7)	−134(3)	C(28)	6 147(9)	1 764(6)	2 661(3)
C(6)	2 361(8)	3 374(6)	254(3)	C(29)	8 318(10)	1 580(6)	3 091(3)
C(7)	2 638(9)	911(6)	335(3)	C(30)	8 223(10)	1 459(6)	2 293(3)
C(8)	2 090(12)	202(8)	17(4)	O(3)	5 076(5)	792(3)	1 579(2)
C(9)	4 188(8)	801(6)	392(3)	C(31)	6 043(9)	163(6)	1 460(3)
C(10)	2 066(10)	720(7)	768(3)	C(32)	5 918(11)	−575(7)	1 758(4)
C(11)	153(11)	2 824(9)	−808(4)	C(33)	4 576(12)	−517(7)	1 890(5)
C(12)	2 851(9)	4 193(6)	484(3)	C(34)	4 117(9)	359(6)	1 831(3)
C(13)	2 326(12)	5 010(7)	249(4)	O(4)	3 141(5)	2 596(3)	1 878(2)
C(14)	2 371(9)	4 241(6)	939(3)	C(35)	3 197(9)	3 101(8)	2 260(3)
C(15)	4 401(8)	4 259(6)	518(3)	C(36)	1 935(11)	3 515(10)	2 262(5)
O(2)	6 603(4)	2 995(3)	1 923(2)	C(37)	984(9)	3 118(9)	1 933(4)
C(16)	7 380(6)	3 383(5)	2 236(2)	C(38)	1 749(8)	2 429(7)	1 757(3)
C(17)	7 686(7)	4 274(5)	2 209(3)	O(5)	7 032(5)	2 167(4)	920(2)
C(18)	8 494(7)	4 647(5)	2 548(3)	C(39)	6 930(10)	2 302(8)	471(3)
C(19)	9 009(7)	4 220(5)	2 912(3)	C(40)	8 198(13)	2 632(9)	366(4)
C(20)	8 709(7)	3 359(5)	2 936(2)	C(41)	9 182(10)	2 556(8)	749(4)
C(21)	7 918(6)	2 910(5)	2 613(2)	C(42)	8 438(8)	2 108(8)	1 058(3)
Disordered thf molecule							
C(43)	4 292(24)	8 262(13)	673(8)	C(43′)	4 873(26)	8 386(12)	888(9)
C(44)	3 658(25)	7 745(16)	1 005(9)	C(44′)	5 920(21)	7 687(18)	952(12)
C(45)	4 534(31)	6 988(17)	1 120(9)	C(45′)	5 293(32)	6 946(16)	689(13)
C(46)	5 488(34)	6 925(15)	777(14)	C(46′)	3 843(29)	7 000(16)	789(11)
C(47)	5 573(21)	7 818(15)	604(8)	C(47′)	3 559(22)	7 947(19)	756(14)

The disordered thf molecule is represented by 'half-carbon' atoms C(43) to C(47′).

Table 4 Selected bond lengths (Å) and angles (°) for three crystalline five-co-ordinate lanthanide(II) aryloxides $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5** and $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}R\text{-}4)_2(thf)_3]\cdot thf$ (R = Me[14] or Bu^t [14b])

	5	R = Me[14]	R = Bu^t [14b]
Ln–O(1)	2.321(5)	2.22(1)	2.21(1)
Ln–O(2)	2.337(5)	2.20(2)	2.22(1)
Ln–O(3)	2.515(6)	2.51(2)	2.44(1)
Ln–O(4)	2.590(5)	2.47(1)	2.47(2)
Ln–O(5)	2.573(5)	2.46(1)	2.48(1)
O(1)–Ln–O(2)	150.3(2)	154.8(10)	149.0(6)
O(1)–Ln–O(3)	104.2(2)	102.5(10)	105.2(5)
O(1)–Ln–O(4)	89.0(2)	89.8(5)	90.5(5)
O(1)–Ln–O(5)	91.6(2)	90.2(5)	88.2(5)
O(2)–Ln–O(3)	105.5(2)	102.6(7)	105.6(5)
O(2)–Ln–O(4)	90.2(2)	89.5(6)	90.2(5)
O(2)–Ln–O(5)	88.7(2)	83.7(7)	89.6(5)
O(3)–Ln–O(4)	89.2(2)	86.4(7)	95.7(5)
O(3)–Ln–O(5)	91.9(2)	109.4(7)	87.0(5)
O(4)–Ln–O(5)	178.6(2)	163.8(7)	177.3(5)

Table 5 Intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for $[YbI_2(thf)_4]$ **8**

Yb–I	3.103(1)	Yb–O(1)	2.399(9)
Yb–O(2)	2.373(8)	O(1)–C(1)	1.43(2)
O(1)–C(4)	1.44(2)	O(2)–C(5)	1.30(2)
O(2)–C(8)	1.40(2)	C(1)–C(2)	1.44(3)
C(2)–C(3)	1.41(3)	C(3)–C(4)	1.36(3)
C(5)–C(6)	1.48(3)	C(6)–C(7)	1.26(3)
C(7)–C(8)	1.43(3)		
I–Yb–O(1)	90.1(2)	I–Yb–O(2)	91.4(2)
O(1)–Yb–O(2)	88.9(3)	Yb–O(1)–C(1)	126(1)
Yb–O(1)–C(4)	129(1)	C(1)–O(1)–C(4)	104(1)
Yb–O(2)–C(5)	127(1)	Yb–O(2)–C(8)	128.7(9)
C(5)–O(2)–C(8)	104(1)	O(1)–C(1)–C(2)	108(2)
C(1)–C(2)–C(3)	109(2)	C(2)–C(3)–C(4)	107(2)
O(1)–C(4)–C(3)	112(2)	O(2)–C(5)–C(6)	114(2)
C(5)–C(6)–C(7)	101(2)	C(6)–C(7)–C(8)	113(2)
O(2)–C(8)–C(7)	106(2)		

Preparation of $[Yb(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(OEt_2)_2]$ **1**.—The compound $K(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)$ (2.0 g, 7.7 mmol) was added to a slurry of YbI_2 (1.7 g, 4.0 mmol) in diethyl ether (60 cm^3) at −30 °C. The solution was allowed to warm to 0 °C, and a change from yellow to orange-red was noted. After stirring for 5 min, the reaction mixture was allowed to warm to room temperature and stirred for a further 30 min. Solid was removed by filtration through Celite. The volume of diethyl ether in the filtrate was reduced to *ca.* 20 cm^3, yielding solid **1**. Orange-red needles of **1** (1.8 g, 2.4 mmol, 62%) were recrystallised from diethyl ether at −30 °C.

Preparation of $[Yb(OC_6H_3Bu^t_2\text{-}2,6)_2(thf)_3]$ **2**.—A slurry of $K(OC_6H_3Bu^t_2\text{-}2,6)$ (2.9 g, 12 mmol) in thf (20 cm^3) was added to YbI_2 (2.6 g, 6 mmol) in thf (30 cm^3) at −30 °C. The reaction mixture was warmed to 0 °C and an intensification of the yellow colour was noted. Stirring was continued at room temperature for a further 30 min. The thf was removed *in vacuo*, diethyl ether (30 cm^3) was added and the solid removed by filtration through Celite. The diethyl ether was then removed from the filtrate *in vacuo* and the solid was again dissolved in thf (30 cm^3). The volume was reduced to *ca.* 10 cm^3, and cooling to −30 °C yielded yellow cubes of **2** (2.7 g, 3.4 mmol, 57%) (Found: C, 55.2; H, 7.9. $C_{40}H_{66}O_5Yb$ requires C, 60.1; H, 8.3%), m.p. 112–114 °C. NMR: ^1H ($C_6D_5CD_3$, 80.13 MHz, 25 °C), δ 1.41 (s, 36 H, Bu^t), 1.6 [br s, 12 H, β-CH_2 (thf)], 3.6 [br s, 12 H, α-CH_2 (thf)], 6.8 (t, 2 H, *p*-H), 7.2 (d, 4 H, *m*-H); $^{171}Yb\text{-}\{^1H\}$ ($C_6H_5Me\text{-}C_6D_5CD_3$, 63.01 MHz, 25 °C), δ 256 ($w_{\frac{1}{2}}$ = 47 Hz).

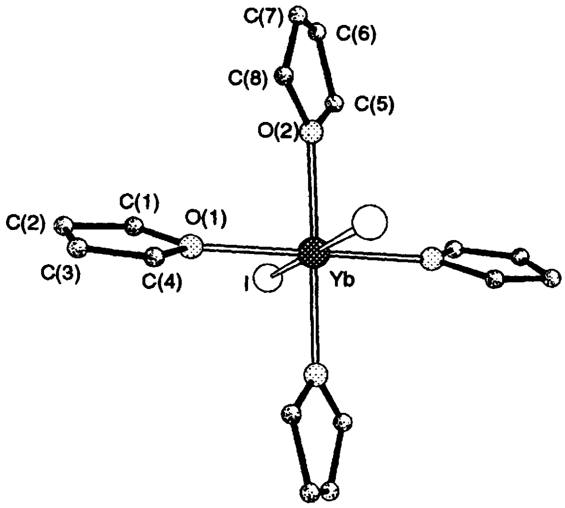

Fig. 2 The molecular structure of $[YbI_2(thf)_4]$ **8** and atom numbering scheme

Table 6 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for $[YbI_2(thf)_4]$ **8**

Atom	*x*	*y*	*z*
Yb	0	0	0
I	2329.8(13)	951.6(8)	−1914.4(10)
O(1)	−1446(10)	1436(6)	211(10)
O(2)	1687(10)	425(7)	1890(8)
C(1)	−794(26)	2353(12)	71(24)
C(2)	−2066(26)	3004(12)	330(30)
C(3)	−3484(27)	2510(12)	611(26)
C(4)	−3087(22)	1588(14)	593(27)
C(5)	3265(25)	356(22)	2028(20)
C(6)	3972(22)	799(22)	3255(18)
C(7)	2713(24)	910(22)	3904(16)
C(8)	1242(23)	811(20)	3096(19)

Preparation of $[Yb(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2(thf)_3]$ **3**.—A slurry of $K(OC_6H_2Bu^t{}_3\text{-}2,4,6)$ (4.3 g, 14.3 mmol) in thf (20 cm^3) was added to YbI_2 (3.1 g, 7.3 mmol) in thf (30 cm^3) at −30 °C. The reaction mixture was warmed to 0 °C and an intensification in the yellow colour was noted. Stirring was continued at room temperature for a further 30 min. The thf was removed *in vacuo*, diethyl ether (30 cm^3) added and the solid removed by filtration through Celite. The diethyl ether was then removed from the filtrate *in vacuo* and the solid again taken-up in thf (30 cm^3). The volume was reduced to *ca.* 10 cm^3, and cooling at −30 °C yielded yellow cubes of **3** (3.45 g, 3.78 mmol, 53%) (Found: C, 61.4; H, 9.2. $C_{48}H_{82}O_5Yb$ requires C, 63.2; H, 9.1%), m.p. 110–115 °C. NMR: ^1H ($C_6D_5CD_3$, 80.13 MHz, −10 °C), δ 1.45 (s, 18 H, *p*-Bu^t), 1.5 [br s, 12 H, β-CH_2 (thf)], 1.60 (s, 36 H, *o*-Bu^t), 3.55 [br s, 12 H, α-CH_2 (thf)], 7.3 (s, 4 H, CH); $^{13}C\text{-}\{^1H\}$ ($C_6D_5CD_3$, 90.56 MHz, 25 °C), δ 25.6 [t, β-C (thf)], 30.3 [q, *p*-$C(CH_3)_3$], 31.3 [q, *o*-$C(CH_3)_3$], 34.7 [s, *p*-$C(CH_3)_3$], 35.9 [s, *o*-$C(CH_3)_3$], 69.2 [t, α-C (thf)], 121.6 (s, C^4), 137.2 (s, C^2 and C^6), 153.1 (s, C^1) (C^3 and C^5 signal not observed; probably hidden under one of the toluene signals); $^{171}Yb\text{-}\{^1H\}$ ($C_6H_5Me\text{–}C_6D_5CD_3$, 63.01 MHz, −75 °C), δ 298 ($w_{\frac{1}{2}}$ = 40 Hz).

Preparation of $[Sm(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]$ **4**.—A slurry of $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ (0.82 g, 3.2 mmol) in thf (20 cm^3) was added to a stirring solution of $SmI_2(thf)_2$ (0.9 g, 1.6 mmol) in thf (30 cm^3) at −30 °C. The reaction mixture was warmed to 0 °C and a change from turquoise blue to an intense red was noted. The solution was allowed to warm to room temperature and stirred for a further 30 min. The thf was removed *in vacuo* and the solid removed by filtration through Celite after prior addition of diethyl ether (30 cm^3). The latter was removed from the filtrate *in vacuo*, to leave a solid, which was recrystallised from thf (*ca.* 10 cm^3) at −30 °C to yield intensely red needles of **4** (0.84 g, 1.04 mmol, 65%) (Found: C, 61.1; H, 8.70. Calc. for $C_{42}H_{70}O_5Sm$: C, 62.6; H, 8.75%), m.p. 133–137 °C.

Preparation of $[Eu(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5**.—A solution of $EuI_2(thf)_2$ (2.03 g, 3.69 mmol) in thf (*ca.* 75 cm^3) was added to a stirred solution of $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ (1.91 g, 7.40 mmol) in thf (*ca.* 100 cm^3). Stirring of the yellow suspension was continued for 20 h at 20 °C, which was then filtered. The solvent was removed from the filtrate *in vacuo*. The resulting yellow solid was extracted into toluene (*ca.* 75 cm^3) and filtered. The filtrate was evaporated to dryness and thf (*ca.* 30 cm^3) added. Cooling to −30 °C yielded yellow X-ray quality crystals of **5** (2.45 g, 2.79 mmol, 76%).

Preparation of $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]$ **6**.—A slurry of $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ (1.55 g, 6 mmol) in thf was added to a solution of $YbI_2(thf)_2$ (1.7 g, 3.0 mmol) in thf at −30 °C. The reaction mixture was warmed to 0 °C and an intensification in the yellow colour was noted. After further stirring at room temperature for 30 min, the thf was removed *in vacuo* and the solid removed by filtration through Celite, after prior addition of diethyl ether (30 cm^3). The latter was removed from the filtrate *in vacuo* and the residue again taken-up into thf (30 cm^3). The volume was reduced to *ca.* 10 cm^3. Cooling to −30 °C afforded yellow cubes of **6** (1.93 g, 2.33 mmol, 78%), m.p. 116–120 °C. NMR: ^1H ($C_6D_5CD_3$, 80.13 MHz, 25 °C): δ 1.35 [br s, 12 H, β-CH_2 (thf)], 1.67 (s, 36 H, Bu^t), 2.47 (s, 6 H, Me), 3.83 [br s, 12 H, α-CH_2 (thf)], 7.20 (s, 4 H, *m*-H); $^{13}C\text{-}\{^1H\}$ ($C_6D_5CD_3$, 90.56 MHz, 25 °C), δ 21.4 (q, Me), 25.7 [t, β-C (thf)], 31.5 [q, $C(CH_3)_3$], 35.3 [s, $C(CH_3)_3$], 70.3 [t, α-C (thf)], 126.1 (s, C^4), 137.9 (s, C^2 and C^6), 149.0 (s, C^1) (C^3 and C^5 signal not observed; probably hidden under one of the toluene signals); $^{171}Yb\text{-}\{^1H\}$ ($C_6H_5Me\text{–}C_6D_5CD_3$, 63.01 MHz, −40 °C), δ 285 ($w_{\frac{1}{2}}$ = 42 Hz).

Preparation of $[Yb(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)I(thf)_x]$ **7**.—A colourless solution of $K(OC_6H_2Bu^t{}_2\text{-}2,6\text{-}Me\text{-}4)$ (0.44 g, 1.70 mmol) in thf (50 cm^3) was added to YbI_2 (0.73 g, 1.71 mmol) at room temperature. The yellow suspension was stirred for 16 h, whereafter the solid was allowed to settle and removed by filtration. The volatiles were removed *in vacuo* to yield a yellow-orange solid (1.0 g). NMR: ^1H ($C_4H_8O\text{–}C_6D_6$, 250.13 MHz, 31 °C), δ 1.41 (s, 36 H, Bu^t), 1.61 [br s, β-CH_2 (thf)], 2.26 (s, 6 H, Me), 3.70 [br s, α-CH_2 (thf)], 6.92 (s, 4 H, CH); $^{13}C\text{-}\{^1H\}$ ($C_4H_8O\text{–}C_6D_6$, 62.90 MHz, 25 °C), δ 21.44 (q, Me), 25.99 [t, β-C (thf)], 31.11 [q, $C(CH_3)_3$], 35.21 [s, $C(CH_3)_3$], 68.27 [t, α-C (thf)], 118.81 (s, C^4), 125.23 (d, C^3 and C^5), 136.94 (s, C^2 and C^6), 164.76 (s, C^1); $^{171}Yb\text{-}\{^1H\}$ ($C_4H_8O\text{–}C_6D_6$, 43.77 MHz, 31 °C), δ 353 ($w_{\frac{1}{2}}$ = 30 Hz).

Crystallographic Data.—The appropriate details are given in Table 7. In each case unique data sets were collected, using a crystal sealed in a capillary under argon.

For complex **5**, raw intensities, collected on a Siemens P4/PC four-circle diffractometer at 294 K, were corrected for absorption using ψ-scan data.[28] Patterson superposition yielded the positions of all non-hydrogen atoms, which were subjected to anisotropic refinement. All hydrogens except those of disordered tetrahydrofuran were generated geometrically (C–H fixed at 0.96 Å) and allowed to ride on their respective parent carbon atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. Computations were performed using the SHELXTL PC program package[29,30] on a PC 486 computer. Analytic expressions of atomic scattering factors were

Table 7 Crystal and refinement data for $[Eu(OC_6H_2Bu^t_2\text{-}2,6\text{-}Me\text{-}4)_2(thf)_3]\cdot thf$ **5** and $[YbI_2(thf)_4]$ **8**

	5	**8**
Formula	$C_{46}H_{78}EuO_6$	$C_{16}H_{32}I_2O_4Yb$
M	897.04	715.3
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	9.962(4)	8.242(2)
b/Å	15.592(6)	14.381(5)
c/Å	31.049(16)	10.033(1)
β/°	95.80(1)	92.97(1)
Z	4	2
U/Å^3	4798(2)	1187.5
D_c/g cm^{-3}	1.217	1.60
F(000)	1860	672
μ/cm^{-1}	13.5	65.1
N	8388	2179
$N_o\,[I > n\sigma(I)]$	5379, $n = 3$	1138, $n = 2$
λ/Å	0.710 73	0.710 69
Specimen size/mm	0.50 × 0.50 × 0.36	0.35 × 0.3 × 0.1
R	0.045	0.043
R'	0.059	0.052
Weighting scheme, *w*	$[\sigma^2(\lvert F_o\rvert) + 0.001\lvert F_o\rvert^2]^{-1}$	$\sigma(F)^{-2}$
Max., min. electron density/e Å^{-3}	0.92, −1.10	0.62, −0.75
Δ/σ_{max}	0.07	0.03

employed, and anomalous dispersion corrections were incorporated.[31]

For complex **8**, the data were collected on an Enraf-Nonius diffractometer in the θ–2θ mode with $\Delta\theta = (0.8 + 0.35 \tan\theta)°$ and a maximum scan time of 1 min. A total of 2179 unique reflections was measured for $2 < \theta < 25°$ and $+h + k \pm l$, and 1138 reflections with $|F^2| > 2\sigma(F^2)$ were used in the refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/Lp$. There was no crystal decay. A correction (max. 1.52, min. 0.49) for absorption was applied using DIFABS[32] after isotropic refinement. The structure was solved by routine heavy-atom methods. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix least squares. The hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent atom. Programs were from the Enraf-Nonius SDP-Plus package.[33]

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

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References

1 (*a*) T. J. Marks and R. D. Ernst, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 3, p. 173; (*b*) H. Schumann, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 474; (*c*) C. Schaverien, *Adv. Organomet. Chem.*, 1994, **36**, 283.

2 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 1007; J. L. Atwood, M. F. Lappert, R. G. Smith and H. Zhang, *J. Chem. Soc., Chem. Commun.*, 1988, 1308.

3 J. S. Ghotra, M. B. Hursthouse and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669; D. C. Bradley, J. S. Ghotra and F. A. Hart, *J. Chem. Soc., Dalton Trans.*, 1973, 1021; D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1977, 1166; R. A. Andersen, D. H. Templeton and A. Zalkin, *Inorg. Chem.*, 1978, **17**, 2317.

4 (*a*) R. C. Mehrotra, A. Singh and U. M. Tripathi, *Chem. Rev.*, 1991, **91**, 1287; (*b*) P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499; (*c*) P. B. Hitchcock, M. F. Lappert and R. G. Smith, *Inorg. Chim. Acta*, 1987, **139**, 183; (*d*) H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem.*, 1988, **27**, 1130; (*e*) G. B. Deacon, S. Nickel, P. MacKinnon and E. R. T. Tiekink, *Aust. J. Chem.*, 1990, **43**, 1245; (*f*) G. B. Deacon, T. Feng, S. Nickel, M. I. Ogden and A. H. White, *Aust. J. Chem.*, 1992, **45**, 671; (*g*) D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, R. L. Vincent, J. G. Watkin and B. D. Zwick, *Inorg. Chem.*, 1994, **33**, 3487.

5 H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem.*, 1989, **28**, 3280; D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1991, **10**, 1049; M. Wedler, J. W. Gilje, U. Pieper, D. Stalke, M. Noltemeyer and F. T. Edelmann, *Chem. Ber.*, 1991, **124**, 1163; W. J. Evans, R. E. Golden and J. W. Ziller, *Inorg. Chem.*, 1991, **30**, 4963; W. A. Herrmann, R. Anwander, M. Kleine and W. Scherer, *Chem. Ber.*, 1992, **125**, 1971; W. A. Herrmann, R. Anwander and M. Denk, *Chem. Ber.*, 1992, **125**, 2399; W. A. Herrmann, R. Anwander and W. Scherer, *Chem. Ber.*, 1993, **126**, 1533; D. M. Barnhart, D. L. Clark, J. C. Huffman, R. L. Vincent and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 4077; D. M. Barnhart, D. L. Clark, J. C. Gordon, J. C. Huffman, J. G. Watkin and B. D. Zwick, *J. Am. Chem. Soc.*, 1993, **115**, 8461.

6 A. Greco, S. Cesca and G. Bertolini, *J. Organomet. Chem.*, 1976, **113**, 321.

7 K. Rossmanith, *Monatsh. Chem.*, 1979, **110**, 1019; M. Wedler, A. Recknagel and F. T. Edelmann, *J. Organomet. Chem.*, 1990, **395**, C26.

8 W. J. Evans, *Polyhedron*, 1987, **6**, 803.

9 P. Girard, J. L. Namy and H. B. Kagan, *J. Am. Chem. Soc.*, 1980, **102**, 2693.

10 P. B. Hitchcock, M. F. Lappert and S. Prashar, *J. Organomet. Chem.*, 1991, **413**, 79.

11 W. J. Evans, T. A. Ulibarri and J. W. Ziller, *J. Am. Chem. Soc.*, 1988, **110**, 6877.

12 (*a*) T. D. Tilley, A. Zalkin, R. A. Andersen and D. H. Templeton, *Inorg. Chem.*, 1981, **20**, 551; (*b*) T. D. Tilley, Ph.D. Thesis, University of California, 1982; cited in ref. 12(*e*); (*c*) T. D. Tilley, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725; (*d*) T. D. Tilley, R. A. Andersen, B. Spencer and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271; (*e*) J. M. Boncella and R. A. Andersen, *Organometallics*, 1985, **4**, 205; (*f*) G. B. Deacon, C. M. Forsyth and R. H. Newnham, *Polyhedron*, 1987, **6**, 1143; (*g*) W. J. Evans, D. K. Drummond, H. Zhang and J. L. Atwood, *Inorg. Chem.*, 1988, **27**, 575; (*h*) T. D. Tilley, J. M. Boncella, D. J. Berg, C. J. Burns and R. A. Andersen, *Inorg. Synth.*, 1990, **27**, 146.

13 (*a*) Yu. F. Rad'kov, E. A. Fedorova, S. Ya. Khorshev, G. S. Kalinina, M. N. Bochkarev and G. A. Razuvaev, *Zh. Obshch. Khim.*, 1985, **55**, 2153; (*b*) F. G. N. Cloke, C. I. Dalby, P. B. Hitchcock, H. Karamallakis and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 779; (*c*) Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1992, 722; (*d*) B. Çetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932; (*e*) D. R. Cary and J. Arnold, *Inorg. Chem.*, 1994, **33**, 1791; (*f*) J. R. van den Hende, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1994, 1413.

14 (*a*) G. B. Deacon, P. B. Hitchcock, S. A. Holmes, M. F. Lappert, P. MacKinnon and R. H. Newnham, *J. Chem. Soc., Chem. Commun.*, 1989, 935; (*b*) G. B. Deacon, T. Feng, P. MacKinnon, R. H. Newnham, S. Nickel, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1993, **46**, 387.

15 I. Gümrükçü, Ph.D. Thesis, University of Sussex, 1980.

16 P. L. Watson, T. H. Tulip and I. Williams, *Organometallics*, 1990, **9**, 1999.

17 (*a*) W. J. Evans, J. W. Grate, H. W. Choi, I. Bloom, W. E. Hunter and J. L. Atwood, *J. Am. Chem. Soc.*, 1985, **107**, 941; (*b*) J. M. Boncella, T. D. Tilley and R. A. Andersen, *J. Chem. Soc., Chem. Commun.*, 1984, 710.

18 A. G. Avent, M. A. Edelman, M. F. Lappert and G. A. Lawless, *J. Am. Chem. Soc.*, 1989, **111**, 3423.

19 P. B. Hitchcock, J. A. K. Howard, M. F. Lappert and S. Prashar, *J. Organomet. Chem.*, 1992, **437**, 177.

20 W. J. Evans, L. A. Hughes and T. P. Hanusa, *Organometallics*, 1986, **5**, 1285.

21 W. J. Evans, I. Bloom, J. W. Grate, L. A. Hughes, W. E. Hunter and J. L. Atwood, *Inorg. Chem.*, 1985, **24**, 4620.

22 A. Sen, V. Chebolu and A. L. Rheingold, *Inorg. Chem.*, 1987, **26**, 1821.

23 V. Chebolu, R. R. Whittle and A. Sen, *Inorg. Chem.*, 1985, **24**, 3082.

24 W. J. Evans, G. W. Rabe and J. W. Ziller, *Inorg. Chem.*, 1994, **33**, 3072.

25 M. N. Bochkarev, V. V. Khramenkov, Yu. F. Rad'kov, L. N. Zakharov and Yu. T. Struchkov, *J. Organomet. Chem.*, 1991, **408**, 329.

26 L. N. Bochkarev, V. M. Makarov, Y. N. Hrzhanovskaya, L. N. Zakharov, G. K. Fukin, A. I. Yanovsky and Yu. T. Struchkov, *J. Organomet. Chem.*, 1994, **467**, C3.

27 L. N. Bochkarev, O. V. Grachev, N. E. Molosnova, S. F. Zhiltsov, L. N. Zakharov, G. K. Fukin, A. I. Yanovsky and Yu. T. Struchkov, *J. Organomet. Chem.*, 1993, **443**, C26.

28 G. Kopfmann and R. Hubber, *Acta Crystallogr., Sect. A*, 1968, **24**, 348.

29 G. M. Sheldrick, in *Crystallographic Computing 3: Data Collection, Structure Determination, Proteins, Databases*, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, New York, 1985, p. 175.

30 G. M. Sheldrick, *SHELXTL PC Manual*, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.

31 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 55, 99 and 149.

32 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

33 SDP-Plus Structure Determination Package, Enraf-Nonius, Delft, 1985.

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