Synthesis and ^{171}Yb-{^{1}H} Nuclear Magnetic Resonance Spectra of Ytterbium(II) Aryloxides [Yb(OR')$_2$(L)$_n$] [(L)$_n$ = (OEt$_2$)$_2$, (thf)$_2$, (thf)$_3$, (pyridine)$_2$ or Me$_2$PCH$_2$CH$_2$PMe$_2$] and [{Yb(μ-OR')(X)}$_2$] (X = OR' or NR$_2$) (R' = C$_6$H$_2$Bu$^t_2$-2,6-Me-4, R = SiMe$_3$, thf = tetrahydrofuran)†

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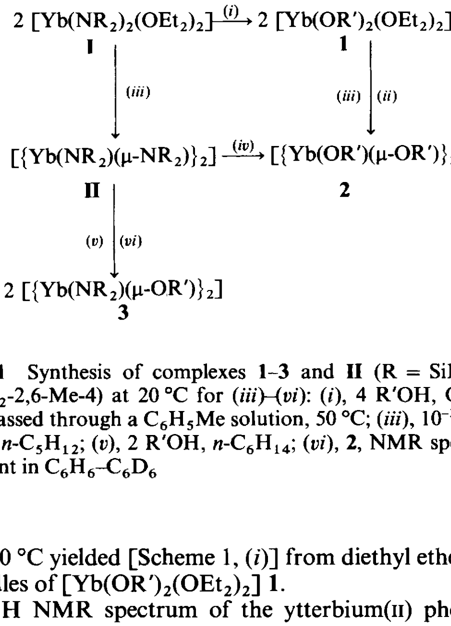
Crystalline homo- and hetero-leptic ytterbium(II) aryloxides derived from bulky 2,6-di-*tert*-butyl-4-methylphenol (R'OH) were prepared as follows: (*a*) [Yb(OR')$_2$(OEt$_2$)$_2$] **1** from 2 R'OH and [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] **I** (R = SiMe$_3$); (*b*) [{Yb(OR')(μ-OR')}$_2$] **2** by desolvating **1** or from [{Yb(NR$_2$)(μ-NR$_2$)}$_2$] **II** and 4 R'OH; and (*c*) [{Yb(NR$_2$)(μ-OR')}$_2$] **3** from **II** and 2 R'OH or **II** and **2**. Single-crystal X-ray diffraction studies established complex **1** to be monomeric with a distorted tetrahedral configuration and **2** to be dimeric with asymmetrically bridging $^-$OR' ligands. Complexes **1**–**3** were characterised by multinuclear (^{1}H, ^{13}C, ^{29}Si and ^{171}Yb) NMR spectroscopy and elemental (C, H, N) analysis. Variable-temperature ^{1}H and ^{13}C NMR spectral data for **2** led to $\Delta G^{\ddagger}$ for the terminal/bridge $^-$OR' site-exchange process. The known aryloxide [Yb(OR')$_2$(thf)$_3$] **4** was obtained from **1** and an excess of tetrahydrofuran (thf); reacting **1** with the appropriate stoichiometric amount of thf, pyridine (py) or 1,2-bis(dimethylphosphino)ethane (dmpe) yielded [Yb(OR')$_2$(thf)$_2$] **5**, [Yb(OR')$_2$(py)$_2$] **6** or [Yb(OR')$_2$(dmpe)] **7**, respectively. The δ [^{171}Yb-{^{1}H}] NMR spectral data for complexes **4**–**7** showed that displacement of diethyl ether from **1** (δ 238 at 193 K) by another neutral coligand had a marked effect on the magnitude of the chemical shift, ranging from δ 286 at 233 K for **4** to δ 999 at 296 K for **7**.

The lanthanide (Ln) bis(trimethylsilyl)amides have been shown to be convenient starting materials for the synthesis of halide-free organolanthanide compounds.[2–10] Thus, various lanthanide(III) complexes were easily prepared by reacting an appropriate lanthanide(III) amide under mild conditions with acetylacetone,[2] an alcohol,[3] a cyclopentadiene,[4] fluorinated alcohol,[5] a phenol,[6] a secondary phosphine,[7] a selenol,[8] a silanol[9] or a thiol.[10] Only a few homoleptic lanthanide(II) complexes have been obtained by this route, *i.e.*, by reactions of a lanthanide(II) amide with an alcohol,[8,11a] phenol,[11b] selenol,[8,11c] tellurol[11c] or thiols.[8,11d]

We now report the synthesis and structures of various homo- and hetero-leptic ytterbium(II) aryloxides derived from 2,6-di-*tert*-butyl-4-methylphenol (R'OH) using [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] **I**[12] or [{Yb(NR$_2$)(μ-NR$_2$)}$_2$] **II**[13] (R = SiMe$_3$) as substrate. The role of ^{171}Yb NMR spectroscopy[14] in this study has been significant. Parts of this work have previously been briefly communicated;[11a,b] Part 1 of this series described the preparation of lanthanide(II) aryloxides by anionic ligand exchange using the appropriate potassium aryloxide and LnI$_2$ and reviewed other methods for their preparation.[1]

Results and Discussion

Synthesis of [Yb(OR')$_2$(OEt$_2$)$_2$] **1**.—The reaction of [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] **I**[12] (R = SiMe$_3$) with a stoichiometric amount of 2,6-di-*tert*-butyl-4-methylphenol (R'OH) in diethyl ether at 0 °C yielded [Scheme 1, (*i*)] from diethyl ether orange-red needles of [Yb(OR')$_2$(OEt$_2$)$_2$] **1**.



Scheme 1 Synthesis of complexes 1–3 and II (R = SiMe$_3$, R' = C$_6$H$_2$Bu$^t_2$-2,6-Me-4) at 20 °C for (*iii*)–(*vi*): (*i*), 4 R'OH, OEt$_2$, 0 °C; (*ii*), Ar passed through a C$_6$H$_5$Me solution, 50 °C; (*iii*), 10^{-2} Torr; (*iv*), 4 R'OH, *n*-C$_5$H$_{12}$; (*v*), 2 R'OH, *n*-C$_6$H$_{14}$; (*vi*), **2**, NMR spectroscopic experiment in C$_6$H$_6$–C$_6$D$_6$

The ^{1}H NMR spectrum of the ytterbium(II) phenoxide **1** showed singlets representing the *tert*-butyl and methyl protons at δ 1.59 and 2.37, respectively, and the triplet/quartet pattern characteristic of co-ordinated diethyl ether at δ 1.05/3.21. Integration was consistent with the formulation of **1** as [Yb(OR')$_2$(OEt$_2$)$_2$]. Complex **1** was further characterised by ^{171}Yb-{^{1}H} NMR spectroscopy[14] (Table 1) and elemental (C, H, N) analysis.

Synthesis of [{Yb(OR')(μ-OR')}$_2$] **2**.—Passing a stream of argon through a solution of **1** in toluene at 50 °C for 2 h yielded the red, homoleptic complex [{Yb(OR')(μ-OR')}$_2$] **2** [Scheme

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† Lanthanide(II) Alkyls, Amides, Alkoxides and Aryloxides. Part 2.[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.

Table 1 The ^{171}Yb-{^{1}H} NMR chemical shift (δ) data[a]

Compound	Solvent[b]	T/K	δ(^{171}Yb)	$w_{\frac{1}{2}}$/Hz	Ref.
1 $[Yb(OR')_2(OEt_2)_2]$	PhMe	193	238	240	11(*b*)
2 $[\{Yb(OR')(\mu\text{-}OR')\}_2]$	PhMe	304	314	50	This work
3 $[\{Yb(NR_2)(\mu\text{-}OR')\}_2]$	PhH	304	536	150	This work
4 $[Yb(OR')_2(thf)_3]$	PhMe	233	286	42	11(*b*)
5 $[Yb(OR')_2(thf)_2]$	PhMe	298	345	85	This work
6 $[Yb(OR')_2(py)_2]$	PhMe	298	745	80	This work
7 $[Yb(OR')_2(dmpe)]$	PhMe	296	999	170	This work
II $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$	PhMe	263	796	90	14

[a] Spectra were recorded at 43.77 MHz (for **2** and **3**) or 63.01 MHz for (**1**, **4**–**7** and **II**) relative to $[Yb(\eta\text{-}C_5Me_5)_2(thf)_2]$ in 10% $C_6D_5CD_3$ at 273 K. [b] 10–20% v/v C_6D_6 or $C_6D_5CD_3$ was used as lock.

1, (*ii*)]. Alternatively, complex **2** was obtained by desolvating **1** *in vacuo* at 20 °C [Scheme 1, (*iii*)]. That **2** was unsolvated was evident from the ^{1}H and ^{13}C-{^{1}H} NMR spectra (in C_5D_5N), which showed no OEt_2 signals; moreover, δ [^{171}Yb-{^{1}H}] was considerably shifted compared with **1**, Table 1.

An alternative route to **2** used $[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2]$ **II**[13] as the precursor. The latter, an orange solid, was obtained from complex **I** upon desolvation *in vacuo* at 20 °C. Treatment of **II** with 4 R'OH yielded [Scheme 1, (*iv*)] red crystals of **2**. The ^{1}H and ^{13}C-{^{1}H} NMR spectral data for **2** in benzene at ambient temperature showed that the terminal and bridging $^-$OR' ligands gave distinct and separate signals. A variable-temperature ^{1}H and ^{13}C-{^{1}H} NMR study showed that these coalesced at higher temperatures. The ^{1}H NMR (250.13 MHz) spectrum of **2** in $C_6D_5CD_3$ showed that the two methyl signals merged at 323 ± 2.5 K, the coalescence temperature T_c, corresponding to $\Delta G^\ddagger = 66.2 \pm 0.5$ kJ mol^{-1}, while the *tert*-butyl signals coalesced at 323 ± 2.5 K, corresponding to $\Delta G^\ddagger = 66.5 \pm 0.5$ kJ mol^{-1}. The ^{13}C-{^{1}H} NMR (125.76 MHz) spectrum showed that $T_c = 338 \pm 1$ K for the *tert*-butyl groups $[C(CH_3)_3]$, corresponding to $\Delta G^\ddagger = 65.5 \pm 0.2$ kJ mol^{-1}. This fluxional process is believed to arise from terminal/bridge $^-$OR' site-exchange.

Synthesis of $[\{Yb(NR_2)(\mu\text{-}OR')\}_2]$ **3**.—The heteroleptic aryloxide $[\{Yb(NR_2)(\mu\text{-}OR')\}_2]$ **3** was obtained [Scheme 1, (*v*)] from **II** with 2 R'OH in hexane, contrary to our earlier report.[11a] The formation of complex **3** was also demonstrated by an NMR tube reaction between **II** and **2** in benzene [Scheme 1, (*vi*)]. Moreover, complex **3** was isolated from the benzene solution and obtained from pentane as red crystals; it was fully characterised by multinuclear (^{1}H, ^{13}C-{^{1}H}, ^{29}Si-{^{1}H}) NMR spectroscopy and elemental (C, H, N) analysis.

To confirm that the observed ^{171}Yb signal (see Table 1) was that of the heteroleptic complex **3** and not the average signal of **II** and **2**, an excess of **II** was added to a solution of **3** in benzene. Again the same signal δ [^{171}Yb-{^{1}H}] 536 was observed.

Synthesis of $[Yb(OR')_2(L)_n]$ (n = 3, L = thf **4**; n = 2, L = thf **5** *or* py **6**; *or* n = 1, L = dmpe **7**).—The reaction of complex **1** with an excess of tetrahydrofuran (thf) in hexane at 0 °C yielded, from hexane at −30 °C, the yellow microcrystalline $[Yb(OR')_2(thf)_3]$ **4**; alternatively, the reaction of **1** with a stoichiometric amount of thf, pyridine (py), or 1,2-bis(dimethylphosphino)ethane (dmpe) in hexane at 0 °C yielded, from hexane at −30 °C, the compounds $[Yb(OR')_2(thf)_2]$ **5**, $[Yb(OR')_2(py)_2]$ **6** and $[Yb(OR')_2(dmpe)]$ **7** as red, blue-green or purple microcrystalline materials, respectively, equation (1).

$$\underset{\mathbf{1}}{[Yb(OR')_2(OEt_2)_2]} \xrightarrow{L} [Yb(OR')_2(L)_n] \qquad (1)$$

	n L
4:	3 thf
5:	2 thf
6:	2 py
7:	1 dmpe

These reactions were not reversible; **1** was not obtained upon addition of an excess of diethyl ether to **5**, **6** or **7**.

The solution ^{171}Yb-{^{1}H} NMR chemical shifts were of particular diagnostic value (Table 1). It was evident that, as for the bis(amide) **I**,[14] displacement of diethyl ether by another neutral coligand had a marked effect on the magnitude of the chemical shift.

Crystal Structure of $[Yb(OR')_2(OEt_2)_2]$ **1**.—The molecular structure and atom numbering scheme for compound **1** are shown in Fig. 1; bond lengths and angles are given in Table 2, fractional atomic coordinates in Table 3.

The molecule was shown to be a monomer in the solid state, the ytterbium being four-co-ordinate with the substituted phenoxo and the diethyl ether ligands being arranged in a distorted tetrahedral environment about the metal.

Lanthanide metal complexes having solely monodentate ligands often have high metal co-ordination numbers due to the large Ln^{2+} or Ln^{3+} radii. Previous crystal structure determinations of low (⩽5) co-ordination number Ln^{2+} complexes have included: **II**,[13] $[Yb(NR_2)_2(dmpe)]$,[15] $[Ln(NR_2)(\mu\text{-}NR_2)_2Na]$[16] (R = $SiMe_3$: Ln = Eu **III** or Yb **IV**) and $[Yb\{Sn(CH_2CMe_3)_3\}_2(thf)_2]$.[17] Work independent of the present study led to the X-ray characterisation of complexes **4**,[11b] **5**,[11b] $[Yb(OR')_2(hmpa)_2]$ **V**[18a] (hmpa = hexamethylphosphoramide) and $[Yb(OC_6H_2Bu^t{}_3\text{-}2,4,6)_2(thf)_3]\cdot thf$ **VI**.[18b]

Evidently the four-co-ordinate complexes **5** and **V** have a similar distorted tetrahedral configuration as **1**, whereas the five-co-ordinate complexes **4** and **VI** adopt a distorted square-pyramidal configuration. Differences in the Yb–OR' bond lengths and angles in **1**, **5** and **V** may be attributed to the different steric demands imposed by OEt_2, thf and hmpa. Consistent with this conclusion is the observation that the average Yb–OR' bond lengths increase in the sequence **V** [2.298(7)], **5** [2.376(10)] and **1** [2.428(11) Å].

Analysis of the bond angles in the complexes **1** and **5** reveals similarities in the angles subtended at the metal by the aryloxides [O(1)–Yb–O(2) 119.8(3) **1** and 118.7(3)° **5** and the ethers O(3)–Yb–O(4) 89.7(4) **1** and 89.9(4)° **5**]; but again the greater bulk of the diethyl ether ligand in **1** than that of thf in **5** is evident from the significant differences in the bond angles O(1)–Yb–O(3) [124.1(4) **1** and 119.9(4)° **5**] and O(2)–Yb–O(4) [115.2(3) **1** and 121.1(4)° **5**], the cyclic thf ligands allowing a less strained tetrahedral conformation to be favoured.

For complex **1**, the average Yb–OR' distance is *ca.* 0.15 Å shorter than Yb–OEt_2. If the steric bulk of the phenoxide ligand were the only consideration in the determination of the conformation of the molecule, then the Yb–O–R' bond angle would be such as to provide maximum shelter for the metal centre. However, the Yb–O–R' angles in **1** exhibit a near linearity, with Yb–O(1)–C(1) and Yb–O(2)–C(16) at 170.9(8) and 167.3(8)°, respectively, perhaps due to significant Yb–O–R' π conjugation. Comparison with other metal(II) bis(phenoxides) indicates that the M–O–R' angle varies widely from *ca.* 128 to

176°.[19] Approximation to linearity in the M–O–R' bond angle appears to occur when there is the possibility of oxygen-to-metal donation through orbitals of π symmetry.

Crystal Structure of [{Yb(OR')(μ-OR')}$_2$] **2**.—The molecular structure and atom numbering scheme for compound **2** are shown in Fig. 2; bond lengths and angles are in Table 4, fractional atomic coordinates in Table 5.

The crystal structure of complex **2** establishes it to be dimeric with asymmetrically bridging $^-$OR' ligands and ytterbium in a three-co-ordinate environment. For a lanthanide metal complex, this is relatively rare, being restricted to several [LnX$_3$] complexes with X = CHR$_2$,[20] NR$_2$,[21] OR'[6] or OCBu$^t_3$;[3a] for Ln^{2+} complexes, the sole examples were **II**,[13] **III**[16] and **IV**.[16] Complexes having bridging $^-$OR' ligands (*cf.* **2** and **3**) are rare; an earlier example was [{Li(μ-OR')(OEt$_2$)}$_2$].[22]

The structure of **2** can be rationalised as being composed of a pair of Yb(OR')$_2$ monomers joined through a central Yb$_2$O$_2$ four-membered ring. While the Yb–μ-O distances are nearly symmetric the Yb–μ-O–C angles are not. Each 'monomer' unit Yb(1)O(1)R'O(3)R' and Yb(2)O(2)R'O(4)R' has one unperturbed terminal $^-$OR' ligand with Yb–O–C angles of 171 and 166°, while the bridging $^-$OR' ligand, being slightly affected by the interaction with the adjacent 'monomer', has reduced exocyclic Yb–O–C angles of 153 and 146°. This view of the bonding implies that there are two different types of Yb–O bonds within the Yb$_2$O$_2$ ring as is reflected in the Yb(1)–O(1) and Yb(2)–O(2) bonds [2.25(2) and 2.30(2) Å] being slightly shorter than the Yb(2)–O(1) and Yb(1)–O(2) bonds [2.37(2) and 2.31(2) Å]. Whereas the Yb–O bond lengths suggest almost symmetrically bridging $^-$OR' ligands, the geometry at O(1) and O(2) indicates that there is significant asymmetric bridging. The Yb–OR' terminal bonds are the shorter [2.10(2) and 2.08(2) Å], and are similar in length to those in **1** [av. 2.15(1) Å] and **5** [av. 2.14(1) Å].[11b] The Yb$_2$O$_2$ ring in **2** is planar within 0.03 Å and the atoms C(16) and O(4) are coplanar with it, whilst C(1) and O(3) are displaced by -0.21 and $+0.62$ Å out of the plane, presumably for steric reasons.

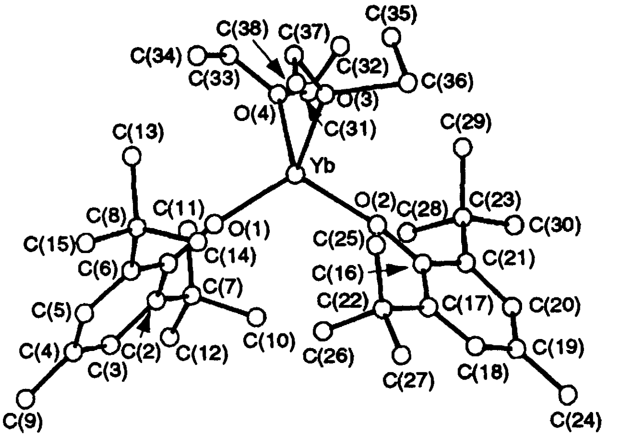

Fig. 1 The molecular structure of [Yb(OR')$_2$(OEt$_2$)$_2$] **1** and atom numbering scheme

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 known procedures: [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] **I**,[12] NaNR$_2$,[23] YbI$_2$[12] and KOR';[1] 2,6-di-*tert*-butyl-4-methylphenol (R'OH) was purchased from Aldrich and used without further purification. Microanalyses were carried out by Medac Ltd., Uxbridge, Middlesex. The NMR spectra were recorded using Bruker WP80, WM250, WM360 or WM500 spectrometers; IR spectra were recorded using a Perkin-Elmer 1720 spectrometer.

Synthesis of [Yb(OR')$_2$(OEt$_2$)$_2$] **1**.—The phenol R'OH (0.73 g, 3.3 mmol) in OEt$_2$ (20 cm^3) was added to compound **I** (1.06 g, 1.7 mmol) in OEt$_2$ at 0 °C. An immediate colour change from orange-brown to red was noted. After stirring for 5 min the reaction mixture was allowed to warm up to room temperature and stirred for a further 30 min. As stirring was continued,

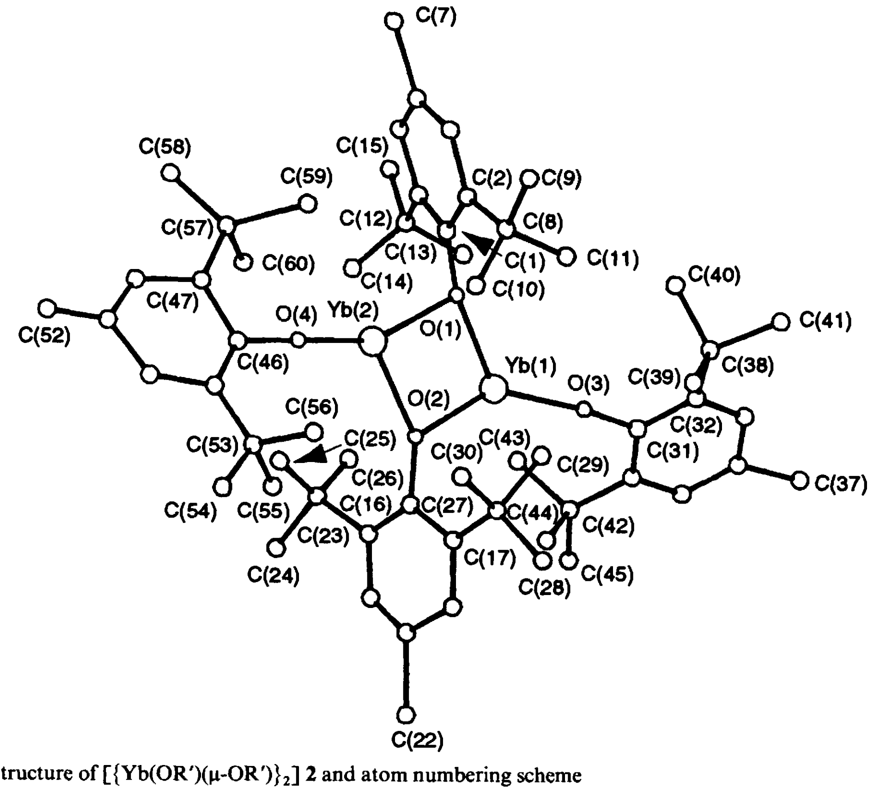

Fig. 2 The molecular structure of [{Yb(OR')(μ-OR')}$_2$] **2** and atom numbering scheme

compound **1** was observed to precipitate as orange-red needles. The volume of OEt_2 was reduced (to *ca.* 20 cm^3) and the solution cooled (−30 °C). Recrystallisation from OEt_2 at −30 °C yielded compound **1** (0.87 g, 1.1 mmol, 67%) (Found: C, 58.1; H, 8.9. $C_{38}H_{66}O_4Yb$ requires C, 60.1; H, 8.75%), m.p. 110–112 °C. NMR: ^1H ($C_6D_5CD_3$, 80.13 MHz, 25 °C), δ 1.05 (t, 12 H, OCH_2CH_3), 1.59 (s, 36 H, Bu^t), 2.37 (s, 6 H, Me), 3.21 (q, 8 H, OCH_2CH_3), 7.15 (s, 4 H, CH); ^{13}C-{^1H} ($C_6D_5CD_3$, 90.56 MHz, 25 °C), δ 21.4 (q, Me), 31.6 [q, $C(CH_3)_3$], 35.2 [s,$C(CH_3)_3$], 125.0 (s, C^4), 137.7 (s, C^2 and C^6), 150.1 (s, C^1) (C^3 and C^5 signal not observed; probably hidden under one of the toluene signals).

Synthesis of [{Yb(NR_2)(μ-NR_2)}$_2$] **II**.—A solution of $NaNR_2$ (4.1 g, 22.4 mmol) in OEt_2 (300 cm^3) was added to a suspension of YbI_2 (5.35 g, 12.5 mmol) in OEt_2 (50 cm^3) at 0 °C. The green suspension was stirred at 0 °C for 1 h and then slowly warmed to room temperature. After stirring for 16 h an orange suspension was obtained. The solid material was allowed to settle and the suspension filtered. The solvent was removed from the filtrate *in vacuo* to yield an orange solid, which was dried for 2 d at 20 °C (10^{-2} Torr) yielding orange solid **II** (5.2 g, 5.3 mmol, 95%). NMR: ^1H (C_5D_5N, 360.13 MHz, 20 °C), δ 0.30 (s, $SiMe_3$). IR (KBr/Nujol): 1378mw, 1250s, 1183m, 1031s, 972s, 933s, 875s, 830vs, 764s, 663m, 610m, 593m cm^{-1}.

Table 2 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for [Yb(OR′)$_2$(OEt_2)$_2$] **1**

Yb–O(1)	2.126(9)	Yb–O(2)	2.182(8)
Yb–O(3)	2.443(10)	Yb–O(4)	2.413(12)
O(1)–C(1)	1.34(2)	O(2)–C(16)	1.321(14)
O(3)–C(36)	1.89(4)	O(3)–C(37)	1.36(4)
O(4)–C(31)	1.67(3)	O(4)–C(33)	1.43(3)
O(1)–Yb–O(2)	119.8(3)	O(1)–Yb–O(3)	124.1(4)
O(1)–Yb–O(4)	103.9(4)	O(2)–Yb–O(3)	100.8(4)
O(2)–Yb–O(4)	115.2(3)	O(3)–Yb–O(4)	89.7(4)
Yb–O(1)–C(1)	170.9(8)	Yb–O(2)–C(16)	167.3(8)
Yb–O(3)–C(36)	113(1)	Yb–O(3)–C(37)	132(2)
C(36)–O(3)–C(37)	115(2)	Yb–O(4)–C(31)	125(1)
Yb–O(4)–C(33)	130(1)	C(31)–O(4)–C(33)	101(2)
O(1)–C(1)–C(2)	119(1)	O(1)–C(1)–C(6)	123(1)

Synthesis of [{Yb(OR′)(μ-OR′)}$_2$] **2**.—(*a*) A suspension of YbI_2 (2.6 g, 6.1 mmol) and KOR′ (3.3 g, 12.8 mmol) in OEt_2 (100 cm^3) was stirred at room temperature for 18 h, yielding an orange suspension. The solvent was removed *in vacuo* and the residue extracted into toluene (80 cm^3). Argon gas was passed through the extract for 2 h at 50 °C. Removing the solvent *in vacuo* yielded the dark red solid **2** (2.4 g, 2.0 mmol, 66%). NMR: ^1H (C_5D_5N, 360.13 MHz, 20 °C), δ 1.51 (s, 36 H, Bu^t), 2.37 (s, 6 H, Me), 7.26 (s, 4 H, CH); ^{13}C-{^1H} (C_5D_5N, 62.90 MHz, 20 °C), δ 36.03 (q, Me), 45.88 [q, $C(CH_3)_3$], 49.63 [s, $C(CH_3)_3$], 133.09 (s, C^4), 140.26 (d, C^3 and C^5), 151.99 (s, C^2 and C^6), 179.79 (s, C^1).

(*b*) Diethyl ether (400 cm^3) was added to YbI_2 (4.32 g, 10.12 mmol) and KOR′ (4.70 g, 18.19 mmol) at room temperature. After stirring for 18 h an orange suspension was obtained. The solid material was allowed to settle and the suspension filtered. The solvent was removed from the filtrate *in vacuo* to yield a red solid, which was dried for 2 d at 20 °C (10^{-2} Torr) yielding red solid **2** (3.05 g, 2.49 mmol, 55%).

(*c*) Pentane (120 cm^3) was added to **II** (2.65 g, 2.7 mmol) and R′OH (2.50 g, 11.3 mmol) at room temperature. The red suspension was stirred for 17 h; the volatiles were removed *in vacuo* and the residue extracted into toluene (100 cm^3). The red extract was concentrated and cooled (−30 °C), yielding red crystals of **2** (1.95 g, 1.6 mmol, 59%) (Found: C, 59.0; H, 8.10. $C_{60}H_{92}O_4Yb_2$ requires C, 58.9; H, 7.60%). NMR ^1H (C_6D_6, 250.13 MHz, 25 °C): δ 1.37 (s, 36 H, Bu^t), 1.57 (s, 36 H, Bu^t), 2.18 (s, 6 H, Me), 2.39 (s, 6 H, Me), 7.04 (s, 8 H, R′); ^{13}C-{^1H} (C_6H_6–C_6D_6, 125.76 MHz, 30 °C), 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^4), 125.40 (d, C^3 and C^5), 127.49 (d, C^3 and C^5), 136.32 (s, C^2 and C^6), 137.74 (s, C^2 and C^6), 155.93 (s, C^1), 162.79 (s, C^1).

Synthesis of [{Yb(NR_2)(μ-OR′)}$_2$] **3**.—(*a*) Hexane (80 cm^3) was added to compound **II** (0.60 g, 0.6 mmol) and R′OH (0.27 g, 1.23 mmol) at room temperature, yielding a red solution which was stirred for 4 h; the volatiles were removed *in vacuo* to yield a red solid, which was dissolved in benzene (2.5 cm^3) and introduced into an NMR tube. After obtaining the NMR spectral data, the tube was opened and the solution transferred into a Schlenk tube. The volatiles were removed *in vacuo* to afford the red solid **3** (0.50 g, 0.45 mmol, 74%).

(*b*) A solution of **II** (0.41 g, 0.4 mmol) in benzene (2.5 cm^3) was

Table 3 Fractional atomic coordinates (× 10^4) with e.s.d.s in parentheses for [Yb(OR′)$_2$(OEt_2)$_2$] **1**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Yb	2656.3(5)	1506.6(3)	3434.4(2)	C(19)	−1658(11)	−1098(8)	2938(6)
O(1)	2317(8)	2146(5)	4139(3)	C(20)	−1498(12)	−572(8)	2525(6)
O(2)	1196(8)	647(5)	3141(3)	C(21)	−511(11)	23(7)	2572(5)
O(3)	4764(8)	853(8)	3283(5)	C(22)	1034(12)	−443(7)	4029(5)
O(4)	3179(10)	2469(6)	2785(5)	C(23)	−366(15)	576(8)	2120(5)
C(1)	1910(12)	2498(7)	4579(5)	C(24)	−2722(19)	−1736(9)	2862(8)
C(2)	665(13)	2919(8)	4539(5)	C(25)	2548(12)	−438(9)	3934(6)
C(3)	170(16)	3247(9)	5018(7)	C(26)	650(15)	289(9)	4335(6)
C(4)	901(15)	3193(10)	5524(7)	C(27)	740(18)	−1132(9)	4391(6)
C(5)	2137(15)	2800(9)	5538(6)	C(28)	−821(18)	1402(8)	2298(8)
C(6)	2622(12)	2453(8)	5083(6)	C(29)	1114(16)	581(10)	1930(6)
C(7)	−186(16)	3048(10)	4008(6)	C(30)	−1363(17)	408(10)	1625(6)
C(8)	4036(14)	2063(10)	5150(6)	C(31)	2177(30)	2709(19)	2245(13)
C(9)	329(23)	3560(12)	6006(8)	C(32)	2847(37)	2480(23)	1892(16)
C(10)	−773(15)	2246(11)	3808(8)	C(33)	4005(30)	3135(18)	2847(13)
C(11)	663(25)	3440(13)	3619(8)	C(34)	4885(33)	3007(20)	3322(14)
C(12)	−1429(19)	3544(11)	4068(9)	C(35)	5035(40)	568(22)	2515(16)
C(13)	5048(14)	2440(12)	4767(8)	C(36)	4555(39)	37(23)	2783(15)
C(14)	3844(19)	1186(10)	5027(9)	C(37)	6053(41)	994(28)	3469(17)
C(15)	4661(18)	2158(13)	5756(7)	C(38)	6249(39)	467(22)	3864(16)
C(16)	327(11)	78(7)	3076(5)	O(5)	5000(0)	5000(0)	5000(0)
C(17)	137(11)	−476(7)	3486(5)	C(39)	5830(52)	5080(37)	5091(25)
C(18)	−784(13)	−1058(8)	3406(5)	C(40)	7018(43)	5095(26)	5228(18)

added to **2** (0.55 g, 0.4 mmol) at room temperature, and stirred for 0.5 h; the dark red solution was introduced into an NMR tube. After obtaining the NMR spectral data, the tube was opened and the solution transferred into a Schlenk tube. The volatiles were removed *in vacuo* and the residue extracted into pentane. Concentrating and cooling (−30 °C) the extract afforded red, sticky crystals of **3** (Found: C, 44.2; H, 7.10; N, 2.00. Calc. for $C_{42}H_{82}N_2O_2Si_4Yb_2$: C, 45.6; H, 7.50; N, 2.55%), m.p. *ca.* 150 °C (decomp.). NMR: ^1H (C_6D_6, 360.13 MHz, 20 °C), δ 0.08 (s, 36 H, $SiMe_3$), 1.50 (s, 36 H, Bu^t), 2.21 (s, 6 H, Me), 7.05 (s, 4 H, R′); $^{13}C-\{^1H\}$ (C_6D_6, 125.76 MHz, 20 °C), 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^4), 128.02 (d, C^3 and C^5), 137.06 (s, C^2 and C^6), 156.96 (s, C^1); $^{29}Si-\{^1H\}$ (C_6D_6, 99.36 MHz, 20 °C), δ −15.44.

Synthesis of [Yb(OR′)$_2$(thf)$_2$] **5**.—Tetrahydrofuran (0.53 g, 7.3 mmol) was added to a solution of **1** (2.78 g, 3.7 mmol) in hexane (30 cm^3) at 0 °C. A slight change from orange-red to red was noted. The volume was reduced to *ca.* 10 cm^3 and compound **5** (2.2 g, 2.9 mmol, 79%) precipitated as red microcrystals.

Synthesis of [Yb(OR′)$_2$(py)$_2$] **6**.—Pyridine (0.41 g, 5.2 mmol) was added to a solution of **1** (1.96 g, 2.6 mmol) in hexane (30

Table 4 Selected intramolecular distances (Å) and angles (°) with e.s.d.s in parentheses for [{Yb(OR′)(μ-OR′)}$_2$] **2**

Yb–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)
O(1)–C(1)	1.32(3)	O(2)–C(16)	1.37(3)
O(3)–C(31)	1.35(3)	O(4)–C(46)	1.42(4)
O(1)–Yb(1)–O(2)	80.6(6)	O(1)–Yb(1)–O(3)	130.1(6)
O(2)–Yb(1)–O(3)	141.3(6)	O(1)–Yb(2)–O(2)	78.5(6)
O(1)–Yb(2)–O(4)	155.4(7)	O(2)–Yb(2)–O(4)	125.9(7)
Yb(1)–O(1)–Yb(2)	100.1(7)	Yb(1)–O(1)–C(1)	153(2)
Yb(2)–O(1)–C(1)	104(1)	Yb(1)–O(2)–Yb(2)	100.5(7)
Yb(1)–O(2)–C(16)	114(2)	Yb(2)–O(2)–C(16)	146(2)
Yb(1)–O(3)–C(31)	171(2)	Yb(2)–O(4)–C(46)	166(2)
O(1)–C(1)–C(2)	118(2)	O(1)–C(1)–C(6)	122(2)

Table 6 Crystal and refinement data* for [Yb(OR′)$_2$(OEt$_2$)$_2$]·0.5 OEt$_2$ and [Yb(OR′)(μ-OR′)}$_2$] **2**

	1·0.5OEt$_2$	**2**
Formula	$C_{38}H_{66}O_4Yb\cdot 0.5C_4H_{10}O$	$C_{60}H_{92}O_4Yb_2$
M	797.05	1223.5
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$P2_12_12_1$
a/Å	9.966(10)	13.240(2)
b/Å	17.472(2)	15.520(8)
c/Å	24.872(7)	32.091(6)
β/°	93.95(5)	90
Z	4	4
U/Å^3	4320.5	6594.3
D_c/g cm^{-3}	1.23	1.23
F(000)	1668	2496
Unique reflections	7561	6410
Observed reflections	4537	3365
μ_{Mo}/cm^{-1}	21.9	28.5
Specimen/mm	1.0 × 0.3 × 0.2	0.4 × 0.3 × 0.2
$A_{min,max}$	0.63, 1.20	0.47, 1.87
R	0.068	0.073
R′	0.108	0.090
$\Delta\rho_{max,min}$	1.2, −0.5	0.9, −0.2
Δ/σ_{max}	0.3	0.2

* Details in common: maximum 2θ 25°; $w = 1/\sigma^2(F)$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

Table 5 Fractional atomic coordinates with e.s.d.s in parentheses for [{Yb(OR′)(μ-OR′)}$_2$] **2**

Atom	*x*	*y*	*z*
Yb(1)	0.109 73(10)	0.422 71(9)	0.214 98(4)
Yb(2)	0.272 34(11)	0.385 22(11)	0.129 15(5)
O(1)	0.106 4(13)	0.431 3(12)	0.144 9(5)
O(2)	0.269 1(13)	0.370 3(12)	0.200 4(5)
O(3)	−0.008 9(12)	0.408 8(12)	0.257 7(5)
O(4)	0.391 9(16)	0.351 8(13)	0.090 2(6)
C(1)	0.073 0(19)	0.464 0(18)	0.109 5(8)
C(2)	0.037 1(18)	0.407 2(19)	0.078 9(7)
C(3)	0.013 5(21)	0.436 3(20)	0.037 7(8)
C(4)	0.019 9(22)	0.522 6(21)	0.030 6(9)
C(5)	0.048 5(23)	0.583 6(23)	0.061 5(9)
C(6)	0.068 6(19)	0.553 5(18)	0.102 3(8)
C(7)	−0.002 2(29)	0.559 5(27)	−0.015 8(11)
C(8)	0.023 4(21)	0.314 0(20)	0.086 6(8)
C(9)	−0.028 4(24)	0.264 9(23)	0.048 7(10)
C(10)	0.116 6(25)	0.267 1(22)	0.097 6(9)
C(11)	−0.046 7(27)	0.305 6(25)	0.124 0(11)
C(12)	0.087 3(22)	0.618 5(21)	0.134 3(9)
C(13)	0.024 3(24)	0.608 1(23)	0.172 9(10)
C(14)	0.191 2(31)	0.631 5(29)	0.147 0(13)
C(15)	0.053 3(30)	0.711 0(27)	0.121 6(12)
C(16)	0.323 6(22)	0.349 0(20)	0.235 1(9)
C(17)	0.305 8(19)	0.262 1(19)	0.249 1(8)
C(18)	0.354 6(21)	0.238 6(20)	0.284 9(9)
C(19)	0.421 9(26)	0.303 0(25)	0.303 1(11)
C(20)	0.434 2(21)	0.376 1(21)	0.288 8(9)
C(21)	0.390 6(20)	0.400 4(18)	0.254 0(7)
C(22)	0.484 8(31)	0.261 8(28)	0.343 7(12)
C(23)	0.420 6(25)	0.489 0(23)	0.235 6(10)
C(24)	0.500 9(29)	0.534 5(26)	0.267 8(10)
C(25)	0.457 2(27)	0.478 1(26)	0.196 3(11)
C(26)	0.335 8(44)	0.541 9(40)	0.239 7(18)
C(27)	0.239 1(21)	0.196 6(18)	0.226 8(8)
C(28)	0.227 8(26)	0.103 6(23)	0.249 0(10)
C(29)	0.129 8(24)	0.232 3(22)	0.219 2(10)
C(30)	0.279 4(30)	0.168 9(26)	0.183 7(11)
C(31)	−0.076 2(17)	0.407 9(17)	0.289 4(7)
C(32)	−0.173 7(17)	0.384 4(17)	0.285 0(8)
C(33)	−0.237 6(22)	0.398 5(20)	0.318 6(9)
C(34)	−0.207 0(21)	0.431 1(21)	0.355 6(8)
C(35)	−0.111 8(22)	0.450 1(19)	0.359 3(8)
C(36)	−0.046 6(17)	0.439 6(17)	0.327 2(7)
C(37)	−0.293 1(26)	0.441 6(25)	0.391 8(11)
C(38)	−0.210 6(22)	0.341 4(20)	0.246 8(9)
C(39)	−0.142 9(24)	0.254 0(22)	0.235 8(10)
C(40)	−0.214 7(20)	0.399 6(19)	0.210 4(8)
C(41)	−0.323 4(26)	0.305 1(24)	0.245 3(10)
C(42)	0.055 2(22)	0.473 9(20)	0.335 1(8)
C(43)	0.081 9(25)	0.553 2(23)	0.307 7(10)
C(44)	0.129 7(26)	0.395 6(24)	0.323 4(10)
C(45)	0.080 3(38)	0.504 2(32)	0.376 7(15)
C(46)	0.483 0(24)	0.348 0(23)	0.067 0(10)
C(47)	0.480 6(20)	0.419 0(21)	0.035 5(8)
C(48)	0.575 5(26)	0.423 2(26)	0.011 7(11)
C(49)	0.653 3(23)	0.374 7(23)	0.013 4(10)
C(50)	0.644 4(24)	0.304 1(23)	0.042 6(10)
C(51)	0.558 8(20)	0.291 7(19)	0.069 7(8)
C(52)	0.734 1(25)	0.384 2(23)	−0.013 3(10)
C(53)	0.556 7(20)	0.219 1(20)	0.099 9(8)
C(54)	0.644 2(27)	0.160 5(26)	0.098 1(12)
C(55)	0.545 8(24)	0.246 9(22)	0.141 7(9)
C(56)	0.476 7(31)	0.154 0(29)	0.095 8(13)
C(57)	0.392 1(38)	0.483 3(33)	0.029 4(15)
C(58)	0.423 7(35)	0.555 5(32)	−0.003 9(14)
C(59)	0.279 0(43)	0.408 1(38)	0.023 4(17)
C(60)	0.373 0(34)	0.546 2(32)	0.077 1(14)

cm^3) at 0 °C. A change from red-orange to blue-green was noted. The volume was reduced to *ca.* 10 cm^3 and the solution was stored at −30 °C. Compound **6** (1.9 g, 2.5 mmol, 96%) was obtained as a green waxy solid.

Synthesis of [Yb(OR′)$_2$(dmpe)] **7**.—1,2-Bis(dimethylphosphino)ethane (0.51 g, 3.4 mmol) was added to a solution of **1** (2.53 g, 3.3 mmol) in hexane (30 cm^3) at 0 °C. A change from red-orange to purple was noted. The volume was reduced to *ca.* 10 cm^3. Storing at −30 °C yielded purple needles of compound **7** (1.6 g, 2.1 mmol, 64%).

Crystallographic Data.—The appropriate details are in Table 6. In each case unique data sets were collected, using a single crystal sealed in a capillary under argon on an Enraf-Nonius CAD4 diffractometer in the θ-2θ mode with monochromated Mo-Kα radiation (λ = 0.710 69 Å). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarisation effects (*Lp*) and also for absorption using DIFABS[24] after isotropic refinement. Reflections with $|F^2| > \sigma(F^2)$ for **1** or $|F^2| > 2\sigma(F^2)$ for **2**, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/Lp$ were considered observed.

For complex **1**, the structure was solved by the heavy-atom method and refined by full-matrix least squares with most non-hydrogen atoms anisotropic. The atoms of the ether solvate molecule and the carbon atoms of the co-ordinated ether molecules were refined isotropically, otherwise the refinement became unstable. The occupancy of the ether solvate molecule refined to 0.5. Programs from the Enraf-Nonius SDP-Plus package[25] were run on a Micro Vax computer.

For complex **2**, the Yb atoms were found from the Patterson map, and a difference map was used to locate the rest of the atoms which were all refined by full-matrix least squares, only the Yb atoms anisotropic. Attempts to refine the O and C anisotropically resulted in some non-positive values. The hydrogen atoms were held fixed at calculated positions with $U_{iso} = 1.3\ U_{eq}$ for the parent atom. The absolute structure was checked by refinement of both alternatives and the results quoted are for the preferred absolute structure.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengtns and angles.

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References

1 Part 1, J. R. van den Hende, P. B. Hitchcock, S. A. Holmes, M. F. Lappert, W.-P. Leung, T. C. W. Mak and S. Prashar, preceding paper.

2 E. H. Barash, P. S. Coan, E. B. Lobkovsky, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1992, **32**, 497.

3 (*a*) H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem.*, 1989, **28**, 3280; (*b*) D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1991, **10**, 1049; (*c*) M. Wedler, J. W. Gilje, U. Pieper, D. Stalke, M. Noltemeyer and F. T. Edelmann, *Chem. Ber.*, 1991, **124**, 1163; (*d*) W. J. Evans, R. E. Golden and J. W. Ziller, *Inorg. Chem.*, 1991, **30**, 4963; (*e*) W. A. Herrmann, R. Anwander, M. Kleine and W. Scherer, *Chem. Ber.*, 1992, **125**, 1971; (*f*) W. A. Herrmann, R. Anwander and M. Denk, *Chem. Ber.*, 1992, **125**, 2399; (*g*) W. A. Herrmann, R. Anwander and W. Scherer, *Chem. Ber.*, 1993, **126**, 1533; (*h*) D. M. Barnhart, D. L. Clark, J. C. Huffman, R. L. Vincent and J. G. Watkin, *Inorg. Chem.*, 1993, **32**, 4077; (*i*) 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.

4 M. Booij, N. H. Kiers, H. J. Heeres and J. H. Teuben, *J. Organomet. Chem.*, 1989, **364**, 79; S. D. Stults, R. A. Andersen and A. Zalkin, *Organometallics*, 1990, **9**, 115; W. A. Herrmann, R. Anwander, F. C. Munck and W. Scherer, *Chem. Ber.*, 1993, **126**, 331.

5 D. C. Bradley, H. Chudzynska, M. E. Hammond, M. B. Hursthouse, M. Motevalli and W. Ruowen, *Polyhedron*, 1992, **11**, 375; D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1993, **12**, 1907; D. C. Bradley, H. Chudzynska, M. B. Hursthouse, M. Motevalli and R. Wu, *Polyhedron*, 1994, **13**, 1; D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1994, **13**, 7.

6 P. B. Hitchcock, M. F. Lappert and A. Singh, *J. Chem. Soc., Chem. Commun.*, 1983, 1499; P. B. Hitchcock, M. F. Lappert and R. G. Smith, *Inorg. Chim. Acta*, 1987, **139**, 183; H. A. Stecher, A. Sen and A. L. Rheingold, *Inorg. Chem.*, 1988, **27**, 1130; 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.

7 H. C. Aspinall, D. C. Bradley and K. D. Sales, *J. Chem. Soc., Dalton Trans.*, 1988, 2211; H. C. Aspinall, D. C. Bradley and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1992, 153; H. C. Aspinall, S. R. Moore and A. K. Smith, *J. Chem. Soc., Dalton Trans.*, 1993, 993.

8 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.

9 M. J. McGeary, P. S. Coan, K. Folting, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1989, **28**, 3283; M. J. McGeary, P. S. Coan, K. Folting, W. E. Streib and K. G. Caulton, *Inorg. Chem.*, 1991, **30**, 1723.

10 H. C. Aspinall, D. C. Bradley, M. D. Hursthouse, K. D. Sales and N. P. C. Walker, *J. Chem. Soc., Chem. Commun.*, 1985, 1585.

11 (*a*) J. R. van den Hende, P. B. Hitchcock and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1994, 1413; (*b*) 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; (*c*) D. R. Cary and J. Arnold, *Inorg. Chem.*, 1994, **33**, 1791; (*d*) B. Çetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, *J. Chem. Soc., Chem. Commun.*, 1992, 932.

12 T. D. Tilley, J. M. Boncella, D. J. Berg, C. J. Burns and R. A. Andersen, *Inorg. Synth.*, 1990, **27**, 146.

13 T. D. Tilley, Ph.D. Thesis, University of California, Berkeley, 1982; cited in J. M. Boncella and R. A. Andersen, *Organometallics*, 1985, **4**, 205.

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

15 T. D. Tilley, R. A. Andersen and A. Zalkin, *J. Am. Chem. Soc.*, 1982, **104**, 3725.

16 T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, **23**, 2271.

17 F. G. N. Cloke, C. I. Dalby, P. B. Hitchcock, H. Karamallakis and G. A. Lawless, *J. Chem. Soc., Chem. Commun.*, 1991, 779.

18 (*a*) Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiwara and H. Taniguchi, *J. Chem. Soc., Chem. Commun.*, 1992, 722; (*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.

19 B. Çetinkaya, I. Gümrükçü, M. F. Lappert, J. L. Atwood, R. D. Rogers and M. J. Zaworotko, *J. Am. Chem. Soc.*, 1980, **102**, 2088; R. L. Geerts, J. C. Huffman and K. G. Caulton, *Inorg. Chem.*, 1986, **25**, 1803; J. Calabrese, M. A. Cushing and S. D. Ittel, *Inorg. Chem.*, 1988, **27**, 867; S. C. Goel, M. Y. Chiang and W. E. Buhro, *J. Am. Chem. Soc.*, 1990, **112**, 6724; P. B. Hitchcock, M. F. Lappert, G. A. Lawless and B. Royo, *J. Chem. Soc., Chem. Commun.*, 1990, 1441; D. Meyer, J. A. Osborn and M. Wesolek, *Polyhedron*, 1990, **9**, 1311.

20 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, *J. Chem. Soc., Chem. Commun.*, 1988, 1007.

21 J. S. Ghotra, M. B. Hursthouse and A. J. Welch, *J. Chem. Soc., Chem. Commun.*, 1973, 669; D. C. Bradley, J. S. Ghotra, F. A. Hart, M. B. Hursthouse and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, 1977, 1166.

22 B. Çetinkaya, I. Gümrükçü, M. F. Lappert, J. L. Atwood and R. Shakir, *J. Am. Chem. Soc.*, 1980, **102**, 2086.

23 C. R. Krüger and H. Niederprüm, *Inorg. Synth.*, 1966, **8**, 15.

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

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

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