Reactions of Ytterbium(II) Amides with Various Brønsted Acids, CS₂ or LiNR₂; Crystal Structures of [{Yb(NR₂)(μ -OCBu^t₃)}₂] and [Yb(OCBu^t₃)₂(thf)₂] (R = SiMe₃, thf = tetrahydrofuran)*

Johannes R. van den Hende, Peter B. Hitchcock and Michael F. Lappert School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK

The reactions of $[\{Yb(NR_2)(\mu-NR_2)\}_2]$ I or $[Yb(NR_2)_2(OEt_2)_2]$ II (R = SiMe_3) with various Brønsted acids, carbon disulfide or LiNR₂ with *N.N.N'*, *N'*-tetramethylethylenediamine (tmen) afforded the following complexes: (a) $[\{Yb(NR_2)(\mu-OCBu^*_3)\}_2]$ 1 from I and 2 Bu*₃COH; (b) $[\{Yb(OCBu^*_3)(\mu-OCBu^*_3)\}_2]$ 2 and $[Yb(OCBu^*_3)_2(thf)_2]$ 3 from I and 4 Bu*₃COH in hexane or tetrahydrofuran (thf), respectively; (c) $[\{Yb(OCBu^*_3)_2(OR')\}_2]$ 4a (R' = C₆H₂Bu*₂-2,6-Me-4) from 1 and 2 HOR'; (d) $[Yb(OCBu^*_3)(OR')(thf)_2]$ 4b from 4a and an excess of thf; (e) $[Yb(OCBu^*_3)(OR')(py)_2]$ 4c from 4b and an excess of pyridine (py); (f) $Yb(O_3SCF_3)_2(dme)$ 5 (dme = 1,2-dimethoxyethane) from II and 2 HO_3SCF_3 ; (g) $[Yb(tmhd)_3]$ 6 from I and 4 Htmhd (= Bu*COCH₂COBu*); (h) $Yb(S_2CNR_2)_2$ 7 from II and 2 CS₂: and (i) $[Li\{Yb(NR_2)_3\}(tmen)]$ 8 from II, LiNR₂ and tmen. A single-crystal X-ray diffraction study established 1 to be dimeric with asymmetrically bridging $\neg OCBu*_3$ ligands. In this molecule the fourmembered Yb_2O_2 ring has a fold angle of 24° about the O(1) \cdots O(2) direction, reducing the steric strain between adjacent bulky groups by bringing the two NR₂ groups slightly above the plane. Complex 3 is monomeric with the alkoxo and the tetrahydrofuran ligands in a distorted-tetrahedral configuration about the ytterbium. One of the alkoxo ligands is bound in a conventional way with the Yb-O-C angle almost linear $[175(2)^\circ]$, while the other Yb-O-C angle is significantly smaller $[155(3)^\circ]$.

Previous reactions of ytterbium(II) amides studied were those with an alcohol,^{2,3} aluminium alkyl,⁴ diazacrown ether,⁵ phenol,^{1,2,6} phosphine,⁷ selenol,^{2,8} sodium amide,⁹ tellurol⁸ or thiol.^{2,10} We now report reactions of $[{Yb(NR_2)(\mu-NR_2)}_2]$ I¹¹ or $[Yb(NR_2)_2(OEt_2)_2]$ II¹² with various Brønsted acids, carbon disulfide or LiNR₂ with tmen (R = SiMe₃, tmen = N, N, N', N'-tetramethylethylenediamine).

We have previously briefly communicated the preparation and NMR spectra of the two ytterbium(II) alkoxides [{YbX(μ -OCBu¹_3)}₂] (X = NR₂ 1 or OCBu¹_3 2; R = SiMe₃) and the crystal structure of 1.³ We report here new data on these complexes and the synthesis and characterisation of further ytterbium(II) alkoxides, an ytterbium(II) dithiocarbamate, a heterobimetallic ytterbium(II) amide, an ytterbium(II) trifluoromethanesulfonate and an ytterbium(III) β -diketonate. The crystal structures of complex 1³ and [Yb(OCBu¹_3)₂(thf)₂] 3 (thf = tetrahydrofuran) are presented.

Lanthanide(III) alkoxides have been prepared by (i) protolytic ligand exchange between an appropriate lanthanide(III) amide and an alcohol, ¹³ or (ii) anionic ligand exchange, using an appropriate lanthanide(III) halide and an alkali-metal derivative of the alcohol.¹⁴ However, no well characterised lanthanide(III) alkoxides had previously been reported in detail. Part 2 of this Series described the preparation of ytterbium(II) aryloxides by protolytic ligand exchange using I or II and 2,6-di-*tert*-butyl-4-methylphenol.¹

Results and Discussion

Synthesis of Ytterbium Alkoxides.—The ytterbium(II) amide $[{Yb(NR_2)(\mu-NR_2)}_2] I^{11}$ with 2 equivalents of Bu'₃COH in

hexane gave the red, crystalline complex [{ $Yb(NR_2)(\mu - OCBu^t_3)$ }_2] 1, equation (1). Complex 1 was fully characterised

$$[{Yb(NR_2)(\mu-NR_2)}_2] + 2 Bu'_3COH \xrightarrow{\text{nexanc}} I$$

$$[{Yb(NR_2)(\mu-OCBu'_3)}_2] + 2 NHR_2 \quad (1)$$

$$1$$

by NMR [${}^{1}H$, ${}^{13}C-{}^{1}H$ }, ${}^{29}Si-{}^{1}H$ }, ${}^{171}Yb-{}^{1}H$ } spectroscopy, elemental (C, H, N) analysis and a single-crystal X-ray diffraction study.

The red, solid homoleptic alkoxide $[{Yb(OCBu_3)(\mu - OCBu_3)}_2]$ **2** was obtained from I and 4 equivalents of Bu₃COH in hexane, equation (2). Complex **2** is probably

$$[\{Yb(NR_2)(\mu-NR_2)\}_2] + 4 Bu^{t_3}COH \xrightarrow{hexane} I \\ [\{Yb(OCBu^{t_3})(\mu-OCBu^{t_3})\}_2] + 4 NHR_2 \quad (2)$$
2

dimeric in the solid state, like the aryloxide analogue $[{Yb(OC_6H_2Bu'_2-2,6-Me-4)(\mu-OC_6H_2Bu'_2-2,6-Me-4)}_2]$

III.^{1,3} Suitable crystals for a single-crystal X-ray diffraction study were not obtained, but mass spectrometry established **2** to be dimeric in the gas phase. Using NMR (¹H, ¹³C-{¹H}) spectroscopy it was shown that the alkoxo ligands were equivalent at ambient temperature; at -50 °C, the ¹H NMR spectrum showed only slight broadening of the ⁻OCBu¹₃ signal. This indicates that the fluxional process, believed to arise from terminal/bridging ⁻OCBu¹₃ site exchange, has a low energy barrier.

When reaction (2) was carried out in tetrahydrofuran (thf) instead of hexane, dark green crystals of the bis(tetrahydrofuran) adduct [Yb(OCBu¹₃)₂(thf)₂] **3** were obtained, equation (3). It was evident from NMR (¹H, ¹³C-{¹H}) spectra in

^{*} Lanthanide(11) Alkyls, Amides, Alkoxides and Aryloxides. Part 3.¹ No reprints available.

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

Table 1 Some 171 Yb-{ 1 H} NMR spectral chemical shift (δ) data " for compounds 1–8, I, XI, XXI and XXIV

Compound	Solvent ^b	T/\mathbf{K}	δ(¹⁷¹ Yb)	w ₁ /Hz	Ref.
$1 [{Yb(NR_2)(\mu - OCBu_3)}_2]$	C ₆ H ₆	304	758	80	3
$2\left[\left\{Yb(OCBu_{3}^{t})(\mu - OCBu_{3}^{t})\right\}_{2}\right]$	C ₆ H ₆	304	705	200	3
$3 [Yb(OCBu_3)_2(thf)_2]$	C ₆ H ₆	304	552	20	This work
$4b [Yb(OCBu'_3)(OR')(thf)_2]$	C ₆ H ₆	304	387	50	This work
4c $[Yb(OCBu_3^t)(OR')(py)_x]$	C ₅ H ₅ N	304	830	60	This work
5 Yb(O_3 SCF $_3$) ₂ (dme)	C_5H_5N	304	620	1000	This work
	$C_5 D_5 N$	213	757	65	This work
8 [Li{ $Yb(NR_2)_3$ }(tmen)]	C ₆ H ₆	304	745	350	This work
$I[{Yb(NR_2)(\mu-NR_2)}_2]$	C ₆ H ₆	304	779	200	This work
XI [$(R_2N)Yb(\mu-NR_2)_2Na$]	C ₆ H ₅ Me	193	947	190	15
XXI $[Yb(NR_2)_2(py)_2]$	C5H5N	213	919	60	This work
XXIV Na[Yb(O ₃ SCF ₃) ₃]•thf	C ₄ H ₈ O		32		16

^a Spectra were recorded at 43.77 (for 1-8, I and XXI) or 63.01 MHz (for XI and XXIV) relative to $[Yb(\eta-C_5Me_5)_2(thf)_2]$ in 10% $C_6D_5CD_3$ at 273 K.^{15 b} 10-20% v/v C_6D_6 , $C_6D_5CD_3$ or C_5D_5N was used as lock. ^c Ref. 15 records δ 796, $w_{\frac{1}{2}}$ 90 at 263 K. Comparisons of complexes 5 and I shows that the temperature effect on 5 is partly dissociative.



Fig. 1 Molecular structure of $[{Yb(NR_2)(\mu-OCBu_3)}_2]$ 1 and atom numbering scheme



Fig. 2 Alternative view of the molecular structure of $[{Yb(NR_2)(\mu - OCBu^t_3)}_2]$ **1** and atom numbering scheme; the *tert*-butyl groups of the $^{-}OCBu^t_3$ ligands have been omitted for clarity

$$[{Yb(NR_2)(\mu-NR_2)}_2] + 4 Bu^{\iota}_3 COH \xrightarrow{\text{thr}} I$$

$$2 [Yb(OCBu^{\iota}_3)_2(\text{thf})_2] + 4 NHR_2 \quad (3)$$

$$3$$

benzene solution at ambient temperature that, unlike in the solid state, the alkoxo ligands are equivalent on the NMR time-scale.

The benzene solution ¹⁷¹Yb-{¹H} NMR¹⁵ spectral chemical shifts of complexes 1–3 (Table 1) may be compared with those for $[{Yb(NR_2)(\mu-NR_2)}_2]$ I (δ 779), $[Yb(NR_2)_2(OEt_2)_2]$ II

(614),¹⁵ [{Yb(OR')(μ -OR')}₂] III (R' = OC₆H₂Bu^t₂-2,6-Me-4) (314),³ [{Yb(NR₂)(μ -OR')}₂] IV (536),³ [Yb(OR')₂(OEt₂)₂] V (238),⁶ [Yb(OR')₂(thf)₂] VI (345)¹ and [Yb(OR')₂(thf)₃] VII (234).¹⁷ As observed for complex IV,³ the shift for the heteroleptic complex 1 was intermediate between those for the homoleptic analogues: the alkoxide 2 and the amide I.

When $[Yb(NR_2)_2(dme)]$ VIII (dme = 1,2-dimethoxyethane) was treated with 2 equivalents of the sterically less demanding Bu'OH, a white solid was isolated. The ¹H NMR spectrum of this product showed a combination of broad and sharp peaks, indicating that it might be a mixture of paramagnetic ytterbium(III) compounds. This contrasts with an earlier report of the same reaction under similar conditions said to result in a quantitative yield of the blue, pentane-insoluble ytterbium(III) complex [{Yb(OBu¹)₂}_n] IX, which was characterised by IR spectroscopy and (poor) elemental (C, H, Yb) analysis.²

Single-crystal Structure of $[{Yb(NR_2)(\mu-OCBu'_3)}_2]$ 1.— The molecular structure and atom numbering scheme for compound 1 are shown in Figs. 1 and 2; bond lengths and angles are in Table 2, fractional atomic coordinates in Table 3 and the crystal data and refinement parameters in Table 6.

The structure shows a Yb_2O_2 four-membered ring in which there appear to be asymmetrically bridging $\neg OCBu_3^{t}$ groups. The Yb(1)-O(1) and Yb(2)-O(2) bonds [2.297(4) and 2.294(5) Å] are significantly shorter than the Yb(2)-O(1) and Yb(1)-O(2)bonds [2.319(5) and 2.320(5) Å]; these bond lengths are similar to those found for the bridging $^{-}OR'$ ligands in [{Yb(OR')(μ -OR')}₂] III [average 2.31(2) Å].^{1.3} However, the asymmetry is less marked in the angles at O(1) and O(2) with Yb(1)-O(1)-C(13) and Yb(2)-O(2)-C(26) [136.2(4) and 135.3(4)°] only slightly larger than Yb(1)-O(2)-C(26) and Yb(2)-O(1)-C(13) [130.8(4) and 129.6(4)°]. This is in contrast



Fig. 3 Molecular structure of $[Yb(OCBu_3^i)_2(thf)_2]$ 3 and atom numbering scheme

Table 2 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for $[\{Yb(NR_2)(\mu-OCBu^1_3)\}_2]$ 1

$\mathbf{V}_{\mathbf{b}}(1) = \mathbf{O}(1)$	2 207(4)	Vb(1) O(2)	2 220(5)
10(1)=0(1)	2.297(4)	10(1) = 0(2)	2.320(3)
Y b(1) - N(1)	2.332(6)	Yb(2)-O(1)	2.319(5)
Yb(2)O(2)	2.294(5)	Yb(2) - N(2)	2.327(6)
$Yb(1) \cdots Yb(2)$	3.356(1)		
O(1)-Yb(1)-O(2)	84.0(2)	O(1)-Yb(1)-N(1)	139.5(2)
O(2)-Yb(1)-N(1)	136.3(2)	O(1) - Yb(2) - O(2)	84.1(2)
O(1)-Yb(2)-N(2)	135.7(2)	O(2)-Yb(2)-N(2)	135.7(2)
Yb(1)-O(1)-Yb(2)	93.3(2)	Yb(1)-O(1)-C(13)	136.2(4)
Yb(2)-O(1)-C(13)	129.6(4)	Yb(1)-O(2)-Yb(2)	93.3(2)
Yb(1)-O(2)-C(26)	130.8(4)	Yb(2)-O(2)-C(26)	135.3(4)

to the angles found in the asymmetrically bridged aryloxide III [153(2), 146(2), 114(2) and 104(1)°, respectively],^{1.3} perhaps as a consequence of the more spherical nature of the \neg OCBu¹₃ ligand. In 1 the four-membered Yb₂O₂ ring has a fold angle of 24° about the O(1) · · · O(2) direction, reducing the steric strain between adjacent bulky groups by bringing the two NR₂ groups slightly above the plane, as illustrated in Fig. 2. Bonding at the N atoms is planar, the SiNSi planes being orthogonal to the YbO₂ plane. The Yb–N bond lengths [2.332(6) and 2.327(6) Å] are similar to those in [Yb(NR₂)₂(dmpe)] X [dmpe = 1,2-bis(dimethylphosphino)ethane] [2.331(13) Å]¹⁸ and to the terminal Yb–N bond in [(R₂N)Yb(µ-NR₂)₂Na] XI (R = SiMe₃) [2.38(2) Å].⁹

The following additional features are noteworthy. (i) Complex 1 has two LnX₂ precedents, the amide I¹¹ and the aryloxide III.^{1,3} (ii) Complex 1 is the first LnX(X') analogue. (iii) Three-co-ordination for a lanthanide metal complex is relatively rare, being restricted to several [LnX₃] complexes with X = CHR₂,¹⁹ NR₂,²⁰ OC₆H₂Bu¹₂-2,6-Y-4 (Y = H, Me or Bu¹)²¹ or OCBu¹₃;²² for Ln²⁺ complexes, the sole examples were III,^{1,3} XI and its europium analogue.⁹ (iv) Complexes having a bridging \neg OCBu¹₃ ligand (cf. 1) are rare; earlier examples include [{Li(μ -OCBu¹₃)}₂].²³ (v) In 1, the bridging ligand is \neg OCBu¹₃ rather than \neg NR₂, although the latter is known to have this potential, as in [{Li(NR₂)(OEt₂)}₂].²⁴ (vi) Alkoxides of Ln²⁺ were previously unknown, although aryloxides are established, including III–VII,^{1,3,6} [Yb-(OR')₂(hmpa)₂] XII [hmpa = P(NMe₂)₃O],²⁵ [Yb(OC₆H₂-Bu¹₃-2,4,6)₂(thf)₃].thf XIII,²⁶ [Eu(OR')₂(thf)₃].thf XIV,¹⁷ [Sm(OR')₂(thf)₃] XV,²⁷ [{KSm(OR')₃}_n] XVI²⁷ and [{KSm-(μ -OR')₃(thf)}∞] XVII.²⁷

Single-crystal Structure of $[Yb(OCBu^t_3)_2(thf)_2]$ 3.—The molecular structure and atom numbering scheme for compound 3 are shown in Fig. 3; selected bond lengths and angles are in Table 4, fractional atomic coordinates in Table 5 and the crystal data and refinement parameters in Table 6.

The structure reveals it be monomeric, with the alkoxo and the tetrahydrofuran ligands in a distorted-tetrahedral configuration about the four-co-ordinated ytterbium. The bonding of one of the alkoxo ligands is unprecedented for lanthanide(II) complexes. In all the structurally characterised lanthanide(II) aryloxide analogues of 3 both aryloxo ligands are co-ordinated

Table 3 Fractional atomic coordinates with estimated standard deviations in parentheses for $[{Yb(NR_2)(\mu-OCBu_3)}_2]$ 1

Atom	X	у	z	Atom	x	у	z
Yb(1)	0.164 74(2)	0.235 43(2)	$0.078\ 81(1)$	C(15)	-0.1401(6)	0.164 7(4)	0.019 5(3)
Yb(2)	-0.04722(3)	$0.260\ 26(2)$	0.156 21(1)	C(16)	-0.0045(6)	0.246 7(5)	-0.0430(3)
Si(1)	$0.403\ 27(17)$	0.181 49(15)	0.005 96(11)	C(17)	-0.2316(6)	0.331 2(5)	0.058 6(4)
Si(2)	0.347 46(18)	0.354 42(15)	0.040 21(12)	C(18)	-0.2064(7)	0.352 5(5)	-0.0428(4)
Si(3)	$-0.266\ 26(19)$	0.304 61(17)	0.242 69(11)	C(19)	-0.0869(7)	0.4100(5)	0.028 6(4)
Si(4)	-0.10451(21)	0.433 04(15)	0.219 90(11)	C(20)	-0.169 9(6)	0.150 3(5)	0.0810(4)
O(1)	0.008 0(3)	0.254 9(3)	0.060 9(2)	C(21)	-0.2401(6)	0.158 9(5)	-0.0172(4)
O(2)	0.111 3(4)	0.199 7(3)	0.168 8(2)	C(22)	-0.0810(7)	0.084 9(5)	0.007 0(4)
N(1)	0.322 0(4)	0.252 4(3)	0.034 1(3)	C(23)	-0.0586(7)	0.218 0(6)	-0.0976(4)
N(2)	-0.1569(5)	0.338 4(4)	0.211 8(3)	C(24)	0.089 0(6)	0.188 6(6)	-0.0333(4)
C(1)	0.497 7(7)	0.138 6(6)	0.058 3(4)	C(25)	0.044 8(7)	0.329 2(7)	-0.057 8(4)
C(2)	0.481 1(7)	0.220 8(6)	-0.053 5(4)	C(26)	0.158 5(6)	0.148 5(4)	0.211 1(3)
C(3)	0.331 7(7)	0.091 9(6)	-0.0233(4)	C(27)	0.173 9(6)	0.058 4(4)	0.181 0(3)
C(4)	0.240 3(8)	0.402 9(5)	0.081 1(4)	C(28)	0.268 5(6)	0.190 2(5)	0.229 0(3)
C(5)	0.350 3(9)	0.412 9(6)	-0.0274(5)	C(29)	0.080 7(6)	0.141 4(5)	0.262 5(3)
C(6)	0.466 5(8)	0.381 7(7)	0.080 6(6)	C(30)	0.204 7(7)	0.066 7(5)	0.118 9(3)
C(7)	-0.247 3(10)	0.273 0(8)	0.318 5(4)	C(31)	0.253 2(8)	-0.0002(5)	0.209 5(4)
C(8)	-0.319 0(8)	0.210 8(7)	0.206 8(5)	C(32)	0.076 9(8)	0.005 8(5)	0.173 4(4)
C(9)	-0.372 7(8)	0.381 2(8)	0.240 6(6)	C(33)	0.351 7(7)	0.183 5(6)	0.183 7(4)
C(10)	0.024 5(7)	0.432 5(5)	0.184 5(4)	C(34)	0.257 4(8)	0.284 6(5)	0.235 3(4)
C(11)	-0.176 3(9)	0.517 5(6)	0.185 1(5)	C(35)	0.320 9(8)	0.158 1(7)	0.283 1(4)
C(12)	-0.078 8(10)	0.465 6(6)	0.294 6(5)	C(36)	0.102 2(9)	0.072 6(7)	0.306 0(4)
C(13)	-0.075 1(5)	0.250 5(4)	0.012 6(3)	C(37)	0.076 3(9)	0.220 1(7)	0.298 2(4)
C(14)	-0.148 0(6)	0.332 7(4)	0.013 0(3)	C(38)	-0.031 7(8)	0.133 4(6)	0.242 6(4)

in a similar fashion, 1,6,17,25,26 while the structure of 3 shows the two alkoxo ligands to be in a different environment. A similar phenomenon has previously been observed for $[Ln(C_5Me_5)(OC_6H_3Bu_2^2-2,6)_2]$ complexes (Ln = Y XVIII or Ce XIX having one aryloxo ligand bound in an almost linear fashion [Ln-O-C: XVIII, 168.0(3); XIX, 158.5(2)°] and the other substantially bent [Ln-O-C: XVIII, 128.6(3); XIX, 105.1(2)°].²⁸ In XVII the Sm-O-C angles are 152.2(7), 155.5(6) and 160.8(7)°.27

One of the alkoxo ligands in complex 3 is bound in a conventional way, the Yb-O(2)-C(14) angle being almost linear [175(2)°], comparing well with the angles found for electrondeficient O-bonded lanthanide, actinide and early transition-metal complexes.^{1,6,25,26,28} The Yb-O(1)-C(1) angle is significantly smaller, 155(3)° (cf. XVII²⁷). Generally, large M-O-C angles are associated with short M-O distances, rationalised by assuming partial double-bond character in the M-O-C linkage due to π donation from the oxygen to the metal.^{29,30} However, the two Yb-O distances in 3 are essentially identical [2.092(14) and 2.07(2) Å], a situation mirrored also in XIX, the Ce-O distances also being virtually identical.28a,b

The origin of the distortion in the bonding of one of the alkoxo ligands is not obvious. Reduction of the Yb-O-C angle increases the steric shielding around the metal centre.

Table 4 Selected intramolecular distances (Å) and angles (°) with estin f),] 3, [

Yb(OR') ₂ (OEt ₂) ₂]	V ^{1,6} and [Yb(C	(1110 sets for [100 se	6,26
	3	v	VI
Yb-O(1)	2.092(14)	2.126(9)	2.139(10)
Yb-O(2)	2.07(2)	2.182(8)	2.135(9)
Yb-O(3)	2.38(2)	2.443(10)	2.369(10)
Yb-O(4)	2.39(3)	2.413(12)	2.382(10)
O(1)-C(1)	1.51(3)	1.34(2)	1.344(11)
$O(2)-C(x)^*$	1.41(3)	1.321(14)	1.338(10)
O(1)-Yb-O(2)	132(2)	119.8(3)	118.7(3)
O(1)-Yb-O(3)	115(1)	124.1(4)	119.9(4)
O(1)-Yb-O(4)	93(1)	103.9(4)	105.5(4)
O(2)-Yb-O(3)	108.5(8)	100.8(4)	98.9(4)
O(2)-Yb-O(4)	110.0(8)	115.2(3)	121.1(4)
O(3)-Yb-O(4)	84.8(8)	89.7(4)	89.9(4)
Yb-O(1)-C(1)	155(3)	170.9(8)	172.7(8)
Yb- $O(2)-C(x)^*$	175(2)	167.3(8)	177.8(8)

* x = 14 (3) or 16 (V and VI).

Table 5 Fractional atomic coordinates for [Yb(OCBu'₃)₂(thf)₂] 3

The O(1)–Yb–O(2) angle is larger $[132(2)^{\circ}]$ than those in the aryloxides V $[119.8(3)^{\circ}]^{1.6}$ VI $[118.7(3)^{\circ}]^{6.26}$ and XII $[110.3(3)^{\circ}]^{25}$ presumably due to the fact that OCBu'₃ is significantly more bulky than OR'.³¹ As a consequence, the O(3)-Yb-O(4) angle is reduced $[84.8(8)^{\circ}]$ in comparison with those seen in V $[89.7(4)^{\circ}]^{1.6}$ VI $[89.9(4)^{\circ}]^{6.26}$ and XII $[97.0(3)^{\circ}]^{.25}$ The Yb-O bond lengths are similar to the terminal Yb–O bond lengths of III [average 2.09(2) Å],^{1,3} but are slightly shorter than those in V [average 2.15(1) Å],^{1,6} VI [average 2.14(1) Å],^{6,26} and XII [average 2.18(1) Å].²⁵ The Yb-O (thf) bond lengths are similar to those in the aryloxide analogue VI [average 2.38(1) Å].^{6,26}

Synthesis of $[{Vb(OCBu_3)(OR')}_x]$ 4a and the Lewis-base Adducts [Yb(OCBuⁱ₃)(OR')L_n] ($\dot{L} = \text{thf}, n = 2$ 4b; L = C₅H₅N, n = x 4c.—The dark red, solid heteroleptic ytterbium(II) complex [{ $Yb(OCBu_3)(OR')$ }] 4a was obtained by treating 1 with 2 equivalents of the phenol, equation (4). In

$$[{Yb(NR_2)(\mu-OCBu_3)}_2] + 2 HOR' \xrightarrow{hexane} 1$$

$$\frac{2}{x} [{Yb(OCBu_3)(OR')}_x] + 2 NHR_2 \quad (4)$$
49

Table 6 Crystal data for [{Yb(NR₂)(µ-OCBu¹₃)}₂] 1 and [Yb(OC- $Bu_{3}^{t}(thf)_{2}$ 3

	1	3
Formula	C ₃₈ H ₉₀ N ₂ O ₂ Si ₄ Yb ₂	C ₃₄ H ₇₀ O ₄ Yb
М	1065.6	716.0
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	P21
a/Å	12.987(2)	8.751(6)
b/Å	16.179(4)	17.011(16)
c/Å	23.621(4)	12.192(7)
β/°	91.03(1)	99.14(5)
Z	4	2
U/Å ³	4962.1	1791.9
$D_{\rm c}/{\rm g~cm^{-3}}$	1.43	1.33
F(000)	2176	752
N (total unique)	9068	3279
N_{o} (observed)	5731	2269
μ_{Mo}/cm^{-1}	38.6	26.3
Specimen/mm	$0.4 \times 0.25 \times 0.2$	$0.3 \times 0.2 \times 0.2$
A _{min,max}	0.79, 1.38	0.51, 1.53
R	0.042	0.080
R'	0.043	0.086

Atom	x	у	Z	Atom	x	у	Z
Yb	0.268 01(12)	0	0.312 44(8)	C(16)	0.098 6(25)	-0.0845(12)	0.076 6(17)
O(1)	0.357 7(17)	0.003 4(34)	0.482 0(12)	C(17)	0.130 9(24)	-0.189 7(13)	0.092 8(18)
O(2)	0.131 2(23)	-0.0819(12)	0.217 6(16)	C(18)	-0.2069(32)	-0.2179(21)	0.213 2(26)
O(3)	0.412 9(24)	0.070 2(13)	0.194 9(17)	C(19)	-0.066 8(44)	-0.121 0(19)	0.353 4(19)
O(4)	0.128 6(30)	0.120 6(16)	0.318 1(21)	C(20)	0.066 3(40)	-0.247 8(19)	0.309 6(27)
C(1)	0.452 1(15)	-0.026 7(7)	0.588 2(12)	C(21)	-0.190 7(36)	-0.135 4(20)	-0.022 2(24)
C(2)	0.345 8(15)	-0.014 5(8)	0.681 8(13)	C(22)	0.023 8(42)	-0.013 1(18)	0.018 8(31)
C(3)	0.595 2(15)	0.032 4(8)	0.598 0(10)	C(23)	-0.227 0(42)	-0.046 4(25)	0.139 7(28)
C(4)	0.496 9(17)	-0.116 3(8)	0.570 6(12)	C(24)	0.054 8(42)	-0.273 7(15)	0.061 7(32)
C(5)	0.415 7(31)	-0.054 4(16)	0.797 2(14)	C(25)	0.296 8(28)	-0.207 2(25)	0.163 2(32)
C(6)	0.176 8(20)	-0.050 8(15)	0.648 5(23)	C(26)	0.163 2(53)	-0.152 5(23)	-0.021 5(28)
C(7)	0.320 6(29)	0.076 0(11)	0.709 0(22)	C(27)	0.394 5(44)	0.069 7(22)	0.073 9(22)
C(8)	0.696 4(22)	0.033 0(15)	0.718 8(15)	C(28)	0.488 3(47)	0.134 0(20)	0.034 0(31)
C(9)	0.544 0(26)	0.121 4(10)	0.572 3(23)	C(29)	0.505 7(52)	0.189 6(24)	0.129 9(26)
C(10)	0.712 3(22)	0.011 7(15)	0.514 2(18)	C(30)	0.518 2(44)	0.135 7(20)	0.227 5(30)
C(11)	0.644 3(24)	-0.144 4(12)	0.655 5(21)	C(31)	0.078 4(50)	0.149 9(26)	0.419 2(29)
C(12)	0.537 3(33)	-0.133 1(13)	0.449 6(17)	C(32)	-0.046 1(62)	0.209 1(33)	0.385 5(39)
C(13)	0.361 5(25)	-0.176 2(10)	0.586 2(22)	C(33)	-0.045 4(58)	0.227 4(32)	0.265 8(38)
C(14)	0.026 2(21)	-0.134 8(11)	0.156 8(14)	C(34)	0.074 0(56)	0.175 4(27)	0.228 4(34)
C(15)	-0.042 4(24)	-0.178 6(12)	0.254 2(15)				

F

contrast to 1, complex 4a had poor solubility in non-coordinating solvents. The ¹H NMR spectrum was complicated, but the observed shifts and integrals were consistent with its formulation. When 4a was dissolved in thf the dark red, crystalline complex [Yb(OCBu¹₃)(OR')(thf)₂] 4b was obtained, equation (5). Complex 4b was soluble in light petroleum and

$$[\{Yb(OCBu'_{3})(OR')\}_{x}] \xrightarrow{\text{thf}} 4a \qquad x[Yb(OCBu'_{3})(OR')(thf)_{2}] \quad (5)$$
4b

aromatic solvents and was characterised by NMR [¹H, ¹³C-{¹H}, ¹⁷¹Yb-{¹H}] spectroscopy and elemental (C, H) analysis. The benzene solution ¹⁷¹Yb-{¹H} NMR spectral chemical shift (Table 1) was characteristic for a heteroleptic complex, being intermediate between those observed for the homoleptic analogues VII (δ 234)¹⁷ and 3.

The pyridine (py) complex 4c was formed upon addition of an excess of pyridine to 4b, equation (6). The 171 Yb-{ 1 H} NMR

$$[Yb(OCBu'_3)(OR')(thf)_2] \xrightarrow{pyridine}$$

4b

$$[Yb(OCBu'_3)(OR')(py)_x] + 2 thf (6)$$
4c

spectrum (Table 1) showed only one signal, at δ 830, indicating that no redistribution to the homoleptic alkoxide and aryloxide complexes had occurred. The observed shift is typical for a pyridine adduct and may be compared with those for [Yb(OR')₂(py)₂] XX (δ 745),¹ [Yb(NR₂)₂(py)₂] XXI (R = SiMe₃) (δ 919) and [Yb(C₅Me₅)₂(py)₂] XXII (δ 949).¹⁵

When a related reaction to that shown in equation (4) was carried out with Bu'OH instead of HOR' a purple-black solid was obtained, which was insoluble in many solvents but soluble in pyridine. This product was not characterised by ¹H NMR spectroscopy, due to its paramagnetism. Hence it appears that oxidation to ytterbium(III) had occurred.

Reactions with Bronsted Acids.—Trifluoromethane sulfonate OSO_2CF_3 has often found use in inorganic chemistry as one of the best available leaving groups.³² Its utility in lanthanide(III) chemistry was demonstrated in the synthesis of (i) the cyclopentadienyls [Lu(n-C₅H₅)(O₃SCF₃)₂(thf)₃]^{33a} and [{Yb(n-C₅H₅)₂(µ-O₃SCF₃)₂],^{33b} (ii) the diphosphinomethanides [Ln{(PMe₂)₂CR}₃] (Ln = Sc, La or Lu; R = SiMe₃),³⁴ (iii) the hydridotris(3,5-dimethylpyrazol-1-yl)borate [Yb{HB(dmpz)₃}₂(O₃SCF₃)]³⁵ and (iv) homoleptic lanthanide(III) bis(trimethylsilyl)amides and 2,6-di-*tert*-butyl-4methylphenoxides.¹⁶ A previous attempt to synthesise a ytterbium(II) trifluoromethane sulfonate by reduction of Yb(O₃SCF₃)₃ XXIII with a stoichiometric amount of 5% Na/Hg amalgam in thf yielded blue-white Na[Yb(O₃SCF₃)₃ + LiBu^{s 36b} (or MgEtBr)^{36a} in thf] and used as a reagent in reactions with aldehydes or ketones.

The ytterbium amide $[Yb(NR_2)_2(OEt_2)_2]$ II reacted with 2 equivalents of trifluoromethanesulfonic acid in dme to afford white, crystalline $Yb(O_3SCF_3)_2(dme)$ 5, equation (7). The

$$[Yb(NR_2)_2(OEt_2)_2] + 2 HO_3SCF_3 \xrightarrow{dme}$$

$$II$$

$$Yb(O_3SCF_3)_2(dme) + 2 NHR_2 + 2 OEt_2 \quad (7)$$

presence of the ${}^{-}O_3SCF_3$ ligand in 5 was evident from NMR spectroscopy. A characteristic quartet was observed for the CF₃ group in the ${}^{13}C{}^{1}H$ NMR spectrum at δ 129.04; the ${}^{19}F{}^{1}H$ NMR spectrum showed a singlet at δ – 76.0. The ${}^{171}Yb{}^{1}H$ NMR spectrum of 5 in pyridine (at 304 K) showed a very

2255

broad signal ($w_{\pm} \approx 1000$ Hz) at δ 620 (Table 1), indicating fluxional behaviour of the $^{-}O_3SCF_3$ and/or pyridine ligands. This process is much slower at 213 K, resulting in a sharp 171 Yb signal at δ 757 ($w_{\pm} \approx 65$ Hz) (Table 1). Elemental (C, H) analysis was consistent with the formulation of 5. A singlecrystal X-ray diffraction study was unsuccessful due to broad reflections.

No reaction was observed between complex 5 and 2 equivalents of LiCHR₂ in benzene at ambient temperature. A similar observation was made when an alkaline-earth-metal analogue $M'(O_3SCF_3)_2$ was allowed to react with MCHR₂ $(M' = Ca, Ba \text{ or } Sr; M = \text{Li or } K; R = \text{SiMe}_3).^{37}$

Addition of 4 equivalents of 2,2,6,6-tetramethylheptane-3,5dione (Bu'COCH₂COBu^t, Htmhd) in toluene to complex I in hexane gave a dark green solution. Work-up and crystallisation from pentane afforded white, crystalline [Yb(tmhd)₃] 6,³⁸ equation (8). The dark green solution suggests that a ytterbium-

$$[{Yb(NR_2)(\mu-NR_2)}_2] + 4 \text{ Htmhd} \xrightarrow{\text{hexane}} I$$

$$\frac{2}{n} (Yb(tmhd)_2)_n + 4 NHR_2 \xrightarrow{\text{pentane} - 30 \circ C} [Yb(tmhd)_3] \quad (8)$$

(II) complex '{Yb(tmhd)₂}_n' may initially have formed, but was then oxidised to afford 6. A similar observation has recently been reported for an analogous samarium(II) compound; attempts to crystallise Sm(tmhd)₂(dme)₂ led to the formation of colourless crystals of [Sm(tmhd)₃(dme)] XXV.³⁹

Related homoleptic tmhd complexes $Ln(tmhd)_3$ were previously prepared from (i) $Ln(NO_3)_3(H_2O)_6$ (Ln = Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu)³⁸ and 3 equivalents of Htmhd in a NaOH–ethanol solution or (ii) from Y₅O(OPr)₁₃ with an excess of Htmhd in refluxing toluene.⁴⁰ Complex 6 had been characterised previously by elemental (C, H) analysis and melting point.³⁸ The La to Gd complexes are dimeric, while those of Y and Ho to Lu are monomers, as exemplified by the crystal structures in the cases of Y,⁴⁰ Pr⁴¹ and Er.⁴²

New data on complex 6 were obtained by NMR (¹H, ¹³C-{¹H}) spectroscopy and mass spectrometry. The NMR spectral data for 6 showed characteristic shifts for a paramagnetic complex.⁴³ Thus, the ¹H NMR spectrum showed a singlet for both the Bu' (δ 0.08) and the CH (δ 4.02) protons, while the ¹³C-{¹H} NMR spectrum showed signals assigned as follows: CMe₃ (δ 24.24), CMe₃ (δ 42.65), CH (δ 45.72) and CO (δ 143.45). The electron-impact mass spectrum showed the parent molecular ion (\equiv M⁺; m/z = 723). The most intense peak (m/z = 540) corresponds to [M - tmhd]⁺. Only one peak with a m/z value (1274) higher than that of M⁺ was observed; this corresponds to [Yb₂(tmhd)₃(Bu'COCHCO)₃]⁺.

Insertion Reactions.—Addition of 2 equivalents of carbon disulfide in thf to complex II afforded the yellow-brown solid $Yb(S_2CNR_2)_2$ 7 equation (9). The insertion product 7, an

$$[Yb(NR_2)_2(OEt_2)_2] + 2 CS_2 \xrightarrow{\text{thf}}$$

II
$$Yb(S_2CNR_2)_2 + 2 OEt_2 \quad (9)$$

7

ytterbium(II) dithiocarbamate, was characterised by NMR (¹H, ¹³C-{¹H}, ²⁹Si-{¹H}) spectroscopy. A singlet was observed for the SiMe₃ group in both the ¹H (δ 0.08) and ²⁹Si-{¹H} (δ 29.00) spectra, while the ¹³C spectrum showed a quartet a δ 2.57 (SiMe₃) and a singlet at δ 271.90 (CS₂). An ¹⁷¹Yb resonance was not observed; this is probably a result of the poor solubility of 7 in thf or pyridine.

Reaction with $LiNR_2$ (R = SiMe₃).—A heterobimetallic complex was obtained when complex I and $LiNR_2$ (R =

$$\frac{1}{2}[\{Yb(NR_2)(\mu - NR_2)\}_2] + LiNR_2 + tmen \xrightarrow{hexane} I$$

$$[Li\{Yb(NR_2)_3\}(tmen)] \quad (10)$$
8

crystals of [Li{Yb(NR₂)₃}(tmen)] **8**. Complex **8** was fully characterised by NMR (¹H, ⁷Li-{¹H}, ¹³C-{¹H}, ²⁹Si-{¹H} and ¹⁷¹Yb-{¹H}) spectroscopy, mass spectrometry and elemental (C, H, N) analysis. At ambient temperature only one signal was observed for the silyl group in the ¹H, ¹³C-{¹H} or ²⁹Si-{¹H} NMR spectrum. However at -55 °C, the ²⁹Si-{¹H} NMR spectrum showed two peaks at δ –14.90 and –21.10 in a 2:1 ratio, indicating two bridging and one terminal N(SiMe₃)₂ group. A similar structure was reported for [(R₂N)Yb(µ-NR₂)₂Na] XI with the sodium positioned between two of the amido ligands.⁹ Other examples of related ytterbium(II) complexes are Na[Yb(O₃SCF₃)₃]-thf XXIV¹⁶ and Yb(CHR₂)₃Na XXVI.⁴⁴ The ¹⁷¹Yb NMR spectral data (Table 1) showed a low-frequency shift for complex **8** relative to I. By contrast, a high-frequency shift was observed (Table 1) for XI compared with I.¹⁵

Mass spectrometry showed complex 8 to be monomeric in the gas phase. The electron-impact mass spectrum showed a peak (m/z = 661) assigned to $[M - \text{tmen}]^+$. The most intense peak (m/z = 493) is attributed to $[M - \text{LiNR}_2 - \text{tmen}]^+$. Several attempts to obtain good elemental (C, H, N) analytical data for 8 were unsuccessful; this may have been due to loss of tmen as a result of prolonged drying *in vacuo*.

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: $[{Vb(NR_2)(\mu-NR_2)}_2]$ I,¹¹ [Yb-(NR_2)₂(OEt₂)₂] II,¹² tri-*tert*-butylmethanol (Bu'₃COH),⁴⁵ Li(CHR₂)⁴⁶ and LiNR₂;⁴⁷ Bu'OH, 2,6-di-*tert*-butyl-4-methylphenol, trifluoromethanesulfonic acid, 2,2,6,6tetramethylheptane-3,5-dione and carbon disulfide were obtained from Aldrich and used without further purification. *N*,*N*,*N'*,*N'*-Tetramethylethylenediamine was obtained from Aldrich and distilled from KOH.

Microanalyses were carried out by Medac Ltd., Uxbridge, Middlesex. The NMR spectra were recorded using Bruker WP-80, AC-250, WM-360 or AMX-500 spectrometers, IR spectra using a Perkin-Elmer 1720 spectrometer and mass spectra using a VG Autospec instrument. Melting points are uncorrected and were determined under argon in sealed capillary tubes using an Electrothermal melting-point apparatus.

Syntheses.—[{Yb(NR₂)(μ -OCBu¹₃)}₂] 1. Addition of Bu¹₃COH (1.73 g, 8.63 mmol) in hexane (100 cm³) to an orangered solution of [{Yb(NR₂)(μ -NR₂)}₂] I (4.08 g, 4.13 mmol) in hexane (100 cm³) at room temperature yielded a dark red solution. After stirring for 3 h at room temperature, the volatiles were removed *in vacuo* and the residue was extracted into pentane (150 cm³). The red extract was concentrated and cooled (-30 °C), yielding red crystals of complex 1 (3.85 g, 3.62 mmol, 88%) (Found: C, 40.7; H, 8.40; N, 2.05. C₃₈H₉₀-N₂O₂Si₄Yb₂ requires C, 42.8; H, 8.50; N, 2.65%) NMR (C₆D₆, 25 °C): ¹H (360.13 MHz), δ 0.36 (s, 36 H, SiMe₃) and 1.31 (s, 54 H, Bu¹); ¹³C-{¹H} (62.90 MHz), δ 6.00 (q, SiMe₃), 34.41 [q, C(CH₃)₃], 46.12 [s, C(CH₃)₃], and 92.07 (s, OCBu¹₃); ²⁹Si-{¹H} (49.70 MHz), δ -15.49.

 $[{Yb(OCBu_{3}^{i})(\mu - OCBu_{3}^{i})}_{2}]$ 2. Addition of hexane (60 cm³)

to Bu¹₃COH (0.50 g, 2.50 mmol) and complex I (0.58 g, 0.59 mmol) at room temperature afforded a green suspension, which was stirred at room temperature for 60 h, the colour changing to red-green. The solid material was allowed to settle. The supernatant liquor was decanted and filtered. Removing the volatiles from the filtrate *in vacuo* yielded the red solid **2** (0.90 g, 0.79 mmol, 68%) (Found: C, 52.3; H, 9.35. $C_{52}H_{108}O_4Yb_2$ requires C, 54.6; H, 9.50%). Electron impact (EI), mass spectrum: *m*/*z* 1142 (1%, *M*⁺) NMR: ¹H (C₆D₆, 250.13 MHz, 25 °C), δ 1.54 (s); ¹³C-{¹H} (C₆H₆-C₆D₆, 62.90 MHz, 31 °C), δ 33.54 [q, C(CH₃)₃], 46.13 [s, C(CH₃)₃] and 89.67 (s, OCBu¹₃).

[Yb(OCBu¹₃)₂(thf)₂] **3**. Tetrahydrofuran (70 cm³) was added to Bu¹₃COH (0.85 g, 4.24 mmol) and complex **I** (0.97 g, 0.98 mmol) at room temperature to yield a dark red solution, which was stirred at room temperature for 16 h. The volatiles were removed *in vacuo* and the green residue was extracted into pentane (100 cm³). The red extract was concentrated and cooled (-30 °C), yielding green crystals of **3** (0.90 g, 1.26 mmol, 64%) NMR: ¹H (C₆D₆, 360.13 MHz, 25 °C), δ 1.36 [br s, 8 H, β -CH₂ (thf)], 1.56 (s, 54 H, Bu¹) and 3.61 [br s, 8 H, α -CH₂ (thf)]; ¹H (C₅D₅N, 360.13 MHz, 25 °C), δ 0.77 [t, 8 H, β -CH₂ (thf)], 1.36 (s, 54 H, Bu¹), and 3.62 [t, 8 H, α -CH₂ (thf)]; ¹³C-{¹H} (C₆H₆-C₆D₆, 62.90 MHz, 25 °C), δ 25.48 [t, β -CH₂ (thf)], 33.77 [q, C(CH₃)₃], 46.39 [s, C(CH₃)₃], 69.08 [t, α -CH₂ (thf)] and 89.92 (s, OCBu¹₃).

Reaction of [Yb(NR₂)₂(dme)] VIII with Bu'OH.—A solution of Bu'OH in hexane (10.9 cm³, 0.235 mol dm⁻³, 2.56 mmol) was added to a red solution of [Yb(NR₂)₂(dme)] VIII (0.75 g, 1.28 mmol) in pentane (80 cm³) at room temperature, yielding a pale yellow solution. After stirring for 1.5 h, the volatiles were removed *in vacuo* and the residue was washed with pentane (15 cm³) to afford a white solid (0.53 g), m.p. > 290 °C. IR (KBr– Nujol): 1378m, 1354m, 1259m, 1206s, 1014s, 936m, 897mw, 841m, 771mw, 685w and 479w cm⁻¹.

[{Yb(OCBu⁴₃)(OR')}_x] **4a**. A solution of HOR' (1.03 g, 4.67 mmol) in hexane (30 cm³) was added to a red solution of complex 1 (2.49 g, 2.34 mmol) in hexane (30 cm³) at room temperature, the colour changing to a brighter red. The solution was stirred at room temperature for 2 h. The volatiles were removed *in vacuo* to afford the dark red solid **4a** (1.85 g, 3.13 mmol, 67%) ¹H NMR (C₆D₆, 360.13 MHz, 25 °C): δ 1.05–1.45 (m, 27 H, Bu⁴), 1.45–1.85 (m, 18 H, Bu⁴), 2.1–2.45 (m, 3 H, Me), and 6.9–7.4 (m, 2 H, aryl).

[Yb(OCBu¹₃)(OR')(thf)₂] **4b**. Tetrahydrofuran (30 cm³) was added to complex **4a** (1.01 g, 1.71 mmol) at room temperature; the red solution was stirred for 4 h. The thf was removed *in vacuo*, the residue was extracted into toluene (40 cm³) and the extract concentrated. Cooling to -30 °C yielded dark red crystals of **4b** (1.0 g, 1.36 mmol, 80%) (Found: C, 58.8; H, 8.15. C₃₆H₆₆O₄ Yb requires C, 58.8; H, 9.05%). NMR: ¹H (C₆D₆, 360.13 MHz, 25 °C), δ 1.22 (s, 18 H, Bu¹), 1.59 [s, 8 H, β -CH₂ (thf)], 1.68 (s, 27 H, Bu¹), 2.47 (s, 3 H, Me), 3.54 [br s, 8 H, α -CH₂ (thf)] and 7.30 (s, 2 H, aryl); ¹³C-{¹H</sup>} (C₆H₆-C₆D₆, 62.90 MHz, 25 °C), δ 21.84 (q, Me), 24.97 [t, β -CH₂ (thf)], 31.15 [q, C(CH₃)₃], 32.50 [q, OC{C(CH₃)₃], 35.14 [s, C(CH₃)₃], 31.492 [s, OC{C(CH₃)₃], 69.77 [t, α -CH₂ (thf)], 85.08 [s, OC(Bu¹)₃], 119.99 (s, CMe), 125.56 (d, CH), 136.74 (s, CBu¹) and 164.08 (s, CO).

[Yb(OCBu¹₃)(OR')(py)_x] 4c. After obtaining the NMR spectral data for complex 4b, the tube was opened and the solution transferred to a Schlenk tube. The volatiles were removed *in vacuo*, the residue was dissolved in pyridine (2.5 cm³) and the dark green solution introduced into an NMR tube. After obtaining the NMR spectral data for 4c, the tube was opened and the solution transferred to a Schlenk tube. The volatiles were removed *in vacuo* to afford the dark green solid 4c. ¹³C-{¹H} NMR: (C₅H₅N-C₅D₅N, 62.90 MHz, 25 °C): δ 21.30 (q, Me), 31.23 [q, C(CH₃)₃], 32.48 [q, OC{C(CH₃)₃], 34.98 [s, C(CH₃)₃], 44.88 [s, OC{C(CH₃)₃], 85.05 [s,

 $OC(Bu')_3$], 118.62 (s, CMe), 125.70 (d, CH), 137.87 (s, CBu'), and 165.33 (s, CO).

Yb(O₃SCF₃)₂(dmc) 5. A diethyl ether solution of HO₃SCF₃ (2.0 cm³, 0.7 mol dm⁻³, 1.4 mmol) was added to [Yb(NR₂)₂(OEt₂)₂] II (0.44 g, 0.7 mmol) in dme (50 cm³) at -70 °C. When the solution was slowly warmed to room temperature it changed from green to yellow. After stirring at room temperature for 1 h the solution was concentrated and cooled (-30 °C) to afford the white, crystalline complex 5 (0.3 g, 0.5 mmol, 77%) (Found: C, 12.5; H, 2.10. C₆H₁₀F₆O₈-S₂Yb requires C, 12.8; H, 1.80%). NMR (C₅D₅N, 25 °C): ¹H (360.13 MHz); δ 3.24 (s, 6 H, OMe) and 3.48 (s, 4 H, CH₂O); ¹³C-{¹H} (125.76 MHz), δ 58.60 (q, OMe), 72.06 (t, CH₂O), and 129.04 (q, ¹J_{CF} = 93.3 Hz, CF₃); ¹⁹F (75.38 MHz), δ -76.0 (s, $w_{\pm} \approx 200$ Hz, CF₃).

[Yb(tmhd)₃] **6**. A toluene solution of Htmhd (11.1 cm³, 0.24 mol dm³, 2.66 mmol) was slowly added to complex **I** (0.62 g, 0.63 mmol) in hexane (40 cm³) at 0 °C. The resulting dark green solution was stirred for 3 h, while slowly warming to room temperature. Removal of the volatiles *in vacuo* yielded a brown oil, which was taken up in pentane (20 cm³) and filtered. The filtrate was concentrated and cooled (-30 °C) to afford white, crystalline **6** (0.59 g, 0.82 mmol, 65%) (Found: C, 54.8; H, 7.85. C₃₃H₅₇O₆Yb requires C, 54.8; H, 7.95%), m.p. 164–168 °C (lit.,³⁸ 166–169 °C). EI mass spectrum: *m/z* 1274 {20, [Yb₂(tmhd)₃], 666 {77, [*M* – Bu']⁺} and 540 {83%, [*M* – tmhd]⁺}. NMR (C₆D₆, 20 °C): ¹H (360.13 MHz), δ 0.08 (s, 54 H, Bu') and 4.02 (s, 3 H, CH); ¹³C-{¹H} (125.76 MHz), δ 24.24 (q, *CMe*₃), 42.65 (s, *CMe*₃), 45.72 (d, CH), and 143.45 (s, CO).

Yb(S₂CNR₂)₂ 7. A thf solution of CS₂ (52.0 cm³, 0.1 mol dm ³, 5.2 mmol) was added to complex II (1.6 g, 2.49 mmol) at -50 °C. The yellow-green solution was stirred for 5 h, while slowly warming to room temperature. The volatiles were removed *in vacuo*, the residue was washed with hexane (10 cm³) and dried *in vacuo* to yield the yellow-brown solid 7 (1.1 g, 1.7 mmol, 68%). NMR: ¹H (C₆D₆, 360.13 MHz, 20 °C), δ 0.08 (s, SiMe₃); ¹³C-{¹H} (C₆D₆, 62.90 MHz, 25 °C), δ 2.57 (q, SiMe₃) and 271.90 (s, CS₂); ²⁹Si-{¹H} (C₆D₆, 49.70 MHz, 25 °C), δ 29.00 (SiMe₃).

 $[Li{Yb(NR_2)_3}(tmen)]$ 8. Hexane (50 cm³) was added to complex I (1.02 g, 1.03 mmol) and LiNR₂ (0.35 g, 2.07 mmol) at room temperature. The resulting red suspension was stirred for 17 h, without any changes being observed. Addition of tmen (0.3 cm³, 2.0 mmol) at room temperature afforded a red precipitate. The volatiles were removed in vacuo. The red solid residue was extracted into toluene (40 cm³). The extract was filtered and concentrated. Cooling (-30 °C) yielded magenta, microcrystalline 8 (1.44 g, 1.85 mmol, 90%) (Found: C, 30.9; H, 7.70; N, 7.75. $C_{18}H_{54}LiN_3Si_6Yb$ requires C, 32.7; H, 8.25; N, 6.35%). EI mass spectum: m/z 661 {2, $[M - \text{tmen}]^+$ } and 493 $\{45\%, [M - \text{LiNR}_2 - \text{tmen}]^+\}$. NMR: ¹H (C₆D₆, 360.13) MHz, 20 °C), δ 0.38 (s, 54 H, SiMe₃), 1.45 (s, 4 H, *CH*₂NMe₂), and 1.83 (s, 12 H, *CH*₂N*Me*₂); ⁷Li-{¹H} (C₆D₆-C₆H₆, 97.21 MHz, 20 °C), δ 3.22; ¹³C-{¹H} (C₆D₆-C₆H₆, 62.90 MHz, 20 °C), δ 6.04 (q, SiMe₃), 46.32 (q, CH₂NMe₂), and 56.17 (t, CH₂NMe₂); ²⁹Si-{¹H} (C₆D₆-C₆H₆, 49.70 MHz, 25 °C), $\delta - 12.68 (SiMe_3); {}^{29}Si-{}^{1}H (C_6D_5CD_3-C_6H_5Me, 49.70 MHz,$ -55 °C), $\delta = -14.90$ (bridge \tilde{SiMe}_3) and -21.10 (terminal SiMe₃).

X-Ray Crystallography for Compounds 1 and 3.—The appropriate details are in Table 6. In each case unique data sets were collected, using a single crystal on an Enraf-Nonius CAD4 diffractometer in the θ -2 θ mode with monochromated Mo-K $_{\alpha}$ radiation ($\lambda = 0.710.69$ Å). Two standard reflections monitored every hour showed no significant change. Data were corrected for Lorentz and polarisation effects (L_p) and also for absorption using DIFABS⁴⁸ after isotropic refinement. Reflections with $|F^2| > 2\sigma(F^2)$, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/L_p$, were

considered to be observed. A weighting scheme $w = 1/\sigma^2(F)$ was employed.

The structure of complex 1 was solved by the heavy-atom method using SHELXS 86⁴⁹ and refined by full-matrix least squares with H atoms at fixed positions. For 3 the Yb atom was 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 using SHELX 76,50 with only the Yb atom anisotropic. Although most C atoms could be located on an electron-density map phased by Yb and the O atoms, the geometry was poor and attempts at free refinement resulted in the C atoms of the Bu' group moving away from the map positions without convergence. Refinement was therefore continued with bond length and next-nearest-neighbour distance constraint within the Bu'₃C units and bond-length constraints within the thf ligands. All C-C bonds within the Bu'₃C groups were set equal to a single free variable, the distance between the central C atoms of the three Bu' groups to a second free variable, the C · · · C distances between the methyl groups in each Bu' group to a third, the C-C bonds in the thf ligands to a fourth and the O-C bonds in the thf ligands to a fifth free variable. Hydrogen atoms were included at calculated positions riding on the C atoms with a common isotropic thermal parameter. A refinement as the opposite absolute structure gave identical R factors.

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

Acknowledgements

We thank Shell Research BV (Koninklijke/Shell-Laboratorium, Amsterdam) for providing a studentship to J. R. v. d. H. (and Dr. R. W. Chorley for his support and interest) and the EPSRC for other support.

References

- 1 Part 2, J. R. van den Hende, P. B. Hitchcock, S. A. Holmes and M. F. Lappert, J. Chem. Soc., Dalton Trans., 1995, 1435.
- 2 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.
- 3 J. R. van den Hende, P. B. Hitchcock and M. F. Lappert, J. Chem. Soc., Chem. Commun., 1994, 1413.
- 4 J. M. Boncella and R. A. Andersen, Organometallics, 1985, 4, 205.
- 5 L. Lee, D. J. Berg and G. W. Bushnell, Inorg. Chem., 1994, 33, 5302.
- 6 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.
- 7 T. D. Tilley, R. A. Andersen and A. Zalkin, J. Am. Chem. Soc., 1982, 104, 3725.
- 8 D. R. Cary and J. Arnold, Inorg. Chem., 1994, 33, 1791.
- 9 T. D. Tilley, R. A. Andersen and A. Zalkin, *Inorg. Chem.*, 1984, 23, 2271.
- 10 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert and R. G. Smith, J. Chem. Soc., Chem. Commun., 1992, 932.
- 11 T. D. Tilley, Ph. D. Thesis, University of California, Berkeley, 1982; cited in ref. 4.
- 12 T. D. Tilley, J. M. Boncella, D. J. Berg, C. J. Burns and R. A. Andersen, *Inorg. Synth.*, 1990, 27, 146.
- 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; D. C. Bradley, H. Chudzynska, M. E. Hammond, M. B. Hursthouse, M. Motevalli and W. Ruowen, *Polyhedron*, 1992, 11, 375; W. A. Herrmann, R. Anwander and W. Scherer, *Chem. Ber.*, 1993, 126, 1533; D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1993, 12, 1907; D. M. Barnhart, D. L. Clark, J. C. Huffman, R. L. Vincent and J. G. Watkin, *Inorg. Chem.*, 1993,

2257

- 14 R. C. Mehrotra, A. Singh and U. M. Tripathi, Chem. Rev., 1991, 91, 1287; C. J. Schaverien, Adv. Organomet. Chem., 1994, 36, 283; F. T. Edelmann, A. Steiner, D. Stalke, J. W. Gilje, S. Jagner and M. Håkansson, Polyhedron, 1994, 13, 539.
- 15 A. G. Avent, M. A. Edelman, M. F. Lappert and G. A. Lawless, J. Am. Chem. Soc., 1989, 111, 3423.
- 16 S. A. Holmes, D. Phil. Thesis, University of Sussex, 1992.
- 17 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, J. Chem. Soc., Dalton Trans., 1995, 1427.
- 18 T. D. Tilley, R. A. Andersen and A. Zalkin, J. Am. Chem. Soc., 1982, 104, 3725
- 19 P. B. Hitchcock, M. F. Lappert, R. G. Smith, R. A. Bartlett and P. P. Power, J. Chem. Soc., Chem. Commun., 1988, 1007.
- 20 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.
- 21 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.
- 22 H. A. Stecher, A. Sen and A. L. Rheingold, Inorg. Chem., 1989, 28, 3280.
- 23 G. Beck, P. B. Hitchcock, M. F. Lappert and I. A. MacKinnon, J. Chem. Soc., Chem. Commun., 1989, 1312.
- 24 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers
- and R. Shakir, J. Am. Chem. Soc., 1983, 105, 302.
 Z. Hou, H. Yamazaki, K. Kobayashi, Y. Fujiv
 H. Taniguchi, J. Chem. Soc., Chem. Commun., 1992, 722. 25 Z. Fujiwara and
- 26 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.
- 27 W. J. Evans, R. Anwander, M. A. Ansari and J. W. Ziller, Inorg. Chem., 1995, 34, 5.
- 28 (a) H. J. Heeres, A. Meetsma and J. H. Teuben, J. Chem. Soc., Chem. Commun., 1988, 962; (b) H. J. Heeres, A. Meetsma, J. H. Teuben and R. D. Rogers, Organometallics, 1989, 8, 2637; (c) C. J. Schaverien, J. H. G. Frijns, H. J. Heeres, J. R. van den Hende, J. H. Teuben and A. L. Spek, J. Chem. Soc., Chem. Commun., 1991, 642.
- 29 I. P. Rothwell, Acc. Chem. Res., 1988, 21, 153 and refs. therein.
- 30 W. J. Evans, T. P. Hanusa and K. R. Levan, Inorg. Chim. Acta, 1985, 110. 191.

View Article Online

- 31 A. Sen, H. A. Stecher and A. L. Rheingold, Inorg. Chem., 1992, 31, 473
- 32 N. E. Dixon, W. G. Jackson, M. J. Lancaster, G. A. Lawrance and A. M. Sargeson, Inorg. Chem., 1981, 20, 470.
- 33 (a) H. Schumann, J. A. Meese-Marktscheffel and A. Dietrich, J. Organomet. Chem., 1989, 377, C5; (b) J. Stehr and R. D. Fischer, J. Organomet. Chem., 1992, 430, C1.
- 34 H. H. Karsch, G. Ferazin, O. Steigelmann, H. Kooijman and W. Hiller, Angew. Chem., Int. Ed. Engl., 1993, 32, 1739.
- 35 G. H. Maunder, A. Sella and D. A. Tocher, J. Chem. Soc., Chem. Commun., 1994, 885.
- 36 (a) T. Hanamoto, Y. Sugimoto, A. Sugino and J. Inanaga, Synlett., 1994, 377; (b) S. Fukuzawa, T. Tsuchimoto and T. Kanai, Chem. Lett., 1994, 1981.
- 37 A. D. Frankland, personal communication.
- 38 K. J. Eisentraut and R. E. Sievers, J. Am. Chem. Soc., 1965, 87, 5254. 39 W. J. Evans, J. L. Shreeve and J. W. Ziller, Inorg. Chem., 1994, 33, 6435
- 40 A. Gleizes, S. Sans-Lenain, D. Medus, N. Hovnanian, P. Miele and J.-D. Foulon, Inorg. Chim. Acta, 1993, 209, 47.
- 41 C. S. Erasmus and J. C. A. Boeyens, Acta Crystallogr., Sect. B, 1970, 26, 1843.
- 42 J. P. R. de Villiers and J. C. A. Boeyens, Acta Crystallogr., Sect. B, 1971, 27, 2335.
- 43 M. Wedler, F. Knösel, U. Pieper, D. Stalke, F. T. Edelmann and H.-D. Amberger, Chem. Ber., 1992, 125, 2171; R. D. Fischer in Fundamental and Technological Aspects of Organo-f-Element Chemistry, eds. T. J. Marks and I. L. Fragalá, NATO ASI Ser. D, Reidel P, Dordrecht, Boston, Lancaster, 1985, S. 277.
- 44 P. B. Hitchcock, S. A. Holmes, M. F. Lappert and S. Tian, J. Chem. Soc., Chem. Commun., 1994, 2691
- 45 R. Syper, Rocz. Chem., 1973, 47, 433.
- 46 N. Wiberg and G. Wagner, Chem. Ber., 1986, 119, 1455.
- 47 P. J. Davidson, D. H. Harris and M. F. Lappert, J. Chem. Soc., Dalton Trans., 1976, 2286.
- 48 N. Walker and D. Stuart, Acta Crystallogr., Sect. A, 1983, 39, 158.
- 49 G. M. Sheldrick, in Crystallographic Computing 3, eds. G. M. Sheldrick, C. Krüger and R. Goddard, Oxford University Press, 1985, pp. 175-189.
- 50 G. M. Sheldrick, SHELX 76, A program for crystal structure refinement, University of Cambridge, 1976.

Received 6th March 1995; Paper 5/01339I

2258