Reactions of Ytterbium(II) Amides with Various Brønsted Acids, CS2 or LiNR2; Crystal Structures of [{Yb(NR2)(μ-OCBut3)}2] and [Yb(OCBut3)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(NR2)(μ-NR2)}2] I or [Yb(NR2)2(OEt2)2] II (R = SiMe3) with various Brønsted acids, carbon disulfide or LiNR2 with N,N,N',N'-tetramethylethylenediamine (tmen) afforded the following complexes: (a) [{Yb(NR2)(μ-OCBut3)}2] 1 from I and 2 But3COH; (b) [{Yb(OCBut3)(μ-OCBut3)}2] 2 and [Yb(OCBut3)2(thf)2] 3 from I and 4 But3COH in hexane or tetrahydrofuran (thf), respectively; (c) [{Yb(OCBut3)(OR')}x] 4a (R' = C6H2But2-2,6-Me-4) from 1 and 2 HOR'; (d) [Yb(OCBut3)(OR')(thf)2] 4b from 4a and an excess of thf; (e) [Yb(OCBut3)(OR')(py)x] 4c from 4b and an excess of pyridine (py); (f) Yb(O3SCF3)2(dme) 5 (dme = 1,2-dimethoxyethane) from II and 2 HO3SCF3; (g) [Yb(tmhd)3] 6 from I and 4 Htmhd (≡ ButCOCH2COBut); (h) Yb(S2CNR2)2 7 from II and 2 CS2; and (i) [Li{Yb(NR2)3}(tmen)] 8 from II, LiNR2 and tmen. A single-crystal X-ray diffraction study established 1 to be dimeric with asymmetrically bridging ⁻OCBut3 ligands. In this molecule 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. 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)°], while the other Yb–O–C angle is significantly smaller [155(3)°].

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] tellurol[8] or thiol.[2,10] We now report reactions of [{Yb(NR2)(μ-NR2)}2] I[11] or [Yb(NR2)2(OEt2)2] II[12] with various Brønsted acids, carbon disulfide or LiNR2 with tmen (R = SiMe3, tmen = N,N,N',N'-tetramethylethylenediamine).
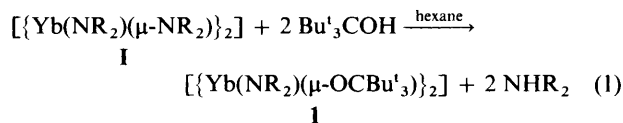
We have previously briefly communicated the preparation and NMR spectra of the two ytterbium(II) alkoxides [{YbX(μ-OCBut3)}2] (X = NR2 1 or OCBut3 2; R = SiMe3) and the crystal structure of 1.[3] We report here new data on these complexes and the synthesis and characterisation of further ytterbium(II) 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 1[3] and [Yb(OCBut3)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(II) 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]
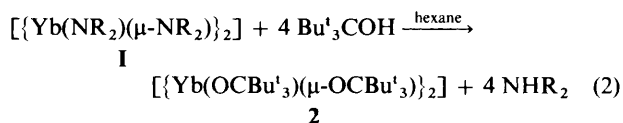
Results and Discussion

Synthesis of Ytterbium Alkoxides.—The ytterbium(II) amide [{Yb(NR2)(μ-NR2)}2] I[11] with 2 equivalents of But3COH in

hexane gave the red, crystalline complex [{Yb(NR2)(μ-OCBut3)}2] 1, equation (1). Complex 1 was fully characterised

$$[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2] + 2\ Bu^t_3COH \xrightarrow{\text{hexane}}$$
$$\mathbf{I}$$
$$[\{Yb(NR_2)(\mu\text{-}OCBu^t_3)\}_2] + 2\ NHR_2 \quad (1)$$
$$\mathbf{1}$$

by NMR [¹H, ¹³C-{¹H}, ²⁹Si-{¹H}, ¹⁷¹Yb-{¹H}¹⁵] spectroscopy, elemental (C, H, N) analysis and a single-crystal X-ray diffraction study.

The red, solid homoleptic alkoxide [{Yb(OCBut3)(μ-OCBut3)}2] 2 was obtained from I and 4 equivalents of But3COH in hexane, equation (2). Complex 2 is probably

$$[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2] + 4\ Bu^t_3COH \xrightarrow{\text{hexane}}$$
$$\mathbf{I}$$
$$[\{Yb(OCBu^t_3)(\mu\text{-}OCBu^t_3)\}_2] + 4\ NHR_2 \quad (2)$$
$$\mathbf{2}$$

dimeric in the solid state, like the aryloxide analogue [{Yb(OC6H2But2-2,6-Me-4)(μ-OC6H2But2-2,6-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 ⁻OCBut3 signal. This indicates that the fluxional process, believed to arise from terminal/bridging ⁻OCBut3 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(OCBut3)2(thf)2] 3 were obtained, equation (3). It was evident from NMR (¹H, ¹³C-{¹H}) spectra in

Table 1 Some ^{171}Yb-$\{^1H\}$ NMR spectral chemical shift (δ) data[a] for compounds 1–8, I, XI, XXI and XXIV

Compound	Solvent[b]	T/K	δ(^{171}Yb)	$w_{\frac{1}{2}}$/Hz	Ref.
1 [{Yb(NR$_2$)(μ-OCBu$^t_3$)}$_2$]	C$_6$H$_6$	304	758	80	3
2 [{Yb(OCBu$^t_3$)(μ-OCBu$^t_3$)}$_2$]	C$_6$H$_6$	304	705	200	3
3 [Yb(OCBu$^t_3$)$_2$(thf)$_2$]	C$_6$H$_6$	304	552	20	This work
4b [Yb(OCBu$^t_3$)(OR')(thf)$_2$]	C$_6$H$_6$	304	387	50	This work
4c [Yb(OCBu$^t_3$)(OR')(py)$_x$]	C$_5$H$_5$N	304	830	60	This work
5 Yb(O$_3$SCF$_3$)$_2$(dme)	C$_5$H$_5$N	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$_2$)(μ-NR$_2$)}$_2$]	C$_6$H$_6$	304	779	200	This work[c]
XI [(R$_2$N)Yb(μ-NR$_2$)$_2$Na]	C$_6$H$_5$Me	193	947	190	15
XXI [Yb(NR$_2$)$_2$(py)$_2$]	C$_5$H$_5$N	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(η-C$_5$Me$_5$)$_2$(thf)$_2$] in 10% C$_6$D$_5$CD$_3$ at 273 K.[15] [b] 10–20% v/v C$_6$D$_6$, C$_6$D$_5$CD$_3$ or C$_5$D$_5$N 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.
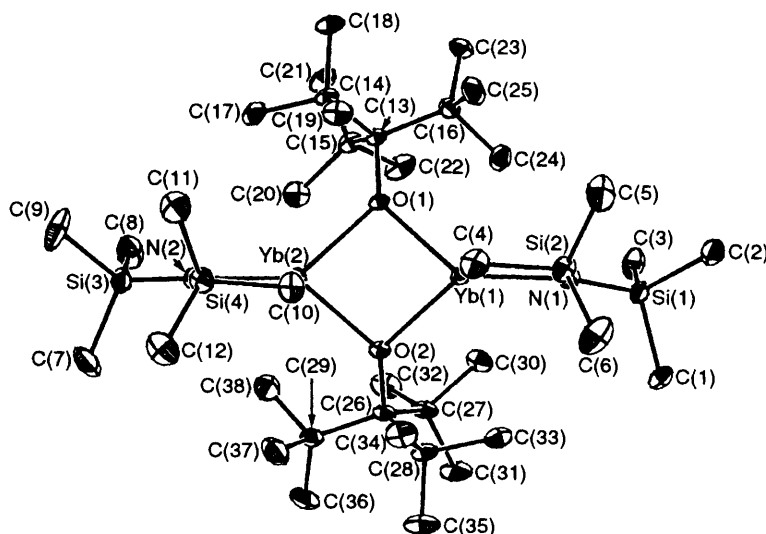
Fig. 1 Molecular structure of [{Yb(NR$_2$)(μ-OCBu$^t_3$)}$_2$] 1 and atom numbering scheme
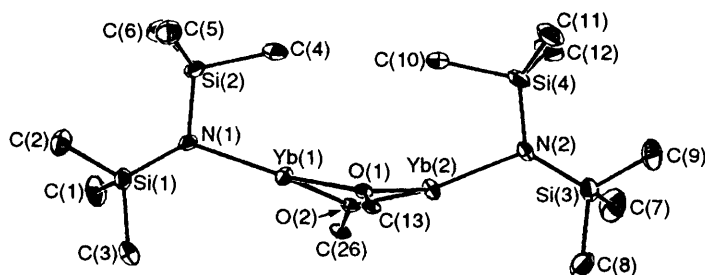
Fig. 2 Alternative view of the molecular structure of [{Yb(NR$_2$)(μ-OCBu$^t_3$)}$_2$] 1 and atom numbering scheme; the *tert*-butyl groups of the $^-$OCBu$^t_3$ ligands have been omitted for clarity

$$[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2] + 4\,Bu^t_3COH \xrightarrow{\text{thf}}$$
$$\mathbf{I}$$
$$2\,[Yb(OCBu^t_3)_2(thf)_2] + 4\,NHR_2 \quad (3)$$
$$\mathbf{3}$$
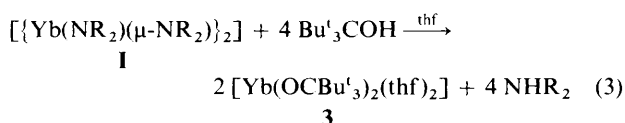
benzene solution at ambient temperature that, unlike in the solid state, the alkoxo ligands are equivalent on the NMR time-scale.

The benzene solution ^{171}Yb-$\{^1H\}$ NMR[15] spectral chemical shifts of complexes 1–3 (Table 1) may be compared with those for [{Yb(NR$_2$)(μ-NR$_2$)}$_2$] I (δ 779), [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] II

(614),[15] [{Yb(OR')(μ-OR')}$_2$] III (R' = OC$_6$H$_2$Bu$^t_2$-2,6-Me-4) (314),[3] [{Yb(NR$_2$)(μ-OR')}$_2$] IV (536),[3] [Yb(OR')$_2$(OEt$_2$)$_2$] 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^{t}OH, a white solid was isolated. The ^{1}H 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(II) complex [{Yb(OBu^t)$_2$}$_n$] IX, which was characterised by IR spectroscopy and (poor) elemental (C, H, Yb) analysis.[2]

Single-crystal Structure of [{Yb(NR$_2$)(μ-OCBu$^t_3$)}$_2$] 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$_2$O$_2$ four-membered ring in which there appear to be asymmetrically bridging $^-$OCBu$^t_3$ 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
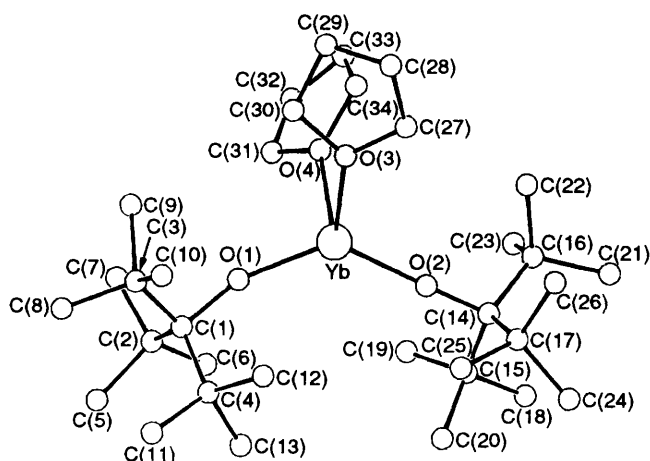

Fig. 3 Molecular structure of [Yb(OCBu$^t_3$)$_2$(thf)$_2$] 3 and atom numbering scheme

Table 2 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [{Yb(NR$_2$)(μ-OCBu$^t_3$)}$_2$] 1

Yb(1)–O(1)	2.297(4)	Yb(1)–O(2)	2.320(5)
Yb(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)···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 $^-$OCBu$^t_3$ ligand. In 1 the four-membered Yb$_2$O$_2$ 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 NR$_2$ groups slightly above the plane, as illustrated in Fig. 2. Bonding at the N atoms is planar, the SiNSi planes being orthogonal to the YbO$_2$ plane. The Yb–N bond lengths [2.332(6) and 2.327(6) Å] are similar to those in [Yb(NR$_2$)$_2$(dmpe)] X [dmpe = 1,2-bis(dimethylphosphino)ethane] [2.331(13) Å][18] and to the terminal Yb–N bond in [(R$_2$N)Yb(μ-NR$_2$)$_2$Na] XI (R = SiMe$_3$) [2.38(2) Å].[9]

The following additional features are noteworthy. (i) Complex 1 has two LnX$_2$ precedents, the amide I[11] 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 [LnX$_3$] complexes with X = CHR$_2$,[19] NR$_2$,[20] OC$_6$H$_2$Bu$^t_2$-2,6-Y-4 (Y = H, Me or Bu^t)[21] or OCBu$^t_3$;[22] for Ln^{2+} complexes, the sole examples were III,[1,3] XI and its europium analogue.[9] (iv) Complexes having a bridging $^-$OCBu$^t_3$ ligand (cf. 1) are rare; earlier examples include [{Li(μ-OCBu$^t_3$)}$_2$].[23] (v) In 1, the bridging ligand is $^-$OCBu$^t_3$ rather than $^-$NR$_2$, although the latter is known to have this potential, as in [{Li(NR$_2$)(OEt$_2$)}$_2$].[24] (vi) Alkoxides of Ln^{2+} were previously unknown, although aryloxides are established, including III–VII,[1,3,6] [Yb-(OR')$_2$(hmpa)$_2$] XII [hmpa = P(NMe$_2$)$_3$O],[25] [Yb(OC$_6$H$_2$-Bu$^t_3$-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')$_3$}$_n$] XVI[27] 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$_2$)(μ-OCBu$^t_3$)}$_2$] 1

Atom	x	y	z	Atom	x	y	z
Yb(1)	0.164 74(2)	0.235 43(2)	0.078 81(1)	C(15)	−0.140 1(6)	0.164 7(4)	0.019 5(3)
Yb(2)	−0.047 22(3)	0.260 26(2)	0.156 21(1)	C(16)	−0.004 5(6)	0.246 7(5)	−0.043 0(3)
Si(1)	0.403 27(17)	0.181 49(15)	0.005 96(11)	C(17)	−0.231 6(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)	−0.206 4(7)	0.352 5(5)	−0.042 8(4)
Si(3)	−0.266 26(19)	0.304 61(17)	0.242 69(11)	C(19)	−0.086 9(7)	0.410 0(5)	0.028 6(4)
Si(4)	−0.104 51(21)	0.433 04(15)	0.219 90(11)	C(20)	−0.169 9(6)	0.150 3(5)	0.081 0(4)
O(1)	−0.008 0(3)	0.254 9(3)	0.060 9(2)	C(21)	−0.240 1(6)	0.158 9(5)	−0.017 2(4)
O(2)	0.111 3(4)	0.199 7(3)	0.168 8(2)	C(22)	−0.081 0(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)	−0.058 6(7)	0.218 0(6)	−0.097 6(4)
N(2)	−0.156 9(5)	0.338 4(4)	0.211 8(3)	C(24)	0.089 0(6)	0.188 6(6)	−0.033 3(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)	−0.023 3(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)	−0.027 4(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)	−0.000 2(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$_5$Me$_5$)(OC$_6$H$_3$Bu$^t_2$-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 electron-deficient 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. **XVII**[27]). 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.

The O(1)–Yb–O(2) angle is larger [132(2)°] than those in the aryloxides **V** [119.8(3)°],[1,6] **VI** [118.7(3)°][6,26] and **XII** [110.3(3)°],[25] presumably due to the fact that OCBu$^t_3$ is significantly more bulky than OR'.[31] As a consequence, the O(3)–Yb–O(4) angle is reduced [84.8(8)°] in comparison with those seen in **V** [89.7(4)°],[1,6] **VI** [89.9(4)°][6,26] and **XII** [97.0(3)°].[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 [{Yb(OCBu$^t_3$)(OR')}$_x$] **4a** *and the Lewis-base Adducts* [Yb(OCBu$^t_3$)(OR')L$_n$] (L = thf, n = 2 **4b**; L = C$_5$H$_5$N, n = x **4c**.—The dark red, solid heteroleptic ytterbium(II) complex [{Yb(OCBu$^t_3$)(OR')}$_x$] **4a** was obtained by treating **1** with 2 equivalents of the phenol, equation (4). In

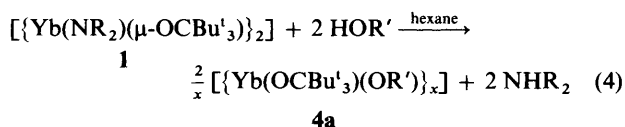$$[\{Yb(NR_2)(\mu\text{-OCBu}^t_3)\}_2] + 2 \text{ HOR}' \xrightarrow{\text{hexane}}$$

$$\mathbf{1}$$

$$\frac{2}{x}[\{Yb(OCBu^t_3)(OR')\}_x] + 2\,NHR_2 \quad (4)$$

$$\mathbf{4a}$$

Table 4 Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses for [Yb(OCBu$^t_3$)$_2$(thf)$_2$] **3**, [Yb(OR')$_2$(OEt$_2$)$_2$] **V**[1,6] and [Yb(OR')$_2$(thf)$_2$] **VI**[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 6 Crystal data for [{Yb(NR$_2$)(μ-OCBu$^t_3$)}$_2$] **1** and [Yb(OCBu$^t_3$)$_2$(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
M	1065.6	716.0
Crystal system	Monoclinic	Monoclinic
Space group	P2$_1$/n	P2$_1$
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$_c$/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 × 0.25 × 0.2	0.3 × 0.2 × 0.2
A$_{min,max}$	0.79, 1.38	0.51, 1.53
R	0.042	0.080
R'	0.043	0.086

Table 5 Fractional atomic coordinates for [Yb(OCBu$^t_3$)$_2$(thf)$_2$] **3**

Atom	x	y	z	Atom	x	y	z
Yb	0.268 01(12)	0	0.312 44(8)	C(16)	−0.098 6(25)	−0.084 5(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)	−0.081 9(12)	0.217 6(16)	C(18)	−0.206 9(32)	−0.217 9(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)				

contrast to **1**, complex **4a** had poor solubility in non-co-ordinating solvents. The ^{1}H 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(OCBu^t$_3$)(OR')(thf)$_2$] **4b** was obtained, equation (5). Complex **4b** was soluble in light petroleum and

$$[\{Yb(OCBu^t{}_3)(OR')\}_x] \xrightarrow{\text{thf}}$$
$$\textbf{4a}$$

$$x[Yb(OCBu^t{}_3)(OR')(thf)_2] \quad (5)$$
$$\textbf{4b}$$
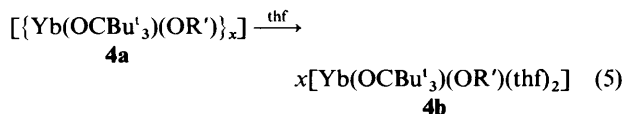
aromatic solvents and was characterised by NMR [^{1}H, ^{13}C-$\{^1$H$\}$, ^{171}Yb-$\{^1$H$\}$] spectroscopy and elemental (C, H) analysis. The benzene solution ^{171}Yb-$\{^1$H$\}$ NMR spectral chemical shift (Table 1) was characteristic for a heteroleptic complex, being intermediate between those 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
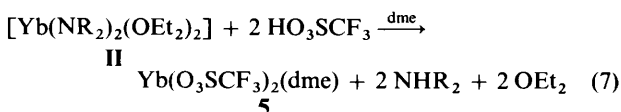
$$[Yb(OCBu^t{}_3)(OR')(thf)_2] \xrightarrow{\text{pyridine}}$$
$$\textbf{4b}$$

$$[Yb(OCBu^t{}_3)(OR')(py)_x] + 2 \text{ thf} \quad (6)$$
$$\textbf{4c}$$
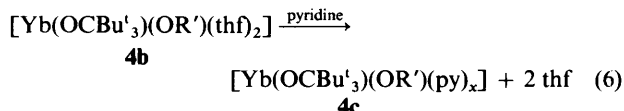
spectrum (Table 1) showed only one signal, at δ 830, indicating that no redistribution to the homoleptic alkoxide and aryloxide complexes had occurred. The observed shift is typical for a pyridine adduct and may be compared with those for [Yb(OR')$_2$(py)$_2$] **XX** (δ 745),[1] [Yb(NR$_2$)$_2$(py)$_2$] **XXI** (R = SiMe$_3$) (δ 919) and [Yb(C$_5$Me$_5$)$_2$(py)$_2$] **XXII** (δ 949).[15]

When a related reaction to that shown in equation (4) was carried out with Bu^{t}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 ^{1}H NMR spectroscopy, due to its paramagnetism. Hence it appears that oxidation to ytterbium(III) had occurred.

Reactions with Brønsted Acids.—Trifluoromethane sulfonate $^-$OSO$_2$CF$_3$ 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(η-C$_5$H$_5$)(O$_3$SCF$_3$)$_2$(thf)$_3$] [33a] and [$\{$Yb(η-C$_5$H$_5$)$_2$(μ-O$_3$SCF$_3$)$\}_2$],[33b] (*ii*) the diphosphinomethanides [Ln$\{$(PMe$_2$)$_2$CR$\}_3$] (Ln = Sc, La or Lu; R = SiMe$_3$),[34] (*iii*) the hydridotris(3,5-dimethylpyrazol-1-yl)borate [Yb$\{$HB(dmpz)$_3\}_2$(O$_3$SCF$_3$)] [35] and (*iv*) homoleptic lanthanide(III) bis(trimethylsilyl)amides and 2,6-di-*tert*-butyl-4-methylphenoxides.[16] A previous attempt to synthesise a ytterbium(II) trifluoromethane sulfonate by reduction of Yb(O$_3$SCF$_3$)$_3$ **XXIII** with a stoichiometric amount of 5% Na/Hg amalgam in thf yielded blue-white Na[Yb(O$_3$SCF$_3$)$_3$-(thf)] **XXIV**.[16] A 'samarium(II) triflate'[36] or the ytterbium analogue[36a] was prepared *in situ* [from Sm(O$_3$SCF$_3$)$_3$ + 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$_3$SCF$_3$)$_2$(dme) **5**, equation (7). The

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

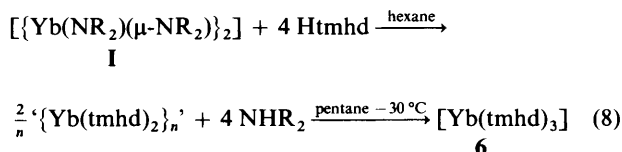$$Yb(O_3SCF_3)_2(\text{dme}) + 2 NHR_2 + 2 OEt_2 \quad (7)$$
$$\textbf{5}$$

presence of the $^-$O$_3$SCF$_3$ ligand in **5** was evident from NMR spectroscopy. A characteristic quartet was observed for the CF$_3$ 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

broad signal ($w_{\frac{1}{2}} \approx 1000$ Hz) at δ 620 (Table 1), indicating fluxional behaviour of the $^-$O$_3$SCF$_3$ and/or pyridine ligands. This process is much slower at 213 K, resulting in a sharp ^{171}Yb signal at δ 757 ($w_{\frac{1}{2}} \approx 65$ Hz) (Table 1). Elemental (C, H) analysis was consistent with the formulation of **5**. A single-crystal X-ray diffraction study was unsuccessful due to broad reflections.

No reaction was observed between complex **5** and 2 equivalents of LiCHR$_2$ in benzene at ambient temperature. A similar observation was made when an alkaline-earth-metal analogue M'(O$_3$SCF$_3$)$_2$ was allowed to react with MCHR$_2$ (M' = Ca, Ba or Sr; M = Li or K; R = SiMe$_3$).[37]

Addition of 4 equivalents of 2,2,6,6-tetramethylheptane-3,5-dione (Bu^{t}COCH$_2$COBu^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-

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

$$\frac{2}{n} \text{'}\{Yb(tmhd)_2\}_n\text{'} + 4 NHR_2 \xrightarrow{\text{pentane } -30 \text{ °C}} [Yb(tmhd)_3] \quad (8)$$
$$\textbf{6}$$
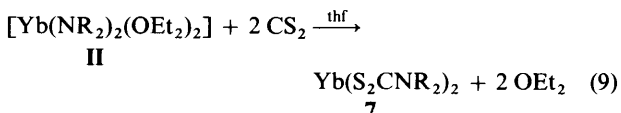
(II) complex '$\{$Yb(tmhd)$_2\}_n$' may initially have formed, but was then oxidised to afford **6**. A similar observation has recently been reported for an analogous samarium(II) compound; attempts to crystallise Sm(tmhd)$_2$(dme)$_2$ led to the formation of colourless crystals of [Sm(tmhd)$_3$(dme)] **XXV**.[39]

Related homoleptic tmhd complexes Ln(tmhd)$_3$ were previously prepared from (*i*) Ln(NO$_3$)$_3$(H$_2$O)$_6$ (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 Y$_5$O(OPr^i)$_{13}$ 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] Pr[41] and Er.[42]

New data on complex **6** were obtained by NMR (^{1}H, ^{13}C-$\{^1$H$\}$) spectroscopy and mass spectrometry. The NMR spectral data for **6** showed characteristic shifts for a paramagnetic complex.[43] Thus, the ^{1}H NMR spectrum showed a singlet for both the Bu^t (δ 0.08) and the CH (δ 4.02) protons, while the ^{13}C-$\{^1$H$\}$ NMR spectrum showed signals assigned as follows: C*Me*$_3$ (δ 24.24), *C*Me$_3$ (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 [Yb$_2$(tmhd)$_3$(Bu^{t}COCHCO)$_3$]$^+$.

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

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

$$Yb(S_2CNR_2)_2 + 2 OEt_2 \quad (9)$$
$$\textbf{7}$$

ytterbium(II) dithiocarbamate, was characterised by NMR (^{1}H, ^{13}C-$\{^1$H$\}$, ^{29}Si-$\{^1$H$\}$) spectroscopy. A singlet was observed for the SiMe$_3$ group in both the ^{1}H (δ 0.08) and ^{29}Si-$\{^1$H$\}$ (δ 29.00) spectra, while the ^{13}C spectrum showed a quartet a δ 2.57 (SiMe$_3$) and a singlet at δ 271.90 (CS$_2$). An ^{171}Yb resonance was not observed; this is probably a result of the poor solubility of **7** in thf or pyridine.

Reaction with LiNR$_2$ (R = SiMe$_3$).—A heterobimetallic complex was obtained when complex **I** and LiNR$_2$ (R =

SiMe$_3$) were mixed in the presence of 1 equivalent of tmen equation (10). Crystallisation from toluene afforded magenta

$$\tfrac{1}{2}[\{Yb(NR_2)(\mu\text{-}NR_2)\}_2] + LiNR_2 + tmen \xrightarrow{\text{hexane}}$$
I
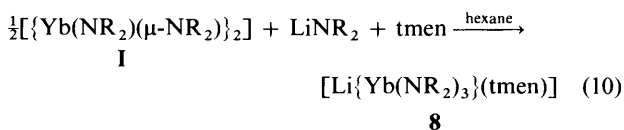
$$[Li\{Yb(NR_2)_3\}(tmen)] \quad (10)$$
8

crystals of [Li{Yb(NR$_2$)$_3$}(tmen)] **8**. Complex **8** was fully characterised by NMR (^{1}H, ^{7}Li-{^{1}H}, ^{13}C-{^{1}H}, ^{29}Si-{^{1}H} and ^{171}Yb-{^{1}H}) spectroscopy, mass spectrometry and elemental (C, H, N) analysis. At ambient temperature only one signal was observed for the silyl group in the ^{1}H, ^{13}C-{^{1}H} or ^{29}Si-{^{1}H} NMR spectrum. However at $-55\,^\circ$C, the ^{29}Si-{^{1}H} NMR spectrum showed two peaks at δ -14.90 and -21.10 in a 2:1 ratio, indicating two bridging and one terminal N(SiMe$_3$)$_2$ group. A similar structure was reported for [(R$_2$N)Yb(μ-NR$_2$)$_2$Na] **XI** with the sodium positioned between two of the amido ligands.[9] Other examples of related ytterbium(II) complexes are Na[Yb(O$_3$SCF$_3$)$_3$]·thf **XXIV**[16] and Yb(CHR$_2$)$_3$Na **XXVI**.[44] The ^{171}Yb 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 $-$ tmen]$^+$. The most intense peak ($m/z = 493$) is attributed to [M $-$ LiNR$_2$ $-$ 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: [{Yb(NR$_2$)(μ-NR$_2$)}$_2$] **I**,[11] [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] **II**,[12] tri-tert-butylmethanol (Bu$^t_3$COH),[45] Li(CHR$_2$)[46] and LiNR$_2$;[47] Bu^{t}OH, 2,6-di-tert-butyl-4-methyl-phenol, trifluoromethanesulfonic acid, 2,2,6,6-tetramethylheptane-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(NR$_2$)(μ-OCBu$^t_3$)}$_2$] **1**. Addition of Bu$^t_3$COH (1.73 g, 8.63 mmol) in hexane (100 cm^3) to an orange-red solution of [{Yb(NR$_2$)(μ-NR$_2$)}$_2$] **I** (4.08 g, 4.13 mmol) in hexane (100 cm^3) 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 cm^3). The red extract was concentrated and cooled ($-30\,^\circ$C), yielding red crystals of complex **1** (3.85 g, 3.62 mmol, 88%) (Found: C, 40.7; H, 8.40; N, 2.05. C$_{38}$H$_{90}$-N$_2$O$_2$Si$_4$Yb$_2$ requires C, 42.8; H, 8.50; N, 2.65%) NMR (C$_6$D$_6$, 25 $^\circ$C): ^{1}H (360.13 MHz), δ 0.36 (s, 36 H, SiMe$_3$) and 1.31 (s, 54 H, Bu^t); ^{13}C-{^{1}H} (62.90 MHz), δ 6.00 (q, SiMe$_3$), 34.41 [q, C(CH$_3$)$_3$], 46.12 [s, C(CH$_3$)$_3$], and 92.07 (s, OCBu$^t_3$); ^{29}Si-{^{1}H} (49.70 MHz), δ -15.49.

[{Yb(OCBu$^t_3$)(μ-OCBu$^t_3$)}$_2$] **2**. Addition of hexane (60 cm^3)

to Bu$^t_3$COH (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$_4$Yb$_2$ requires C, 54.6; H, 9.50%). Electron impact (EI), mass spectrum: m/z 1142 (1%, M^+) NMR: ^{1}H (C$_6$D$_6$, 250.13 MHz, 25 $^\circ$C), δ 1.54 (s); ^{13}C-{^{1}H} (C$_6$H$_6$–C$_6$D$_6$, 62.90 MHz, 31 $^\circ$C), δ 33.54 [q, C(CH$_3$)$_3$], 46.13 [s, C(CH$_3$)$_3$] and 89.67 (s, OCBu$^t_3$).

[Yb(OCBu$^t_3$)$_2$(thf)$_2$] **3**. Tetrahydrofuran (70 cm^3) was added to Bu$^t_3$COH (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 cm^3). The red extract was concentrated and cooled ($-30\,^\circ$C), yielding green crystals of **3** (0.90 g, 1.26 mmol, 64%) NMR: ^{1}H (C$_6$D$_6$, 360.13 MHz, 25 $^\circ$C), δ 1.36 [br s, 8 H, β-CH$_2$ (thf)], 1.56 (s, 54 H, Bu^t) and 3.61 [br s, 8 H, α-CH$_2$ (thf)]; ^{1}H (C$_5$D$_5$N, 360.13 MHz, 25 $^\circ$C), δ 0.77 [t, 8 H, β-CH$_2$ (thf)], 1.36 (s, 54 H, Bu^t), and 3.62 [t, 8 H, α-CH$_2$ (thf)]; ^{13}C-{^{1}H} (C$_6$H$_6$–C$_6$D$_6$, 62.90 MHz, 25 $^\circ$C), δ 25.48 [t, β-CH$_2$ (thf)], 33.77 [q, C(CH$_3$)$_3$], 46.39 [s, C(CH$_3$)$_3$], 69.08 [t, α-CH$_2$ (thf)] and 89.92 (s, OCBu$^t_3$).

Reaction of [Yb(NR$_2$)$_2$(dme)] **VIII** *with* Bu^{t}OH.—A solution of Bu^{t}OH in hexane (10.9 cm^3, 0.235 mol dm^{-3}, 2.56 mmol) was added to a red solution of [Yb(NR$_2$)$_2$(dme)] **VIII** (0.75 g, 1.28 mmol) in pentane (80 cm^3) 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 cm^3) to afford a white solid (0.53 g), m.p. > 290 $^\circ$C. IR (KBr–Nujol): 1378m, 1354m, 1259m, 1206s, 1014s, 936m, 897mw, 841m, 771mw, 685w and 479w cm^{-1}.

[{Yb(OCBu$^t_3$)(OR′)}$_x$] **4a**. A solution of HOR′ (1.03 g, 4.67 mmol) in hexane (30 cm^3) was added to a red solution of complex **1** (2.49 g, 2.34 mmol) in hexane (30 cm^3) 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%) ^{1}H NMR (C$_6$D$_6$, 360.13 MHz, 25 $^\circ$C): δ 1.05–1.45 (m, 27 H, Bu^t), 1.45–1.85 (m, 18 H, Bu^t), 2.1–2.45 (m, 3 H, Me), and 6.9–7.4 (m, 2 H, aryl).

[Yb(OCBu$^t_3$)(OR′)(thf)$_2$] **4b**. Tetrahydrofuran (30 cm^3) 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 cm^3) and the extract concentrated. Cooling to $-30\,^\circ$C yielded dark red crystals of **4b** (1.0 g, 1.36 mmol, 80%) (Found: C, 58.8; H, 8.15. C$_{36}$H$_{66}$O$_4$Yb requires C, 58.8; H, 9.05%). NMR: ^{1}H (C$_6$D$_6$, 360.13 MHz, 25 $^\circ$C), δ 1.22 (s, 18 H, Bu^t), 1.59 [s, 8 H, β-CH$_2$ (thf)], 1.68 (s, 27 H, Bu^t), 2.47 (s, 3 H, Me), 3.54 [br s, 8 H, α-CH$_2$ (thf)] and 7.30 (s, 2 H, aryl); ^{13}C-{^{1}H} (C$_6$H$_6$–C$_6$D$_6$, 62.90 MHz, 25 $^\circ$C), δ 21.84 (q, Me), 24.97 [t, β-CH$_2$ (thf)], 31.15 [q, C(CH$_3$)$_3$], 32.50 [q, OC{C(CH$_3$)$_3$}$_3$], 35.14 [s, C(CH$_3$)$_3$], 44.92 [s, OC{C(CH$_3$)$_3$}$_3$], 69.77 [t, α-CH$_2$ (thf)], 85.08 [s, OC(Bu^t)$_3$], 119.99 (s, CMe), 125.56 (d, CH), 136.74 (s, CBu^t) and 164.08 (s, CO).

[Yb(OCBu$^t_3$)(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 cm^3) 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**. ^{13}C-{^{1}H} NMR: (C$_5$H$_5$N–C$_5$D$_5$N, 62.90 MHz, 25 $^\circ$C): δ 21.30 (q, Me), 31.23 [q, C(CH$_3$)$_3$], 32.48 [q, OC{C(CH$_3$)$_3$}$_3$], 34.98 [s, C(CH$_3$)$_3$], 44.88 [s, OC{C(CH$_3$)$_3$}$_3$], 85.05 [s,

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

Yb(O$_3$SCF$_3$)$_2$(dme) 5. A diethyl ether solution of HO$_3$SCF$_3$ (2.0 cm^3, 0.7 mol dm^{-3}, 1.4 mmol) was added to [Yb(NR$_2$)$_2$(OEt$_2$)$_2$] II (0.44 g, 0.7 mmol) in dme (50 cm^3) 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. C$_6$H$_{10}$F$_6$O$_8$-S$_2$Yb requires C, 12.8; H, 1.80%). NMR (C$_5$D$_5$N, 25 °C): ^{1}H (360.13 MHz); δ 3.24 (s, 6 H, OMe) and 3.48 (s, 4 H, CH$_2$O); ^{13}C-$\{^1$H$\}$ (125.76 MHz), δ 58.60 (q, OMe), 72.06 (t, CH$_2$O), and 129.04 (q, $^1J_{CF}$ = 93.3 Hz, CF$_3$); ^{19}F (75.38 MHz), δ −76.0 (s, $w_{\frac{1}{2}}$ ≈ 200 Hz, CF$_3$).

[Yb(tmhd)$_3$] 6. A toluene solution of Htmhd (11.1 cm^3, 0.24 mol dm^{-3}, 2.66 mmol) was slowly added to complex I (0.62 g, 0.63 mmol) in hexane (40 cm^3) 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 cm^3) 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. C$_{33}$H$_{57}$O$_6$Yb requires C, 54.8; H, 7.95%), m.p. 164–168 °C (lit.,^{38} 166–169 °C). EI mass spectrum: m/z 1274 {20, [Yb$_2$(tmhd)$_3$(Bu^{t}COCHCO)$_3$]$^+$}, 723 [37, M^+ = Yb(tmhd)$_3$], 666 {77, [M − Bu^t]$^+$} and 540 {83%, [M − tmhd]$^+$}. NMR (C$_6$D$_6$, 20 °C): ^{1}H (360.13 MHz), δ 0.08 (s, 54 H, Bu^t) and 4.02 (s, 3 H, CH); ^{13}C-$\{^1$H$\}$ (125.76 MHz), δ 24.24 (q, CMe_3), 42.65 (s, CMe$_3$), 45.72 (d, CH), and 143.45 (s, CO).

Yb(S$_2$CNR$_2$)$_2$ 7. A thf solution of CS$_2$ (52.0 cm^3, 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 cm^3) and dried *in vacuo* to yield the yellow-brown solid 7 (1.1 g, 1.7 mmol, 68%). NMR: ^{1}H (C$_6$D$_6$, 360.13 MHz, 20 °C), δ 0.08 (s, SiMe$_3$); ^{13}C-$\{^1$H$\}$ (C$_6$D$_6$, 62.90 MHz, 25 °C), δ 2.57 (q, SiMe$_3$) and 271.90 (s, CS$_2$); ^{29}Si-$\{^1$H$\}$ (C$_6$D$_6$, 49.70 MHz, 25 °C), δ 29.00 (SiMe$_3$).

[Li$\{$Yb(NR$_2$)$_3\}$(tmen)] 8. Hexane (50 cm^3) was added to complex I (1.02 g, 1.03 mmol) and LiNR$_2$ (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 cm^3, 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 cm^3). 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$_3$Si$_6$Yb requires C, 32.7; H, 8.25; N, 6.35%). EI mass spectum: m/z 661 {2, [M − tmen]$^+$} and 493 {45%, [M − LiNR$_2$ − tmen]$^+$}. NMR: ^{1}H (C$_6$D$_6$, 360.13 MHz, 20 °C), δ 0.38 (s, 54 H, SiMe$_3$), 1.45 (s, 4 H, CH_2NMe$_2$), and 1.83 (s, 12 H, CH$_2$NMe_2); ^{7}Li-$\{^1$H$\}$ (C$_6$D$_6$–C$_6$H$_6$, 97.21 MHz, 20 °C), δ 3.22; ^{13}C-$\{^1$H$\}$ (C$_6$D$_6$–C$_6$H$_6$, 62.90 MHz, 20 °C), δ 6.04 (q, SiMe$_3$), 46.32 (q, CH$_2$NMe_2), and 56.17 (t, CH_2NMe$_2$); ^{29}Si-$\{^1$H$\}$ (C$_6$D$_6$–C$_6$H$_6$, 49.70 MHz, 25 °C), δ −12.68 (SiMe$_3$); ^{29}Si-$\{^1$H$\}$ (C$_6$D$_5$CD$_3$–C$_6$H$_5$Me, 49.70 MHz, −55 °C), δ −14.90 (bridge SiMe$_3$) and −21.10 (terminal SiMe$_3$).

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–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 (L_p) and also for absorption using DIFABS^{48} 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 86^{49} 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^t 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$^t_3$C units and bond-length constraints within the thf ligands. All C–C bonds within the Bu$^t_3$C groups were set equal to a single free variable, the distance between the central C atoms of the three Bu^t groups to a second free variable, the C ··· C distances between the methyl groups in each Bu^t 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.

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