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VOLATILE TRIS-TERTIARY-ALKOXIDES OF YTTRIUM AND LANTHANUM. THE X-RAY CRYSTAL STRUCTURE OF $[La_3(OBu^t)_9(Bu^tOH)_2]$

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Abstract—Tertiary alkoxides of yttrium and lanthanum have been prepared by addition of excess tertiary alcohol to the metal tris-(bis-trimethylsilylamides), $M\{N(SiMe_3)_2\}_3$ (M = Y, La), and characterized by elemental analyses, NMR, IR and mass spectroscopy. With t-butanol and t-amyl alcohol the alcoholates $[Y_3(OBu^t)_9(Bu^tOH)_2]$ (**1**), $[Y_3(OAm^t)_9(Am^tOH)_2]$ (**2**) and $[La_3(OBu^t)_9(Bu^tOH)_2]$ (**3**) were isolated. With higher tertiary alcohols the tris-t-alkoxides $[M(OR)_3]$ were obtained [M = Y, R = CMe_2Pr^i (**4**), $CMeEtPr^i$ (**5**), CEt_3 (**6**); M = La, R = CMe_2Pr^i (**7**), $CMeEtPr^i$ (**8**)] as dimers. The coordinated Bu^tOH in **1** could be replaced by THF or pyridine but not by trimethylamine. The X-ray crystal structure of **3** showed that the La_3 triangle is capped by two μ_3-OBu^t groups with three μ_2-OBu^t bridges as in $[La_3(\mu_3\text{-}OBu^t)_2(\mu\text{-}OBu^t)_3(OBu^t)_4(Bu^tOH)_2]$. The variable temperature NMR data suggest that compounds **1** and **2** have the same structure in solution as compound **3**.

The alkoxides of yttrium and some of the lanthanides have been known for many years,[1–4] but hitherto have not been fully characterized. In recent years the interest in these compounds has been greatly boosted by their applications in ceramics and electronic materials.[5] The need for volatile or soluble (in organic solvents) metallo-organic compounds containing metal—oxygen bonds, which could serve as precursors for the MOCVD or the sol–gel technique has prompted several workers to reinvestigate the older data[6,7] and to search for new compounds.[8,14] The yttrium and lanthanide alkoxides are known to form polymeric structures which are responsible for their low volatility and solubility.[4] Recently it has been shown[6,7] that yttrium, ytterbium and scandium isopropoxides form pentanuclear complexes $[M_5O(OPr^i)_{13}]$ around a five-coordinated (μ_5) oxygen atom. Evans *et al.*[9] attempted the preparation of yttrium t-butoxide from YCl_3 and $NaOBu^t$ or $LiOBu^t$ in THF and obtained products such as $[Y_3(\mu_3\text{-}OCMe_3)(\mu_3\text{-}Cl)(\mu\text{-}OCMe_3)_3(OCMe_3)_4(THF)_2]$ and $[Y_4(\mu_5\text{-}OCMe_3)_2(\mu\text{-}OCMe_3)_4(OCMe_3)_4(\mu\text{-}O)(\mu\text{-}Cl)_2Li_4(\mu\text{-}OCMe_3)_2]_2$. They succeeded in isolating a chlorine-free compound $[La_3(OBu^t)_9(THF)_2]$, although they were unable to solve the crystal structure due to disorder problems. Further work[10] produced more structures of chloro-t-butoxo complexes of yttrium and demonstrated the general complexity of the system and its dependence on small changes in the preparative conditions.

RESULTS AND DISCUSSION

We have prepared the following tris-t-alkoxides of yttrium and lanthanum: $[M_3(OR)_9(ROH)_2]$ [M = Y, R = Bu^t (**1**), Am^t (**2**); M = La, R = Bu^t (**3**)] and $[M(OR)_3]_n$ [M = Y, R = CMe_2Pr^i (**4**), $CMeEtPr^i$ (**5**), CEt_3 (**6**); M = La, R = CMe_2Pr^i (**7**), $CMeEtPr^i$ (**8**)].

We chose the t-alkoxides because the branched OR groups give greatest shielding of the metal atoms thereby decreasing the degree of oligomerization and enhancing the volatility and solubility.

We were also interested in comparing the t-alkoxides with the isopropoxides which we found previously to form the oxo-complexes $[M_5O$

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$(\mathrm{OPr^i})_{13}]$. The mechanism of the formation of the oxo-complexes could be either:

(i) by elimination of propene ($\mathrm{MOPr^i} \rightarrow \mathrm{MOH} + \mathrm{C_3H_6}$), or
(ii) by formation of di-isopropyl ether ($2\ \mathrm{MOPr^i} \rightarrow \mathrm{M_2O} + \mathrm{Pr^i{}_2O}$).

Some t-alkoxides (e.g. $\mathrm{Al_2OBu^t{}_6}$) are known to undergo β-elimination with formation of an alkene on thermolysis. However, we have found that all of the yttrium and lanthanum t-alkoxides are tris compounds thermally stable at least up to 150°C. Since t-alkoxide groups should eliminate alkenes much more readily than the isopropoxide group this appears to rule out mechanism (i) for the formation of the $[\mathrm{M_5O(OPr^i)_{13}}]$ compounds.

Preparations

To preclude the formation of the chloride alkoxides obtained by Evans *et al.*,[9,10] we chose to prepare the t-alkoxides from a chlorine-free starting material. For this purpose we used the reaction of $\mathrm{M\{N(SiMe_3)_2\}_3}$ (M = Y or La)[11] with tertiary alcohols in benzene solution:

$$\mathrm{M\{N(SiMe_3)_2\}_3 + 3\ R^tOH \rightarrow [M(OR^t)_3] + 3\,HN(SiMe_3)_2}.$$

This approach was recently used by other workers in synthesizing $[\mathrm{Y(OSiPh_3)_3}]$,[12] although they were unsuccessful when applying it to the t-butoxide.

The alcohol in at least 30% excess was added to $\mathrm{M\{M(SiMe_3)_2\}_3}$ in benzene solution. The mixture was stirred and refluxed for 1 h and the completion of the reaction checked by NMR. The solvents were evaporated *in vacuo* and the residue either sublimed *in vacuo* or crystallized from toluene or pentane. The compounds were characterized by elemental analysis, NMR, IR and mass spectra. An X-ray crystal structure of $[\mathrm{La_3(\mu_3\text{-}OBu^t)_2(\mu\text{-}OBu^t)_3(OBu^t)_4(Bu^tOH)_2}]$ was obtained.

All the compounds were obtained as white solids. Compounds **1** and **3** were moderately soluble in organic solvents, while the higher t-alkoxides were very easily soluble in benzene and pentane. Some data on melting points, volatilities and mass spectra of these compounds are presented in Table 1. It is noteworthy that three of these compounds (**1**–**3**) are formulated as $[\mathrm{M_3(OR)_9(ROH)_2}]$ with coordinated alcohol, which was identified by IR and NMR spectroscopy. Such complexes are rare in metal alkoxide chemistry[4] since alkoxide bridging is the preferred mode of metal coordination expansion. The coordinated alcohol could be removed by heating (**1**, 60–70°C; **2**, 40–50°C; **3**, 100°C) *in vacuo* with the lanthanum complex (**3**) being the most stable. Therefore, the volatilities observed for these compounds probably relate to the unsolvated tri-t-alkoxides and their melting points are complicated by decomposition caused by loss of coordinated alcohol. The coordinated t-butanol in **1** was readily replaced by THF giving $[\mathrm{Y_3(OBu^t)_9(THF)_2}]$ (**9**) which lost THF when heated to 70°C *in vacuo*. Pyridine also displaced the alcohol from **1** but trimethylamine did not. It is noteworthy that Evans *et al.*[9] obtained $[\mathrm{Y_3(OBu^t)_8Cl(THF)_2}]$ and showed that the THF could be replaced by pyridine.

None of the higher t-alkoxides ($\mathrm{C_6}$ or $\mathrm{C_7}$) gave complexes with coordinated alcohol, presumably

Table 1.

Compound	Melting point (°C)	Volatility (°C/torr)	Mass spectra *m/z* Obs.	Mass spectra *m/z* Calc.	Mass spectra Species
$[\mathrm{Y_3(OBu^t)_9(Bu^tOH)_2}]$ (**1**)	171	$235/10^{-2}$	851.2463	851.2403	$[\mathrm{Y_3(OBu^t)_8}]^+$
			721.1046	721.1046	$[\mathrm{Y_3(OBu^t)_6O}]^+$
$[\mathrm{Y_3(OAm^t)_9(Am^tOH)_2}]$ (**2**)	84	$150/10^{-3}$	None observed		
$[\mathrm{La_3(OBu^t)_9(Bu^tOH)_2}]$ (**3**)	192	$240/10^{-3}$	610.7948	610.7972	$[\mathrm{La_3O_6C_7H_{14}}]^+$
$[\mathrm{Y(OCMe_2Pr^i)_3}]$ (**4**)	161	$170/10^{-3}$	742.3499	742.3445	$[\mathrm{Y_2(OCMe_2Pr^i)_6\text{-}2Me}]^+$
			683.3007	683.2949	$[\mathrm{Y_2(OCMe_2Pr^i)_5}]^+$
$[\mathrm{Y(OCMeEtPr^i)_3}]$ (**5**)	196	$170/10^{-3}$	753.3739	753.3731	$[\mathrm{Y_2(OCMeEtPr^i)_5}]^+$
$[\mathrm{Y(OCEt_3)_3}]$ (**6**)	198	$225/10^{-2}$	753.3713	753.3731	$[\mathrm{Y_2(OCEt_3)_5}]^+$
			709.3106	709.3106	$[\mathrm{Y_2(OCEt_3)_5\text{-}Me\text{-}Et}]^+$
$[\mathrm{La(OCMe_2Pr^i)_3}]$ (**7**)	119	$135/10^{-3}$	783.3023	783.2953	$[\mathrm{La_2(OCMe_2Pr^i)_5}]^+$
			597.0961	597.0969	$[\mathrm{La_2(OCMe_2Pr^i)_3O}]^+$
$[\mathrm{La(OCMeEtPr^i)_3}]$ (**8**)	112	$150/10^{-3}$	853.3729	853.3735	$[\mathrm{La_2(OCMeEtPr^i)_5}]^+$

because of steric hindrance which prevents the metals attaining the octahedral coordination required for the trinuclear species $[M_3(OR)_9(ROH)_2]$. Instead it seems that dimeric compounds $[M_2(OR)_6]$ are formed with tetrahedral metal coordination. Although the volatility data in Table 1 are not very precise it does appear that for both $[M(OCMe_2Pr^i)_3]$ and $[M(OCMeEtPr^i)_3]$ the heavier lanthanum compounds are distinctly more volatile than the corresponding yttrium compounds.

Bradley and Swanwick[13] showed several years ago that in the series $[M(OR^t)_4]$ (M = Ti, Zr, Hf; R = Bu or Am) the volatilities were in the unexpected order Hf > Zr > Ti. This was explained in terms of the mass-entropy effect which becomes apparent when the central metal atom is effectively screened by the bulky ligands and prevented from contributing to intermolecular attractive forces. The rather large difference in volatility between the yttrium and lanthanum compounds suggests that other factors must also be involved. For example the dimeric lanthanum compounds may dissociate more readily to monomers than the yttrium dimers. Nevertheless, the mass spectral data show evidence of gaseous dimeric species for both metals.

Mass spectra

None of the compounds gave parent molecular ions but some important fragment ions were identified by accurate masses as shown in Table 1.

Considering first of all the trinuclear species $[M_3(OR)_9(ROH)_2]$, it is clear that loss of coordinated alcohol has occurred but the presence of trinuclear fragment ions $[Y_3(OBu^t)_8]^+$ (*m*/*z*, 851), $[Y_3O(OBu^t)_6]^+$ (*m*/*z*, 721) and $[La_3O_6C_7H_{14}]^+$ (*m*/*z*, 610.8) suggests that the trimer species $[M_3(OR)_9]$ is present in the vapour state. Although $[Y_3(OBu^t)_9(THF)_2]$ gave no identifiable fragment ions, the pyridine complex gave a peak at 856 corresponding to $[Y_3O_9C_{31}H_{45}N_2]^+$.

For all of the higher t-alkoxides a fragment ion corresponding to $[M_2(OR)_5]^+$ was observed, suggesting that these compounds are dimeric in the vapour state. In addition to the agreement between observed and calculated accurate masses, these species were also confirmed by the presence in the correct proportion of the M+1 ion corresponding to the species containing one ^{13}C atom in place of a ^{12}C atom.

NMR spectra

Variable temperature ^1H and ^{13}C NMR studies were carried out in order to derive structural information on these t-alkoxides in solution. All of the compounds were fluxional and required low temperatures to slow down the exchange between distinguishable alkoxide groups.

The limiting low temperature ^1H NMR spectra of the trinuclear species $[M_3(OR)_9(ROH)_2]$ (**1**–**3**) were very complex and a knowledge of the molecular structure of the lanthanum compound (**3**) obtained by single crystal X-ray analysis was invaluable in their interpretation. The structure (Fig. 1) shows that in $[La_3(OBu^t)_9(Bu^tOH)_2]$ (**3**) there is a triangle of metal atoms bound by two capping μ_3-OBu^t groups (above and below the triangle) and three bridging μ_2-OBu^t groups. Each metal has two terminal ligands of which two out of six are probably the coordinated alcohols.

The t-butoxides (**1**) and (**3**) exhibit very similar spectra which are detailed in Table 2. At around 230 K, each has five major peaks with intensities in the ratio 2:2:2:1:4, reading from left to right lower field to higher field. Assuming that the two coordinated alcohol molecules are bonded to different metals then one μ_2-OBu^t is unique since the other two will be equivalent. If the two μ_3-OBu^t groups are also equivalent then it follows that the six terminal groups are in a 2:4 ratio corresponding to two alcohols and four alkoxides. Closer inspection of the spectra reveals that there are some significant minor peaks adjacent to some of the major peaks and at low temperature the OH peak for the coordinated alcohol splits into two peaks in a 3:1 ratio. This suggests that more than one structure is present and indeed the molecular structure (Fig. 1) depends on whether the coordinated alcohols are both above (or below) the plane of the M_3 triangle (isomer **A**) or one is above and one below (isomer **B**). The X-ray structure unfortunately does not clearly identify the positions of the alcohol ligands, but it is reasonable to suppose that the OH chemical shifts of isomers **A** and **B** will be slightly different. The unique μ_2-OBu^t resonance at *ca* δ 1.50 is also split into an approximately 2:1 ratio, although the two peaks are not sufficiently resolved to give accurate values of integration. The lowest field peak at *ca* δ 1.80, which is believed to be due to the μ_3-OBu^t groups, also has a small satellite as do the other major peaks, but even at 400 MHz it has not been possible to completely resolve the spectra. At higher temperature (300 K) the spectra simplify to three main peaks in the ratio (left to right from lower field to higher field) 2:3:6 corresponding to $2\times\mu_3$, $3\times\mu_2$ and $6\times$terminal groups due, presumably, to rapid exchange involving the coordinated alcohols and the terminal alkoxide groups. The OH peaks also coalesce into a single peak in the correct proportion to the t-butyl peaks of 2:99

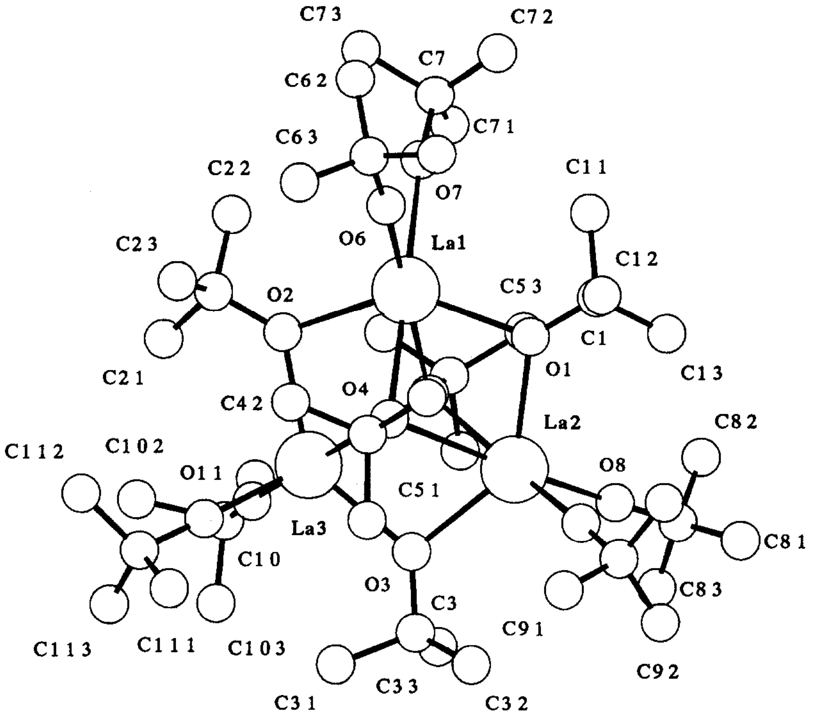

Fig. 1. The molecular structure of $[La_3(\mu_3\text{-}OBu^t)_2(\mu\text{-}OBu^t)_3(OBu^t)_4(Bu^tOH)_2]$ showing the atom numbering scheme: hydrogen atoms omitted for clarity.

required by the formula. On raising the temperature to *ca* 330 K the three t-butyl peaks all coalesced into a single, broad peak due to exchange of terminal, μ_2-bridging and μ_3-bridging alkoxide groups. Addition of t-butanol (δ 1.15 Bu^t, 2.37 OH) to the yttrium compound (**1**) in toluene (d_8) at 300 K had no effect on the lowest field t-butoxide peak (μ_3-OBu^t), or on the peak at intermediate field (μ_2-OBu^t), but caused a substantial shift from δ 1.43 to 1.26 in the highest field peak (terminal OBu^t groups). This behaviour was taken as further confirmation that the highest field peak was due to the terminal alkoxide groups including the coordinated alcohols. The alcohol OH peak was also shifted to higher field (δ 2.52) as expected showing rapid exchange between free and coordinated alcohol molecules.

The t-amyloxide of yttrium (**2**) gave more complex ^1H NMR spectra than the t-butoxide because of the presence of singlets (methyl bonded to the quaternary carbon), triplets (methyl of the ethyl) and quartets (methylene of the ethyl). Nevertheless, the overall pattern was similar to that of the t-butoxides with broad singlets, triplets and quartets at 353 K each giving five resonances at low temperatures (253 K). In the case of the singlets, which were best resolved, the ratios of intensities were 2 : 2 : 2 : 1 : 4 (from low to high field) exactly as found in the t-butoxides. It is therefore reasonable to conclude that the t-amyloxide has the same trinuclear structure as the t-butoxide.

The ^{13}C NMR spectra of compounds **1**–**3** showed splitting of peaks similar to that found in the ^1H spectra, but were less well resolved and not amenable to quantitative evaluation. The ^{89}Y NMR spectra of **1** and **2** at 310 K showed single peaks at δ 166.8 and 199.1 in C_6D_6. No doubt the fluxional nature of these complexes prevented the resolution into two peaks in the 2 : 1 ratio required by the structure assuming that the yttrium atoms bonded to one terminal alkoxide and one alcohol would have a slightly different chemical shift from the yttrium bonded to two terminal alkoxides.

The ^1H NMR spectrum of **9** at 273 K was rather complex corresponding to the presence of a major species having two broad unresolved peaks at δ 1.78 and 1.35 and a minor species with sharp lines at δ 1.92, 1.72, 1.70, 1.53 and 1.49 in the ratios of 1 : 3 : 1 : 2 : 1 : 1, respectively. The peaks due to THF were present at δ 1.43 and 3.59. It appears that more than one species is present but one of them could well have the trinuclear structure of **1** with the t-butanol molecules replaced by THF, analogous to the complex $[Y_3Cl(OBu^t)_8(THF)_2]$ obtained by Evans *et al.*[9]

By careful heating *in vacuo* the coordinated

Table 2. ^{1}H NMR spectra

Compound	Temperature (K)	Chemical shifts[a]
$[Y_3(OBu^t)_9(Bu^tOH)_2]$ (**1**)	323	4.20 (2H), 1.53 (99H)
	297[b]	3.83, 1.83, 1.68, 1.43
	253	1.83, 1.77, 1.76, 1.74, 1.54, 1.52, 1.30
	227	1.83 (18H), 1.81 (18H), 1.77 (18H), [1.56, 1.51, 9H], [1.33, 1.28, 36H].
$[Y_3(OAm^t)_9(Am^tOH)_2]$ (**2**)	353	1.84 (q, 2H), 1.48 (s, 6H), 0.95 (t, 3H)
	297[b]	2.73 (s, 2H) [1.76, 1.56, 1.38, 0.95br, 122H]
	253	5.53 (s, 2H), 2.40q, 2.22q, 1.98q, 1.78 (s, 22H), 1.74q, 1.69 (s, 22H), 1.66 (s, 22H), 1.51q, 1.49 (s, 11H), 1.31 (s, 44H), 1.21t, 1.08t, 0.96t, 0.92t, 0.88t.
$[La_3(OBu^t)_9(Bu^tOH)_2]$ (**3**)	338	4.06 (s, 2H), 1.48 (s, 99H)
	297[b]	4.96 (2H), 1.81 (18H), 1.70 (27H), 1.45 (54H)
	273	5.00, 1.74, 1.70, 1.64, 1.50, 1.39
	263	1.75, 1.70, 1.66, 1.49, 1.46, 1.32
	242	5.42, 5.36, 1.77, 1.72, 1.68, 1.49, 1.46, 1.30
	233	[5.42, 5.36, 2H], 1.78 (18H), 1.77 (18H), 1.70 (18H), [1.49, 1.47, 9H], [1.32, 1.28, 36H].
$[Y(OCMe_2Pr^i)_3]$ (**4**)	297[b]	1.63 (sept. 1H), 1.30 (s, 6H), 1.05 (d, 6H)
	203	[1.92, 1.77, 1H], [1.46, 1.41, 6H], [1.22, 1.16, 1.07, 6H].
$[Y(OCMeEtPr^i)_3]$ (**5**)	300[b]	1.90 (sept), 1.72 (sept), 1.54q, 1.39s, 1.13 mult.
$[Y(OCEt_3)_3]$ (**6**)	353	1.54q, 0.97t
	303[b]	1.57 mult, 1.00t
	273	1.61 (q, 2H), 1.54 (q, 4H), [1.04t, 1.00t, 9H].
$[La(OCMe_2Pr^i)_3]$ (**7**)	297[b]	1.72 (sept, 1H), 1.36 (s, 6H), 1.03 (d, 6H)
	233	[2.52, 2.21, 1.89, sept], [1.69, 1.53, 1.45, 1.40, s], [1.34, 1.15, 1.02, 0.94, d].
$[La(OCMeEtPr^i)_3]$ (**8**)	298[b]	1.66 (sept, 1H), 1.55 (q, 2H), 1.20 (s, 3H), 1.07 (d, 3H), 1.03 (t, 3H), 0.98 (t, 3H).
$[Y(OBu^t)_3]_n$[c]	297[b]	1.62–1.50 (two broad overlapping peaks)
	217	1.80, 1.77, 1.73, 1.69, 1.58, 1.55, 1.49, 1.44, 1.27.
$[Y(OAm^t)_3]_n$[d]	300[b]	Broad peaks overlapping 1.75, 1.55, 1.43, 0.98
	233	2.20q, 2.05q, 1.95q, 1.70 (s, 2H), 1.63 (s, 2H), 1.52 (s, 2H), 1.52 (s, 2H), 1.45 (s, 2H), 1.35 (s, 2H), 1.28t, 1.22t, 1.0t, 0.97t, 0.84t.

[a] Relative to TMS, in $C_6D_5CD_3$ except when designated [b].

[b] In C_6D_6.

[c] Obtained by removing Bu^tOH from **1** *in vacuo* (see Experimental).

[d] Obtained by removing Am^tOH from **2** *in vacuo*.

t-butanol could be removed from **1** leaving the unsolvated tris-t-butoxide $(Y(OBu^t)_3]_n$, which gave a very broad ^{1}H NMR signal at *ca* δ 1.56 at 297 K. At low temperature (217 K) this was resolved into a complex spectrum of nine peaks (δ 1.80, 1.77, 1.73, 1.69, 1.58, 1.55, 1.49, 1.44 and 1.27) suggesting the presence of polymeric species.

Removal of coordinated t-amyl alcohol from **2** left a solid whose ^{1}H NMR spectrum at 233 K gave five resolved singlets at δ 1.70, 1.63, 1.52, 1.45 and 1.35 in the ratio 2 : 2 : 2 : 1 : 2, respectively, together with several quartets (δ 2.20, 2.05 and 1.95) and triplets (δ 1.28, 1.22, 1.06, 0.97 and 0.84). Interestingly, the pattern of singlets could be ascribed to trinuclear $[Y_3(\mu_3\text{-}OAm^t)_2(\mu_2\text{-}OAm^t)_3(OAm^t)_4]$, based on the structure in Fig. 1, without the coordinated alcohol molecules. In such a structure the μ_2-ligands would be distinguishable in a 1 : 2 ratio and the four terminal ligands in a 2 : 2 ratio. It would seem that the slightly more bulky t-amyloxide groups do not allow the trinuclear cluster to undergo further polymerization resulting in a molecular structure containing one six-coordinate and two five-coordinated yttrium atoms.

The yttrium and lanthanum derivatives of the C_6 t-alcohol dimethylisopropylcarbinol (**4** and **7**) showed different ^1H NMR behaviour compared with the t-butoxides and t-amyloxides. At room temperature, **4** gave a septet (δ 1.63), singlet (δ 1.30) and doublet (δ 1.05) in the correct proportions for the alkyl group. Cooling to 203 K was required to cause splitting to two septets (δ 1.92 and 1.77), two singlets (δ 1.46 and 1.41) and three doublets (δ 1.22, 1.16 and 1.07) which were all broad. The lanthanum analogue (**7**), which also showed only a single alkoxide species at room temperature (δ 1.72 sept., 1.36 sing., 1.03 doub.) gave a more complex spectrum at lower temperatures (233 K) comprising three septets, four singlets and four doublets.

The mass spectra of **4** and **7** gave evidence of dinuclear fragment ions, but the ^1H NMR spectra for dimers should give only two alkoxide environments and it may well be that a trinuclear species is present in equilibrium with the dimer. It is noteworthy that for both compounds the signals all moved downfield on cooling. The ^{13}C NMR spectrum of **4** showed no splitting down to 233 K, whereas in **7** splitting into two signals was observed for $C(CH_3)_2$ and $CCH(CH_3)_2$ carbon atoms at 233 K. Interestingly, the ^{89}Y NMR spectrum of **4** gave a single peak at δ 36.8 at very much higher field than the trinuclear compounds **1** and **2**, which contain octahedrally coordinated yttrium. This strongly suggests that in **4** the yttrium is in a lower coordination environment.

The ^1H NMR spectrum of **5** gave, at room temperature, two septets, one quartet, two singlets and a multiplet consisting of overlapping triplets and doublets. The ratio of the two septets and two singlets was 2 : 1 in each case, suggesting the presence of a dimer. The spectrum was unchanged on lowering the temperature. The ^{13}C NMR spectrum of **5** showed two unequal signals for the quaternary, CH, CH_2 and CH_3 (ethyl) carbon atoms, but two large (equal) and two small (equal) signals for the CH_3 (isopropyl) carbon atoms. This suggests a dimeric structure in which restricted rotation renders the two methyls of the isopropyl groups non-equivalent. The ^{89}Y NMR signal for **5** was at δ 45.6, which is in the same region as for **4** and also suggests a lower coordination than in **1** and **2**. The ^1H NMR spectrum of **8** at room temperature gave a septet, a quartet, a singlet, a triplet and two equal doublets and was unchanged on lowering the temperature. The splitting of the isopropyl methyl doublets suggests non-equivalence as in the yttrium compound (**5**).

The ^{13}C NMR spectrum of **8** also showed one signal for the quaternary, CH, CH_2 and CH_3 (ethyl) carbons, but two (equal) signals for the CH_3 (isopropyl) carbons in agreement with the ^1H NMR spectrum.

Finally we mention the ^1H NMR spectrum of **6**, which at 353 K gave a quartet (δ 1.54) and a triplet (δ 0.97). At around 303 K the quartet broadens and at 273 K is resolved into two quartets (δ 1.61 and 1.54) in a 2 : 1 ratio. The triplet also broadens and splits into two overlapping triplets (δ 1.04 and 1.00) at 273 K. The ^{13}C NMR spectrum of **6** showed splitting of the quaternary and CH_2 carbon atoms at room temperature, whilst the ^{89}Y spectrum gave one peak at δ 37.5. These data together with the mass spectrum suggest that compound **6** is dimeric with distorted tetrahedral yttrium.

Infrared spectra

Compounds **1**–**3**, containing coordinated alcohols, have broad bands corresponding to OH-stretching vibrations at 3420, 3439 and 3386 cm^{-1}, respectively. Compound **9** shows one of the characteristic THF bands at 1075 cm^{-1} (cf. 1072 cm^{-1} in free ligand), but the other band at *ca* 913 cm^{-1} is obscured by strong bands due to t-butoxide groups.

X-ray crystal structure of $[La_3(OBu^t)_9(Bu^tOH)_2]$ (3)

The molecular structure of **3** was determined by single crystal X-ray diffraction and is shown in Figs 1 and 2. Some bond lengths are listed in Table 3 and bond angles in Table 4. The trinuclear species with the M_3O_{11} metal–oxygen framework has already been described under the NMR section. The presence of two molecules of Bu^tOH in the trinuclear molecule is shown by elemental analysis, IR spectra and ^1H NMR spectra, but it was not possible to locate the OH hydrogen atoms in the X-ray structure. It is reasonable to suggest that the coordinated alcohols occupy terminal positions on two of the three lanthanum atoms and their presence might be revealed by longer La—O bond distances compared with the La—OBu^t groups. Looking at the terminal La—O bonds it is noticeable that La(1) has one long (2.604) and one short (2.195 Å) bond suggesting that O(7)C(7)(C71, C72, C73) is one of the alcohol molecules. La(2) is equally bonded to O(8) and O(9) (La—O, 2.304 and 2.308 Å) which must be covalently bonded t-butoxides and therefore La(3) should carry the other alcohol ligand. In fact La(3) is almost equally bonded to O(10) and O(11) (La—O, 2.350 and 2.315 Å) and the difference is barely significant. If the coordinated alcohols are bonded to La(1) and La(3) this would make the μ_2-bridging t-butoxide group O(2)C(2)(C21, 22, 23) slightly different in environment from the other two equivalent μ_2-bridging groups. In fact O(2) forms a symmetrical bridge to La(1) (2.449 Å) and La(3) (2.447 Å), whereas O(3)

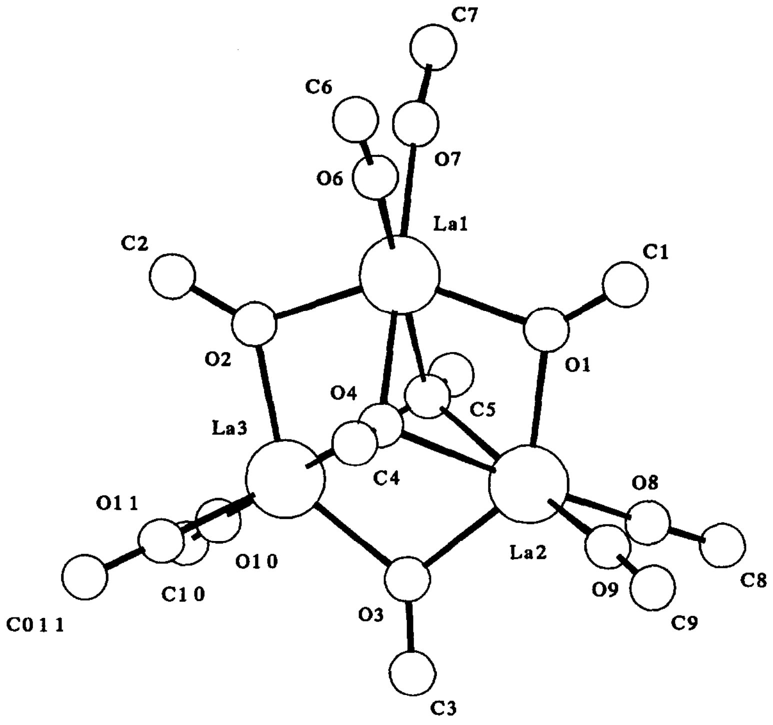

Fig. 2. The structure of the La$_3$(OAlk)$_{11}$ core. All Bu^t methyls omitted for clarity.

and O(1) form slightly unsymmetrical bridges [La(3)—O(3), 2.417; La(2)—O(3), 2.458; La(1)—O(1), 2.408; and La(2)—O(1), 2.460 Å]. Bearing in mind the uncertainties in these bond distances the data are inconclusive. The presence of coordinated alcohol might be expected to show up in a comparison of La—O—C bond angles. Thus the oxygen atom on a covalently bound alkoxide has two lone pairs of electrons available for π-donation into vacant metal orbitals with a limiting angle of 180° for full π-bonding. The oxygen of a coordinated alcohol has only one lone pair for π-donation leading to an angle nearer to 120°. The data in Table 4 show that three of the terminal groups have LaOC angles very close to 180° (178.9, 178.7 and 177.0), one is 175.1, another is 173.7 and the smallest angle is 167.5°. It is significant that the smallest angle involves La(1)—O(7) which has the longest terminal La—O bond length and was accordingly identified as a coordinated alcohol. The

Table 3. Selected bond lengths (Å) for [La$_3$(μ_3-OBu^t)$_2$(μ-OBu^t)$_3$(OBu^t)$_4$(Bu^{t}OH)$_2$]

O(1)—La(1)	2.408(14)	O(2)—La(1)	2.449(14)
O(4)—La(1)	2.505(13)	O(5)—La(1)	2.548(13)
O(6)—La(1)	2.195(13)	O(7)—La(1)	2.604(15)
O(1)—La(2)	2.460(12)	O(3)—La(2)	2.458(14)
O(4)—La(2)	2.622(14)	O(5)—La(2)	2.573(14)
O(8)—La(2)	2.304(18)	O(9)—La(2)	2.308(18)
O(2)—La(3)	2.447(13)	O(3)—La(3)	2.417(14)
O(4)—La(3)	2.594(14)	O(5)—La(3)	2.586(14)
O(10)—La(3)	2.350(19)	O(11)—La(3)	2.315(16)
C(1)—O(1)	1.442(20)	C(2)—O(2)	1.451(27)
C(3)—O(3)	1.457(22)	C(4)—O(4)	1.461(20)
C(5)—O(5)	1.475(22)	C(6)—O(6)	1.409(23)
C(7)—O(7)	1.500(27)	C(8)—O(8)	1.449(29)
C(9)—O(9)	1.441(29)	C(10)—O(10)	1.423(32)
C(011)—O(11)	1.427(27)		

Table 4. Selected bond angles (°) for [La$_3$(μ_3-OBu^t)$_2$(μ-OBu^t)$_3$(OBu^t)$_4$(Bu^{t}OH)$_2$]

O(2)—La(1)—O(1)	140.9(4)	O(4)—La(1)—O(1)	73.9(5)
O(4)—La(1)—O(2)	74.4(5)	O(5)—La(1)—O(1)	73.3(5)
O(5)—La(1)—O(2)	73.2(5)	O(5)—La(1)—O(4)	65.9(4)
O(6)—La(1)—O(1)	105.1(5)	O(6)—La(1)—O(2)	107.0(5)
O(6)—La(1)—O(4)	110.4(5)	O(6)—La(1)—O(5)	176.2(4)
O(7)—La(1)—O(1)	107.1(5)	O(7)—La(1)—O(2)	102.8(5)
O(7)—La(1)—O(4)	175.3(4)	O(7)—La(1)—O(5)	109.8(5)
O(7)—La(1)—O(6)	73.9(5)	O(3)—La(2)—O(1)	137.0(4)
O(4)—La(2)—O(1)	71.0(4)	O(4)—La(2)—O(3)	72.1(5)
O(5)—La(2)—O(1)	72.0(4)	O(5)—La(2)—O(3)	72.4(5)
O(5)—La(2)—O(4)	63.9(4)	O(8)—La(2)—O(1)	106.6(5)
O(8)—La(2)—O(3)	105.1(5)	O(8)—La(2)—O(4)	168.4(5)
O(8)—La(2)—O(5)	104.5(6)	O(9)—La(2)—O(1)	100.5(5)
O(9)—La(2)—O(3)	110.6(5)	O(9)—La(2)—O(4)	106.5(6)
O(9)—La(2)—O(5)	169.0(4)	O(9)—La(2)—O(8)	85.1(7)
O(3)—La(3)—O(2)	139.3(4)	O(4)—La(3)—O(2)	72.8(5)
O(4)—La(3)—O(3)	73.2(5)	O(5)—La(3)—O(2)	72.6(5)
O(5)—La(3)—O(3)	72.8(5)	O(5)—La(3)—O(4)	64.1(4)
O(10)—La(3)—O(2)	106.6(6)	O(10)—La(3)—O(3)	103.4(6)
O(10)—La(3)—O(4)	170.7(5)	O(10)—La(3)—O(5)	106.7(6)
O(11)—La(3)—O(2)	101.9(5)	O(11)—La(3)—O(3)	108.3(5)
O(11)—La(3)—O(4)	105.6(5)	O(11)—La(3)—O(5)	169.2(4)
O(11)—La(3)—O(10)	83.7(7)	La(2)—O(1)—La(1)	101.0(5)
C(1)—O(1)—La(1)	129.9(11)	C(1)—O(1)—La(2)	129.1(11)
La(3)—O(2)—La(1)	99.7(5)	C(2)—O(2)—La(1)	130.0(11)
C(2)—O(2)—La(3)	130.1(10)	La(3)—O(3)—La(2)	102.1(5)
C(3)—O(3)—La(2)	127.0(13)	C(3)—O(3)—La(3)	130.9(12)
La(2)—O(4)—La(1)	94.2(4)	La(3)—O(4)—La(1)	94.4(4)
La(3)—O(4)—La(2)	93.3(4)	C(4)—O(4)—La(1)	123.8(10)
C(4)—O(4)—La(2)	122.6(11)	C(4)—O(4)—La(3)	120.8(10)
La(2)—O(5)—La(1)	94.4(4)	La(3)—O(5)—La(1)	93.6(4)
La(3)—O(5)—La(2)	94.6(4)	C(5)—O(5)—La(1)	120.3(10)
C(5)—O(5)—La(2)	123.4(12)	C(5)—O(5)—La(3)	123.0(12)
C(6)—O(6)—La(1)	175.1(10)	C(7)—O(7)—La(1)	167.5(12)
C(8)—O(8)—La(2)	178.7(14)	C(9)—O(9)—La(2)	177.0(13)
C(10)—O(10)—La(3)	173.7(15)	C(011)—O(11)—La(3)	178.9(13)

next smallest angle (173.7°) corresponds to La(3)—O(10), which on bond length considerations could be the other alcohol molecule. It is noteworthy that the LaOC angles in the bridging alkoxides are much smaller (μ_2, 127.0–130.1° and μ_3, 120.8–123.8°). In the absence of any clear cut evidence for the position of the second alcohol, we presume it is disordered, together with an alkoxy group, over sites O(10) and O(11).

All of the lanthanum atoms in **3** are in distorted octahedral coordination with each metal bonded to two terminal, two μ_2-bridging and two μ_3-bridging t-butoxide groups. The μ_3-bridging oxygen atoms cannot be involved in π-donation to the metals and it is significant that they are positioned *trans* to the strongly π-donating terminal oxygen atoms. The overall molecular structure of **3** is similar to that reported for [Y$_3$Cl(OBu^t)$_8$(THF)$_2$] by Evans *et al.*[9] who were unable to remove the final chlorine atom in their synthetic procedure. Further work by Evans *et al.*[10] led to the isolation of [Y$_3$Cl(OBu^t)$_8$(THF)$_3$][BPh$_4$] which contains the interesting trinuclear cation [Y$_3$(μ_3-Cl)(μ_3-OBu^t)(μ-OBu^t)$_3$(OBu^t)$_3$(THF)$_3$]$^+$ which also has the same framework structure as **3**.

We believe that in solution compound **1** obtained in this research has the same structure as the lanthanum analogue **3**. Although we have grown a single crystal of **1**, the X-ray crystallographic analysis has so far been thwarted by disorder problems. Work is continuing on the X-ray structure determination for compounds **1** and **4**–**6**. It is interesting to note even the very bulky t-alkoxo groups, OCMe$_2$Pr^i, OCMeEtPr^i and OCEt$_3$, result in the formation of dimeric yttrium and lanthanum trialkoxides. By using the bulky substituted phenoxo ligand, $2,6\text{-}\mathrm{Bu_2^tC_6H_3O}$, Lappert *et al.*[8] have obtained the monomeric $[\mathrm{Y(OC_6H_3Bu_2^t)_3}]$ compound which sublimed at 250–255°C/10^{-3} torr and is considerably less volatile than compounds **4–6** reported here. Clearly the gain in volatility expected to result from a monomeric species has been more than compensated for by the lowering in volatility caused by the increased number of atoms in the substituted phenoxo group. Work in progress suggests that enhanced volatility of the metal tris-t-alkoxides will be obtained by substituting $\mathrm{CF_3}$ groups for $\mathrm{CH_3}$ due to the anomalously weak intermolecular forces between fluoroalkyl groups.

EXPERIMENTAL

All operations were carried out under an atmosphere of purified $\mathrm{N_2}$ using vacuum line, glove box and Schlenk-style apparatus. Solvents were dried over and distilled from sodium benzophenone and stored over molecular sieves. $\mathrm{Bu^tOH}$ was refluxed over sodium butoxide and distilled. $\mathrm{Am^tOH}$, $\mathrm{Pr^i}$ $\mathrm{Me_2COH}$, $\mathrm{Pr^iEtMeCOH}$ and $\mathrm{Et_3COH}$ were dried first over molecular sieves, then the amount required for the reaction was put in excess benzene and finally dried azeotropically. The commercial yttrium and lanthanum chlorides were refluxed in $\mathrm{SOCl_2}$ (freshly distilled from linseed oil) for 48 h. The $\mathrm{SOCl_2}$ was then evaporated off *in vacuo* and the chlorides heated at 50°C for 20 h to remove residual traces of $\mathrm{SOCl_2}$. Hexamethyldisilazane was purchased from Aldrich and dried over molecular sieves. Butyl lithium was used as purchased. The compounds $\mathrm{M\{N(SiMe_3)_2\}_3}$ (M = Y or La) were prepared as previously described.[11]

NMR spectra were obtained using Bruker WP80FT, WM250FT and WH400FT spectrometers. Calibration was made using solvent signals from incomplete deuteration and made relative to TMS for ^{1}H and ^{13}C; ^{89}Y was relative to $\mathrm{YCl_3}$. Mass spectra were obtained using a MS-902 EI mass spectrometer, recorded at 70 eV. IR spectra were obtained as Nujol mulls in the range 4000–200 cm^{-1} using a Perkin–Elmer FT 1720× spectrometer.

Microanalytical data on carbon and hydrogen were obtained from University College, London and from B.M.A.C. The metals were analysed gravimetrically as metal oxides.

Crystallography

Crystal data for **3**: $\mathrm{C_{44}H_{101}O_{11}La_3}$, $M = 1223.0$, monoclinic space group $P2_1/a$, $a = 28.163(5)$, $b = 10.987(2)$, $c = 19.974(5)$ Å, $\alpha = \beta = 90$, $\gamma = 99.79°$, $V = 6090.49$ Å^3, $Z = 4$, $D_c = 1.33$ g cm^{-3}, $\mu(\text{Mo-}K_\alpha) = 21.2$ cm^{-1}. Data were collected at room temperature with an Enraf–Nonius CAD4 diffractometer and monochromated Mo-K_α radiation. The data were corrected for Lorentz, polarization and absorption effects. Full-matrix least-squares refinement of 514 parameters gave $R = 0.041$, $R_w = 0.037$ for 4170 unique, observed reflections from 7443 measured. The weighting scheme, $\mathrm{w} = [\sigma^2(F_0)+]^{-1}$, gave acceptable agreement analyses. Atomic coordinates, full lists of bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

Preparation of $[\mathrm{Y_3(OBu^t)_9(Bu^tOH)_2}]$ (**1**)

To $\mathrm{Y\{N(SiMe_3)_2\}_3}$ (3.1 g) in benzene (85 cm^3) was added $\mathrm{Bu^tOH}$ (15 cm^3) and the solution was refluxed for 2 h. Solvent and $\mathrm{(Me_3Si)_2NH}$ were then removed by evaporation *in vacuo* and the residue was crystallized from toluene giving white crystals (1.3 g, 67% yield based on yttrium, m.p. 171°C). Found: 25.0; C, 47.6; H, 9.4. Calc. for $[\mathrm{Y_3(OBu^t)_9(Bu^tOH)_2}]$: Y, 24.9; C, 49.2; H, 9.5%. ^{13}C NMR ($\mathrm{C_6D_5CD_3}$) at 298 K: δ 74.9, 72.2 (O*C*Me$_3$); 36.3, 34.3 (*C*H$_3$); at 233 K: δ 74.9, 72.5, 72.2, 72.1 (O*C*Me$_3$); 36.5, 36.3, 35.7, 34.0 (*C*H$_3$). ^{89}Y NMR ($\mathrm{C_6D_6}$) at 310 K: δ 166.8. IR: 3420br, 1241m, 1207s, 1165m, 983s, 936s, 901s, 877m, 768m, 741w, 530s, 496s, 478s, 391m, 256s, 230w cm^{-1}.

A sample of **1** was heated *in vacuo* at 60–80°C until no more $\mathrm{Bu^tOH}$ remained. Found: Y, 2.85. $\mathrm{Y(OBu^t)_3}$ requires: Y, 28.8%. Compound **1** appears to sublime at 235°C/10^{-2} torr with decomposition, yielding a white sublimate (47%, m.p. 240°C). Found: C, 39.6; H, 8.1. $\mathrm{Y(OBu^t)_3}$ requires: C, 46.8; H, 8.8%.

Preparation of $[\mathrm{Y_3(OAm^t)_9(AM^tOH)_2}]$ (**2**)

A solution of $\mathrm{Am^tOH}$ (6 cm^3) in benzene (40 cm^3) was added to a solution of $\mathrm{Y\{N(SiMe_3)_2\}_3}$ (6.2 g) in benzene (160 cm^3) and left overnight. After removing solvent, $\mathrm{(Me_3Si)_2NH}$ and excess $\mathrm{Am^tOH}$ by evaporation *in vacuo* the residue was recrystallized from $\mathrm{Am^tOH}$ (2.8 g, 63% based on yttrium, m.p. 84°C). Found: Y, 21.7. $\mathrm{Y_3(OAm^t)_9(Am^tOH)}$ requires: Y, 21.7%. ^{13}C NMR ($\mathrm{C_6D_6}$) at 297 K: δ 75.2 (O*C*Me$_2$Et); 40.7 (C*C*H$_2$Me); 31.3 (C*C*H$_3$); 11.2 (CCH$_2$*C*H$_3$); at 253 K ($\mathrm{C_6D_5CD_3}$): 77.4, 77.0, 74.4 (O*C*Me$_2$Et); 41.4, 40.7, 39.5 (C*C*H$_2$Me); 31.3, 31.2, 29.6 (C*C*H$_3$); 12.1, 11.0, 10.8 (CCH$_2$*C*H$_3$). ^{89}Y NMR ($\mathrm{C_6D_6}$) at 310 K: δ 199.1. IR: 3386br, 1360m, 1331w, 1316w, 1287w, 1227m, 1162s, 1151s, 1059m, 1017m, 981s, 949s, 935m, 890s, 878m, 793w, 735m, 534m, 512s, 480m, 464m, 390w, 305w, 242w, 235w, 228s, 225m cm^{-1}.

A sample of **2** was heated *in vacuo* at 70°C until no more Am^{t}OH remained. The white solid (m.p. 110°C) was analysed for $Y(OAm^t)_3$. Found: Y, 25.8. $Y(OAm^t)_3$ requires: Y, 25.4%. Compound **2** appeared to distil at 150°C/10^{-3} torr with decomposition, giving a glue-like condensate which could not be crystallized.

Preparation of $[La_3(OBu^t)_9(Bu^tOH)_2]$ (**3**)

To a solution of $La\{N(SiMe_3)_2\}_3$ (4.8 g) in benzene (150 cm^3) was added Bu^{t}OH (5 cm^3) and the solution was refluxed for 1 h and left overnight. After removing volatiles by evaporation *in vacuo*, the residue was crystallized from toluene (3.2 g, 100% based on lanthanum, m.p. 192°C). Found: La, 34.2; C, 42.3; H, 8.6. $[La_3(OBu^t)_9(Bu^tOH)_2]$ requires: La, 34.1; C, 43.2; H, 8.3%. ^{13}C NMR (C_6D_6) at 297 K: δ 73.7, 73.0, 71.6 ($O\mathit{C}Me_3$); 36.2, 35.5, 34.4 ($C\mathit{C}H_3$); at 253 K ($C_6D_5CD_3$): 73.4, 72.0, 70.8 ($O\mathit{C}Me_3$); 35.0, 34.6, 32.6 ($C\mathit{C}H_3$). IR: 3439br, 1378s, 1356s, 1349s, 1202s, 1022w, 972s, 936s, 911s, 889m, 826w, 746m, 513s, 488s, 457m, 379m, 353m, 229s, 226s cm^{-1}.

Preparation of $[Y(OCMe_2Pr^i)_3]$ (**4**)

Me_2Pr^iCOH (8 cm^3) in benzene (50 cm^3) was added to a solution of $Y\{N(SiMe_3)_2\}_3$ (8 g) in benzene (200 cm^3) and refluxed for 2 h and left overnight. After removal of the volatiles *in vacuo* the residue was distilled at 170°/10^{-3} torr (5.0 g, 91% based on yttrium, m.p. 161°C). Found: Y, 22.7; C, 53.4; H, 10.5. $Y(OCMe_2Pr^i)_3$ requires: Y, 22.7; C, 55.1; H, 10.0%. The compound dissolves readily in hydrocarbon solvents. ^{13}C NMR (C_6D_6) at 297 K: δ 76.5 ($O\mathit{C}Me_2Pr_i$); 41.2 ($C\mathit{C}HMe_2$); 30.1 ($C\mathit{C}H_3$); at 233 K ($C_6D_5CD_3$): 76.7, 41.2, 29.6, 19.4. ^{89}Y NMR ($C_6D_5CD_3$) at 310 K: δ 36.8. IR: 1366s, 1353m, 1321w, 1223m, 1175s, 1149s, 1103s, 1051s, 1010s, 947s, 923m, 911m, 869w, 852w, 795w, 714m, 574s, 558w, 532s, 478m, 429m, 378w, 359w, 300w, 254w, cm^{-1}.

Preparation of $[Y(OCMeEtPr^i)_3]$ (**5**)

Compound **5** was obtained from the reaction of $Y\{N(SiMe_3)_2\}_3$ (7 g) and $MeEtPr^iCOH$ (8 cm^3) in benzene, in the same manner as for **4**, as a white solid by sublimation at 170°C/10^{-3} torr (5.0 g, 94% based on yttrium, m.p. 196°C). Found: Y, 20.7; C, 53.8; H, 10.7. $Y(OCMeEtPr^i)_3$ requires: Y, 20.5; C, 58.0; H, 10.4%. Compound **5** dissolves readily in hydrocarbon solvents. ^{13}C NMR (C_6D_6) at 297 K: δ 80.0, 78.2 ($O\mathit{C}MeEtPr^i$); 38.4, 37.0 ($C\mathit{C}HMe_2$); 36.0, 35.3 ($C\mathit{C}H_2Me$); 26.9, 25.2 ($C\mathit{C}H_3$); 19.2, 19.0, 18.8, 18.7 ($CCH\mathit{C}H_3$); 10.2, 9.8 ($CCH_2\mathit{C}H_3$). ^{89}Y NMR ($C_6D_5CD_3$) at 310 K: δ 45.6. IR: 1362s, 1329m, 1313w, 1281w, 1202m, 1169s, 1147s, 1104s, 1063m, 1023s, 994s, 957m, 941s, 908s, 853m, 792w, 724m, 699m, 580m, 563s, 485m, 442m, 393w, 363w, 328w, 281w, cm^{-1}.

Preparation of $[Y(OCEt_3)_3]$ (**6**)

Compound **6** was prepared in the same manner as **4** and **5** from the reaction of $Y\{N(SiMe_3)_2\}_3$ (7 g) and Et_3COH (8 cm^3) in benzene, and the residual white solid was distilled at 225°C/10^{-2} torr (4.0 g, 75% based on yttrium, m.p. 198°C). Found: Y, 20.4; C, 55.8; H, 10.8. $Y(OCEt_3)_3$ requires: Y, 20.5; C, 58.0; H, 10.4%. Compound **6** dissolves readily in hydrocarbon solvents. ^{13}C NMR (C_6D_6) at 297 K: δ 80.2, 78.0 ($O\mathit{C}Et_3$); 33.7, 33.3 ($C\mathit{C}H_2CH_3$); 9.7 ($CH_2\mathit{C}H_3$). ^{89}Y NMR at 310 K: δ 47.8 (C_6D_6), 37.5 ($C_6D_5CD_3$). IR: 1344m, 1324m, 1295w, 1277w, 1259w, 1212m, 1158s, 1050s, 996s, 948s, 923m, 851w, 813w, 795w, 762w, 713m, 669w, 578m, 534s, 479m, 456w, 374m, 314w, 283w, cm^{-1}.

Preparation of $[La(OCMe_2Pr^i)_3]$ (**7**)

Pr^iMe_2COH (4.5 cm^3) in benzene (50 cm^3) was added to a solution of $La\{N(SiMe_3)_2\}_3$ (5.86 g) in benzene (150 cm^3), and after refluxing for 2 h was left overnight. After removal of volatiles *in vacuo* the residue was distilled at 135°C/10^{-3} torr (1.75 g, 42% based on lanthanum, m.p. 119°C). Found: La, 31.9. $La(OCMe_2Pr^i)_3$ requires: La, 31.4%. ^{13}C NMR (C_6D_6) at 297 K: δ 77.2 ($O\mathit{C}Me_2Pr^i$); 40.5 ($C\mathit{C}HMe_2$); 28.6 ($C\mathit{C}H_3$); 19.4 ($CH\mathit{C}H_3$); at 233 K ($C_6D_5CD_3$): δ 29.7, 29.1 ($C\mathit{C}H_3$); 19.9, 19.4 ($CH\mathit{C}H_3$). IR: 1308w, 1235vw, 1189m, 1169s, 1146s, 1099s, 1061w, 985s, 974s, 945m, 927m, 905m, 858m, 800w, 706w, 552m, 513m, 492m, 437w, 388w, 312w, cm^{-1}.

Preparation of $[La(OCMeEtPr^i)_3]$ (**8**)

Compound **8** was prepared in the same manner as **7** from the reaction of $La\{N(SiMe_3)_2\}_3$ (4.41 g) and $MeEtPr^iCOH$ (4 cm^3) in benzene and the residual white solid was distilled at 150°C/10^{-3} torr (2.1 g, 61% based on lanthanum, m.p. 112°C). Found, La, 29.5; C, 49.8; H, 9.4. $La(OCMeEtPr^i)_3$ requires: La, 28.7; C, 52.1; H, 9.4%. ^{13}C NMR (C_6D_6) at 297 K: δ 79.7 ($O\mathit{C}MeEtPr^i$); 38.6 ($\mathit{C}HMe_2$); 35.5 ($C\mathit{C}H_2Me$); 26.0 ($OC\mathit{C}H_3$); 19.1, 19.0 ($CH\mathit{C}H_3$); 10.1 ($CH_2\mathit{C}H_3$). IR: 1361s, 1327w, 1279w, 1259w, 1181s, 1165s, 1147s, 1102s, 1035m, 1007s, 953m, 932s, 911s, 851w, 787w, 715m, 694w, 574m, 557w, 516s, 437w, 416w, 392w, 330w, 233w, cm^{-1}.

Preparation of $[Y_3(OBu^t)_9(THF)_2]$ **(9)**

A sample of **1** was dissolved in THF, refluxed for 1 h and left overnight. After evaporation of the volatiles *in vacuo* the residue was redissolved in THF and compound **9** crystallized out. Found: Y, 24.5; C, 44.9; H, 8.9. $[Y_3(OBu^t)_9(THF)_2]$ requires: Y, 24.9; C, 49.4; H, 9.1%. On heating *in vacuo* at 70°C the THF was pumped off. Compound **9** begins melting at 142°C with decomposition. ^1H NMR ($C_6D_5CD_3$) at 303 K: δ 3.59, 1.88, 1.68, 1.52, 1.46; at 273 K: 3.59 (THF), 1.92, 1.78, 1.72, 1.70, 1.53, 1.52, 1.49, 1.43 (THF). IR: 1354m, 1239m, 1207s, 1075w, 1002s, 985m, 935m, 903m, 876w, 767w, 528m, 497m, 481m, 391w, 256m, 230m, cm^{-1}.

Reaction of **1** *with pyridine*

A sample of **1** was dissolved in pyridine and left overnight. After evaporating off the volatiles *in vacuo* the residue was crystallized from toluene and recrystallized from pentane to give colourless crystals (m.p. 118°C). Found: Y, 26.2; C, 48.3; H, 8.2; N, 2.5. Calc. for $Y_3(OBu^t)_9(C_5H_5N)_2$: Y, 24.6; C, 51.0; H, 8.5; N, 2.6%. ^1H NMR (C_6D_6) at 297 K: δ 9.25, 7.00, 6.81 (multiplets, 2H, 1H, 2H, C_5H_5N); 1.55 (singlet, 28H, $OCCH_3$).

Addition of NMe_3 *to* **1**

(a) Trimethylamine (3.5 cm^3) was condensed at -90°C onto **1** (1.24 g) and allowed to warm to 0°C. After 1 h at 0°C the volatiles were evaporated off *in vacuo* and **1** was recovered unchanged.

(b) NMe_3 (11 cm^3) was condensed onto **1** in toluene (20 cm^3) and allowed to warm to 0°C. After 2 h at 0°C it was kept at -20°C for a further 60 h and the volatiles then evaporated off *in vacuo*. The residue was unchanged (**1**).

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