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PENTANUCLEAR OXOALKOXIDE CLUSTERS OF SCANDIUM, YTTRIUM, INDIUM AND YTTERBIUM, X-RAY CRYSTAL STRUCTURES OF $[M_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_5]$ (M = In, Yb)

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Abstract—Attempts to prepare the metal tri-isopropoxides $M(OPr^i)_3$ (M = Sc, Y, In, Yb) by various methods always produced the pentanuclear oxoalkoxide clusters $[M_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_5]$ as the stable products. X-ray single crystal diffraction showed (M = In, Yb) the presence of the μ_5-oxygen atom bonded in a square pyramidal configuration to five metal atoms which had terminal isopropoxo groups *trans* to the oxo atom. The μ_3- and μ_2-isopropoxo groups contribute to the distorted octahedral coordination of each metal atom. The scandium, yttrium and ytterbium clusters could be sublimed *in vacuo* and gave mass spectra containing pentanuclear cluster ions. The ^1H NMR spectra for each compound was consistent with the X-ray crystal structure and variable-temperature studies showed fluxionality in the indium complex.

In recent years there has been a resurgence of interest in the application of metal alkoxides as precursors for the deposition of pure metal oxides using either sol–gel or MOCVD techniques.[1] The metal oxides and heterometal oxides are currently of considerable importance in the electronics, ceramics, glass and optical industries.

The alkoxides of yttrium,[2] indium[3] and ytterbium[4] have been known for some time whilst those of scandium[5,6] have received less attention. In attempting to prepare indium tri-isopropoxide from the reaction of indium trichloride with the requisite amount of sodium isopropoxide we obtained a crystalline product which surprisingly had the analysis corresponding to the novel pentanuclear oxoalkoxide $In_5O(OPr^i)_{13}$. Further work established that analogous compounds were given by scandium, yttrium and ytterbium and this was reported in a preliminary communication[7] which included the single crystal X-ray structure of the indium compound. We now report full details of our work including the single crystal X-ray structure of $Yb_5O(OPr^i)_{13}$. Quite independently the yttrium analogue $Y_5O(OPr^i)_{13}$ was discovered and fully characterized jointly by Professor Liliane Hubert-Pfalzgraf at Nice and Professor K. Caulton at Bloomington and their co-workers.[8]

RESULTS AND DISCUSSION

All attempts to prepare the tri-isopropoxides $M(OPr^i)_3$ (M = AC, Y, In, Yb) by a variety of methods resulted in the isolation of the pentanuclear species $M_5O(OPr^i)_{13}$ which were characterized by elemental analyses, NMR spectra, IR spectra and in some cases mass spectra (Sc, Y, Yb) and single crystal X-ray structures (In, Yb). Our results on the yttrium compound are in agreement with the independent work of Hubert-Pfalzgraf and co-workers.[8]

Preparation of $M_5O(OPr^i)_{13}$ (M = Sc, Y, In, Yb)

It was realized that our initial preparation of $In_5O(OPr^i)_3$ may have been caused by hydrolysis but repeated preparations using exceptional precautions to exclude water always resulted in the formation of the pentanuclear oxoalkoxide. The indium compound was prepared by reaction of

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anhydrous $InCl_3$ with $NaOPr^i$ in a 1 : 3 molar ratio in a benzene–isopropanol mixed solvent. To check whether the isopropanol was implicated in the formation of the oxo species a reaction was carried out in benzene with sodium isopropoxide powder, from which all isopropanol had been removed, but the product was still $In_5O(OPr^i)_{13}$. The yields of $In_5O(OPr^i)_{13}$ were always less than 50% and the precipitated NaCl was heavily contaminated with some insoluble indium compound. When heated to 145°C/10^{-2} mm Hg this "NaCl" gave an off-white sublimate and the volatile products were isopropanol and acetone. This off-white indium-containing sublimate was extraordinarily air-sensitive rendering it practically impossible to characterize. However, an ^1H NMR spectrum (C_6D_6, 80 MHz) was obtained with signals at δ 1.50 (6 H, d, CH_3) and 4.67 (1H, CH) corresponding to a single isopropoxide species in contrast to the complex spectrum of $In_5O(OPr^i)_{13}$. The off-white sublimate contained no chloride and on heating to 130°C/10^{-2} mm Hg gave a small amount of sublimate but the major part decomposed to metallic indium. A solution of the sublimate in toluene at room temperature decomposed to indium within a few hours but was stable for several days at -20°C, during which colourless crystals were deposited. The behaviour of this compound suggests that it may be indium monoisopropoxide which would be expected to have a cubane tetrameric structure $(InOPr^i)_4$ analogous to the thallium(I) alkoxides.[9] In fact, further heating of the original precipitated "NaCl" to 230°C/10^{-2} mm Hg gave a red sublimate of InCl. When the pentanuclear oxo cluster $In_5O(OPr^i)_{13}$ was heated to 80°C/10^{-2} mm Hg some acetone and isopropanol were released but no indium compound was sublimed up to 170°C.

Treatment of anhydrous $ScCl_3$ with $NaOPr^i$ (1 : 3 molar ratio) in isopropanol gave, after removal of sodium chloride and solvent, a white solid which sublimed at 220–280°C/10^{-2} mm Hg accompanied by a more volatile liquid. The sublimate which contained no sodium gave a complex ^1H NMR spectrum, but after recrystallization from isopropanol gave a spectrum consistent with $Sc_5O(OPr^i)_{13}$. The volatile liquid was shown by ^1H NMR to be almost entirely isopropanol contaminated with a scandium species (peaks in the mass spectrum at *m*/*z*, 355, 281, 207 in addition to OPr^i, 59 and Sc, 45).

In another experiment freshly sublimed $Sc\{N(SiMe_3)_2\}_3$, obtained from the reaction of $ScCl_3$ and $LiN(SiMe_3)_2$,[10] suspended in a benzene–pentane mixture was treated with excess isopropanol under reflux. On cooling, a high yield of $Sc_5O(OPr^i)_{13}$ crystallized out and sublimed at 220–280°C/10^{-2} mm Hg.

The analogous pentanuclear clusters $M_5O(OPr^i)_{13}$ (M = Y, Yb) were obtained from the reaction of the respective metal with isopropanol catalysed by $HgCl_2$, although it had been reported previously that this method gave the metal tri-isopropoxides.[3] Indeed, both compounds could be sublimed at *ca* 220°C/10^{-2} mm Hg which is similar to the sublimation temperatures (Y, 200–210°C/0.1 mm Hg; Yb, 190–200°C/0.2 mm Hg) reported for the "tri-isopropoxides". Addition of excess isopropanol to $Y\{N(SiMe_3)_2\}_3$ at room temperature followed by removal of excess alcohol and $HN(SiMe_3)_2$ *in vacuo* left a solid which gave a ^1H NMR spectrum which was complex and different from that of $Y_5O(OPr^i)_{13}$. It remained unchanged in isopropanol solution for several days at room temperature but upon heating under reflux for 1 h it was converted into the pentanuclear oxoalkoxide. This suggests that $Y(OPr^i)_3$ is thermally unstable and is converted in boiling isopropanol to $Y_5O(OPr^i)_{13}$. It is noteworthy that Hubert-Pfalzgraf and co-workers[8] found that $Y_5O(OPr^i)_{13}$ did not react with aluminium tri-isopropoxide whereas their initial product of the reaction of yttrium and Pr^iOH did react to give the heterometal alkoxide $YAl_3(OPr^i)_{12}$.

It is significant that in spite of exceptional precautions to prevent hydrolysis we have isolated $M_5O(OPr^i)_{13}$ as the thermally stable species and not the previously reported metal tri-isopropoxides. The analytical data presented in Table 1 show that the two types of compound can be distinguished on the basis of their elemental analyses. The comparison of the IR data in Table 2 of $M_5O(OPr^i)_{13}$ and "$M(OPr^i)_3$" compounds shows striking similarities between them. This was also noted for $Y_5O(OPr^i)_{13}$ by Hubert-Pfalzgraf and co-workers.[8] The mechanism of the breakdown of the tri-isopropoxides to give the pentanuclear oxoalkoxides has not yet been elucidated because the presence of isopropanol renders it diffult to identify other volatile products such as propene or di-isopropyl ether. Elimination of alkene is facile for metal tertiary alkoxides[12] but we have found that yttrium tritertiary alkoxides can be prepared under similar conditions of reaction and can be sublimed unchanged.[13] It appears therefore that elimination of di-isopropyl ether may account for the presence of the oxo atom in the pentanuclear clusters:

$$5M(OPr^i)_3 \longrightarrow M_5O(OPr^i)_{13} + Pr^i_2O.$$

Mass spectra of $M_5O(OPr^i)_{13}$

The scandium, yttrium and ytterbium complexes all gave positive ions containing the pentanuclear

Table 1. Analytical and spectroscopic data for the compounds

Compound	Analysis (%)[a,b]		Accurate mass[c]		^{1}H NMR (δ ppm)[d]	
	M	OPr^i	Species	m/z	CH	CH$_3$
$Sc_5O(OPr^i)_{13}$	22.5 (22.3) [20.2]	75.6 (76.1) [79.8]	$[P-OPr^i]^+$	949.371 (949.371)	4.40–4.65[e]	1.70, 1.54, 1.41, 1.37[f] (4:4:4:1)
$Y_5O(OPr^i)_{13}$	36.0 (36.2) [33.4]	62.5 (62.5) [66.6]	$[P-OPr^i]^+$	1169.118 (1169.121)	4.35–4.70[e]	1.65, 1.48, 1.40, 1.36[f] (4:4:4:1)
$In_5O(OPr^i)_{13}$	42.9 (42.3) [39.4]	56.6 (56.6) [60.4]	Not obtained		4.57[g]	1.63, 1.49[f] (8:5)
$Yb_5O(OPr^i)_{13}$	52.5 (52.5) [49.4]	47.5 (46.6) [50.6]	$[P-3(OPr^i)]^+$	1476.188 (1476.186)[h]	191, 111, −46, +134[i] (4:4:1:4)	97, 61, 1, −70[i] (4:4:1:4)

[a] Calculated values for oxo cluster in parentheses.

[b] Calculated values for $M(OPr^i)_3$ in brackets.

[c] $P = M_5O(OPr^i)_{13}$ calculated in parentheses.

[d] Obtained in C_6D_6 except for Yb compound in $C_6D_5CD_3$; relative integrations in parentheses.

[e] Cluster of septets, J 6 Hz.

[f] Doublets, J 6 Hz.

[g] Broad septet, J 6 Hz.

[h] Calculated with ^{174}Yb isotope.

[i] Broad signals.

cluster (Table 1) but the indium complex was thermally unstable and gave no mass spectrum. For scandium, $[P-OPr^i]^+$ (where $P = M_5O(OPr^i)_{13}$; M = Sc) was the most abundant metal-containing species, whereas for yttrium the highest mass peak was $[P-Me]^+$ but the $[P-OPr^i]^+$ peak was considerably more abundant. For ytterbium, the highest mass peak corresponded to $[P-3(OPr^i)]^+$. In each case the fragmentation pattern was complex and attention was focussed on those peaks closest to the parent molecular ion P^+. The fact that numerous peaks near the parent ion were observed emphasizes the stability of the $M_5(\mu_5\text{-}O)O_{13}$ cluster.

NMR spectra of $M_5O(OPr^i)_{13}$

The ^{1}H NMR chemical shifts are presented in Table 1. The room temperature spectra of the scandium and yttrium clusters in C_6D_6 at 250 MHz were in agreement with the requirements of the single crystal X-ray structures found for $M_5O(OPr^i)_{13}$ (M = In and Yb, which are discussed later), namely four sharp doublets and associated septets in the ratio 4:4:4:1. The scandium compound in $C_6D_5CD_3$ gave a similar spectrum which was unchanged on heating to 90°C, thus showing that the alkoxo ligands were non-fluxional on the NMR timescale and even the terminal groups remained resolved in the 4:1 ratio (basal–apical). On some occasions the spectrum of the yttrium compound at room temperature (C_6D_6) was collapsed into one resolved peak and two broad peaks in the ratio 4:4:5 possibly due to exchange caused by the presence of a trace of isopropanol. In $C_6D_5CD_3$, the 4:4:5 spectrum was always observed and it remained unchanged up to 80°C showing that the μ_3- and μ_2-isopropoxides remained distinguishable from the terminal groups which had collapsed into one signal.

The paramagnetic ytterbium compound at 30°C gave four broad signals between δ +97 and −70 in approximately a 4:4:1:4 ratio due to the methyl groups, and four corresponding peaks for the methine protons between δ +191 and −134. On changing the temperature all of the peaks change in chemical shift due to the paramagnetism but the overall spectrum is unchanged. Thus at 90°C the spectrum covers the range δ +144 to −101. Whilst at −60°C the highest field signal is at δ −169.5 and the lowest field signal is beyond the range of the instrument (i.e. $> \delta$ +200).

By contrast, the ^{1}H NMR spectrum of the indium complex at room temperature showed only two ligand environments in the ratio 8:5. The minor doublet at higher field remained unchanged down to −80°C ($C_6D_5CD_3$, 400 MHz), whereas the major

Table 2. Comparison between IR bands below 1375 cm^{-1} for the oxo clusters and literature values for M(OPr^i)$_3$ (M = Y, Yb)

Sc$_5$O(OPr^i)$_{13}$	Y$_5$O(OPr^i)$_{13}$	Y(OPr^i)$_3$^{a}	In$_5$O(OPr^i)$_{13}$	Yb$_5$O(OPr^i)$_{13}$	Yb(OPr^i)$_3$^{a}
1368s	1366s	1363sh	1371s	1368s	1365sh
1356s	1355s	1354m	1359m	1353s	1356s
1342m	1338s	1336m	1342m br	1335m	1337s
1254w	1260w	—	1263w	1257w	—
1173vs	1170vs br	1168vs	1164m	1169vs br	1172vs
1158s sh	—	—	—	—	—
1130vs	1124vs br	1123s	1126vs	1123vs br	1123s
1015vs	1007vs	1005vs	988s	1006vs	1010vs
980s	975s sh	974s	—	—	—
970s	970s br	—	970 m sh	971s	976s
960s	952s sh	950s	952s	950s	953s
868w	—	—	—	—	—
842m	831s	835m	832m	835m sh	839m
832m		830m			833m
—	—	822m	—	826m	825m
780w	830w sh	—	805w sh	799w	—
—	—	—	730m	—	—
720w	721w	—	720m	719w	—
—	—	—	570s br	—	—
559vs br	533s	532s	554s br	530vs	534s
515vs br	512s sh	—	502s br	498s br	497m
489m	496s	493s	—	486s sh	—
461m sh	—	—	—	—	—
450m	452s	450s	455m br	445s	447m
416m	421m	418m	—	414m	416m
—	399s br	393s	401vs br	391s	393m
350m br	343w sh	^{b}	—	—	^{b}
330m br	332w br	^{b}	—	328w br	^{b}
296m br	292w br	^{b}	305w br	299w	^{b}
279m sh	—	^{b}	—	—	^{b}
245w br	259m br	^{b}	240m br	252w	^{b}

[a] From ref. 11.

[b] Beyond reported range.

doublet collapsed at *ca* −30°C (250 MHz) but gave two broad equal peaks at −60°C straddling the minor doublet. This behaviour demonstrated a greater lability of the isopropoxide groups in the indium cluster. Thus the μ_2- and μ_3-ligands were exchanging rapidly above −30°C (ΔG 43–49 kJ mol^{-1}) whilst the terminal ligands were inseparable down to −80°C. This suggests either that the terminal basal–apical exchange is much more facile than μ_2–μ_3 bridging exchange or, more likely, that the chemical shifts of the basal and apical terminal ligands are very close in value.

X-ray crystal structures of [In$_5$O(OPr^i)$_{13}$] *and* [Yb$_5$O(OPr^i)$_{13}$]

We have already reported the molecular structure of [In$_5$(μ_5-O)(μ_3-OPr^i)$_4$(μ_2-OPr^i)$_4$(OPr^i)$_5$] which was determined by single crystal X-ray diffraction.[7] We have now found that the ytterbium analogue [Yb$_5$(μ_5-O)(μ_3-OPr^i)$_4$(μ_2-OPr^i)$_4$(OPr^i)$_5$] is isostructural with the same M$_5$O$_{14}$ cluster framework. Whilst our work was in progress Hubert–Pfalzgraf and Caulton and their co-workers[8] independently determined the crystal structure of [Y$_5$(μ_5-O)(μ_3-OPr^i)$_4$(μ_2-OPr^i)$_4$(OPr^i)$_5$] and this compound is isostructural with the indium and ytterbium clusters. The structural unit M$_5$O$_{14}$ is shown in Fig. 1 and the more important bond distances and bond angles are listed in Table 3. In essence, the structure contains a μ_5-oxygen bonded to five metal atoms in a square pyramidal configuration with four μ_2-isopropoxy groups bridging the four basal metal atoms. The four μ_3-isopropoxy groups occupy the triangular faces of the square pyramid. Each metal has one terminal isopropoxy group completing a

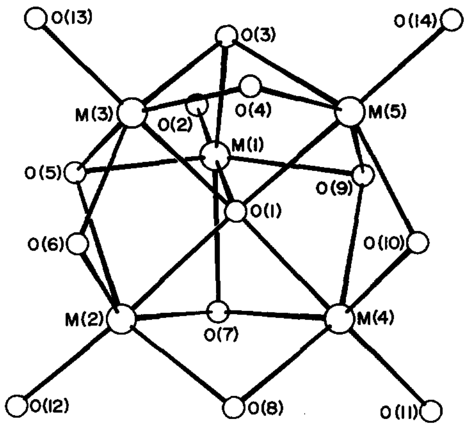

Fig. 1. The metal–oxygen core in $[M_5O(\mu_3\text{-}OPr^i)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_5]$.

distorted octahedral coordination. It is interesting to note that the first example of a structurally characterized cluster molecular containing a μ_5-oxo atom was the organoyttrium methoxo compound $[Y_5(\mu_5\text{-}O)(\mu_3\text{-}OMe)_4(\mu_2\text{-}OMe)_4(C_5H_5)_5]$ reported by Evans and Sollberger.[14] In this case the terminal alkoxo groups have been replaced by η^5-Cp ligands. This reinforces our view that the $[M_5(\mu_5\text{-}O)(\mu_3\text{-}OR)_4(\mu_2\text{-}OR)_4]$ framework (M_5O_9) possesses special stability and must be the driving force for the breakdown of the tri-isopropoxides of scandium, yttrium, indium and ytterbium. Presumably the more stable tritertiary alkoxides[13] cannot attain the M_5O_4 cluster grouping because of steric hindrance and the metals are compelled to adopt a lower coordination number (except Y which gives trinuclear t-butoxide).

The metal–metal distances basal–basal and basal–apical are, respectively, 3.16 and 3.26 Å for indium and 3.26 and 3.38 Å for ytterbium and thus, as expected, there is no evidence for metal–metal bonding within these cluster molecules. The four basal metal atoms are virtually in a square with the μ_5-oxygen atoms slightly above this plane, e.g. 0.16 Å (In) and 0.19 Å (Yb). The apical metal atoms are closer to the μ_5-oxygen (2.21 Å In—O; 2.28 ÅYb—O) than the basal metal atoms (average 2.24 Å, In—O; 2.31 Å, Yb—O). The shortest M—O bonds involve the terminal isopropoxo groups with average bond lengths of 1.96 (In) and 2.00 Å (Yb). The μ_2-isopropoxo groups are symmetrically bonded to the basal metal atoms with average M—O bond lengths of 2.14 (In) and 2.19 Å (Yb). The μ_3-isopropoxy groups have shorter apical M—O bond lengths [average 2.22 (In) and 2.28 Å (Yb)] than the basal M—O bond lengths [average 2.34 (In) and 2.39 Å (Yb)]. The mean bond angles about the μ_5-oxygen are the same for each compound with the mean apical metal–oxygen–basal metal angles of 94.2 ± 0.6 (In) and 94.6 ± 0.4° (Yb), reflecting the slight displacement of the μ_5-oxygen above the plane of the four basal metals. The angles subtended by the μ_5-oxygen and the basal metals are *cis*: 89.7 ± 0.7 (In) and 89.6 ± 0.5° (Yb) and *trans*: 171.5 ± 1.1 (In) and 170.7 ± 0.9° (Yb).

Hubart-Pfalzgraf and co-workers[8] have discussed the structure of $Y_5O(OPr^i)_{13}$ in relation to other cluster alkoxides of yttrium, viz. $[Y_3(OBu^t)_8Cl(THF)_2]$ and $[Y_4O(OBu^t)_{10}Cl_2]^{2-}$ isolated by Evans *et al.*[15] from reactions involving YCl_3 with $LiOBu^t$ or $NaOBu^t$, respectively. The formation of an octahedral configuration for yttrium was considered to be a driving force for the formation of the $Y_5O(OPr^i)_{13}$ structure with the interesting suggestion that the ultimate structure could be the anion $[Y_6O(\mu_2\text{-}OR)_{12}(OR)_6]^{2-}$ containing a μ_6-O octahedrally coordinated to six equivalent metal atoms. It is possible that the sodium salt of such a species is precipitated with NaCl in the reaction between MCl_3 and NaOR. In this respect it is also relevant to note that Andersen *et al.*[16] had earlier reported the neodymium complex chloride isopropoxide $[Nd_6(\mu_6\text{-}Cl)(\mu_3\text{-}OPr^i)_2(\mu_2\text{-}OPr^i)_9(OPr^i)_6]$ which contains a μ_6-Cl at the centre of a trigonal prismatic cluster of neodymium atoms.

EXPERIMENTAL

All operations were performed under an atmosphere of purified nitrogen using Schlenk-style apparatus and a glove box. Solvents were distilled from sodium benzophenone under nitrogen, and isopropanol was initially heated under reflux with CaO (preheated to 700°C) for several hours. Then a small quantity of dried benzene was added and the azeotropes (benzene–isopropanol–water, if still present, then benzene–isopropanol) were removed by fractional distillation; the remaining isopropanol was distilled onto activated 3 Å molecular sieves prior to use. Anhydrous $ScCl_3$ was prepared from the reaction of Sc_2O_3 with concentrated HCl followed by removal of H_2O/HCl *in vacuo*, then heating under reflux for 7 days with $SOCl_2$ (freshly distilled from linseed oil) and finally $SOCl_2$ was removed by distillation *in vacuo*. Anhydrous $InCl_3$ was obtained from commercial sources and heated *in vacuo* for several hours prior to use. Yttrium and ytterbium powder (40 mesh, 99.9%), sodium metal (lumps), and Bu^nLi (solution in hexane), were obtained from commercial sources. Hexamethyldisilazane was prepared by a literature route from reacting Me_3SiCl with ammonia.[11]

^1H NMR spectra were obtained using Bruker WP80 FT, WM250 FT and WH400 FT spec-

Table 3. Selected bond lengths (Å) and angles (°) for $M_5O(OPr^i)_{13}$ (M = In, Yb)

	In	Yb	Category
M(1)—O(1)	2.208(8)	2.285(23)	M_5O core
M(2)—O(1)	2.260(8)	2.339(24)	
M(3)—O(1)	2.242(9)	2.311(24)	
M(4)—O(1)	2.220(9)	2.300(24)	
M(5)—O(1)	2.235(8)	2.301(24)	
M(1)—O(2)	1.957(15)	2.003(24)	Terminal M—O
M(2)—O(12)	1.988(16)	2.026(29)	
M(3)—O(13)	1.984(16)	1.991(33)	
M(4)—O(11)	1.984(15)	2.015(32)	
M(5)—O(14)	1.982(15)	1.981(29)	
M(2)—O(6)	2.140(11)	2.192(29)	Basal M—μ_2-O
M(3)—O(6)	2.154(10)	2.181(25)	
M(3)—O(4)	2.162(11)	2.219(35)	
M(5)—O(4)	2.135(11)	2.177(29)	
M(5)—O(10)	2.147(11)	2.173(31)	
M(4)—O(10)	2.126(11)	2.183(30)	
M(4)—O(8)	2.147(10)	2.171(28)	
M(2)—O(8)	2.123(11)	2.229(34)	
M(1)—O(3)	2.219(10)	2.306(26)	Basal M—μ_3-O
M(1)—O(5)	2.204(10)	2.262(29)	
M(1)—O(9)	2.222(10)	2.305(27)	
M(2)—O(5)	2.326(9)	2.397(24)	
M(3)—O(5)	2.340(10)	2.285(3)	
M(3)—O(3)	2.318(9)	2.371(25)	
M(5)—O(3)	2.327(9)	2.379(27)	
M(5)—O(9)	2.297(10)	2.370(27)	
M(4)—O(9)	2.382(10)	2.368(25)	
M(4)—O(7)	2.330(10)	2.390(27)	
M(2)—O(7)	2.361(10)	2.371(24)	
M(1)—O(1)—M(2)	93.6(3)	93.9(9)	
M(1)—O(1)—M(3)	94.4(3)	94.7(9)	
M(1)—O(1)—M(4)	95.0(4)	95.2(9)	
M(1)—O(1)—M(5)	94.2(3)	94.7(8)	
M(2)—O(1)—M(3)	88.9(3)	88.9(8)	
M(3)—O(1)—M(5)	89.7(3)	90.0(9)	
M(5)—O(1)—M(4)	90.4(3)	90.3(9)	
M(4)—O(1)—M(2)	89.7(3)	89.3(9)	
M(2)—O(1)—M(5)	172.2(3)	171.4(10)	
M(3)—O(1)—M(4)	170.5(3)	170.1(10)	

trometers; chemical shifts are quoted relative to tetramethylsilane, although calibration was made from the solvent signals from incomplete deuteration. IR spectra were recorded as Nujol mulls between CsI plates in the range 4000–200 cm^{-1} using a Perkin–Elmer 577 spectrophotometer, and mass spectra using a Kratos MS50 TC spectrometer. Metals were analysed gravimetrically as the oxide M_2O_3 by hydrolysis of a sample in a platinum crucible followed by heating in air to 650°C for In and 750°C for the others (for Y and Yb this was followed by heating in a roaring bunsen flame). The isopropoxide analyses were by the method of Bradley *et al.*[17]

(1) $Sc_5O(OPr^i)_{13}$

(a) Sodium (5.0 g, 0.22 mol) was added to isopropanol (250 cm^3) and heated under reflux for 2 h, after which dissolution of metal was complete. This was cooled to room temperature whereupon a solution of anhydrous $ScCl_3$ (11 g, 73 mmol) in isopropanol (250 cm^3) was added. The mixture was heated under reflux for a further 2 h and then stirred at room temperature for 60 h. The white precipitate was filtered off and the solvent was removed *in vacuo* to leave a white residue. This was heated to 220°C/10^{-2} mm Hg whereupon sublimation began to occur, but was slow, and was therefore continued at up to 280°C/10^{-2} mm Hg; a more volatile liquid was also obtained in a trap held at −196°C (see Results and Discussion). The sublimate was recrystallized from isopropanol to give white needle *crystals* of $Sc_5O(OPr^i)_{13}$ (m.p. > 320°C, 2.5 g, 17% based upon $ScCl_3$). Further washing of the precipitate with isopropanol enhanced the yield slightly.

(b) The $(Me_3Si)_2NH$ (34.6 cm^3, 164 mmol) was cautiously added to Bu^nLi (53 cm^3 of 3.15 M solution, 0.17 mol) and then solvent was removed *in vacuo*. The residue was dissolved in tetrahydrofuran (100 cm^3) and to this a solution of $ScCl_3$ (8.4 g, 56 mmol) in tetrahydrofuran (100 cm^3) was added dropwise. After stirring at room temperature overnight the solvent was removed *in vacuo* and the residue was triturated with pentane (200 cm^3) and any undissolved solid was filtered off. The trituration, etc., was repeated with fresh pentane (200 cm^3) and the two filtrates were combined, concentrated *in vacuo* and held at −25°C, whereupon white crystals of $Sc[N(SiMe_3)_2]_3$ were obtained. These were sublimed at 110°/10^{-2} mm Hg (20.0 g, 69% based upon $ScCl_3$). A sample of the sublimate (8.5 g, 16 mmol) was suspended in benzene (250 cm^3) and isopropanol was added (20 cm^3, ~ five-fold excess), whereupon all the solid dissolved. The contents were heated under reflux for 1 h, then allowed to cool to room temperature, at which point solvents were removed *in vacuo* to leave a white residue. The residue was recrystallized from isopropanol to give white *crystals* of $Sc_5O(OPr^i)_{13}$ (2.1 g, 65% based upon $Sc[N(SiMe_3)_2]_3$).

(2) $Y_5O(OPr^i)_{13}$

To yttrium powder (25 g, 0.28 mol) were added a few small crystals of $HgCl_2$ followed by isopropanol (400 cm^3, large excess), and the contents were heated under reflux for 60 h. By this time most of the metal had dissolved but a small quantity of black solid remained, which was filtered off and discarded. Solvent was removed from the filtrate and a sample of the residue (6 g) was recrystallized from isopropanol to give white *crystals* of $Y_5O(OPr^i)_{13}$ (4.9 g, 7% yield based upon Y). The bulk of the residue was sublimed at 220°C/10^{-2} mm Hg, although presumably some decomposition also occurred since much non-volatile residue remained (sublimed yield of $Y_5O(OPr^i)_{13}$ was 22.2 g, 32% based upon Y). The combined yield of 39% would presumably have been much higher if the whole sample had been recrystallized.

(3) $In_5O(OPr^i)_{13}$

Sodium (34.7 g, 1.48 mol) was added to a mixture of isopropanol (200 cm^3, large excess) and benzene (800 cm^3) and the contents heated under reflux overnight, after which the metal had dissolved. To this was added a solution of $InCl_3$ (106 g, 0.48 mol) in isopropanol (500 cm^3) and the contents were heated under reflux for 2 h, after which they were cooled to room temperature and the white precipitate filtered off. Further extraction from the precipitate was attempted with isopropanol (200 cm^3), and the filtrates were combined and concentrated *in vacuo*, whereupon colourless *crystals* of $In_5O(OPr^i)_{13}$ were obtained (62 g, 48% based upon $InCl_3$). The compound began to turn yellow when heated to 160°C under an atmosphere of nitrogen.

(4) $Yb_5O(OPr^i)_{13}$

To ytterbium powder (10.2 g, 59 mmol) were added a few small crystals of $HgCl_2$ followed by isopropanol (250 cm^3, large excess), and the contents were heated under reflux for 24 h. The residual black solid was filtered off and solvent was removed from the filtrate *in vacuo*. The white residue was sublimed at 215°C/10^{-2} mm Hg as white *crystals* of $Yb_5O(OPr^i)_{13}$ (17.8 g, 86% based upon Yb). M.p. > 300°C.

X-ray crystallography

Crystals of the indium and ytterbium clusters used for the X-ray work were sealed under nitrogen in thin-walled glass capillaries. All crystallographic measurements were performed at 293 K using a Nonius CAD4 diffractometer and graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å), following previously detailed procedures.[18] The structures were solved by direct methods and refined by full-matrix least-squares analysis. For the indium compound all included atoms were refined anisotropically, but due to large thermal motion in the isopropyl groups, C—O and C—C distances were fixed at 1.40 and 1.50 Å, respectively. These distances were also fixed for the ytterbium compound, but in addition all carbon atoms were refined isotropically. No hydrogens were included for either compound.

Details of the crystal data, data collection and refinement are given in Table 4. Computer pro-

Table 4. Crystal data, details of intensity measurements and structure refinement

Molecular formula	$C_{39}H_{91}O_{14}In_5$	$C_{39}H_{91}O_{14}Yb_5$
Molecular weight	1358.12	1649.12
Crystal system	Monoclinic	Monoclinic
a (Å)	12.665(2)	12.878(4)
b (Å)	21.305(2)	21.621(4)
c (Å)	20.910(6)	21.377(3)
α (°)	90.0	90.0
β (°)	90.70(2)	91.38(2)
γ (°)	90.0	90.0
V (Å^3)	5641.7	5950.39
Space group	$P2_1/n$	$P2_1/n$
Z	4	4
D_c (g cm^{-3})	1.60	1.84
μ (cm^{-3})	20.32	78.05
F(000)	2728	3148
h, k, l, range	±13, 23, 23	±15, 25, 25
Total number of reflections	8323	11084
Number of unique reflections	7828	10471
Number of reflections used; $[F > 3\sigma(F)]$	4680	4164
Number of parameters	525	328
Weighting scheme parameter g in $w = 1/[\sigma^2(F)+gF_o^2]$	0.003486	0.002529
Final R	0.057	0.071
Final R_w	0.080	0.091

grams and sources of scattering factor were as previously described.[18]

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