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Lanthanide silasesquioxanes: monomeric and functionalised complexes

Judith Annand and Helen C. Aspinall *

Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool, Crown Street, Liverpool, UK L69 7ZD. E-mail: hca@liv.ac.uk

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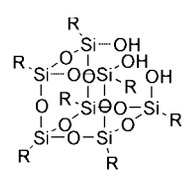
Lanthanide tris(silylamides) LnL_3 reacted with 2/3 equivalents of the trisilanol $(C_6H_{11})_7Si_7O_9(OH)_3$ **1** in THF to give the lanthanide silasesquioxanes $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ which are dimeric in solution at 233 K. Reaction of LnL_3 with 1 equivalent of **1** in THF resulted in complete conversion of **1** into the trisilylated compound $(C_6H_{11})_7Si_7O_9(OSiMe_3)_3$ as does reaction of LnL_3 with 2/3 equivalents of **1** in toluene. Reaction of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ with 1 equivalent of $(Me_2NCH_2CH_2)_2NMe$ (PMDTA) gave the monomeric complex $[(C_6H_{11})_7Si_7O_{12}Ln(PMDTA)]$. The chloro-functionalised lanthanide silasesquioxane $[(C_6H_{11})_7Si_7O_{11}(OSiMe_3)LnCl(THF)]$ was formed by reaction of $[(C_6H_{11})_7SiO_7O_{12}Ln(THF)_2]$with 1 equivalent of Me_3SiCl. New compounds have been characterised by NMR spectroscopy and by elemental analysis.

Introduction

Electrophilic C–H activation by d^0 early transition metal,[1] lanthanide[2,3] and actinide[4] species has been shown to have great potential, and catalysts derived from such metals have activities equalling or surpassing those of more conventional platinum group metal catalysts.[5,6] Lanthanide(III) ions are hard Lewis acids and co-ordination of these large ions in a highly electrophilic environment should lead to useful organometallic chemistry. The silasequioxane framework of the trisilanol $(C_6H_{11})_7Si_7O_9(OH)_3$ **1** provides a highly electrophilic ligand



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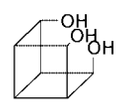

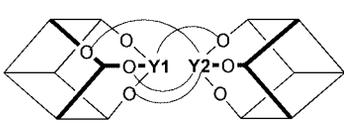

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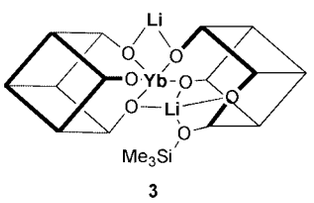

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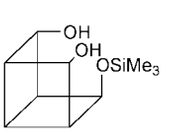
environment and has the advantage of binding facially to the Ln, thus leaving a large open binding site for electrophilic chemistry to take place. When we embarked on this work there was just one published report of a lanthanide silasequioxane,[7] which showed a unique dimeric structure **2** in the solid state, demonstrating the Lewis acidity of the Ln by its ability to co-ordinate to normally non-basic framework O atoms. We have since reported a heterometallic lanthanide–lithium silasequioxane **3** which also shows co-ordination of framework O atoms to a metal centre.[8] Our aim in the present work was to prepare monomeric lanthanide silasequioxanes, to understand their co-ordination chemistry in solution and to prepare chloro derivatives which should be suitable precursors to organolanthanide complexes in highly electrophilic environments.

Results and discussion

Characterisation of the complexes

All the compounds described here could be crystallised by cooling of a concentrated pentane solution, or by careful addition of MeCN to a THF solution. However, despite their superficial appearance of good quality, all of the crystals thus obtained were severely disordered and unsuitable for characterisation by X-ray diffraction. We therefore used NMR spectroscopy as our primary structural tool. The complex resonances due to cyclohexyl groups meant that ^{1}H NMR spectroscopy gave little structural information about the lanthanide silasequioxanes. Although the CH_2 region of the ^{13}C NMR spectrum was very complex due to the different environments of the cyclohexyl groups, the CH (*ipso* C) region of the spectrum was very valuable in determining the symmetry of the complexes. Resonances due to *ipso*-C atoms were assigned unambiguously by using the DEPT pulse sequence. Compounds such as trisilanol **1** with C_{3v} symmetry show 3 signals in the ratio 1:3:3 for the *ipso* C atoms; lowering the symmetry to C_s by a single substitution as in **4** or to C_{2h} by dimer formation as in **5** results in a



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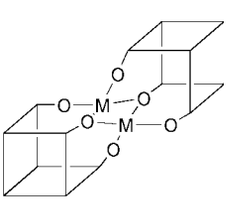

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1:2:2:1:1 pattern. Acceptable signal-to-noise ratios in ^{29}Si NMR were only obtained in a reasonable time by the use of $[Cr(acac)_3]$ as a relaxation agent, and as this technique gave essentially no extra information about the symmetry of the complexes it was not used routinely.

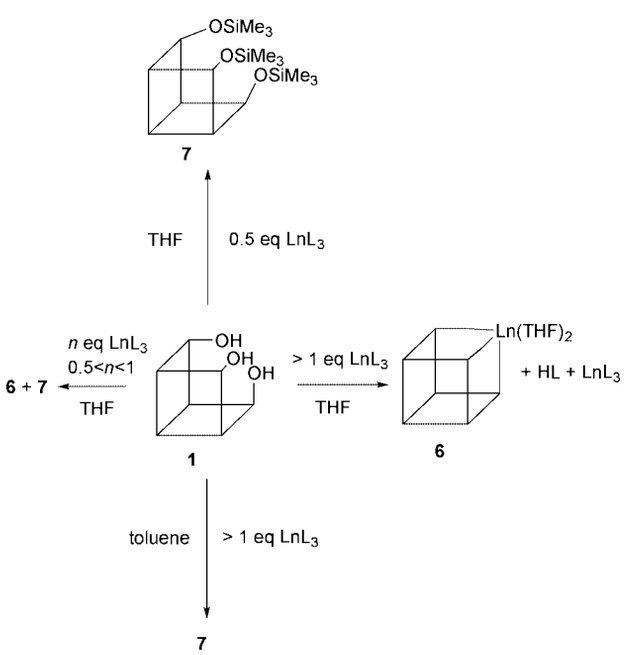
Table 1 Variable temperature ^{13}C NMR spectra of $[(C_6H_{11})_7Si_7O_{12}Y(THF)_2]$[a]

298 K		233 K	
Chemical shift	Assignment	Chemical shift	Assignment
69.59	THF (co-ord.)	71.01 68.01	THF (co-ord.) THF (free)
28.01, 27.72, 27.66, 27.56, 27.02, 26.92, 26.63	CH_2 cyclohexyl	28.13, 27.66, 27.44, 27.12, 26.63, 26.35, 26.21, 25.89	CH_2 cyclohexyl
25.20, 24.18, 23.28	3:3:1, *ipso*-CH cyclohexyl	25.33, 24.68	3:3, *ipso*-CH cyclohexyl (C_{3v} complex)
25.46	THF	25.52 24.21, 23.71, 23.65, 22.66, 22.54	THF 1:2:2:1:1, *ipso*-CH cyclohexyl (C_{2h} complex)

[a] Samples were dissolved in $CDCl_3$.

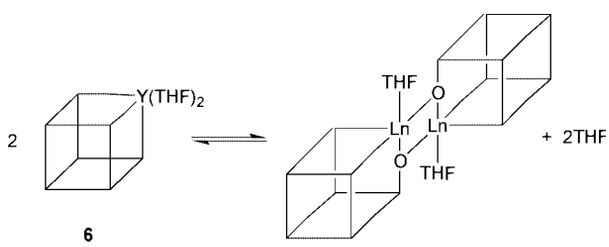
Preparation of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ 6

Lanthanide tris(silylamides) $[Ln\{N(SiMe_3)_2\}_3]$ are popular starting materials for the preparation of lanthanide complexes by reaction with protic reagents, and many complexes have been prepared by this route. Advantages of the 'silylamide route' are that the by-product, HMDS ($HN(SiMe_3)_2$), is volatile and easily removed, and that contamination with alkali metal ions, often a problem with metathesis reactions, cannot occur. The 'silylamide route' therefore seemed a sensible place to start our investigations into lanthanide silasequioxane chemistry. Preparations of other metal silasequioxanes by this method have been reported where M = Ln[7] or Ti.[9] Although the reaction of $[LnL_3]$ (L = $N(SiMe_3)_2$) with 1 equivalent of trisilanol **1** would be expected to lead to quantitative formation of lanthanide silasequioxane $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_n]$, in our hands this reaction was found always to produce a mixture containing the desired product and the trisilylated compound $(C_6H_{11})_7Si_7O_9(OSiMe_3)_3$ **7**. We found that contamination with **7** was only avoided in the presence of an excess of $[LnL_3]$ as shown in Scheme 1. Compounds $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ **6** were



Scheme 1 Reactions of compound **1** with LnL_3 ($Ln\{N(SiMe_3)_2\}_3$).

isolated for Ln = La, Pr, Eu, Y or Yb. Crystals were grown from concentrated pentane solutions, but always too disordered to be characterised by X-ray diffraction. ^1H NMR spectroscopy indicated the presence of two molecules of co-ordinated THF; this was also confirmed by elemental analysis. ^{13}C NMR data for $[(C_6H_{11})_7Si_7O_{12}Y(THF)_2]$ at 298 and at 233 K are summarised in Table 1. At room temperature the complexes have C_{3v} symmetry as demonstrated by the 3:3:1 pattern for the *ipso*-CH resonances in their ^{13}C NMR spectra. This is consistent with the proposed monomeric structure, although it should be noted that a fluxional process has been reported for a boron silasequioxane which gives a time averaged C_{3v} structure at room temperature.[10] On lowering the temperature of a $CDCl_3$ solution of $[(C_6H_{11})_7Si_7O_{12}Y(THF)_2]$ to 243 K some broadening in the low-field *ipso*-CH resonance was observed, though there were no other obvious changes in the spectrum. At 233 K, the *ipso*-CH region of the spectrum became complex and 7 distinct resonances were resolved. Two distinct sets of THF resonances were also observed, consistent with free and co-ordinated THF. This can be explained by a monomer/dimer equilibrium as shown in Scheme 2. The C_{2h} symmetry species could not be completely



Scheme 2 Proposed monomer/dimer equilibrium for compounds **6**.

frozen out even at 218 K, although at this temperature the ratio of free to co-ordinated THF had increased significantly. Related monomer/dimer equilibria have been observed for a vanadium silasequioxane at 253 K[11] and for a titanium silasequioxane at room temperature.[12]

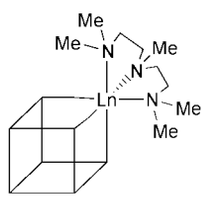
Attempts to prepare 'ligand-free' $[(C_6H_{11})_7Si_7O_{12}Ln]$

Ligand-free $[(C_6H_{11})_7Si_7O_{12}Ln]$ is an attractive synthetic target: the 'bare' Ln co-ordinated to the highly electron-withdrawing silasequioxane framework should be strongly Lewis acidic and highly reactive. We first attempted to prepare the ligand-free complex by reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with compound **1** in toluene. However, as discussed in more detail below, this resulted only in complete conversion of **1** into the silylated compound **7** (Scheme 1). The alternative approach was to remove the co-ordinated THF molecules from $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$. We attempted this by heating samples of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ (Ln = La or Y) to 60 °C *in vacuo* for 5 h. This resulted in removal of almost all of the THF (^1H NMR integration indicated the presence of <1 mol of residual THF per Ln). Apart from the reduction in intensity of THF resonances, the ^1H NMR spectrum showed no obvious change. The ^{13}C NMR spectrum was extremely complex in the *ipso*-CH region; the low-field THF resonance appeared at δ 68.1, consistent with unco-ordinated THF. These data suggest that $[(C_6H_{11})_7Si_7O_{12}Y]$ achieves co-ordinative saturation by bonding with framework O atoms as observed in the solid state for **2**,

although in the absence of crystallographic data the structure cannot unambiguously be determined.

Substitution reactions of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$

It was clear that THF adducts **6** were not going to yield crystals suitable for X-ray diffraction, also that THF was not a strong enough donor to prevent formation of dimeric lanthanide silasequioxanes at low temperature in solution, and presumably in the solid state. We therefore investigated the use of multidentate ligands to cap the Ln atom, starting with multidentate O-donors. Diglyme ($Me(OCH_2CH_2)_2OMe$) has successfully been used as a facially capping ligand in lanthanide alkoxide[13] and β-diketonate[14] chemistry, but was found not to co-ordinate to the lanthanide silasequioxanes. A similar lack of success was encountered with 15-crown-5, and so we moved on to the stronger donor pentamethyldiethylenetriamine, PMDTA. This has been widely used as a ligand for alkali metals but to date there are no reports of its use in lanthanide chemistry. Reaction of **1** with 1.5 equivalents $[Ln\{N(SiMe_3)_2\}_3]$ in the presence of 1.5 equiv PMDTA in THF resulted in formation of crystalline complexes **8** analysing as $[(C_6H_{11})_7Si_7O_{12}Ln(PMDTA)]$. ^{13}C



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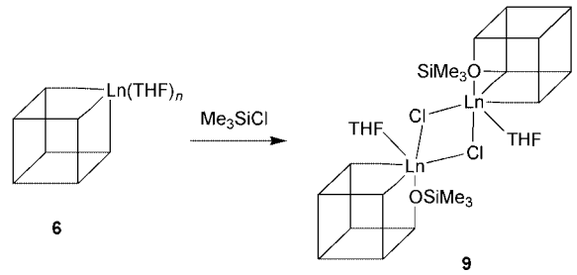
NMR spectroscopy showed that the complexes have C_{3v} symmetry at room temperature (*ipso*-C atoms show 3:3:1 ratio) and also confirmed that PMDTA had co-ordinated. Low temperature ^{13}C NMR spectroscopy showed no change in structure and therefore it is reasonable to conclude that the complexes are monomeric. Unfortunately crystals grown from THF and MeCN were disordered and could not be characterised by X-ray diffraction.

The THF ligands of compounds **6** may also be displaced by H_2O: on opening **6** to the air a soluble complex analysing as $[(C_6H_{11})_7Si_7O_{12}Y(H_2O)_4]$ was formed. The ^{13}C NMR spectrum showed the 3:3:1 pattern for the *ipso*-C atoms indicative of a C_{3v} monomeric structure. TGA of this complex showed weight loss at 242 °C corresponding to loss of 4 H_2O molecules, and loss of organic fragments occurred at 534 °C.

Functionalised lanthanide silasequioxanes

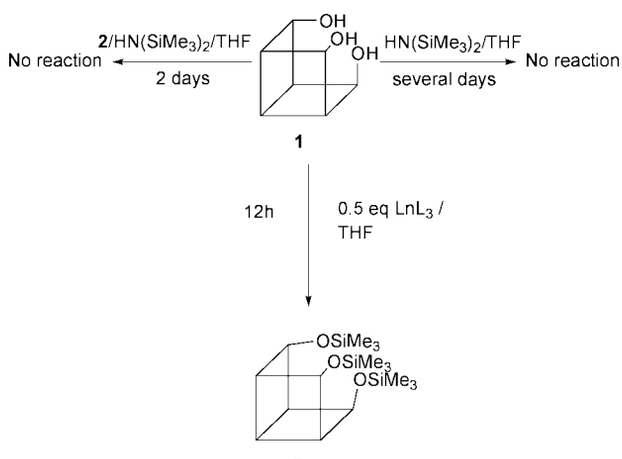
The highly electrophilic silasequioxane ligand would provide a novel environment for organolanthanide chemistry, and our first efforts in this area investigated the reactions of LnL_3 with the monosilylated silanol $(C_6H_{11})_7Si_7O_9(OSiMe_3)(OH)_2$ **4**. We found that reaction of LnL_3 with **4** under a variety of conditions yielded only complex mixtures, possibly containing small quantities of the desired heteroleptic complex $[(C_6H_{11})_7Si_7O_{11}(OSiMe_3)Ln\{N(SiMe_3)_2\}]$ We therefore adopted the novel strategy of silylating a co-ordinated siloxy group by reaction with Me_3SiCl. Addition of 1 equivalent of Me_3SiCl to a THF solution of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ (Ln = La or Y) as shown in Scheme 3 resulted in formation of a new product which was isolated by crystallisation from pentane. Elemental, analytical and NMR spectroscopic data were consistent with the formulation $[(C_6H_{11})_7Si_7O_{11}(SiMe_3)LnCl(THF)]$. The ^{13}C NMR spectrum in $CDCl_3$ showed a 1:2:2:1:1 pattern for the *ipso*-C atoms which would be consistent with either a monomer or a dimer with C_{2h} symmetry. Owing to the large size of the Ln^{3+} ions we believe that the six-co-ordinate dimeric structure **9** with bridging chloride ligands is the most likely.



Scheme 3 Synthesis of chloro-functionalised lanthanide silasesquioxanes.

Formation of $(C_6H_{11})_7Si_7O_9(SiMe_3)_3$ 7

When reactions were carried out between LnL_3 and 1 equivalent of compound **1** in THF the trisilylated compound $(C_6H_{11})_7Si_7O_9(SiMe_3)_3$ **7** was invariably formed as a substantial component of the products. When the reaction was carried out in a non-co-ordinating solvent (toluene) **7** and HMDS were shown by ^{29}Si NMR spectroscopy to be the only Si-containing products. Reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with 2 equivalents of **1** in THF resulted in complete conversion into **7**, which was isolated in almost quantitative yield. However, formation of **7** was completely suppressed in the presence of an excess of $[Ln\{N(SiMe_3)_2\}_3]$. These observations are summarised in Scheme 4. The formation of **7** has not been reported before in the reactions of **1** with metal silylamides.[7,9]



Scheme 4 Formation of $(C_6H_{11})_7Si_7O_9(OSiMe_3)_3$ **7**.

Although HMDS is well known as a silylating agent for alcohols,[15] a catalytic quantity of Me_3SiCl must be added, and the reaction is presumably catalysed by released HCl. Indeed we observed no reaction between compound **1** and HMDS after several days at room temperature, either with or without added **6**. It therefore appears that the catalyst for formation of **7** is an intermediate in the formation of **6**. A related silylation has been reported in the reaction of $[Sc\{N(SiMe_3)_2\}_3]$ with 5 equivalents of $HOSiBu^t_3$[16] in which the products were $Sc(OSiBu^t_3)_3{\cdot}NH_3$, 2HMDS and $2Bu^t_3SiOSiMe_3$. When the reaction was carried out between $[Sc\{N(SiMe_3)_2\}_3]$ and 3 equivalents Bu^t_3SiOH a complex mixture was obtained which contained degradation products of HMDS. No reaction was observed between HMDS and Bu^t_3SiOH, demonstrating that the reaction was catalysed by a scandium complex. A solid state yttrium Lewis acid has also been reported to catalyse the trimethylsilylation of alcohols with HMDS.[17]

Experimental

Unless otherwise stated all the preparations described below were performed under strictly anaerobic conditions using standard Schlenk techniques. Solvents were distilled from

sodium–benzophenone (non-deuteriated) or CaH_2 (deuteriated) and stored under N_2 over 4 Å molecular sieves prior to use. Samples for NMR spectroscopy were sealed under vacuum, and spectra recorded on Bruker WM250 or AC200 spectrometers. ^{29}Si NMR spectra were recorded using inverse gated decoupling and a 5 s pulse delay, in the presence of 0.02 M $Cr(acac)_3$ as a relaxation agent. Elemental analyses were performed in duplicate by Mr S. Apter of this Department. $(C_6H_{11})_7Si_7O_9(OH)_3$ was prepared according to the published method.[18]

Preparation of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$

A solution of $(C_6H_{11})_7Si_7O_9(OH)_3$ (0.706 g, 0.725 mmol) in THF (10 cm^3) was added to a solution of $[Y\{N(SiMe_3)_2\}_3]$ (0.620 g, 1.088 mmol) in THF (10 cm^3). After stirring at room temperature for 1 h the solvent was removed *in vacuo* . Product was extracted into pentane, and the clear pentane solution decanted from a small quantity of undissolved material. Crystals of $[(C_6H_{11})_7Si_7O_{12}Y(THF)_2]$ were isolated from a concentrated pentane solution at −20 °C. Yield = 0.707 g (81%). Found: C, 50.21; H, 7.73%. $C_{50}H_{93}O_{14}Si_7Y$ requires: C, 49.89; H, 7.79%. ^{1}H NMR($CDCl_3$): δ 3.98 (m, THF, 8 H), 1.90 (m, THF, 8 H), 1.73 (vbr, m, 70 H), 1.21 (vbr, m, 70 H) and 0.65 (vbr, m, 14 H). ^{13}C NMR($CDCl_3$): δ 28.01, 27.72, 27.66, 27.56, 27.02, 26.92, 26.63 (CH_2 of cyclohexyl); 25.20, 24.18, 23.28 (*ipso*-C; 3 : 3 : 1); 69.59, 25.46 (THF).

$[(C_6H_{11})_7Si_7O_{12}La(THF)_2]$ was prepared in an analogous manner. Found C, 47.51; H, 7.58%. $C_{50}H_{93}LaO_{14}Si_7$ requires C, 47.45; H, 7.64%. ^{1}H NMR(C_6D_6): δ 4.22 (m, THF, 8 H); 1.92–0.85 (complex set of signals, *ca*. 160 H, cyclohexyl and THF). ^{13}C NMR(C_6D_6): δ 28.92, 28.53, 28.25, 27.90, 27.69 (CH_2 of cyclohexyl); 26.71, 25.40, 24.25 (*ipso*-C; 3 : 3 : 1); 70.63, 26.12 (THF).

Attempted removal of THF from $[(C_6H_{11})_7Si_7O_{12}Y(THF)_2]$

$[(C_6H_{11})_7Si_7O_{12}La(THF)_2]$ (0.070 g, 0.058 mmol) was placed in a 5 mm NMR tube attached to a Young's tap. This was heated to 60 °C *in vacuo* (0.02 mmHg) for 5h. After this time the mass of the sample was 0.067g. The sample was dissolved in $CDCl_3$ (0.5 cm^3) and sealed under vacuum and NMR spectra were recorded. ^{1}H NMR($CDCl_3$): δ 3.86 (br, <1 H, THF), 1.90 (THF), 1.74 (br, 35 H, cyclohexyl), 1.24 (br, 35 H, cyclohexyl) and 0.75 (br, 7 H, cyclohexyl). ^{13}C{-^{1}H} NMR ($CDCl_3$): δ 68.10 (THF), 27.60, 26.88 (broad, CH_2 of cyclohexyl), 25.55 (THF) and 24.46 (complex, broad, *ipso*-CH).

Exposure of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ to air

A sample of $[(C_6H_{11})_7Si_7O_{12}Ln(THF)_2]$ (Ln = La or Y) was exposed to air for 3 days at room temperature. After this time there was no visible change in the sample.

Ln = Y. ^{1}H NMR($CDCl_3$): δ 5.9 (vbr, H_2O), 3.75 (t, J = 6.0, 5 H, THF), 1.86 (t, J = 6.0 Hz, THF), 1.74 (br, 35 H, cyclohexyl), 1.21 (br, 35 H, cyclohexyl) and 0.66 (br, 7 H, cyclohexyl). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 67.97 (THF), 27.99, 27.75, 27.54, 27.37, 27.11, 26.89, 26.43 (CH_2 of cyclohexyl), 25.58 (THF), 25.20, 24.33, 23.11 (3 : 3 : 1, CH of cyclohexyl). IR: $\tilde{\nu}$/cm^{-1} 3322 (O–H), 2925, 1567, 1447, 1377, 1261, 1196, 1110, 894, 848, 800 and 739. Found C, 43.60; H, 7.48%. $C_{42}H_{87}O_{17}Si_7Y$ requires C, 43.88, H, 7.63%.

Ln = La. ^{1}H NMR($CDCl_3$): δ 4.4 (vbr, H_2O), 3.74 (t, J = 6.0, 5 H, THF), 1.86 (t, J = 6.0 Hz, THF), 1.74 (br, 35 H, cyclohexyl), 1.21 (br, 35 H, cyclohexyl) and 0.74 (br, 7 H, cyclohexyl). IR (Nujol): $\tilde{\nu}$/cm^{-1} 3329 (O–H), 2860, 1461, 1376, 1261, 1196, 1110, 1025, 893, 847, 822, 802 and 737. Found C, 40.16; H, 7.40%. $C_{42}H_{87}LaO_{17}Si_7$ requires C, 42.05, H, 7.31%.

Preparation of $[(C_6H_{11})_7Si_7O_{12}Y(PMDTA)]$

To a solution of $[Y\{N(SiMe_3)_2\}_3]$ (0.157 g, 0.275 mmol) in THF (10 cm^3) was added PMDTA (0.032 g, 0.184 mmol) and a solution of $(C_6H_{11})_7Si_7O_9(OH)_3$ (0.178 g, 0.183 mmol) in THF (10 cm^3). The resulting solution was stirred at room temperature for 16h. After this time the solvent was removed *in vacuo* and the resulting solid extracted into toluene. Product was isolated as colourless microcrystals from toluene–petroleum (bp 30–40 °C) at −20 °C. Yield = 0.105 g (46.3%). Found C, 49.30; H, 8.24; N, 3.62%. $C_{51}H_{100}N_3O_{12}Si_7Y$ requires C, 49.69; H, 8.18; N, 3.41%. ^{1}H NMR($CDCl_3$): δ 3.74 (m, THF, 2 H), 2.40 (complex pattern, PMDTA, 18 H), 1.84 (m, THF, 2 H), 1.73 (vbr, m, 35 H) and 1.23 (vbr, m, 35 H) and 0.77 (vbr, m, 7 H). ^{13}C-{^{1}H} NMR} ($CDCl_3$): δ 56.53, 54.46, 45.58, 42.96 (2 : 2 : 4 : 1, PMDTA), 26.47–28.13 (complex pattern, CH_2 of cyclohexyl); 67.93, 25.49 (THF, unco-ord).

Complexes of La and Yb were prepared in an analogous manner. $[(C_6H_{11})_7Si_7O_{12}La(PMDTA)]$: Found C, 46.02; H, 7.79; N, 3.07%; $C_{51}H_{100}LaN_3O_{12}Si_7$ requires C, 47.75; H, 7.86; N, 3.28%. $[(C_6H_{11})_7Si_7O_{12}Yb(PMDTA)]$: Found C, 46.48; H, 7.86; N, 3.30; $C_{51}H_{100}N_3O_{12}Si_7Yb$ requires C, 46.51; H, 7.65; N, 3.19%.

Reaction of $[Yb\{N(SiMe_3)_2\}_3]$ with 2 equivalents $(C_6H_{11})_7Si_7O_9(OH)_3$

A solution of $(C_6H_{11})_7Si_7O_9(OH)_3$ (1.045 g, 1.073 mmol) in THF (10 cm^3) was added to a solution of $[Yb\{N(SiMe_3)_2\}_3]$ (0.351 g, 0.536 mmol) in THF (10 cm^3). After stirring at room temperature for 48 h, the solvent was removed *in vacuo* . Product was extracted into toluene; colourless crystals of $(C_6H_{11})_7Si_7O_9(OSiMe_3)_3$ were obtained by addition of pentane to a concentrated toluene solution and cooling to −20 °C. Yield = 1.112 g (87%). Found: C, 51.70; H, 8.80%. $C_{51}H_{104}O_{12}Si_{10}$ requires C, 51.47; H, 8.81%. ^{29}Si NMR: δ 8.64, −68.35, −69.50 and −70.17. ^{13}C NMR: δ 25.25, 24.87, 23.04 and 1.99.

Preparation of $[(C_6H_{11})_7Si_7O_{11}(OSiMe_3)LaCl(THF)]$

$[(C_6H_{11})_7Si_7O_{12}La(THF)_2]$ (0.451g, 0.382 mmol) was disssolved in THF (10 cm^3). Me_3SiCl (48 µl, 0.378 mmol) was added and the solution stirred at room temperature for 16h. The solvent was removed *in vacuo* and the product extracted into pentane. The pentane solution was evaporated to dryness and the resulting white glass (0.392 g) crystallised from THF (4 cm^3) by slow diffusion of MeCN (4 cm^3). Found C, 44.57; H, 7.50; Cl, 3.42%. $C_{49}H_{94}ClLaO_{13}Si_8$ requires C, 45.61; H, 7.34; Cl, 2.75%. ^{1}H NMR($CDCl_3$): δ 3.88 (m, THF, 8 H); 1.87 (m, THF, 8 H); 1.74 (vbr, m, 70 H), 1.24 (vbr, m, 70 H), 0.75 (vbr, m, 14 H) and 0.16 (s, 18 H, $OSiMe_3$). ^{13}C NMR($CDCl_3$): δ 27.55, 27.52, 27.43, 26.80, 26.75, 26.67, 26.61, 26.55, 26.51 (CH_2 of cyclohexyl); 24.67, 23.68, 23.47, 23.21, 23.09 (*ipso*-C; 1 : 2 : 2 : 1 : 1); 68.59, 25.45 (THF); 1.68 ($OSiMe_3$).

$[(C_6H_{11})_7Si_7O_{11}(OSiMe_3)YCl(THF)]$ was prepared in an analogous manner. Found C, 45.77; H, 7.78%. $C_{49}H_{94}ClO_{13}Si_8Y$ requires C, 47.45; H, 7.64%. ^{1}H NMR($CDCl_3$): δ 3.83 (m, THF, 8 H); 1.87 (m, THF, 8 H); 1.73 (vbr, m, 70 H), 1.24 (vbr, m, 70 H), 0.74 (vbr, m, 14 H) and 0.15 (s, 18 H, $OSiMe_3$). ^{13}C NMR($CDCl_3$): δ 27.53, 27.45, 27.41, 26.75, 26.60 (CH_2 of cyclohexyl); 24.62, 23.82, 23.45, 23.17, 23.05 (*ipso*-C; 1 : 2 : 2 : 1 : 1); 68.44, 25.46 (THF); 1.82 ($OSiMe_3$).

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References

1 I. P. Rothwell, *Polyhedron*, 1985, **4**, 177.
2 P. L. Watson and G. W. Parshall, *Acc. Chem. Res.*, 1985, **18**, 51.

3 H. Raba, J.-Y. Saillard and R. Hoffmann, *J. Am. Chem. Soc.*, 1986, **108**, 4327.
4 J. W. Bruno, G. M. Smith, T. J. Marks, C. K. Fair, A. J. Schultz and J. M. Williams, *J. Am. Chem. Soc.*, 1986, **108**, 40.
5 C. Lecuyer, F. Quignard, A. Choplin, D. Olivier and J.-M. Basset, *Angew. Chem.*, *Int. Ed. Engl.*, 1991, **30**, 1660.
6 M. S. Eisen and T. J. Marks, *J. Mol. Catal.*, 1994, **86**, 23.
7 W. A. Herrmann, R. Anwander, V. Dufaud and W. Scherer, *Angew. Chem.*, *Int. Ed. Engl.*, 1994, **33**, 1285.
8 J. A. Annand, H. C. Aspinall and A. Steiner, *Inorg. Chem.*, 1999, **38**, 3941.
9 F. J. Feher, S. L. Gonzales and J. W. Ziller, *Inorg. Chem.*, 1988, **27**, 3440.
10 F. J. Feher, T. A. Budzichowski and J. W. Ziller, *Inorg. Chem.*, 1992, **31**, 5100.
11 F. J. Feher and J. F. Walzer, *Inorg. Chem.*, 1991, **30**, 1689.
12 T. Maschmeyer, M. C. Klunduk, C. M. Martin, D. S. Shephard, J. M. Thomas and B. F. G. Johnson, *Chem. Commun.*, 1997, 1847.
13 D. C. Bradley, H. Chudzynska, M. B. Hursthouse and M. Motevalli, *Polyhedron*, 1993, **12**, 1907.
14 G. Malandrino, R. Licata, F. Castelli, I. L. Fragala and C. Benelli, *Inorg. Chem.*, 1995 **34**, 6233.
15 B. A. Anderson, in *Encyclopaedia of Reagents for Organic Synthesis*, ed. L. A. Paquette, J. Wiley, New York, 1995, vol. 4, p. 2661.
16 K. J. Covert, D. R. Neithamer, M. C. Zonneville, R. E. LaPointe, C. P. Schaller and P. T. Wolczanski, *Inorg. Chem.*, 1991, **30**, 2494.
17 P. Kumar, G. C. G. Pais and A. Keshavaraja, *J. Chem. Res. (S)*, 1996, 376.
18 F. J. Feher, D. A. Newman and J. F. Walzer, *J. Am. Chem. Soc.*, 1989, **111**, 1741.