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Article

Precursors for MOCVD and ALD of Rare Earth Oxides–Complexes of the Early Lanthanides with a Donor-Functionalized Alkoxide Ligand

Helen C. Aspinall,* Jamie F. Bickley, Jeffrey M. Gaskell, Anthony C. Jones, and Gael Labat

Department of Chemistry, Donnan and Robert Robinson Laboratories, University of Liverpool,
Crown Street, Liverpool L69 7ZD, U.K.

Paul R. Chalker

Department of Engineering, University of Liverpool, Liverpool L69 3BX, U.K.

Paul A. Williams

Epichem Limited, Power Road, Bromborough, Wirral CH62 3QF, U.K.

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Complexes of the early lanthanides with the donor-functionalized alkoxide ligand mmp (Hmmp = $HOCMe_2CH_2$-OMe, 1-methoxy-2-methylpropan-2-ol) are excellent precursors for Metal Organic Chemical Vapor Deposition (MOCVD) and Atomic Layer Deposition (ALD) of lanthanide oxides; however, their coordination chemistry, which is the subject of this paper, is rather complex. Precursors for MOCVD and ALD of lanthanide oxides are prepared by the reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with 3 equiv of the alcohol Hmmp in toluene in the presence of 1 equiv of tetraglyme and are indefinitely stable in solution. Reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with 3 equiv of Hmmp in the absence of stabilizing Lewis bases gives complex condensed products with empirical formula $[\{Ln(mmp)_{3-n}\}_2O_n]$. These condensed products show poor volatility and are unsatisfactory precursors for MOCVD or ALD of oxides. The cluster complex $[La_3(\mu_3,\kappa^2\text{-mmp})_2(\mu_2,\kappa^2\text{-mmp})_3(mmp)_4]$ has been prepared by careful reaction of $[La\{N(SiMe_3)_2\}_3]$ with 4 equiv of Hmmp and has been characterized by single-crystal X-ray diffraction. Salt metathesis reactions using M(mmp) (M = Li or Na) are unreliable routes to $[Ln(mmp)_3]$. Crystals of the heterometallic cluster complex $[NaLa_3(\mu_3\text{-OH})(\mu_3,\kappa^2\text{-mmp})_2(\mu_2,\kappa^2\text{-mmp})_4(mmp)_3]$ were isolated from the reaction of $[La(NO_3)_3(tetraglyme)]$ with 3 equiv of Na(mmp), and crystals of $[Li(\kappa^2\text{-Hmmp})Pr(\mu_2,\eta^2\text{-mmp})_4)LiCl]$ were isolated from the reaction of $PrCl_3$ with 3 equiv of Li(mmp); both of these complexes have been characterized by single-crystal X-ray diffraction.

Introduction

Rare earth oxides are becoming increasingly important in microelectronics: they have the necessary properties to be used as replacements for SiO_2 as the gate dielectric layer in field effect transistors,[1] and they are also attractive as capacitor layers in next generation DRAMs (Dynamic Random Access Memory). They are good insulators due to their large band gaps (3.9 eV for Pr_2O_3, 5.6 eV for Gd_2O_3), and they have high dielectric constants (Gd_2O_3 $\kappa \sim 16$, La_2O_3 $\kappa \sim 27$, Pr_2O_3 $\kappa \sim 26-30$) and good thermodynamic stability on silicon. In addition, Pr_2O_3 and Gd_2O_3 offer the possibility of epitaxial growth on silicon, which eliminates the problem of current leakage along polycrystalline film grain boundaries. Metal organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) are both excellent techniques for the growth of high purity oxide films, but both these techniques require precursor compounds with reasonable volatility, which is not always easy to achieve in lanthanide chemistry. Because of the large radii of Ln^{3+}, complexes of the lanthanides require either multidentate or extremely bulky ligands in order to stabilize the monomeric structures and hence achieve the required volatility. This is a significant challenge for the synthetic chemist.

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* To whom correspondence should be addressed. E-mail: hca@liv.ac.uk.

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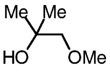
The oldest known class of volatile lanthanide complexes is the tris-β-diketonates which have been known since the early years of the 20th century. They are easily prepared and have excellent ambient stability. [Ln(thd)$_3$] (thd = tetramethyl-3,5-heptanedionate) complexes have been investigated for MOCVD of oxides of La,[2] Pr,[3] Nd,[4] and Gd.[5] However these precursors are thermally quite robust and require high growth temperatures that are generally incompatible with microelectronics applications, where high growth temperatures can lead to problems such as increased dopant diffusion, and the oxide films produced are often contaminated with trace carbon. A number of volatile cyclopentadienyl−rare earth complexes, [Cp$_3$Ln] and [(MeCp)$_3$Ln], have been used for ALD of Ln_2O_3 (Ln = Y,[6] Er,[7] and Gd[8]), but they are not suited for MOCVD due to heavy carbon contamination in the grown layers.

Metal alkoxides have been widely used in MOCVD and ALD,[9] but simple lanthanide alkoxides are involatile. 3-Methoxy-2-methylpropan-2-ol (Hmmp) **(1)** is a donor-functionalized alcohol which was introduced by Anwander and Herrmann in the 1990s, and some complexes of the later lanthanides and Y were reported in 1997.[10] An earlier report had shown that rare earth complexes with donor-functionalized alkoxide ligands have promising volatility,[11] and [Lu(mmp)$_3$]$_2$ was found to sublime at 95 °C and 10^{-3} Torr. Although the crystal structure of [Lu(mmp)$_3$]$_2$ was reported, detailed characterization of complexes of the early lanthanides was conspicuous by its absence.



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Hmmp

We have previously used volatile mmp complexes of Bi,[12] Hf,[13] and Zr[13] for deposition of oxide layers, and so when we began our work on liquid injection MOCVD of lanthanide oxides we chose complexes with mmp as precursors. Using these precursors we have successfully grown thin films of La_2O_3,[14] PrO_x,[15,16] Nd_2O_3,[17] and Gd_2O_3,[18] all of which show exceptionally low, in some cases undetectable, carbon contamination.[18] We have also used mmp complexes of the lanthanides for liquid injection atomic layer deposition (ALD) of lanthanide oxides.[19] It quickly became apparent to us that, although we were able to prepare reproducible and reliable precursors for oxide growth, the chemistry of the early Ln with Hmmp is far from simple. Full details of MOCVD and ALD using mmp complexes of the lanthanides have already been published,[14−19] but to date no homoleptic mmp complexes of the early lanthanides have been structurally characterized. Because of the usefulness of these complexes as precursors for deposition of lanthanide oxides we felt it was important to unravel some of the complexities that we encountered, and in this paper we report on the chemistry of early Ln with Hmmp.

Results and Discussion

Synthesis of Complexes. The Silylamide Route. We began our work with the well-established ‘silylamide route’ i.e. the reaction of 3 equiv of Hmmp with the appropriate lanthanide silylamide [Ln{N(SiMe$_3$)$_2$}$_3$]

$$[\mathrm{Ln}\{\mathrm{N(SiMe_3)_2}\}_3] \xrightarrow{\mathrm{3Hmmp}} [\mathrm{Ln(mmp)_3}] + 3\mathrm{HN(SiMe_3)_2}$$

This route generally results in clean reaction, giving a volatile and easily removed byproduct, and it had been used successfully by Anwander and Herrmann for the synthesis of lanthanide complexes with donor-functionalized alkoxides.[10,11] Preliminary experiments on an NMR tube scale showed that a C_6D_6 solution of [La{N(SiMe$_3$)$_2$}$_3$] reacts cleanly with 3 equiv of Hmmp to eliminate 3 equiv of HN(SiMe$_3$)$_2$, and so we fully expected that reaction on a preparative scale would give a quantitative yield of [La(mmp)$_3$].

Addition of 3 equiv of Hmmp to a toluene solution of [Y{N(SiMe$_3$)$_2$}$_3$] at room temperature followed by removal of volatiles in vacuo gave an oily product analyzing as [Y(mmp)$_3$] and with a simple ^{1}H NMR spectrum (Figure S1) similar to that reported for [Lu(mmp)$_3$]$_2$.[10] However, repeating the reaction under the same conditions with [La{N(SiMe$_3$)$_2$}$_3$] gave an oily product with an extremely complex ^{1}H NMR spectrum; reaction in pentane resulted in precipitation of the product as a white powder, which showed a similar ^{1}H NMR spectrum. When the reaction was performed in toluene at −40 °C and the sample was kept at ≤0 °C, we obtained a much simpler ^{1}H NMR spectrum.

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However, when this sample was allowed to warm to room-temperature, its ^{1}H NMR spectrum increased in complexity until it appeared very similar to that of the product from a room-temperature reaction (see Figure S2(a),(b)).

Elemental analysis of the products isolated from the reaction of $[La\{N(SiMe_3)_2\}_3]$ with 3 equiv of Hmmp gave consistent values that were very low in C and H. Anwander and Herrmann reported formation of a partially hydrolyzed oxo-hydroxo-bridged cluster $[Lu_4(O)(OH)(mmp)_9]$ on reaction of $[Lu\{N(SiMe_3)_2\}_3]$ with wet Hmmp,[10] and the IR spectrum of this complex showed ν(O−H) at 3487 cm^{-1}. A more complete hydrolysis of $[La(mmp)_3]$ could account for the low C and H content; however, we rule out hydrolysis as the cause of the condensation reaction on the following grounds: (i) in our hands no condensation was observed in the reaction of $[Y\{N(SiMe_3)_2\}_3]$ with Hmmp and (ii) we have shown (vide infra) that condensation is prevented in the presence of appropriate additives. Unlike $[Lu_4(O)(OH)(mmp)_9]$, the complexes that we isolated showed no ν(O−H) in the IR spectrum. We propose that the products isolated from the reaction of $[Ln\{N(SiMe_3)_2\}_2]$ with 3 equiv of Hmmp are oxo-bridged clusters of the empirical formula $[\{Ln(mmp)_{3-n}\}_2(\mu\text{-}O)_n]_x$. Elemental analysis indicates that products with $n = 1.5$ and $n = 1.0$ are obtained from the reaction of $[La\{N(SiMe_3)_2\}_3]$ in pentane with 3 or 4 equiv of Hmmp, respectively; the results are much more variable with Pr and Nd. Hydrolysis of all of the isolated complexes gives Hmmp as the only organic product, proving that there is no degradation of mmp ligands within the complexes. There are numerous examples of the condensation of simple lanthanide and yttrium alkoxides to form oxo-bridged clusters, e.g., $[Pr_4O_2(OCH_2CMe_3)_8]_n$,[20] $[Pr_4O_2(OCH_2CH_2OMe)_8]$,[20] $[Y_5(\mu\text{-}O)(OPr^i)_{13}]$,[21] $[Cp_5Y_5(\mu\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)]$,[22] $[Ce_3(OBu^t)_{10}O]$,[23] and $[La_5(\mu\text{-}O)(OBu^t)_{13}]$;[24] in all these cases it is proposed that the bridging O atom is derived from an alkoxide by C−O cleavage, rather than from partial hydrolysis, although the exact mechanism of the process is not discussed. A highly disordered structure $[Dy_6(\mu_6\text{-}O)(OCH_2CMe_3)_{12}]^{4+}$ has been observed on crystallization of $[Dy(OCH_2CMe_3)_3]_4$ from THF, but the origin of the μ_6-O in this structure has not been elucidated.[25]

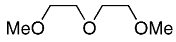
Horii et al. have investigated the decomposition of $[Hf(mmp)_4]$ during MOCVD of HfO_2 and have proposed the process shown in Scheme 1.[26]

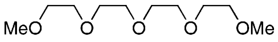
The key step in this reaction is a β-hydrogen elimination from coordinated mmp to give Hf−OH and the alkene $Me_2C{=}CH(OMe)$. In the lanthanide system, it is possible that this process could be catalyzed under mild conditions by a Lewis acidic Ln^{3+} center to form Ln−OH species which then react further by intramolecular H-transfer to form oxo species as the final products.

Our work suggests that a simple homoleptic alkoxide of empirical formula $[Ln(mmp)_3]$ is the initial product of reaction between $[Ln\{N(SiMe_3)_2\}_3]$ and Hmmp in toluene, and our ^{1}H NMR studies show that this product is stable in the reaction mixture in the presence of eliminated $HN(SiMe_3)_2$. However, as soon as the reaction mixture is concentrated, the condensation reaction begins, though it is significantly slowed at low temperature, and, as we show, it is prevented in the presence of some Lewis bases. This suggests that the condensation reaction is catalyzed by the coordinatively unsaturated (and therefore Lewis acidic) Ln^{3+} center.

Attempts To Stabilize the '$[Ln(mmp)_3]$' Moiety. For MOCVD applications it is essential that the precursor has reasonable volatility; the product isolated from the simple reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with 3 equiv of Hmmp was very poor in this respect and did not give good growth rates. It was very soon clear to us that the mmp complexes of the early lanthanides are significantly less stable than those of yttrium and the later lanthanides and that this difference in stability is due to a higher degree of coordinative unsaturation in complexes of the larger early lanthanides. We had two objectives: first, to produce a stabilized volatile precursor suitable for MOCVD and, second, to understand some of the complexities of the coordination chemistry of the early lanthanides with mmp.

The first objective was addressed by an empirical approach: it was necessary to add a donor ligand which would not interfere with oxide growth, and we chose to start with the readily available polyethers diglyme and tetraglyme.


diglyme


tetraglyme

The tridentate ether diglyme gave no stabilization: the product isolated from the reaction of $[Ln\{N(SiMe_3)_2\}_3]$ with 3 equiv of Hmmp in the presence of 1 equiv of diglyme showed a complex ^{1}H NMR spectrum, and its elemental analysis indicated low C and H content. However, addition of 1 equiv of tetraglyme to $[Ln\{N(SiMe_3)_2\}_3]$ prior to addition of 3 equiv of Hmmp gave an oily product with a simple ^{1}H NMR spectrum and an elemental analysis consistent with the empirical formula $[Ln(mmp)_3]\cdot$tetraglyme. This reaction could be performed in either toluene or pentane, and the product was indefinitely stable in solution at room temperature. It had sufficient volatility to be used in liquid injection MOCVD and gave excellent growth rates of highly pure lanthanide oxide, even in the absence of additional O_2.[14,16−19] The ^{1}H NMR spectrum of tetraglyme-stabilized $[Pr(mmp)_3]$ showed no paramagnetic shifting of the tetraglyme resonances, although the resonances due to mmp ligands were shifted as expected. This suggests that the tetraglyme is not in the inner coordination sphere of the complex. Triglyme has been shown to act as an outer-sphere

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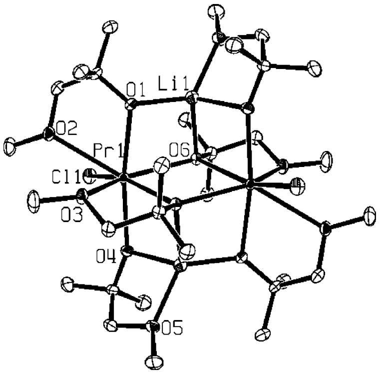

Figure 1. Structure of [LiPr(mmp)$_3$Cl]$_2$.

ligand in [Y(hfac)$_3$(H$_2$O)$_2$]·triglyme,[27] and we propose that tetraglyme is similarly associated with the outer coordination sphere in [Ln(mmp)$_3$]·tetraglyme complexes. Unfortunately detailed structural characterization has so far eluded us: these complexes have resisted all attempts at crystallization.

In the presence of LiCl we were able to isolate the crystalline product [LiPrCl(mmp)$_3$]$_2$ **2**, which was characterized by X-ray diffraction (see Figure 1).[16] This was our first successful crystallographic characterization of stabilized '[Ln(mmp)$_3$]' and proved that, in the presence of a sufficiently strong donor (in this case Cl$^-$), the elusive [Ln(mmp)$_3$] could be trapped before it had the opportunity to condense to more complex species. It also demonstrated that the formation of condensed species in the absence of an additional Lewis base was not due to hydrolysis.

The presence of LiCl is not acceptable in a MOCVD precursor, and so we continued in our quest to find a stable crystalline derivative of [Ln(mmp)$_3$] which would be an acceptable precursor. We found that the presence of excess Hmmp stabilized [Ln(mmp)$_3$], and we obtained relatively simple (though rather broad) ^{1}H NMR spectra of these products (see Figures S3 and S4 for spectra of Pr complexes). Preliminary results show that "[Pr(mmp)$_3$(Hmmp)]" is an effective precursor for MOCVD of PrO$_x$.

We have been able to isolate crystals from a reaction of [La{N(SiMe$_3$)$_2$}$_3$] with 4 equiv of Hmmp in pentane, and X-ray diffraction has shown these crystals to be [La$_3$(μ_3,κ^2-mmp)$_2$(μ_2,κ^2-mmp)$_3$(mmp)$_4$] **3**, shown in Figure 3. Although the crystalline product contains no Hmmp, the presence of the free alcohol in the crystallization solution has prevented the condensation reaction. A summary of reactions of [Ln{N(SiMe$_3$)$_2$}$_3$] (Ln = La, Pr) with Hmmp is shown in Scheme 2.

Salt Methathesis Routes. (a) Salt Metathesis Reactions Starting from [Ln(NO$_3$)$_3$(tetraglyme)]. Although the 'silylamide route' carried out under the correct conditions is effective for the preparation of Ln complexes with mmp, the need to synthesize [Ln{N(SiMe$_3$)$_2$}$_3$] as a starting material may be seen as a disadvantage, and so we investigated some more direct routes to [Ln(mmp)$_3$]. [La(NO$_3$)$_3$(tetraglyme)] is an easily prepared anhydrous lanthanide complex which we have used as a starting material for synthesis of lanthanum aryloxides,[28] and the presence of tetraglyme, which we know to stabilize [La(mmp)$_3$], made this complex an attractive candidate as a starting material for preparation of [La(mmp)$_3$]. Addition of 3 equiv of Na(mmp) in THF to a THF suspension of [La(NO$_3$)$_3$(tetraglyme)] resulted in immediate reaction and precipitation of NaNO$_3$. However, complete replacement of the nitrates was never achieved at room temperature: prolonged reflux was always required to obtain a nitrate-free product, and on some occasions even this resulted in formation of an isolated product which was analyzed as [La(NO$_3$)(mmp)$_2$]. On the occasions when we did succeed in complete replacement of nitrates, the nitrate-free product was obtained as an oil on removal of THF, and a simple ^{1}H NMR spectrum showed that [Ln(mmp)$_3$] had been stabilized. The oily product was very soluble in diethyl ether, but rapid addition of pentane resulted in precipitation of a white solid with low C and H content, identical to that obtained from the unstabilized 'silylamide route'. Complete replacement of nitrates was a difficult to achieve in this synthetic route, and so unreacted Na(mmp) was frequently present in reaction mixtures even after prolonged periods of reflux. On several occasions we were able to isolate very high yields of highly crystalline material from diethyl ether and pentane. X-ray diffraction showed this material to be a heterometallic cluster [NaLa$_3$(μ_3-OH)(mmp)$_9$] **4**, and elemental analysis confirmed that the crystal structure is representative of the bulk material.

The reactions of [La(NO$_3$)$_3$(tetraglyme)] with Na(mmp) are summarized in Scheme 3.

As shown in Scheme 3, if the nitrate substitution reaction goes to 90% completion, there is sufficient unreacted Na(mmp) to account for a high isolated yield of a NaLa$_3$ heterometallic cluster. We propose that the hydroxy group originates from a condensation reaction analogous to that which occurs in unstabilized [La(mmp)$_3$]. We can rule out adventitious H$_2$O as a source of the OH group as **4** is obtained in reproducibly high yields, and an excess of NaH is used in the preparation of Na(mmp) used in this reaction.

(b) Salt Metathesis Reactions Starting from LnCl$_3$. The salt metathesis reaction of [La(NO$_3$)$_3$(tetraglyme)] with Na(mmp) was not a reliable route to stabilized [La(mmp)$_3$], so we turned our attention to reactions with LnCl$_3$. Although reactions of LnCl$_3$ with alkali metal reagents often lead to chloride- or alkali-metal-contaminated products,[29]we considered that this route was worth some preliminary investigation. The reaction of LaCl$_3$ with 3 equiv of Na(mmp) in THF gave an oily product which resisted all attempts at crystallization, and so this route was not pursued further. However, reaction of LnCl$_3$ (Ln = La or Pr) with 3 equiv of Li(mmp) in THF gave products with simple ^{1}H NMR spectra, indicative of a stabilized product. In the case of Pr we were able to isolate a crystalline product, which was shown by X-ray diffraction to be [Li$_2$PrCl(mmp)$_4$(Hmmp)] **5**. The presence of Li(mmp) in the product can be accounted for by an incomplete reaction between Li(mmp) and PrCl$_3$; the

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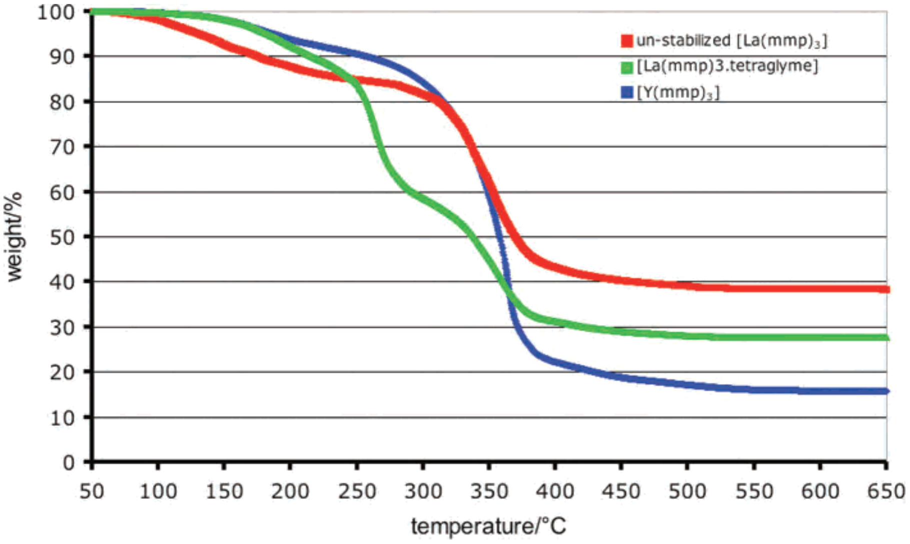


Figure 2. TGA plots for $[Y(mmp)_3]$, unstabilized "$[La(mmp)_3]$", and $[La(mmp)_3]\cdot$tetraglyme.

Scheme 1. Decomposition of $[Hf(mmp)_4]$ during MOCVD

$$[Hf(mmp)_4] \xrightarrow{\beta\text{-H elimination}} [Hf(OH)_4] + 4Me_2C{=}CH(OMe)$$

$$[Hf(OH)_2(mmp)_2] \xrightarrow[\text{intramolecular H-transfer}]{\beta\text{-H elimination}} HfO_2 + 2Hmmp + 2Me_2C{=}CH(OMe)$$

presence of a slight excess of Hmmp during the preparation of Li(mmp) would account for its presence in the final crystalline product, which shows an IR absorption at 3218 cm^{-1} due to the coordinated Hmmp.

TGA Studies. Figure 2 shows TGA plots for unstabilized "$[La(mmp)_3]$", $[La(mmp)_3]\cdot$tetraglyme, and $[Y(mmp)_3]$. Our interest in growth of rare earth oxide films has been limited to the early lanthanides, and so we have not investigated $[Y(mmp)_3]_n$ as a precursor for MOCVD; however, its relative stability compared with mmp complexes of the early lanthanides made it an interesting model compound for TGA studies. The TGA plot shown in Figure 2 shows a first weight loss of approximately 6% between 150 °C and 225 °C, followed by the major weight loss between 350 °C and 370 °C, and the residue after heating to 550 °C corresponds to 16% of the original mass. Although TGA cannot distinguish unequivocally between decomposition and sublimation, there is clearly some sublimation of a Y-containing species: complete decomposition of $[Y(mmp)_3]$ ($M_r = 398.3$) to $0.5Y_2O_3$ ($M_r = 225.8$) would correspond to a residue of 28.3%, significantly higher than the residue we observe.

$[La(mmp)_3\cdot$tetraglyme$]$ is the precursor that we have used with great success for MOCVD of La_2O_3, and therefore its TGA is of most interest to us. Three weight losses are observed; the first (ca. 14%) beginning at around 150 °C, which is consistent with the elimination of 1 equiv of 1-methoxy-2-methylprop-1-ene as shown for the decomposition of $[Hf(mmp)_4]$ in Scheme 1 (theoretical weight loss = 12.8%). It is probable that the next weight loss of ca. 28%, occurring between 250 °C and 310 °C, is due to loss of tetraglyme (bp 275 °C), and the final weight loss, which is complete at 515 °C, is due to loss of the remaining mmp ligands, leaving a residue of La_2O_3.

As we have already shown, unstabilized "$[La(mmp)_3]$" is rather poorly defined, and even freshly prepared material has undergone significant condensation to oxo bridged oligomers. Detailed interpretation of the TGA of unstabilized "$[La(mmp)_3]$" is therefore impossible. However it is clear that the first weight loss occurs at temperatures as low as 50 °C, and a second process begins at ca. 300 °C, which is close to the temperature at which the final weight loss from $[La(mmp)_3\cdot$tetraglyme$]$ begins. The residue of 38% is consistent with complete decomposition to La_2O_3.

In contrast to $[Y(mmp)_3]$, the high residues from unstabilized "$[La(mmp)_3]$"(38%) and $[La(mmp)_3\cdot$tetraglyme$]$ (28%) are consistent with complete thermal decomposition to La_2O_3 with no sublimation. Whereas unstabilized "$[La(mmp)_3]$" loses weight slowly at temperatures above 50 °C; the presence of tetraglyme is seen to increase thermal stability so that there is negligible weight loss below ca. 150 °C, slightly below the evaporator temperature that we use in our liquid injection MOCVD studies.

Although the rare earth mmp complexes that we have investigated show significant residues in atmospheric pressure TGA, this lack of volatility and thermal stability does not preclude their use as precursors for liquid injection MOCVD, where the precursor in solution is kept at ambient temperature until it is injected into the reactor, which has an operating pressure of approximately 1 mBar. Indeed the poor thermal stability of the rare earth mmp complexes gives them a real advantage as MOCVD precursors when compared to $[Ln(thd)_3]$ which require high growth temperatures which are incompatible with microelectronics applications. Our work on liquid injection MOCVD of La_2O_3 using $[La(mmp)_3]\cdot$tetraglyme is consistent with the TGA results: the onset of growth occurs at ca. 250 °C, and the maximum growth rate occurs at 400−450 °C.[14]

Crystal Structures. $[La_3(\mu_3,\kappa^2\text{-mmp})_2(\mu_2,\kappa^2\text{-mmp})_3(mmp)_4]$ 3. An ORTEP plot of **3** is shown in Figure 3, and a plot showing just La and O atoms is shown in Figure 4. The three La atoms of this cluster are linked by face- and edge-bridging mmp ligands so that each La atom is bonded

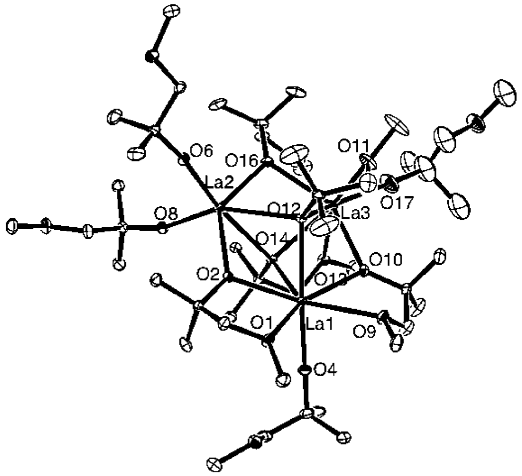


Figure 3. Structure of $[La_3(\mu_3,\kappa^2\text{-mmp})_2(\mu_2,\kappa^2\text{-mmp})_3(\text{mmp})_4]$ **3**. Selected distances (Å) are as follows: La1−O14, 2.507(5); La2−O14, 2.721(5); La3−O14, 2.563(5); La1−O12, 2.550(5); La2−O12, 2.637(5); La3−O12, 2.634(5); O16−La2, 2.440(5); O16−La3, 2.475(5); O2−La1, 2.446(5); O2−La2, 2.434(5); O10−La1, 2.452(5); O10−La3, 2.454(5); La2−O6, 2.239(5); La2−O8, 2.229(5); La3−O17, 2.265(8); La1−O4, 2.219(5); La1−O1, 2.684(5); La1−O9, 2.678(5); La3−O11, 2.618(6); La3−O13, 2.683(5); La3−O15, 2.772(6).

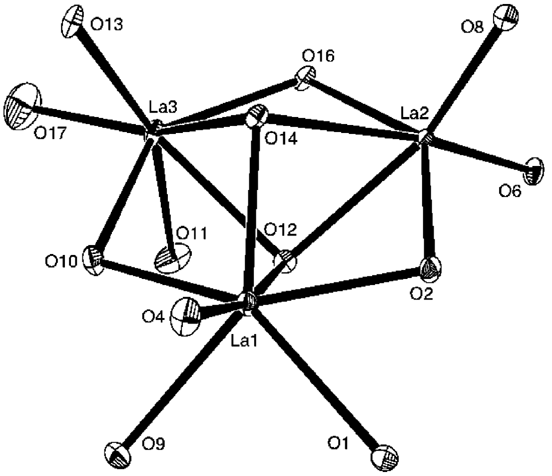
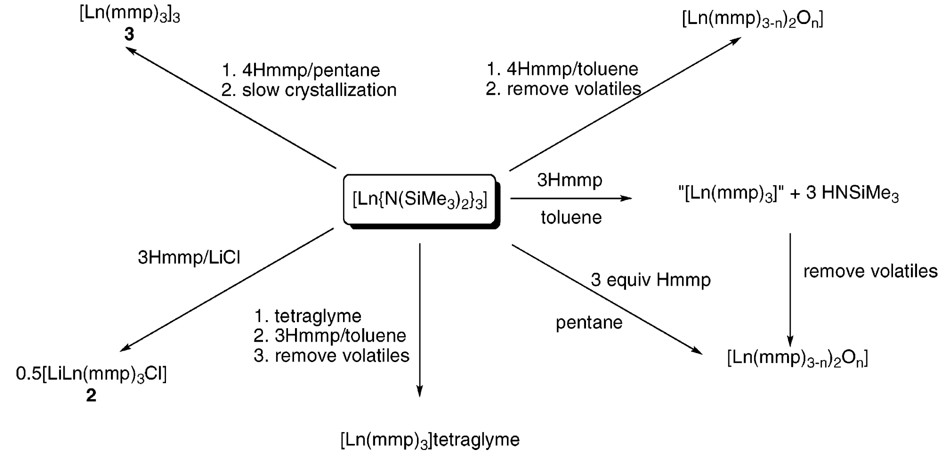


Figure 4. La_3O_{13} core of **3**.

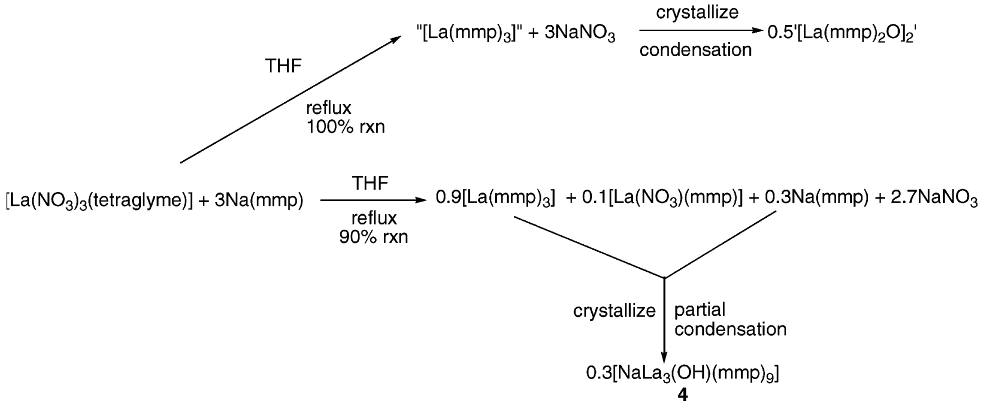
to the alkoxide groups of two face-bridging and two edge-bridging ligands. La2 is six-coordinate; in addition to the bridging alkoxide ligands it is also bonded to two ‘dangling’ alkoxides. La1 is bonded to the OMe groups of two edge-bridging mmp ligands and also has one ‘dangling’ ligand, making it seven-coordinate. La3 is also seven-coordinate, being bonded to the OMe groups of both face-bridging and one edge-bridging ligands as well as having one ‘dangling’ alkoxide. O12 is 1.375 Å out of the La3 plane, and O14 is 1.354 Å out of the plane. The average La−O12 distance is 2.61(5) Å; the average La−O14 distance is 2.6(1) Å.

$[NaLa_3(\mu_3\text{-OH})(\mu_3,\kappa^2\text{-mmp})_2(\mu_2,\kappa^2\text{-mmp})_4(\text{mmp})_3]$ 4. An ORTEP plot of **4** is shown in Figure 5, and a diagram showing just La, Na, and O atoms is shown in Figure 6. The three La atoms of the cluster are linked by face- and edge-bridging and ‘dangling’ mmp ligands as well as by a

Scheme 2. Summary of Reactions of $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La or Pr) with Hmmp



Scheme 3. Summary of Reactions of $[Ln(NO_3)_3(\text{tetraglyme})]$ with Na(mmp)



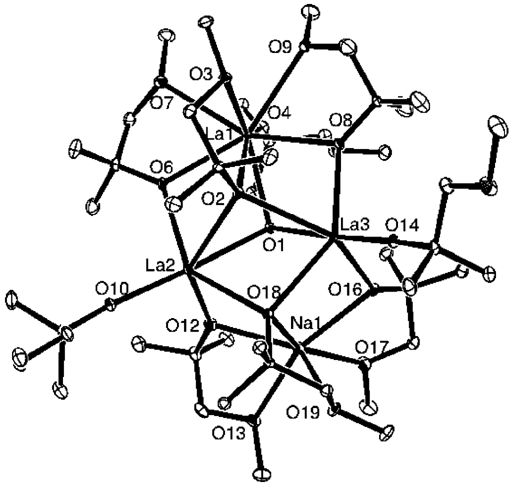


Figure 5. Structure of [$NaLa_3(\mu_3\text{-}OH)(\mu_3,\kappa^2\text{-}mmp)_2(\mu_2,\kappa^2\text{-}mmp)_4(mmp)_3$] **4**. Selected distances (Å) are as follows: La1−O1, 2.417(2); La1−O2, 2.620(2); La1−O3, 2.662(2); La1−O4, 2.231(2); La1−O6, 2.479(2); La1−O7, 2.695(3); La1−O8, 2.433(2); La1−O9, 2.683(3); La2−O1, 2.536(2); La2−O2, 2.590(2); La2−O6, 2.446(2); La2−O10, 2.223(2); La2−O12, 2.285(3); La2−O18, 2.511(2); La3−O1, 2.528(2); La3−O2, 2.607(2); La3−O8, 2.433(2); La3−O14, 2.218(3); La3−O16, 2.305(2); La3−O18, 2.500(2); Na1−O12, 2.411(3); Na1−O13, 2.427(3); Na1−O16, 2.432(3); Na1−O17, 2.376(3); Na1−O18, 2.543(3); Na1−O19, 2.386(3).

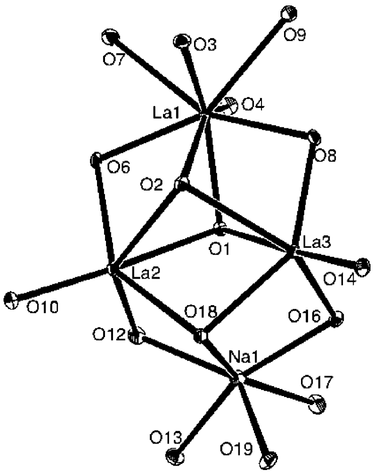


Figure 6. $NaLa_3O_{16}$ core of **4**.

face-bridging μ_3-OH, and each La atom is additionally bonded to one 'dangling' mmp. La1 is unique: it is eight-coordinate, and, in addition to the μ_3-OH, the edge- and face-bridging alkoxide groups, and the 'dangling' mmp ligand, it is also coordinated by the OMe groups of the bridging mmp ligands. The coordination spheres of La2 and La3 are equivalent. Both are six-coordinate, and, in addition to the face bridging alkoxide and hydroxide groups, each is also bonded to a μ_2-alkoxide which bridges with La1, to a μ_3- and a μ_2-alkoxide which form bridges with Na1, and to one 'dangling' mmp. La2 and La3 are not bonded to any OMe groups. The Na atom is bonded to the alkoxide and OMe groups of one μ_3- and two μ_2-mmp ligands, making it six-coordinate. The μ_3-OH group is 1.193 Å out of the La_3 plane and is unsymmetrically bound to the three La atoms, with one short distance (to La1) and two slightly longer distances (to La2 and La3). The average La−μ_3-OH distance is 2.49(6) Å. There are very few crystallographically characterized examples of the [$La_3(\mu_3\text{-}OH)$] motif; the earliest example is in a trinuclear Schiff base complex,[30] where the μ_3-OH group is 1.02 Å out of the La_3 plane and the average La−OH distance is 2.55(3) Å. The μ_3-alkoxide O atom of **4** is 1.41 Å out of the La_3 plane, which is slightly longer than the corresponding μ_3-alkoxide to La_3 plane distances of **3**. The average μ_3-alkoxide to La distance in **4** is 2.61(1) Å, very close to the corresponding value of 2.602 Å found in **3**.

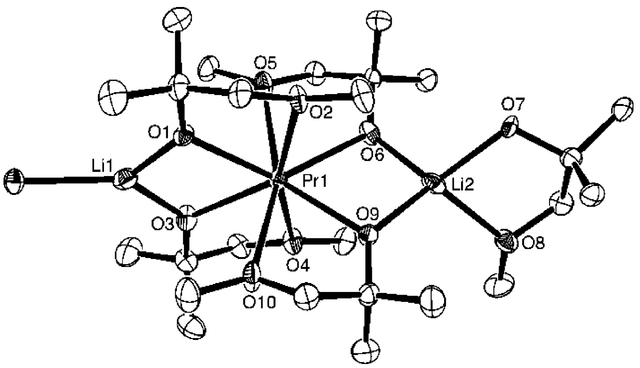


Figure 7. Structure of [$Li(\kappa^2\text{-}Hmmp)Pr(\mu_2,\kappa^2\text{-}mmp)_4)LiCl$] **5**. Selected distances (Å) are as follows: Pr1−O1, 2.363(3); Pr1−O2, 2.624(4); Pr1−O3, 2.368(4); Pr1−O4, 2.624(4); Pr1−O5, 2.616(4); Pr1−O6, 2.343(3); Pr1−O9, 2.340(4); Pr1−O10, 2.620(4); Li1−O1, 1.841(11); Li1−O3, 1.836(10); Li2−O6, 1.919(11); Li2−O7, 2.002(10); Li2−O8, 2.105(11); Li2−O9, 1.913(9).

[$Li(\eta^2\text{-}Hmmp)Pr(\mu_2,\kappa^2\text{-}mmp)_4)LiCl$] 5. The structure of complex **5** is shown in Figure 7. This complex contains one neutral Hmmp ligand, but as we have not located an alcoholic H atom, it is impossible for us to make an unambiguous identification of this neutral ligand. There is no uniquely long Pr−$OCMe_2$ distance, and so it is unlikely that the OH is bonded to Pr. The Li2−O9 distance of 1.913(9) Å is significantly longer than either Li1−O1 (1.841(11) Å) or Li1−O3 (1.836(10) Å), and therefore it seems most likely that O9 is the alcoholic O atom. A search of the Cambridge Crystallographic Database[31] supports this assignment: the average Li−O(alcohol) distance is 1.949 Å (longer than Li2−O9), and the minimum is 1.852 Å (longer than either Li1−O1 or Li1−O3).

Conclusions

Our published work[14−19] has shown that complexes of the lanthanides with the donor functionalized mmp ligand are excellent precursors for MOCVD of lanthanide oxides. The coordination chemistry of the early lanthanides with mmp is much more complex than that of the later lanthanides and yttrium. In the absence of an additional Lewis base, [$Ln(mmp)_3$] (Ln = La or Pr) decompose to form complex species which we propose to have an empirical formula [$\{Ln(mmp)_{3-n}\}_2O_n$]. The presence of tetraglyme (1 equiv per Ln atom) is sufficient to stabilize solutions of "[$Ln(mmp)_3$]" indefinitely although ^{1}H NMR spectroscopy shows that the tetraglyme is not in the inner coordination sphere of Ln. Similarly [$Ln(mmp)_3$] is stabilized in the presence of an

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(30) Aspinall, H. C.; Black, J.; Dodd, I.; Harding, M. M.; Winkley, S. J. *J. Chem. Soc., Dalton Trans.* **1993**, 709.

(31) Fletcher, D. A.; McMeeking, R. F.; Parkin, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 746.

Table 1. Crystallographic Data for Compounds **3**−**5**

	3	**4**	**5**
empirical formula	$C_{45}H_{99}La_3O_{18}$	$C_{45}H_{100}La_3NaO_{19}$	$C_{27}H_{57}Cl_7Li_2O_{10}Pr$
formula weight	1344.97	1384.97	944.67
crystal system	monoclinic	triclinic	monoclinic
space group	$C2/c$	P-1	$P2_1/c$
a/Å	39.443(4)	11.5140(7)	9.9344(11)
b/Å	14.7341(15)	13.5134(8)	19.756(2)
c/Å	20.618(2)	22.3467(13)	22.601(3)
α/deg	90.00	74.7490(10)	90.00
β/deg	100.036(2)	78.4960(10)	95.708(2)
γ/deg	90.00	71.2260(10)	90.00
V/Å^3	11799(2)	3150.9(3)	4413.8(9)
Z	8	2	4
D_c/g cm^{-3}	1.514	1.46	1.422
F(000)	5472	1408	1932
μ/mm^{-1}	2.194	2.064	1.570
crystal dimensions/mm	0.4 × 0.2 × 0.2	0.5 × 0.3 × 0.2	0.3 × 0.2 × 0.2
temp/K	100(2)	100(2)	100(2)
$\theta_{min/max}$/deg	1.05, 25.00	1.70, 25.00	1.37, 28.26
reflections	10394	11105	10932
R1	0.0460	0.0299	0.0510
wR2	0.1222	0.0802	0.1101
$\Delta\rho_{min,max}$/e Å^{-3}	−2.109, 2.424	−0.815, 2.178	−3.118, 1.490
goodness of fit	1.312	1.074	0.761

excess of Hmmp, and [$La_3(mmp)_9$] has been isolated and characterized crystallographically. The most effective route to [$Ln(mmp)_3$] is the reaction of [$Ln\{N(SiMe_3)_2\}_3$] with an excess of Hmmp. Salt metathesis routes to [$Ln(mmp)_3$] starting from $LnCl_3$ or [$Ln(NO_3)_3$(tetraglyme)] are rather unreliable, often resulting in incomplete exchange and incorporation of alkali metal in the product.

Experimental Section

The preparation of all lanthanide complexes was performed under strictly anaerobic and anhydrous conditions using standard Schlenk techniques. Hmmp was dried over activate 4 Å molecular sieves prior to use. Nondeuterated solvents were distilled from sodium/benzophenone ketyl and stored under N_2 over activated 4 Å molecular sieves prior to use. Deuterated solvents were distilled from CaH_2 prior to use. NMR spectra were recorded on a Bruker Avance 400 spectrometer. NMR samples of lanthanide complexes were sealed under vacuum. Elemental analyses were performed in duplicate by Mr. S. Apter of this department, using a Carlo Erba 1106 analyzer.

TGA data were obtained on a Shimadzu TGA51 analyzer housed within a N_2 purged box, and the sample was in a Pt cell. The N_2 flow rate was 50 cm^3/min, and the temperature ramp rate was 20 °C/min.

Crystallographic Studies. All X-ray data were collected at 213-(2) K using a Bruker-AXS Smart Apex CCD diffractometer (Mo-Kα, graphite monochromator) in the ϕ rotation scan mode. The structures were solved by direct methods with the SHELXS97 package and refined using full-matrix least-squares on F^2 (SHELXL97). Crystallographic data are summarized in Table 1.

Preparation of [$Y(mmp)_3$]. Dry Hmmp (0.85 cm^3, 8.1 mmol) was added to a solution of [$Y\{N(SiMe_3)_2\}_3$] (1.41 g, 2.47 mmol) in toluene (30 cm^3). The mixture was stirred for 10 min before the solvent was removed in vacuo to give a pale yellow oil. Yield = 0.91 g (93%). Analysis: found C, 44.7; H, 8.2%. Calcd for $C_{15}H_{33}O_6Y$: C, 45.2; H, 8.35%. ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 6H, CH_3), 3.15 (s, 2H, CH_2), 3.34 (s, 3H, OCH_3).

Reaction of Lanthanum Silylamide with 3 Equiv of Hmmp in Toluene. Dry Hmmp (0.57 cm^3, 5.01 mmol) was added to a stirred solution of [$La\{N(SiMe_3)_2\}_3$] (1.035 g, 1.67 mmol) in toluene (30 cm^3). The solution was stirred for 10 min, and then the solvent was removed in vacuo, to give the product as a pale brown oil. Yield = 0.48 g. Analysis: found C, 29.2; H, 5.4%. Calcd for $La_4(C_5H_{11}O_2)_6O_2$: C, 29.48; H, 5.44%. ^{1}H NMR ($CDCl_3$): δ 1−2 (complex region, CH_3), 3−4 (complex resonances, CH_2, OCH_3). IR (cm^{-1}, neat oil): 2960s, 1457m, 1357m, 1261m, 1229m, 1172m, 1084m, 965m.

Reaction of Lanthanum Silylamide with 3 Equiv of Hmmp in Pentane. Dry Hmmp (0.413 cm^3, 3.7 mmol) was added to a stirred solution of [$La\{N(SiMe_3)_2\}_3$] (0.742 g, 1.19 mmol) in pentane (30 cm^3). Product precipitated as a pale yellow solid. The supernatant was decanted off, and the product was dried under a flow of dry N_2. Yield = 0.33 g. Analysis: found C, 30.0; H, 5.9%. Calcd for $La_4(C_5H_{11}O_2)_6O_2$: C, 29.48; H, 5.44%. ^{1}H NMR ($CDCl_3$): δ ($CDCl_3$): δ 1−2 (complex resonances, CH_3), 3−4 (complex resonances, CH_2, OCH_3).

Reaction of Lanthanum Silylamide with 4 Equiv of Hmmp in Pentane. Hmmp (1.021 cm^3, 8.89 mmol) was added to added to a solution of [$La(N(SiMe_3)_2)_3$] (1.376 g, 2.22 mmol) in pentane. The reaction mixture was stirred at room temperature for 10 min, and then the solvent was removed in vacuo to give product as a pale orange oil. Yield = 0.71 g. Analysis: found: C, 34.7; H, 6.6%. Calcd for [$\{La(C_5H_{11}O_2)_2\}_2O$]: C, 34.01; H, 6.28%. ^{1}H NMR ($CDCl_3$): δ 1.21, 1.44, 1.50, 1.62, 1.71 (s, CH_3) 3.20, 3.21, 3.24, 3.38, 3.40, 3.47, 3.70, 3.72, 3.73, 3.75, 3.89 (singlets, CH_2 and OCH_3). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 25.66, 27.997 (m, CCH_3), 59.48 (m, OCH_3), 70.44, (m, OCH_2), 84.04, (m, CCH$_3$). IR (cm^{-1}, neat oil): 2960s, 1458m, 1358m, 1347m, 1274s, 1250s, 1230s, 1172s, 1109s, 1087s, 957s, 944s, 843s.

Crystals of **3** suitable for single-crystal X-ray diffraction were obtained by a reaction analogous to that described above, except that the oil formed on removal of the solvent from the reaction mixture was immediately cooled to −18 °C and stored at this temperature for several days. Under these conditions the oil crystallized completely.

Stabilization of [$La(mmp)_3$] with Tetraglyme in Pentane. Tetraglyme (0.73 cm^3, 3.29 mmol) was added to a solution of [$La\{N(SiMe_3)_2\}_3$] (2.036 g, 3.29 mmol) in pentane, leading to a slight clouding of the solution. Dry Hmmp (1.13 cm^3, 9.87 mmol) was added to the solution, causing a deepening of the color and a slight increase of temperature. The mixture was stirred for 10 min at room temperature, and the solvent was removed in vacuo to give the product as a viscous brown oil. Analysis: found: C, 43.8; H: 7.9%. Calcd for $C_{25}H_{55}O_{11}La$: C, 44.77; H, 8.26%. ^{1}H NMR main resonances ($CDCl_3$): δ 1.21, 1.45, 1.50, 1.62, 1.71 (s, CH_3) 3.19, 3.21, 3.23, 3.37, 3.40, 3.76, 3.88 (s, CH_2, OCH_3) 3.44, 3.60, 3.61, 3.62, 3.70, 3.71, 3.72 (tetraglyme). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 27.9, 30.3 (m, CCH_3), 61.8, (m, OCH_3), 73.3, (m, OCH_2), 86.7, (m, CCH_3). IR (cm^{-1}, neat oil): 2960s, 2873s, 1458m, 1348m, 1171s, 1108s.

Preparation of $[NaLa_3(\mu_3\text{-OH})(\mu_3,\kappa^2\text{-mmp})_2(\mu_2,\kappa^2\text{-mmp})_4(mmp)_3]$ 4. Na(mmp) was prepared by addition of Hmmp (0.95 cm^3, 8.28 mmol) to a suspension of washed NaH (0.203 g, 8.46 mmol) in THF (30 cm^3). The Na(mmp) solution was added to a stirred suspension of $[La(NO_3)_3(\text{tetraglyme})]$ (1.51 g, 2.75 mmol) in THF, resulting in the formation of a fine white precipitate. The reaction mixture was heated to reflux for 1.5 h. The white precipitate of $NaNO_3$ was allowed to settle, and the clear solution was decanted off. The solvent was removed in vacuo to give a glassy solid. Colorless crystals of the product were grown from toluene/petroleum ether at −18 °C. Yield = 0.84 g (66%). Analysis: found C, 39.85; H, 7.85%. Calcd for $C_{45}H_{100}O_{19}La_3Na$: C, 39.02; H, 7.27%.

Preparation of $[Li(\kappa^2\text{-Hmmp})Pr(\mu_2,\kappa^2\text{-mmp})_4)LiCl]$ 5. A suspension of $PrCl_3$ (2.261 g, 9.14 mmol) in THF (30 cm^3) was sonicated for 2 h. Li(mmp) was prepared by dropwise addition of Bu^{n}Li in hexane (2.37 M, 11.58 cm^3, 27.43 mmol) to a solution of dry Hmmp (3.15 cm^3, 27.43 mmol) in THF (20 cm^3). The THF solution of Li(mmp) was added to the stirred suspension of $PrCl_3$, and stirring was continued at room temperature for 16 h to give a clear, green solution. The solvent was removed in vacuo to give a glassy green solid. Product was extracted into $CHCl_3$, and crystals were grown by addition of petroleum ether to the $CHCl_3$ solution. Yield: 3.4 g (75%). IR (cm^{-1}, Nujol) 3218.

Acknowledgment. We thank EPSRC for financial support (studentship to J.M.G.).

Supporting Information Available: CIF files for compounds **3**, **4**, and **5** and ^{1}H NMR spectra of products from the reaction of $[Ln\{N(SiMe_3)_2\}_3]$ (Ln = La, Pr) with Hmmp and Hmmp/tetraglyme. This material is available free of charge via the Internet at http://pubs.acs.org.

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