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Synthesis of a New Class of Compounds Containing a Ln−O−Al Arrangement and Their Reactions and Catalytic Properties

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Abstract: Synthesis of a new class of compounds containing a Ln−O−Al moiety has been accomplished by the reaction of LAlOH(Me) (L = $\mathrm{HC(CMeNAr)_2}$, Ar = 2,6-$i\mathrm{Pr_2C_6H_3}$) with a series of $\mathrm{Cp_3Ln}$ compounds. The terminal Al−OH group shows selective reactivity, and the complexes $\mathrm{Cp_2Ln(THF)}$−O−AlL(Me) (Ln = Yb, **1**; Er, **2**; Dy, **3**), $\mathrm{Cp_2Yb}$−O−AlL(Me) (**4**), and $\mathrm{Cp_3Ln(\mu\text{-}OH)AlL(Me)}$ (Ln = Er, **5**; Dy, **6**; Sm, **7**) were obtained. This allows further insight into the proton exchange process, and two different mechanisms, intermolecular and intramolecular elimination of CpH, are proposed under different conditions. Complexes **1**−**4**, **6**, and **7** have been characterized by X-ray structural analyses which reveals a Ln−O−Al or Ln(μ-OH)Al core in these complexes. The obtuse Ln−O−Al angles fall in the range 151.9−169.8°. The reaction of **1** or **4** with $\mathrm{Me_3SnF}$ in toluene under refluxing conditions unexpectedly yielded the compounds $\mathrm{[Cp_2Yb(\mu\text{-}OSnMe_3)]_2}$ (**8**) and LAl(Me)F (**9**). Reactions of LAlOH(Me) with the mono- and dicyclopentadienyl complexes LYbCp(Cl) (**10**) and $\mathrm{LYbCp_2}$ (**11**) supported by the bulky β-diketiminate ligand were unsuccessful. However, the reaction of LAl(OH)Me with $\mathrm{LYbN(SiMe_3)_2Cl}$ (**12**) containing a labile Yb−N bond leads to the formation of LYbCl−O−AlL(Me) (**13**) under elimination of $\mathrm{HN(SiMe_3)_2}$. Furthermore, complexes **1**, **3**, **4**, and **6** exhibit good catalytic activity for the polymerization of ϵ-caprolactone.

Introduction

There is widespread interest in the chemistry of lanthanides containing heterometal atoms, especially those where aluminum is present as the other component.[1] One aspect is the synthesis of mixed-metal solid-state materials with unusual physical properties.[2] The other is the fact that lanthanide aluminum heterobimetallic complexes are good catalysts for the polymerization of olefinic monomers, methyl methacrylate (MMA), lactones, and cyclic carbonates;[3] this is analogous in manner to the development of group 4 metal and aluminum bimetallic olefin polymerization catalysts.[4] In this regard, the work of Evans[1a,5] and Yasuda[3b,c,6] on the synthesis and catalytic properties of the lanthanide aluminum heterometallic complexes is notable. Although a variety of structural types and compositions have been identified thus far, the majority of them are aluminum alkyl adducts formed through OR or OAr bridges.[1,5] Thus, it was of interest to develop a synthetic strategy to incorporate rare-earth metals on Al−O systems to generate compounds containing the Ln−O−Al unit, where the oxygen atom is not bonded to alkyl or aryl groups. It was envisaged that the Ln−O−Al unit would provide a stable framework to assemble new complexes of practical application such as catalysts.

We were encouraged with the results we obtained on syntheses, structures, and applications of alumoxanes,[7] aided by the complexes containing terminal Al−OH groups.[7a−d] The utility of such molecules as suitable synthons for the preparation of various building blocks has already been shown by assembling tri- and tetranuclear alumoxanes.[7b,8] Furthermore, we have also shown that the compound $\mathrm{Cp_2Zr(Me)}$−O−AlL(Me) when activated with methylalumoxane (MAO) serves as a good

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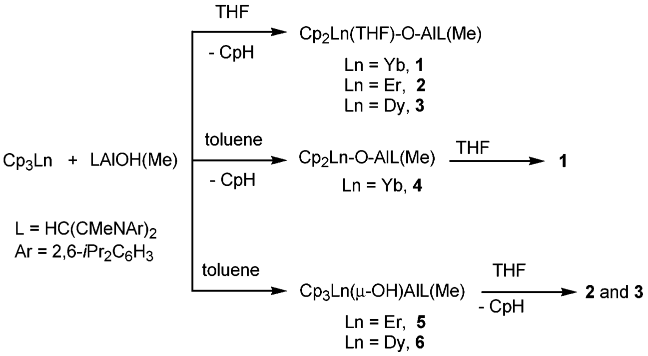
Scheme 1

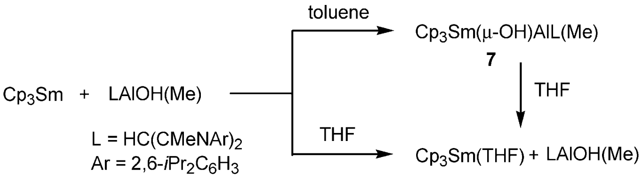


catalyst for ethylene polymerization.[7f] Therefore, in the following we report on the reaction of Cp$_3$Ln (Ln = Yb, Er, Dy, and Sm) with aluminum monohydroxide LAlOH(Me) (L = HC(CMeNAr)$_2$, Ar = 2,6-*i*Pr$_2$C$_6$H$_3$). Complexes of general composition Cp$_2$Ln(THF)−O−AlL(Me) (Ln = Yb, Er, and Dy), Cp$_2$Yb−O−AlL(Me), and Cp$_3$Ln(μ-OH)AlL(Me) (Ln = Er, Dy, and Sm) were obtained. Consequently, it turned out that the complex LAlOH(Me) with terminal Al−OH group is a suitable precursor to prepare a new class of lanthanide aluminum heterobimetallic compounds, which has a selective reactivity for the reported lanthanide series and can act as a Brønsted acid or a Lewis base. In addition, reactions of LAlOH(Me) with ytterbium complexes supported by a bulky β-diketiminate ligand were also examined. The reactivity and catalytic properties of these new complexes have been primarily investigated.

Results and Discussion

Reaction of LAlOH(Me) with Cp$_3$Ln and Formation of Complexes 1−7. Reaction of LAlOH(Me) with 1 equiv of Cp$_3$Ln was carried out in THF at room temperature to afford Cp$_2$Ln(THF)−O−AlL(Me) (Ln = Yb, **1**; Er, **2**; Dy, **3**) (Scheme 1) in good yields accompanied by color change and precipitate formation. The elimination of CpH and the formation of the Ln−O−Al moiety was confirmed by EI-MS, elemental analyses, and X-ray structural analyses. A coordinated THF molecule allows the lanthanide ion to be of preferred tetrahedral geometry. In the meantime, we were also interested in exploring the reactions in noncoordinating solvent such as toluene. Thus, the reaction of Cp$_3$Yb and LAlOH(Me) in toluene yielded the compound Cp$_2$Yb−O−AlL(Me) (**4**) followed by the color change from dark green to yellow-green. However, the reaction of Cp$_3$Ln (Ln = Er and Dy) and LAlOH(Me) in toluene leads to the formation of compounds Cp$_3$Ln(μ-OH)AlL(Me) (Ln = Er, **5**; Dy, **6**), with the Al−OH unit coordinated as a Lewis base to the Ln center. Elimination of CpH was not observed even in refluxing toluene. Compounds **4**−**6** can be converted to **1**−**3**, respectively, when treated with THF.

Scheme 2



The reaction of Cp$_3$Sm and LAlOH(Me) in THF did not occur even under refluxing conditions; instead, Cp$_3$Sm(THF) was formed. However, when the reaction was carried out in toluene the adduct Cp$_3$Sm(μ-OH)AlL(Me) (**7**) was isolated. Furthermore, the dissociation of **7** to Cp$_3$Sm(THF) and LAlOH(Me) was observed when **7** was treated with THF (Scheme 2). This indicates that LAlOH(Me) is a weaker base than THF.

Although Cp$_3$Ln is widely employed to prepare dicyclopentadienyl derivatives through protolytic exchange and elimination of CpH,[9] limited information is available concerning the reaction pathway due to the higher reactivity of the precursor used, such as carboxylic acids[9a] and alcohols.[9b,c] The mild reactivity of the Al−OH unit allows the isolation of some of the intermediates and sheds light on the reaction pathway. On the basis of the facts discussed above, it is obvious that the formation of the Ln−O−Al unit is a multiple-step process. The first step is the coordination of a Lewis base to the unsaturated lanthanide center. The adduct Cp$_3$Ln(THF) is preferentially formed, in the presence of THF, while with toluene as a solvent, LAlOH(Me) acts as a Lewis base and coordinates to the Ln center to yield Cp$_3$Ln(μ-OH)AlL(Me) (Scheme 3). The latter dissociates to Cp$_3$Ln(THF) and LAlOH(Me) when THF was added. The second step involves formation of the Ln−O−Al moiety through a protolytic exchange, which proceeds with either an intermolecular elimination of CpH between Cp$_3$Ln(THF) and LAlOH(Me) in THF or an intramolecular elimination of CpH from Cp$_3$Yb(μ-OH)AlL(Me) in toluene. However, Cp$_3$Sm(THF) and Cp$_3$Ln(μ-OH)AlL(Me) (Ln = Er, Dy, and Sm) are stable enough to be isolated and do not react further under the given conditions.

Compounds **1**−**7** were isolated as crystalline and thermally stable solids, which are moderately air- and moisture-sensitive. Complexes **1**−**3** and **5**−**7** have a poor solubility in THF or toluene at ambient temperature, but can be dissolved under slight heating. Compound **4** is soluble in toluene at room temperature. The melting point of the complexes **5**−**7** lies in the range **5** (205−207 °C) < **6** (258−260 °C) < **7** (323−325 °C). The molecular ions of **1**−**3** were detected in the EI-MS without the coordinated THF molecule albeit in low intensity, followed by the most intense peak corresponding to $[M-THF-Me]^+$, which indicates stability of the Ln−O−Al core. The peaks at *m/z* 758, 754, and 742 can be attributed to $[M-CpH-Me]^+$ for **5**−**7**, respectively. In the IR spectra of **5**−**7**, a broad absorption band near 3500 cm^{-1} is assigned to the stretching frequency of the bridging hydroxide group.

X-ray Structural Analyses. Crystals of complexes **1**−**4**, **6**−**8**, **11**, and **12** have been investigated by single-crystal X-ray technique (Table 1). Unfortunately, due to the poor crystal quality of **5** satisfactory data could not be obtained. Selected structures (**2**, **4**, **7**, and **11**) are shown in Figures 1−4, whereas

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Scheme 3

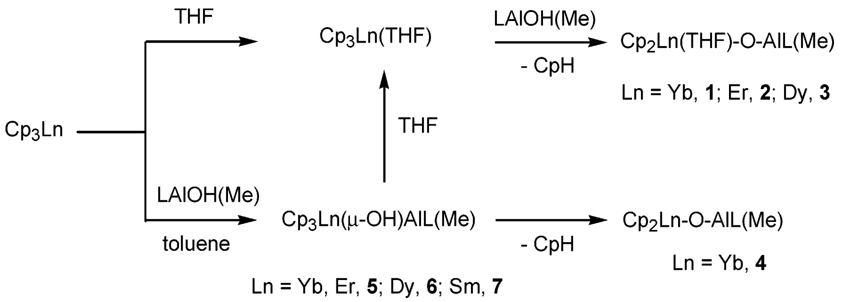

Table 1. Crystallographic Data for Complexes **1**−**4**, **6**−**8**, **11**, and **12**

	1	**2**	**3**	**4**·2 toluene	**6**
formula	$C_{44}H_{62}AlN_2O_2Yb$	$C_{44}H_{62}AlErN_2O_2$	$C_{44}H_{62}AlDyN_2O_2$	$C_{54}H_{70}AlN_2OYb$	$C_{45}H_{60}AlDyN_2O$
fw	850.98	845.20	840.44	963.14	834.43
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/m$
temp, K	100(2)	133(2)	133(2)	133(2)	133(2)
λ, Å	1.54178	0.71073	0.71073	0.71073	0.71073
a, Å	8.812(1)	8.850(1)	8.854(1)	9.130(2)	10.188(2)
b, Å	37.845(2)	37.991(5)	37.975(2)	12.498(3)	19.669(4)
c, Å	12.032(1)	12.072(3)	12.106(1)	42.211(8)	10.536(2)
β, deg	97.06(1)	97.07(3)	97.17(1)	93.36(3)	109.43(3)
V, Å^3	3982(1)	4028(1)	4039(1)	4808(2)	1991(1)
Z	4	4	4	4	2
crystal color	yellow	pink	colorless	yellow	colorless
no. of data/restraints/params	5655/190/512	6766/126/502	6937/191/511	7906/350/594	3476/222/295
GoF on F^2	1.041	0.980	0.917	1.276	1.109
$R1,^a$ w$R2^b$ ($I > 2\sigma(I)$)	0.0199, 0.0503	0.0221, 0.0506	0.0545, 0.0748	0.0340, 0.0808	0.0508, 0.1022
$R1,^a$ w$R2^b$ (all data)	0.0210, 0.0511	0.0294, 0.0523	0.1169, 0.0874	0.0378, 0.0819	0.0575, 0.1046
largest diff. peak/hole, e Å^{-3}	0.415/−0.537	0.496/−0.902	0.714/−1.120	0.780/−1.319	2.238/−2.436

	7	**8**	**11**·0.5 hexane	**12**
formula	$C_{45}H_{60}AlN_2OSm$	$C_{26}H_{38}O_2Sn_2Yb_2$	$C_{42}H_{58}N_2Yb$	$C_{35}H_{59}ClN_3Si_2Yb$
fw	822.28	966.02	763.94	786.524
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/m$	$P2_1/n$	$P2_1/n$	$P2_1/c$
temp, K	100(2)	133(2)	133(2)	133(2)
λ, Å	1.54178	0.71073	0.71073	0.71073
a, Å	10.214(1)	8.288(2)	16.326(2)	17.120(3)
b, Å	19.606(1)	16.180(6)	9.565(1)	18.184(4)
c, Å	10.556(1)	10.394(2)	23.801(4)	12.887(3)
β, deg	109.37(1)	98.53(2)	94.17(1)	104.48(3)
V, Å^3	1994(1)	1378(1)	3707(1)	3884(1)
Z	2	2	4	4
crystal color	yellow	yellow	red	red
no. of data/restraints/params	2950/206/294	2366/0/148	6344/259/500	6663/0/399
GoF on F^2	1.206	1.033	1.031	1.045
$R1,^a$ w$R2^b$ ($I > 2\sigma(I)$)	0.0302, 0.0683	0.0153, 0.0305	0.0174, 0.0379	0.0191, 0.0470
$R1,^a$ w$R2^b$ (all data)	0.0314, 0.0686	0.0186, 0.0313	0.0209, 0.0388	0.0228, 0.0481
largest diff. peak/hole, e Å^{-3}	0.600/−0.526	0.354/−0.492	0.343/−0.470	0.712/−0.839

all the structures and structural fit of compounds **1**−**3**, **6**, and **7** for the sake of comparison are depicted in Figures S1−S12 in the Supporting Information. Compounds **1**−**3** are isomorphous (Figures S1−S4), and the lanthanide ion possesses a pseudo-tetrahedral geometry surrounded by two cyclopentadienyl rings and two oxygen atoms (Figure 1). The central Ln−O−Al core is obtuse (**1**, 169.5°; **2**, 168.6°; **3**, 167.4°). The Ln−O (Yb−O(1) 2.020 Å, Er−O(1) 2.043 Å, Dy−O(1) 2.056 Å) and average Ln−X_{Cp} (X_{Cp} is the centroid of the Cp group, Yb−X_{Cp} 2.37 Å, Er−X_{Cp} 2.40 Å, Dy−X_{Cp} 2.43 Å), Al−O (av 1.69 Å) and Al−N (av 1.94 Å) distances are almost unaffected by the different covalent radii of the corresponding lanthanide ion (Yb 1.94, Er 1.73, Dy 1.75 Å).[10] The Yb−O distances in **1** are similar to the corresponding ones in $[(C_5H_4Me)_2YbTHF]_2$-(μ-O)[11] (2.02 and 2.35 Å) and $(Ar'O)_2(THF)_2Yb(\mu\text{-}OAr')_2AlMe_2$[5b] (Ar′ = 2,6-$Me_2C_6H_3$) (2.06 and 2.37 Å). Compounds **2** and **3** are rare examples of structurally characterized Er and Dy compounds containing Ln−O bonds.

The Yb center in compound **4** is not coordinated to a solvent molecule (Figure 2) and the $O(1)YbX_{Cp1}X_{Cp2}$ core is almost planar with the sum of angles 357°. However, the coordination sphere of the Yb atom is partly saturated by two agostic interactions to two hydrogen atoms H(28A) and H(28C) (2.66 and 2.53 Å) from the *i*Pr moiety of the ligand (Figure 2). The Yb−O−Al angle (168.8°) is similar to that in **1**. The shorter Yb−O (2.000 Å) and longer Al−O (1.713 Å) distances (Table

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[10] For covalent atomic radii see web page of Cambridge Structural Database: http://www.ccdc.cam.ac.uk/products/csd/radii/.

[11] Adam, M.; Massarweh, G.; Fischer, R. D. *J. Organomet. Chem.* **1991**, *405*, C33−C37.

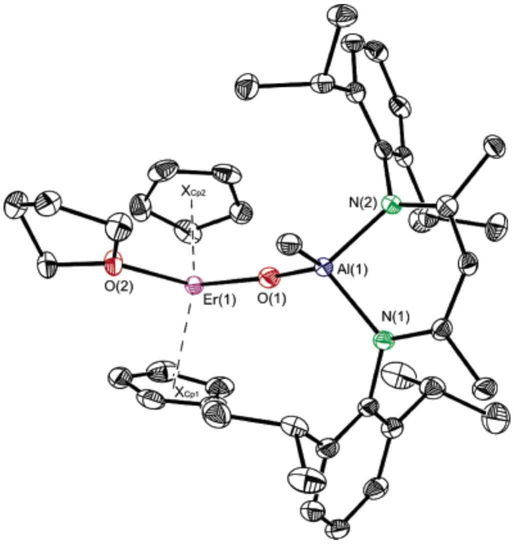

Figure 1. Molecular structure of **2** (50% probability thermal ellipsoids). Hydrogen atoms and the disorder of the THF molecule are omitted for clarity.

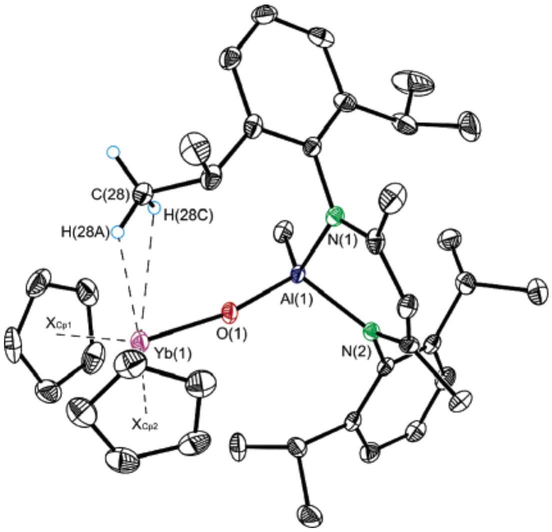

Figure 2. Molecular structure of **4** (50% probability thermal ellipsoids). Solvating toluene molecules and hydrogen atoms, except those on C(28), are omitted for clarity.

2) compared to the corresponding ones in **1** indicate the stronger bonding interaction of the Yb and O atoms in **4**. The Yb−O bond lengths in **1** (2.020 Å) and in **4** (2.000 Å) are the shortest Yb−O separations observed thus far.[11,12] The Yb−X_{Cp} distance (2.34 Å) is a little shorter than that in **1** (2.37 Å) due to the lower coordination number of the Yb center.

Compounds **6** and **7** crystallize in the monoclinic space group $P2_1/m$ with half of a molecule in the asymmetric unit and are isomorphous (Table 1). The mirror plane passes through the Ln(μ-OH)Al unit (Figure 3). The coordination sphere of Dy and Sm in **6** and **7** is similar to that in $Cp_3Dy(THF)$ and $Cp_3Sm(THF)$.[13] The Dy−OH distance (2.431 Å) in **6** can be compared with those of Dy−O(THF) in $Cp_3Dy(THF)$ (2.46 Å)[13] and **3** (2.36 Å) and is longer than that of Dy−O(1) in **3** (2.056 Å). The Sm−OH distance (2.500 Å) in **7** is similar to that in $Cp_3Sm(THF)$ (2.51 Å).[13b] The Al−O distances (1.766 Å) in **6** and (1.758 Å) **7** are much longer than those in complexes **1**−**4** due to their coordinative character and steric bulk of the $LnCp_3$ moiety. However, the Dy−O−Al and Sm−O−Al angles (153.6° and 151.9°) (Table 2) are less obtuse than those in **1**−**4**. Selected bond lengths and angles for complexes **1**−**7** are given in Table 2.

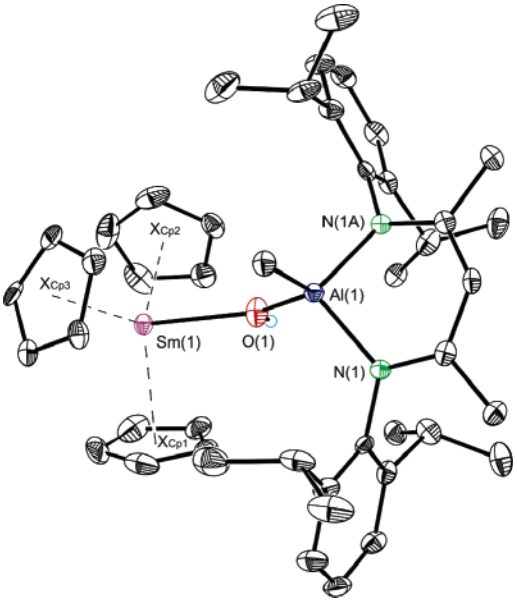

Figure 3. Molecular structure of **7** (50% probability thermal ellipsoids). Hydrogen atoms of the C−H bonds, second positions of the disordered isopropyl, and Cp groups are omitted for clarity.

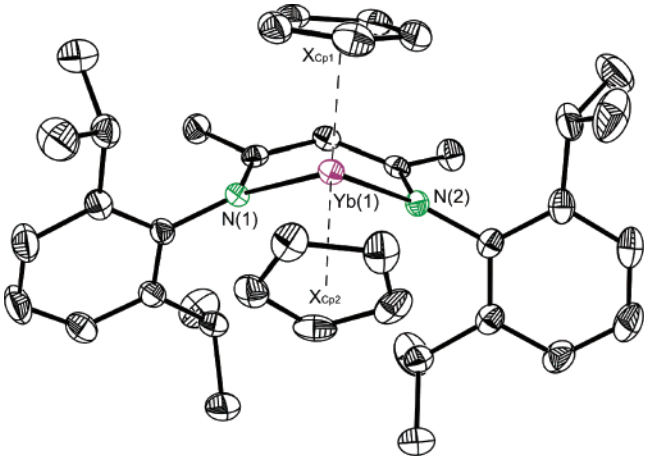

Figure 4. Molecular structure of **11** (50% probability thermal ellipsoids). Solvating hexane molecule and the hydrogen atoms are omitted for clarity.

Reaction of 1 and 4 with Me_3SnF. The Me group in LAlOH(Me) has been used thus far as the fourth substituent on Al and has played only the role of a spectator ligand. It was of interest to prepare other derivatives by using the Me group. It is well-known that the reaction of aluminum alkyls with Me_3SnF results in the formation of aluminum florides;[14] therefore, formation

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Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**−**4**, **6**, and **7**

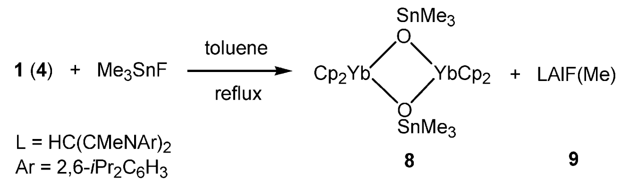
	1[a]	**2**[a]	**3**[a]	**4**·2 toluene[b]	**6**[c]	**7**[c]
Al−N(1)	1.931(2)	1.933(2)	1.920(7)	1.919(4)	1.905(5)	1.906(3)
Al−N(2)	1.939(2)	1.939(2)	1.934(6)	1.921(3)	equiv to Al−N(1)	equiv to Al−N(1)
Al−O(1)	1.692(2)	1.690(2)	1.690(6)	1.713(3)	1.766(6)	1.758(4)
Al−C	1.980(2)	1.976(2)	1.963(8)	1.951(5)	1.956(9)	1.962(5)
Ln−O(1)	2.020(1)	2.043(2)	2.056(5)	2.000(3)	2.431(6)	2.500(4)
Ln−X	2.32(1)	2.34(2)	2.36(1)	2.66(4), 2.53(4)	2.45(2)	2.50(2)
Ln−X_{Cp1}	2.37(1)	2.39(1)	2.42(2)	2.34(3)	2.46(2)	2.51(2)
Ln−X_{Cp2}	2.37(1)	2.40(1)	2.43(2)	2.34(3)	equiv to Ln−X_{Cp1}	equiv to Ln−X_{Cp1}
N(1)−Al−N(2)	94.8(1)	94.9(1)	95.7(3)	94.6(2)	96.7(3)	97.0(2)
C−Al−O(1)	117.8(1)	117.8(1)	118.2(3)	114.3(2)	114.2(4)	113.6(2)
Al−O(1)−Ln	169.8(1)	168.6(1)	167.4(3)	168.8(2)	153.6(4)	151.9(2)
O(1)−Ln−X	94.8(3)	96.1(1)	95.2(7)	68(1), 95(1)	105.4(5)	106.6(4)
O(1)−Ln−X_{Cp1}	112.1(3)	111.8(2)	112.2(5)	112.5(3)	97.0(5)	96.4(4)
O(1)−Ln−X_{Cp2}	109.4(3)	109.4(2)	109.4(4)	114.7(3)	equiv to O−Ln−X_{Cp1}	equiv to O−Ln−X_{Cp1}
X_{Cp1}−Ln−X_{Cp2}	129.1(3)	128.9(2)	128.9(5)	129.6(3)	118.0(5)	118.0(4)

[a] X = O(2) from THF. [b] X = H(28A), H(28C). [c] X = X_{Cp3}.

Table 3. Selected Bond Distances (Å) and Angles (deg) for **8**, **11**, and **12**

8		**11**·0.5 hexane		**12**	
Yb(1)−O(1)	2.187(2)	Yb(1)−N(1)	2.303(2)	Yb(1)−N(1)	2.234(2)
Yb(1)−O(1A)	2.191(2)	Yb(1)−N(2)	2.336(2)	Yb(1)−N(2)	2.258(2)
Yb(1)−X_{Cp1}	2.37(2)	Yb(1)−X_{Cp1}	2.39(2)	Yb(1)−N(3)	2.182(2)
Yb(1)−X_{Cp2}	2.36(2)	Yb(1)−X_{Cp2}	2.31(2)	Yb(1)−Cl(1)	2.491(1)
Sn(1)−O(1)	2.010(2)	N(1)−Yb(1)−N(2)	85.6(2)	Yb(1)−H(12A)	2.67(2)
O(1)−Yb(1)−O(1A)	77.7(1)	X_{Cp1}−Yb(1)−X_{Cp2}	125.9(4)	Yb(1)−H(26A)	2.70(2)
Yb(1)−O(1)−Yb(1A)	102.3(1)	N(1)−Yb(1)−X_{Cp1}	112.8(4)	Yb(1)−H(35A)	2.75(2)
Yb(1)−O(1)−Sn(1)	127.7(1)	N(1)−Yb(1)−X_{Cp2}	106.0(4)	N(1)−Yb(1)−N(2)	85.4(1)
Yb(1)−O(1)−Sn(1A)	129.4(1)	N(2)−Yb(1)−X_{Cp1}	111.1(4)	N(3)−Yb(1)−Cl(1)	113.8(1)
X_{Cp1}−Yb(1)−X_{Cp2}	123.4(4)	N(2)−Yb(1)−X_{Cp2}	107.8(4)	N(1)−Yb(1)−N(3)	129.7(1)
				N(2)−Yb(1)−N(3)	114.9(1)

Scheme 4



of the complexes $Cp_2Ln{-}O{-}AlL(F)$ can be anticipated in the reaction of $Cp_2Ln{-}O{-}AlL(Me)$ with Me_3SnF. On the contrary, reaction of **1** and Me_3SnF in refluxing toluene yielded compound $[Cp_2Yb(\mu\text{-}OSnMe_3)]_2$ (**8**) accompanied by the formation of LAlF(Me) (**9**) (Scheme 4), which was identified by EI-MS, ^1H, and ^{19}F NMR. The same result was obtained when **4** was used instead of **1**. This shows that the Ln−O−Al unit is reactive and affords a new route for the preparation of lanthanide heterobimetallic complexes with a Ln−O−M (M = metal) core.

Compound **8** was obtained as yellow crystals and has been characterized by X-ray structural analysis. The structural investigation reveals a centrosymmetric dimer of composition $[Cp_2Yb(\mu\text{-}OSnMe_3)]_2$. The central Yb_2O_2 core is planar due to the symmetry and is linked to two terminal Me_3Sn groups. The low steric demand of the Me_3Sn groups possibly leads to the aggregation of the monomeric unit. The Yb−O distance (av 2.19 Å) (Table 3) is significantly longer than the corresponding Yb−O(1) distance in **1** and **4** and can be compared to the bridging ones in $[Cp_2Yb(\mu\text{-}OnPr)]_2$[9b] (2.20 Å) and $[(Me_3SiC_5H_4)_2Yb(\mu\text{-}OH)]_2$[15] (2.29 Å), but is shorter than Yb−O(THF) in **1**. The Sn−O distance (2.01 Å) is similar to that for the exocyclic Sn−O distance (2.02 Å) in *cis*-$\{[(Me_3SiCH_2(Cl)SnCH_2(Me_2)Si)_2CC]O\}_2$[16] and is longer than those (1.96−1.98 Å) in Sn_3O_3 heterocycles.[17]

Investigation on Reaction of LAlOH(Me) with *β*-Diketiminate Ytterbium Complexes. Recently, the bulky *β*-diketiminate ligand L (L = $CH(CMeNAr)_2$, Ar = 2,6-$iPrC_6H_3$) was found to be an ideal ligand to stabilize mixed-ligand ytterbium complexes due to its steric and electronic properties.[18] Therefore, *β*-diketiminate complexes containing cyclopentadienyl groups were primarily investigated. The mono- and dicyclopentadienyl ytterbium complexes **10** and **11** were readily obtained from the reaction of $LYbCl_2(THF)_2$ with 1 and 2 equiv of CpNa, respectively, in THF in high yields (Scheme 5). However, compounds **10** and **11** reveal no reactivity toward LAlOH(Me) in toluene or THF, even under refluxing conditions.

Lanthanide amides show a diverse chemistry due to the labile Ln−N bond.[19] Therefore, it was an obvious route to prepare Ln−O−Al units from compounds containing Ln−N bonds. Treatment of $LYbCl_2(THF)_2$ with 1 equiv of $NaN(SiMe_3)_2$ in THF afforded $LYb(N(SiMe_3)_2)Cl$ (**12**) as red crystals in moderate yield. Efforts to prepare $LYb(N(SiMe_3)_2)_2$ under similar conditions resulted in decomposition products. Further reaction of **12** with an equivalent amount of LAlOH(Me) in toluene smoothly yielded LYbCl−O−AlL(Me) (**13**) under elimination of $HN(SiMe_3)_2$ (Scheme 6).

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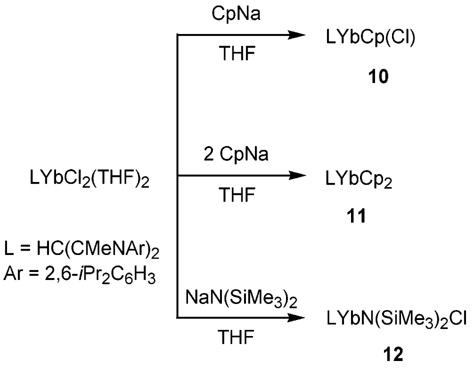
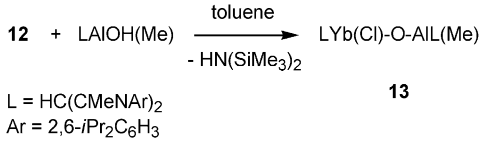
Scheme 5



Scheme 6



Compound **13** was isolated as yellow crystals and is soluble in toluene and THF. The molecular ion of **13** in the EI-MS spectrum is silent, and the most intense peak at m/z 1086 corresponds to $[M - Me]^+$.

Complexes **11**−**13** have been characterized by X-ray structural analyses. The structure of **13** is highly disordered due to the similar coordination sphere of the Yb and Al atoms and can be solved in both $P1$ and $P\bar{1}$ space group. The ball and stick model of **13** refined in $P1$ is depicted in Figure S12. The ytterbium ion in **11** is of pseudotetrahedral geometry surrounded by two cyclopentadienyl substituents and two nitrogen atoms of the chelating ligand (Figure 4). The coordination sphere of the ytterbium atom in **12** is more complicated and is formed by three nitrogen and one chlorine atom and further by agostic interaction to three hydrogen atoms (Yb−H 2.67, 2.70, and 2.75 Å, Figure S11). The C_3N_2Yb six-membered ring in both compounds adopts a boat conformation with the Yb at the prow and C(3) at the stern. The $Yb-N_{(endocyclic)}$ distances in **11** (2.303 and 2.336 Å) are a little longer than those in **12** (2.234 and 2.258 Å) (Table 3) and $LYbCl(\mu\text{-}Cl)_3YbL(THF)$[18a] (2.27 Å) due to the bulky Cp substituents.

Test for Catalytic Activity and the Polymerization of ϵ-Caprolactone. Ring-opening polymerization of lactones is an important process since the polymer is biodegradable and of practical application.[20] Lanthanide alkoxides are known to catalyze polymerization of lactones.[21] Thus, the catalytic property of complexes **1**, **3**, **4**, and **6** for the polymerization of ϵ-caprolactone were preliminarily investigated. These complexes show living catalyst activity at ambient or higher temperature in THF or toluene (Table 4). This indicates that the catalytic activity is maintained even when the R group is replaced by the Al unit. It is notable that compound **6** also shows high activity. This is probably due to the coordinating character of the lactone, which leads to the elimination of CpH and formation of $Cp_2Dy(\epsilon\text{-caprolactone})-O-AlL(Me)$ as the catalytic precursor. The coordination of the lactone has been observed.[21]

The general trend for the catalyst activity shows that the high-temperature polymerization leads to low molecular weight of the polymer and high polydispersity compared to that at ambient temperature for **1**, **3**, and **4**, whereas for **6** polymerization at high temperature shows the opposite trend for the molecular weight with almost similar polydispersity. The polymers obtained have molecular weight (M_n) in the range of 1.8−6.1 × 10^4, and the polydispersity (M_w/M_n) ranges from 1.5 to 2.3. The yield is almost quantitative (Table 4). As discussed before, the M_n and M_w/M_n vary with the temperature of polymerization. The values can be compared with those of polymers obtained with $Ln(O\text{-}iPr)_3$ and organolanthanide(II) complexes.[3b,22] The polydispersity index (1.7−2.3) is larger than that (1.1) obtained with Cp'_2LnOR (Cp′ = Cp, Cp*; Ln = Sm, Y; R = Me, Et). The difference in the results is probably due to the conditions of polymerization (e.g., different temperature and reaction time).[20] The application of such molecules for other polymerization reactions is currently being pursued.

Table 4. Polymerization of ϵ-Caprolactone[a]

compound	solvent	T (°C)	time (h)	yield (%)	M_n	M_w/M_n
1	THF	22	3	96	51766	1.6
1	toluene	70	0.5	95	18556	2.3
1	THF	70	0.5	96	24172	2.1
3	THF	22	3	95	61345	1.7
3	THF	70	0.5	96	33256	1.7
4	toluene	22	5	94	21807	1.5
4	toluene	70	0.5	95	17718	1.8
6	toluene	22	5	95	20934	1.6
6	toluene	70	0.5	97	39690	1.7

[a] Cat. = [0.01 mol/L]; caprolactone/cat. = 100.

Conclusions

In summary, we describe the synthesis of a new class of compounds containing the Ln−O−Al moiety from the reaction of LAlOH(Me) (L = $HC(CMeNAr)_2$, Ar = 2,6-$iPr_2C_6H_3$) and selected lanthanide precursor. The terminal Al−OH group shows selective reactivity for the lanthanide series when Cp_3Ln was used, and different types of lanthanide aluminum complexes containing either oxo-bridged Ln−O−Al or coordinated OH as $Ln(\mu\text{-}OH)Al$ were obtained depending on the varying lanthanide ion and solvent. This shows that the reaction of Cp_3Ln and LAlOH(Me) provides a facile route to synthesize lanthanide aluminum complexes. The formation of Ln−O−Al arrangement is a multiple-step process, and the elimination of CpH occurs through different mechanisms accompanied by the formation of different intermediates under different conditions. Furthermore, complexes **1**, **3**, **4**, and **6** are useful catalysts for the polymerization of ϵ-caprolactone. The reaction of **1** or **4** with Me_3SnF affords **8** containing a Yb−O−Sn core, which indicates that the Ln−O−Al unit is reactive and affords a new route to lanthanide heterobimetallic complexes containing a Ln−O−M unit. In addition, reactions of **10** and **11** with LAlOH(Me) show that mono- and dicyclopentadienyl derivatives are not suitable to act as CpH-eliminating reagents. The labile Ln−N bond can also be exploited as another method to prepare Ln−O−Al complexes. The reaction of LAlOH(Me) with lanthanide complexes containing two or three amide groups in different ratios is presently under investigation.

Experimental Section

General. All reactions were performed using standard Schlenk and drybox techniques. Solvents were appropriately dried and distilled under

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dinitrogen prior to use. Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. ^{1}H NMR spectra were recorded on a Bruker AM-200 instrument. The chemical shifts were reported in ppm with reference to external standards, more explicitly, $SiMe_4$ for ^{1}H nucleus. Mass spectra were obtained on a Finnigan Mat 8230. IR spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer as Nujol mulls between KBr plates. Cp_3Ln,[22] $LYbCl_2(THF)_2$,[18a] Me_3SnF,[23] and LAlOH(Me)[8] (L = $HC(CMeNAr)_2$, Ar = 2,6-$i$$Pr_2C_6H_3$) were prepared according to the literature methods. ϵ-Caprolactone (Aldrich) was dried over molecular sieves and degassed prior to use. Molecular weight data were recorded on a Waters 2410 refractive index detector with a procedure similar to that reported in the literature.[24] The polycaprolactone was characterized by ^{1}H and ^{13}C NMR.

$Cp_2Yb(THF)-O-AlL(Me)$ (1). THF (40 mL) was added to a mixture of LAlOH(Me) (0.48 g, 1 mmol) and Cp_3Yb (0.37 g, 1 mmol) at room temperature. The solution slowly turned from dark green to yellow accompanied by precipitate formation. The slurry was stirred for 12 h, and all the volatiles were removed in vacuo. THF (30 mL) was added and warmed until a clear yellow solution was obtained. The hot solution was filtered and kept at room temperature to give yellow crystals, which were collected by filtration, and the mother liquor was kept at 4 °C to give additional crystalline solid. Total yield: 0.66 g (78%). Mp: 249−251 °C. Anal. Calcd for $C_{44}H_{62}AlN_2O_2Yb$ (850.98): C, 62.05; H, 7.29; N, 3.29. Found: C, 62.15; H, 7.75; N, 3.33. EI-MS: m/z (%) = 778 (1) $[M - THF]^+$, 764 (100) $[M - THF - Me]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1624 (w), 1590 (w), 1552 (w), 1522 (m), 1315 (m), 1261 (m), 1176 (w), 1096 (s), 1021 (s), 917 (s), 875 (w), 801 (s), 761 (w), 722 (m), 663 (w), 643 (w), 605 (w), 534 (w), 452 (w).

$Cp_2Er(THF)-O-AlL(Me)$ (2). The procedure is the same as that described for **1** with Cp_3Er (0.36 g, 1 mmol) instead of the Cp_3Yb. Yield: 0.62 g (73%). Mp: 270−272 °C. Anal. Calcd for $C_{44}H_{62}AlErN_2O_2$ (845.20): C, 62.47; H, 7.34; N, 3.31. Found: C, 62.32; H, 7.54; N, 3.43. EI-MS: m/z (%) = 774 (1) $[M - THF]^+$, 758 (100) $[M - THF - Me]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1624 (w), 1585 (w), 1521 (s), 1344 (w), 1314 (s), 1260 (s), 1196 (w), 1178 (m), 1099 (s), 1058 (w), 1019 (s), 936 (w), 913 (s), 887 (w), 877 (w), 800 (s), 776 (m), 762 (m), 722 (w), 604 (w), 534 (w), 451 (w).

$Cp_2Dy(THF)-O-AlL(Me)$ (3). The procedure is the same as that described for **1** with Cp_3Dy (0.36 g, 1 mmol) instead of the Cp_3Yb. Yield: 0.63 g (75%). Mp: 263−265 °C. Anal. Calcd for $C_{44}H_{62}AlDyN_2O_2$ (840.44): C, 62.82; H, 7.38; N, 3.33. Found: C, 62.54; H, 7.64; N, 3.23. EI-MS: m/z (%) = 768 (1) $[M - THF]^+$, 754 (100) $[M - THF - Me]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1637 (w), 1585 (w), 1521 (s), 1504 (w), 1344 (w), 1321 (w), 1314 (s), 1255 (s), 1196 (w), 1177 (m), 1105 (m), 1958 (w), 1026 (s), 1012 (s), 936 (w), 908 (s), 887 (w), 800 (m), 774 (s), 762 (m), 754 (m), 723 (w), 660 (w), 643 (m), 605 (m), 534 (w), 451 (w).

$Cp_2Yb-O-AlL(Me)$ (4). Toluene (40 mL) was added to a mixture of LAlOH(Me) (0.48 g, 1 mmol) and Cp_3Yb (0.37 g, 1 mmol) at room temperature. The solution slowly turned from dark green to yellow. The resulting yellow solution was stirred for 12 h, and all the volatiles were removed in vacuo. Toluene (15 mL) was added, and a clear yellow solution was obtained. The solution was filtered and kept at −26 °C for 3 weeks to give yellow crystals. Yield: 0.54 g (69%). Mp: 274−276 °C. Anal. Calcd for $C_{40}H_{54}AlN_2OYb$ (779.14): C, 61.61; H, 6.93; N, 3.59. Found: C, 61.31; H,7.24; N, 3.53. EI-MS: m/z (%) = 764 (4) $[M - Me]^+$, 461 (100) $[M - Me - Cp_2Yb]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1658 (w), 1584 (w), 1534 (s), 1348 (m), 1319 (s), 1261 (s), 1182 (m), 1100 (s), 1058 (w), 1021 (s), 939 (w), 889 (s), 798 (s), 773 (s), 722 (w), 664 (w), 645 (w), 626 (m), 534 (w), 451 (w).

$Cp_3Er(\mu$-$OH)AlL(Me)$ (5). The procedure is the same as that described for **2** with toluene instead of THF. Yield: 0.62 g (73%). Mp: 205−207 °C. Anal. Calcd for $C_{45}H_{60}AlErN_2O$ (839.20): C, 64.35; H, 7.15; N, 3.34. Found: C, 64.15; H, 7.33; N, 3.48. EI-MS: m/z (%) = 772 (1) $[M - CpH]^+$, 758 (60) $[M - CpH - Me]^+$, 461 (100) $[M - Me - Cp_3Er]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 3438 (w), 1653 (w), 1625 (w), 1587 (w), 1525 (m), 1311 (m), 1261 (s), 1193 (w), 1175 (w), 1098 (s), 1019 (s), 960 (w), 940 (w), 875 (w), 801 (s), 761 (m), 711 (w), 654 (w), 642 (w), 605 (w), 540 (w), 464 (w), 451 (w).

$Cp_3Dy(\mu$-$OH)AlL(Me)$ (6). The procedure is the same as that for **3** with toluene instead of THF. Yield: 0.68 g (81%). Mp: 258−260 °C. Anal. Calcd for $C_{45}H_{60}AlDyN_2O$ (834.43): C, 64.71; H, 7.19; N, 3.35. Found: C, 64.39; H, 7.21; N, 3.37. EI-MS: m/z (%) = 768 (1) $[M - CpH]^+$, 754 (33) $[M - CpH - Me]^+$, 461 (100) $[M - Me - Cp_3Dy]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 3580 (w), 1624 (w), 1587 (w), 1525 (s), 1312 (s), 1257 (s), 1193 (w), 1177 (w), 1107 (m), 1055 (w), 1019 (s), 942 (m), 877 (m), 846 (w), 802 (s), 777 (s), 760 (s), 714 (s), 625 (w), 643 (m), 606 (m), 537 (w), 450 (w).

$Cp_3Sm(\mu$-$OH)AlL(Me)$ (7). The procedure is the same as that for **6** with Cp_3Sm (0.35 g, 1 mmol) instead of Cp_3Dy. Yield 0.67 g (81%). Mp: 323−325 °C. Anal. Calcd for $C_{45}H_{60}AlN_2OSm$ (822.29): C, 65.67; H, 7.30; N, 3.41. Found: C, 65.26; H, 7.43; N, 3.51. EI-MS: m/z (%) = 758 (1) $[M - CpH]^+$, 742 (30) $[M - CpH - Me]^+$, 461 (100) $[M - Me - Cp_3Sm]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 3588 (w), 1652 (w), 1586 (w), 1523 (s), 1311 (m), 1257 (m), 1193 (w), 1176 (w), 1106 (w), 1055 (w), 1019 (s), 936 (m), 876 (w), 802 (m), 774 (m), 758 (s), 717 (m), 642 (w), 607 (w), 449 (w).

$[Cp_2Yb(\mu$-$OSnMe_3)]_2$ (8). A mixture of **1** (0.85 g, 1 mmol) and Me_3SnF (0.18 g, 1 mmol) was refluxed in toluene until the insoluble Me_3SnF disappeared. All volatiles were removed in vacuo, and toluene (15 mL) was added and warmed until a clear solution was obtained. The hot solution was filtered and kept at room temperature to give yellow crystals of **8**. Yield: 0.26 g (53%). Mp: 230 °C (dec). Anal. Calcd for $C_{26}H_{38}O_2Sn_2Yb_2$ (966.02): C, 32.30; H, 3.93. Found: C, 32.15; H, 3.64. EI-MS: m/z (%) = 951 (4) $[M - Me]^+$, 901 (100) $[M - Cp]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1653 (w), 1624 (w), 1558 (w), 1307 (w), 1264 (m), 1094 (s), 1019 (s), 867 (w), 800 (s), 722 (m), 662 (w), 625 (w), 600 (w), 533 (w), 514 (w), 456 (w). The mother liquor was dried in vacuo and extracted with hexane (20 mL). The hexane solution was concentrated and kept at 4 °C to give a colorless crystalline solid of LAlF(Me) (**9**). Yield: 0.20 g (41%). Mp: 202−204 °C. EI-MS: m/z (%) = 478 (10) $[M]^+$, 463 (100) $[M - Me]^+$. ^{1}H NMR (200 MHz, C_6D_6, ppm): $\delta = -0.83$ (s, 3 H, AlMe), 1.07, 1.18, 1.31, 1.45 (d, 4 × 6 H, $^3J_{HH}$ = 6.9 Hz, CHMe_2), 1.58 (s, 6 H, CH-(CMe)$_2$), 3.18, 3.66 (sept, 2 × 2 H, $^3J_{HH}$ = 6.8 Hz, CHMe$_2$), 4.95 (s, 1 H, CH(CMe)$_2$), 7.03−7.16 (m, 6 H, C_6H_3). ^{19}F NMR (200 MHz, C_6D_6, ppm): −149.9. When **4** was used instead of **1**, the same products were obtained with similar yields.

LYbCp(Cl) (10). CpNa (1.0 mL, 2.0 M in THF, 2.0 mmol) was added to a solution of $LYbCl_2(THF)_2$ (1.61 g, 2 mmol) in THF (30 mL) at −78 °C. The mixture was allowed to warm to room temperature and was stirred for 14 h. All volatiles were removed in vacuo, and the residue was extracted with toluene (2 × 15 mL). The solution was concentrated to ca. 15 mL and kept at 4 °C for 48 h to give red crystals. The crystals were collected by filtration, and the filtrate was concentrated and kept at −26 °C for 7 d to give additional crystals. Total yield: 1.17 g (85%). Mp: 281−283 °C. Anal. Calcd for $C_{34}H_{46}ClN_2Yb$ (690.52): C, 59.09; H, 6.66; N, 4.06. Found: C, 58.94; H, 6.68; N, 4.05. EI-MS: m/z (%) = 691 (14) $[M]^+$, 626 (100) $[M - Cp]^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1633 (w), 1531 (m), 1509 (w), 1435 (w), 1317 (w), 1264 (s), 1173 (w), 1099 (s), 1022 (m), 933 (w), 847 (w), 794 (m), 760 (w), 738 (w), 693 (w), 663 (w).

$LYbCp_2$ (11). The procedure is the same as that for **10** when 2 equiv of CpNa were used. Total yield: 1.25 g (87%). Mp: 267−269 °C. Single crystals suitable for X-ray analysis were obtained by recrystallization from hexane. Anal. Calcd for $C_{39}H_{51}N_2Yb$ (720.94): C, 64.92; H, 7.07; N, 3.88. Found: C, 64.94; H, 6.85; N, 4.21. EI-MS: m/z (%) = 721 (3) $[M]^+$, 656 (100) $[M - Cp]^+$. IR (KBr, Nujol mull, cm^{-1}):

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$\tilde{\nu}$ = 1653 (w), 1521 (m), 1499 (w), 1310 (w), 1261 (m), 1180 (w), 1166 (w), 1097 (m), 1018 (m), 927 (w), 873 (w), 842 (w), 792 (s), 780 (s), 757 (w), 722 (w), 601 (w), 559 (w).

LYbN(SiMe$_3$)$_2$Cl (12). THF (30 mL) was added to a mixture of LYbCl$_2$(THF)$_2$ (0.81 g, 1 mmol) and NaN(SiMe$_3$)$_2$ (0.18 g, 1 mmol) at 0 °C. The resulting solution was warmed to room temperature and was stirred for 14 h. All volatiles were removed in vacuo, and the residue was extracted with hexane (2 × 15 mL). The solution was concentrated to ca. 15 mL and kept at 4 °C for 24 h to give red crystals. Yield: 0.38 g (48%). Mp: 250−252 °C. Anal. Calcd for $C_{35}H_{59}ClN_3Si_2Yb$ (786.52): C, 53.40; H, 7.50; N, 5.34. Found: C, 53.65; H, 7.49; N, 5.21. EI-MS: *m*/*z* (%) = 786 (2) [M]$^+$, 771 (80) [M − Me]$^+$, 625 (100) [M − N(SiMe$_3$)$_2$]$^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1624(w), 1552 (w), 1525 (w), 1504 (w), 1314 (w), 1261 (m), 1176 (w), 1099 (w), 1058 (w), 1020 (w), 940 (s), 875 (m), 850 (w), 819 (w), 795 (w), 757 (w), 722 (m), 673 (w), 625 (w), 603 (w), 521 (w), 445 (w).

LYbCl−O−AlL(Me) (13). Toluene (40 mL) was added to a mixture of LAlOH(Me) (0.24 g, 0.5 mmol) and **12** (0.39 g, 0.5 mmol) at room temperature. The color of the solution slowly turned from orange-red to yellow. The solution was stirred for 12 h, and all the volatiles were removed in vacuo. Toluene (10 mL) was added, and a clear yellow solution was obtained by filtration. Crystals were obtained after the solution was kept at 4 °C for 48 h. The crystals were collected by filtration, and the filtrate was concentrated and kept at −26 °C for 4 d to give additional crystals. Total yield: 0.40 g (72%). Mp: 270−272 °C. Anal. Calcd for $C_{59}H_{85}AlClN_4OYb$ (1100.52): C, 64.33; H, 7.72; N, 5.09. Found: C, 64.54; H, 7.68; N, 5.23. EI-MS: *m*/*z* (%) = 1086 (100) [M − Me]$^+$. IR (KBr, Nujol mull, cm^{-1}): $\tilde{\nu}$ = 1623 (w), 1538 (m), 1315 (w), 1261 (w), 1173 (w), 1098 (m), 1022 (m), 935 (w), 798 (m), 722 (w), 606 (w).

Polymerization of ϵ-Caprolactone. In a typical procedure, 0.1 mmol of catalyst was dissolved in 10 mL of solvent by warming. After the solution was cooled to room temperature, ϵ-caprolactone (1.11 mL, 10 mmol) was added with stirring. HCl (2.0 M) was added to the mixture under N_2 after the designated time. The resulting mixture was washed twice with diluted HCl and twice with H_2O. The organic layer was separated and added to hexane (100 mL) to precipitate the polymer. The polymer was filtered and dried in vacuo. When THF was used as solvent, toluene was added to the reaction mixture before washing with HCl.

X-ray Structure Determination. Crystals were mounted on glass fibers in a rapidly cooled perfluoropolyether. Diffraction data of structures **1** and **7** were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD detector using Cu Kα radiation (λ = 1.54178 Å). Data of structure **4** were collected on a Stoe−Siemens−Huber four-circle diffractometer, and data of structures **2**, **3**, **6**, **8**, **11**, and **12** were collected on a Stoe IPDS II-array detector system using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods using the program SHELXS-97[25] and refined using F^2 on all data by full-matrix least-squares with SHELXL-97.[26] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included in the model at geometrically calculated positions and refined with the riding model except those in disordered *i*Pr moieties, solvated toluene (**4**) and hexane (**11**) molecules, where the riding model was not applied. The coordinated THF molecule in **1**−**3**, one of the Cp rings in **4**, one of the *i*Pr groups and one Cp ring in **6** and **7**, and the hexane molecule in **11** are disordered in two positions and were refined with geometry and distance restraints and restraints for the anisotropic displacement parameters. The crystallographic data of the reported structures are given in Table 1.

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Supporting Information Available: Plots of structures of compounds **1**−**4**, **6**−**8**, and **11**−**13** and two plots comparing the structures **1**−**3**, **6**, and **7** (Figure S1−S12, PDF). Details of the single-crystal X-ray structure determinations of **1**−**4**, **6**−**8**, **11**, and **12** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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