New Bis(allyl)(diketiminato) and Tris(allyl) Lanthanide Complexes and Their Reactivity in the Polymerization of Polar Monomers

Luis F. Sánchez-Barba,[†] David L. Hughes,[†] Simon M. Humphrey,[‡] and
M. Bochmann*,[†]

*Wolfson Materials and Catalysis Centre, School of Chemical Sciences and Pharmacy,
University of East Anglia, Norwich, NR4 7TJ, U.K., and University Chemical Laboratory,
University of Cambridge, Lensfield Road, Cambridge, CB2 1EW, U.K.*

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The reaction of $LnCl_3(THF)_n$ (Ln = La, $n = 4$; Ln = Y, Sm, Nd, $n = 3$) with 3 equiv of allylMgCl in THF/1,4-dioxane followed by crystallization in 1,4-dioxane/toluene proceeds in very high yields to give the tris(η^3-allyl) complexes $[La(\eta^3\text{-}C_3H_5)_3(\kappa^1\text{-dioxane})]_2(\mu\text{-dioxane})$ and $[Ln(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_\infty$ (Ln = Y, **1**; Sm, **2**; Nd). Improved one-pot syntheses for the tris(η^3-allyl) lanthanum and neodymium compounds are reported. The crystal structures of **1** and **2** show that the compounds consist of distorted square-pyramidal lanthanide centers in linear polymer chains. The reaction of $[La(\eta^3\text{-}C_3H_5)_3(\kappa^1\text{-dioxane})]_2(\mu\text{-dioxane})$ and $[Ln(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_\infty$ with the diketimine ligand 2-(2,6-diisopropylphenyl)amino-4-(2,6-diisopropylphenyl)imino-2-pentene (BDI-H) in THF at 60 °C generates cleanly the β-diketiminato complexes $Ln(\eta^3\text{-}C_3H_5)_2\{\kappa^2\text{-}HC(MeCNAr)_2\}$ (Ar = 2,6-$C_6H_3{}^iPr_2$; Ln = La, **3**; Y, **4**; Sm, **5**; Nd, **6**) with propene elimination. The crystal structure of **5** shows a distorted tetrahedral $SmN_2(allyl)_2$ core, with the samarium atom positioned 1.438(4) Å out of the C_3N_2 ligand plane. All complexes are highly effective single-component catalysts for the ring-opening polymerization of ϵ-caprolactone and *rac*-lactide. Polymer end group analysis shows that the polymerization process is initiated by allyl transfer to monomer.

Introduction

Lanthanide catalysts (including group 3) are being widely employed in coordination polymerization to give a range of polymers or copolymers and can work without conventional aluminum alkyl additives to afford materials that do not contain traces of toxic metals.[1,2] In this context, lanthanide allyl complexes[3] have been shown to be excellent precatalysts. For example, Taube et al.[4] reported the synthesis of neutral tris(η^3-allyl)lanthanide complexes $[La(\eta^3\text{-}C_3H_5)_3(\kappa^1\text{-dioxane})]_2(\mu\text{-dioxane})$ and $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-dioxane})]_\infty$, which catalyze the polymerization of butadiene in toluene with high 1,4-*trans*-stereroselectivity. Other allyl complexes have been used in the polymerization of polar monomers; for example, we showed recently that *ansa*-bis(allyl) lanthanide complexes[5a] and allyl-bridged oligonuclear complexes[5b,c] are highly active single-component catalysts for the polymerization of methyl methacrylate, butadiene,[6] and cyclic esters. Allyl complexes of early lanthanides based on the $[Flu\text{-}CMe_2\text{-}Cp]^{2-}$ ligand for the syndiospecific polymerization of styrene have also been reported recently.[7]

Given the recent interest in non-cyclopentadienyl ligand environments in group 3 metal chemistry,[8] and more specifically in the use of the β-diketiminato ("nacnac") donor framework,[9] we became interested in exploring the synthesis of nacnac-based mixed-ligand lanthanide allyl complexes. These ligands have several attractive features. β-Diketiminato ligands can play a role similar to cyclopentadienyls, the steric and electronic properties of β-diketiminato ligands can be readily altered through an appropriate choice of substituents, and they can coordinate to the metal center in different

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* Corresponding author. E-mail: M.Bochmann@uea.ac.uk.

[†] University of East Anglia.

[‡] University of Cambridge.

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bonding modes ranging from purely σ to a combination of σ and π donation.[10] High-activity lanthanide polymerization catalysts incorporating nacnac ligands have been reported. In particular, Piers et al. have developed the chemistry of organo-scandium complexes supported by β-diketiminato ligands[11] and described scandium and yttrium alkyl compounds with related bulky chelating ligands.[12] The syntheses of scandium and yttrium complexes bearing moderately bulky 2-iminophenolato ligands have been reported,[13] and heteroleptic samarium,[14] neodymium,[14] and ytterbium[15] complexes and lanthanide chlorides[16] containing β-diketiminato ligands have also recently been made. In contrast, to the best of our knowledge, no examples of allyllanthanides supported by β-diketiminato ligands are known. Generally, mixed-ligand lanthanide compounds (L)LnR$_2$ are difficult to synthesize, due to the tendency of these types of compounds to undergo ligand redistribution, dimerization, or oligomerization reactions or to retain additional donor molecules in the coordination sphere.

We report here the synthesis and structures of novel tris(η^3-allyl)lanthanides, their facile conversion into bis(η^3-allyl)(nacnac) complexes, and their reactivity as single-component catalysts for the ring-opening polymerization of ϵ-caprolactone and *rac*-lactide.

Results and Discussion

Syntheses. The reaction of LnCl$_3$(THF)$_n$ (Ln = La, $n = 4$; M = Y, Sm, Nd, $n = 3.5$) in a mixture of THF/1,4-dioxane (4:1) with 3 equiv of allylmagnesium chloride affords the corresponding tris(η^3-allyl) complexes [La(η^3-C$_3$H$_5$)$_3$(κ^1-dioxane)]$_2$(μ-dioxane) and [Ln(η^3-C$_3$H$_5$)$_3$(μ-dioxane)]$_\infty$ (Ln = Y, **1**; Sm, **2**; Nd) in very good yields as yellow, orange, red, and green crystals, respectively. Qualitative tests showed the absence of halide. The lanthanum and neodymium tris(η^3-allyl) compounds were reported before by Taube.[4a] However, in that synthesis the tetra(allyl) metalates [Li(μ-dioxane)$_{1.5}$][Ln(η^3-C$_3$H$_5$)$_4$] (Ln = La, Nd) were used as starting materials, followed by the abstraction of allyllithium with BEt$_3$ to afford a dimeric compound for the former and a linear coordination polymer for the latter. An alternative strategy was reported[4c] a few years ago for the synthesis of the complex [Nd(η^3-C$_3$H$_5$)$_3$(μ-dioxane)]$_\infty$ starting from NdI$_3$(THF)$_3$ and the corresponding allyl Grignard reagent. In our case, we used commercially available metal chlorides in one-pot reactions. The tris(η^3-allyl) complexes [La(η^3-C$_3$H$_5$)$_3$(κ^1-dioxane)]$_2$(μ-dioxane) and [Ln(η^3-C$_3$H$_5$)$_3$(μ-dioxane)]$_\infty$ were easily obtained at room temperature after 15 h, followed by several recrystallizations at −26 °C to give yields of >80% (Scheme 1).

The ^{1}H and {^{1}H}^{13}C NMR spectra of the new Y and Sm compounds **1** and **2** in THF-d_8 at room temperature display one set of signals for the η^3-allyl groups, showing the equivalence between H$_{\rm syn}$ and H$_{\rm anti}$ and a single sharp signal for the 1,4-dioxane molecule displaced by THF-d_8. The compounds are extremely air and moisture sensitive, highly soluble in THF or 1,4-dioxane, and insoluble in light petroleum, toluene, or diethyl ether. They decompose in dichloromethane.

Whereas single crystals of **1** suitable for X-ray diffraction crystallography were readily grown from 1,4-dioxane/toluene at −26 °C, the isolation of crystals for the samarium derivative **2** was complicated by the extreme sensitivity and relative instability of this compound. The smallest crystals decomposed almost immediately when removed from the Schlenk tube under nitrogen, whereas the bigger ones degraded on the diffractometer during the course of the acquisition of the intensity data. Suitable crystals of **2** were eventually obtained by recrystallization from a 1:8 mixture of 1,4-dioxane/toluene after several days at −26 °C. The difference in stability between the yttrium and samarium tris(η^3-allyl) complexes was also evident by the fact that **2** decomposed in the inert atmosphere of the glovebox over a period of a few months, while **1** remained unchanged under identical conditions.

Compounds **1** and **2** are isostructural (Figure 1); the bond lengths and angles are very similar in the two molecules; they resemble Taube's neodymium analogue.[4a,d] Selected dimensions are listed in Table 1. The structures confirm the presence of three η^3-allyl groups coordinated to the metal center and bridging 1,4-dioxane molecules linking the Ln(η^3-C$_3$H$_5$)$_3$ units to form linear polymeric chains. The 1,4-dioxane ligands are arranged about centers of symmetry, and the Ln atoms lie on 2-fold symmetry axes; thus the allyl ligands of C(41−43) and C(41′−43′) are related.

The yttrium and samarium atoms have a distorted square-pyramidal coordination pattern, with alternating orientations along the chains. The O−M−O′ angles, across the square base of the pyramid, are 155.1(2)° and 154.72(10)° in **1** and **2**. There are slight differences in the two complexes in the arrangements of the η^3-allyl ligand containing C(31−33), which is disordered about the 2-fold symmetry axis. In **1**, C(31) and C(33′) have been resolved into two overlapping atoms with centers about 0.25 Å apart; however, refinement was not totally satisfactory and both C−C bond lengths in this ligand were constrained at 1.39(1) Å. In **2**, the atoms C(31) and C(33′) were found to be essentially coincident and were refined satisfactorily as a single-site atom; the variation of C−C bond lengths in this ligand suggests however that, assuming the delocalization across the ligand is equal, the two atoms are not perfectly coincident. The corresponding ligand in the Nd analogue appears less well-resolved.[4a,d]

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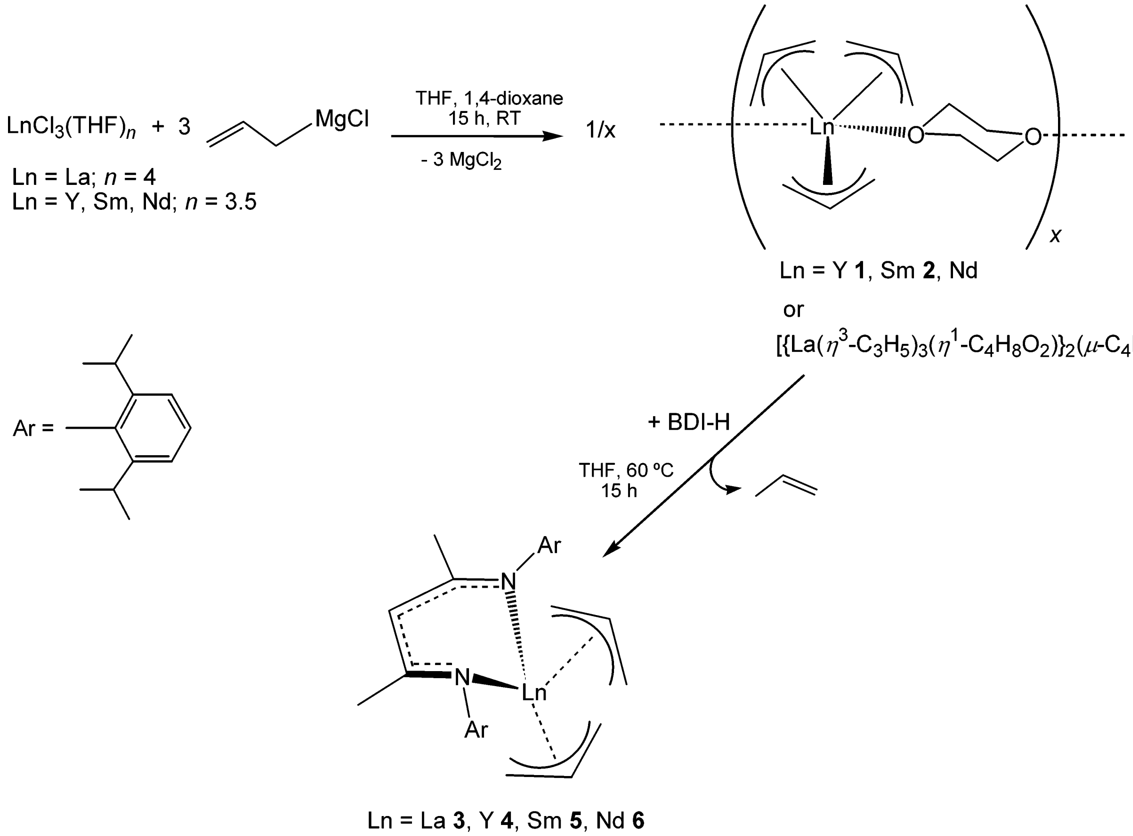
Scheme 1



The allyl ligand of C(41−43) was fully resolved in both complexes and shows more reliable dimensions. Here, the Y−C distances are in the range 2.638(7)−2.676(7) Å and the Sm−C distances are slightly longer at 2.678(4)−2.731(5) Å. All the C−C bonds have essentially the same length, the mean value is 1.375(4) Å, and the C−C−C angles are 126.4(7)° and 126.8(4)° in **1** and **2**, respectively.

The crystal structure packing diagram of **1** and **2** (Figure 2) shows the linear polymeric chains, with the η^3-allyl groups in alternating orientations and the bridging 1,4-dioxane ligands in chair conformation.

Compounds **1**, **2**, and the tris(η^3-allyl)lanthanum and neodymium analogues serve as convenient starting materials for the synthesis of mixed-ligand complexes. Thus stirring with diketimine (BDI-H) in THF at 60 °C for 15 h gives high yields of the first examples of bis(η^3-allyl)(BDI) lanthanide complexes, $Ln(\eta^3\text{-}C_3H_5)_2\{\kappa^2\text{-}HC(MeCNC_6H_3{}^iPr_2\text{-}2,6)_2\}$ (Ln = La, **3**; Y, **4**; Sm, **5**; Nd, **6**), as yellow, orange, red, and green microcrystalline solids, respectively (Scheme 1).

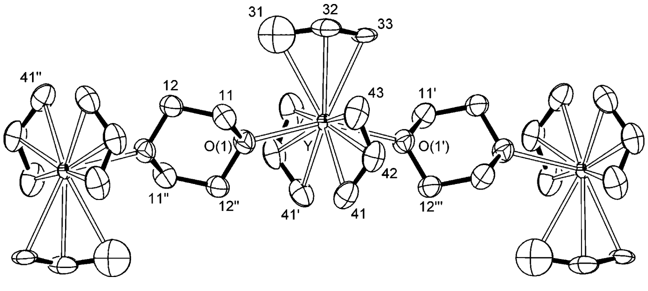


Figure 1. View of a fragment of the polymer complex $[Y(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)]_\infty$, **1**. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 50% probability level. The samarium analogue **2** is isostructural.

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 1 and 2

$[Y(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)]_n$, **1**		$[Sm(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)]_n$, **2**	
Y−O(1)	2.507(4)	Sm−O(1)	2.577(2)
Y−C(31)	2.76(4)	Sm−C(31)	2.725(4)
Y−C(32)	2.656(11)	Sm−C(32)	2.715(7)
Y−C(33)	2.661(17)	Sm−C(33)	2.725(4)
Y−C(41)	2.638(7)	Sm−C(41)	2.678(4)
Y−C(42)	2.650(7)	Sm−C(42)	2.705(4)
Y−C(43)	2.676(7)	Sm−C(43)	2.731(5)
C(31)−C(32)	1.390(10)	C(31)−C(32)	1.281(12)
C(32)−C(33)	1.399(10)	C(32)−C(33)	1.428(12)
C(41)−C(42)	1.389(11)	C(41)−C(42)	1.369(6)
C(42)−C(43)	1.364(11)	C(42)−C(43)	1.379(6)
O(1)−Y−O(1′)	155.1(2)	O(1)−Sm−O(1′)	154.72(10)
O(1)−Y−C(32′)	106.1(4)	O(1)−Sm−C(32′)	104.9(3)
O(1)−Y−C(32)	98.4(4)	O(1)−Sm−C(32)	100.0(3)
O(1)−Y−C(33)	128.3(3)	O(1)−Sm−C(33)	129.48(11)
O(1)−Y−C(42)	92.63(19)	O(1)−Sm−C(42)	92.73(10)
O(1)−Y−C(42′)	78.84(18)	O(1)−Sm−C(42′)	78.40(10)
C(32)−Y−C(42)	100.6(4)	C(32)−Sm−C(42)	100.3(2)
C(32)−Y−C(42′)	119.4(4)	C(32)−Sm−C(42′)	120.6(2)
C(42)−Y−C(42′)	139.9(4)	C(42)−Sm−C(42′)	139.0(2)

The new compounds **3**−**6** were characterized by NMR spectroscopy (^1H, $\{^1H\}^{13}C$, NOESY-2D, HETCOR, for diamagnetic species) and elemental analysis. In all cases, the ^1H spectra in benzene-d_6 at room temperature display one set of signals for the η^3-allyl groups and the β-diketiminato ligand. Complexes **3** and **4** show two different doublets for the H_{anti} and H_{syn} atoms with two different J_{HH} coupling constants, as well as a multiplet for the central CH proton. The BDI ligands show in all cases one signal for the Me and CH groups, but restricted rotation about the $N-C_{aryl}$ bonds gives rise

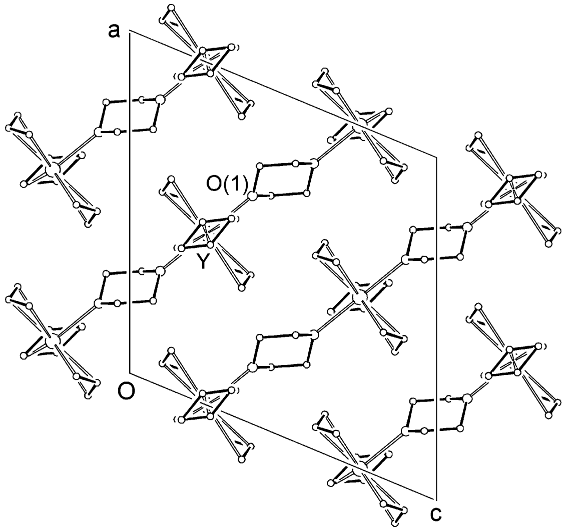


Figure 2. Projection of the linear polymer chains down the *b*-axis in complex **1**; complex **2** is essentially identical.

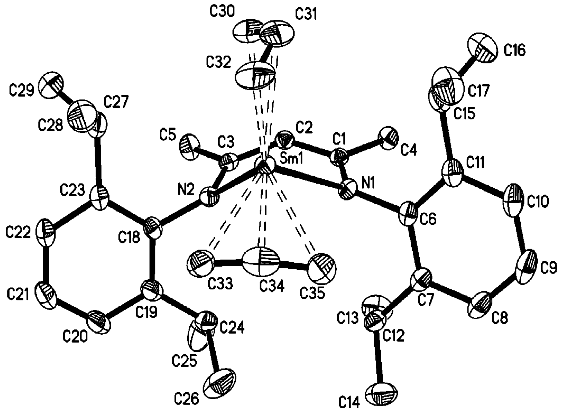


Figure 3. Molecular structure of $Sm(\eta^3-C_3H_5)_2\{HC(MeCN-2,6-{}^iPr_2C_6H_3)_2\}$, **5**. Thermal ellipsoids are drawn at the 30% probability level.

to two separate doublets for the isopropyl methyl groups. The ^{13}C spectra in benzene-d_6 display one set of signals for the η^3-allyl groups and the β-diketiminato ligand. The compounds do not retain donor solvent molecules in the metal coordination sphere. There is a clear NOE (nuclear Overhauser effect) signal in the NOESY-2D spectrum between the H_{anti} and only one ^iPr group in the BDI ligand, which confirms the restricted rotation about the $N-C_{aryl}$ bonds and the proximity between the two different ligands in the same molecule. This experiment eliminates the alternative formulation of the compounds as the ion pairs, $[Ln\{HC(MeCNAr)_2\}_2]^+[Ln(\eta^3-C_3H_5)_4]^-$.

The geometry of these compounds was confirmed by the single-crystal X-ray structure of complex **5** (Figure 3). Selected bond lengths and angles are collected in Table 2. The samarium center exhibits a distorted tetrahedral geometry, in which the N(1) and N(2) occupy two positions and the η^3-allyl groups the other two positions.

The samarium atom lies 1.438(4) Å above the C_3N_2 ligand plane. This displacement is significantly larger than that observed in the related five-coordinated dialkyl yttrium[12d] compounds (0.819(5) Å) incorporating a similar chelating ligand, or an organo-scandium[11a,b] compound (1.232(3) Å) containing a bulky nacnac ligand.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 5

Sm(1)−N(1)	2.372(3)	N(1)−Sm(1)−N(2)	82.92(10)
Sm(1)−N(2)	2.369(3)	N(1)−Sm(1)−C(31)	111.66(15)
Sm(1)−C(30)	2.606(4)	N(1)−Sm(1)−C(34)	110.67(14)
Sm(1)−C(31)	2.692(4)	N(2)−Sm(1)−C(31)	129.07(15)
Sm(1)−C(32)	2.702(4)	N(2)−Sm(1)−C(34)	114.93(13)
Sm(1)−C(33)	2.612(4)	C(31)−Sm(1)−C(34)	105.05(17)
Sm(1)−C(34)	2.674(4)	Sm(1)−N(1)−C(1)	110.1(2)
Sm(1)−C(35)	2.636(4)	Sm(1)−N(1)−C(6)	126.5(2)
N(1)−C(1)	1.327(4)	C(1)−N(1)−C(6)	119.9(3)
C(1)−C(2)	1.421(5)	Sm(1)−N(2)−C(3)	109.1(2)
C(2)−C(3)	1.402(5)	Sm(1)−N(2)−C(18)	128.1(2)
N(2)−C(3)	1.340(4)	C(3)−N(2)−C(18)	119.6(3)
C(30)−C(31)	1.344(7)	N(1)−C(1)−C(2)	124.1(3)
C(31)−C(32)	1.389(8)	C(1)−C(2)−C(3)	132.9(3)
C(33)−C(34)	1.381(7)	C(2)−C(3)−N(2)	124.5(3)
C(34)−C35)	1.373(7)	C(30)−C(31)−C(32)	127.1(6)
		C(33)−C(34)−C(35)	123.9(4)

The two Sm−N bond lengths are closely similar (2.372(3) and 2.369(3) Å). The allyl fragment opposite the N atoms is η^3-bonded, with three very similar Sm−C bond lengths [Sm(1)−C(33) = 2.612(4) Å, Sm(1)−C(34) = 2.674(4) Å, Sm(1)−C(35) = 2.636(4) Å]. Bonding of the second allyl moiety is less symmetrical, with Sm(1)−C(30, 31, 32) distances of 2.606(4), 2.692(4), and 2.702(4) Å.

Polymerization Studies. Complexes **1**−**6** were tested for the ring-opening polymerization of ϵ-caprolactone (CL) and *rac*-lactide (*rac*-LA). In principle, polymerization can be envisaged to occur by one of two mechanisms: either the transfer of the nucleophilic alkyl ligand to the monomer, with formation of a metal alkoxide-propagating species (Scheme 2, path A), or ring opening and propagation via a cationic (activated chain end, ACE) mechanism (path B).

Complexes **1**−**6** act as highly active single-component catalysts for the polymerization of ϵ-caprolactone (CL) to give high molecular weight polymers (Table 3). A variety of polymerization conditions were explored. The tris(η^3-allyl) complexes **1** and **2** initiated very rapid polymerization of CL at room temperature (entries 1 and 4), and **2** gave complete conversion of 200 equiv of CL in 90 s, with a productivity of more than 9×10^5 g PCL (mol Sm)$^{-1}\cdot h^{-1}$. The polymerization was well controlled and gave high molecular weight polymer with narrow polydispersity ($M_w = 51\,000$, $M_w/M_n = 1.4$). For catalyst **1**, productivity and molecular weight decreased on cooling, and at −20 °C only traces of polymer were found. By contrast, complex **2** was still very active at −20 °C and reached a conversion of 47% after 3.5 min, with a polydispersity suggestive of living behavior ($M_w/M_n = 1.1$) (entry 5). The dimeric complex $[La(\eta^3-C_3H_5)_3(\kappa^1-dioxane)]_2(\mu-dioxane)$ proved to be an extremely active catalyst, with productivities of more than 4×10^6 g PCL (mol La)$^{-1}\cdot h^{-1}$ at room temperature (entry 6). This activity was maintained at −20 °C, with $M_w/M_n = 1.1$.

The diketiminato-bis(allyl) complexes **3**−**6** also showed very high CL polymerization activity. For instance, **3** gave complete conversion within 15 s at 0 °C, with a productivity of $>6.7 \times 10^5$ g PCL (mol La)$^{-1}\cdot h^{-1}$. The polymer had a high molecular weight, while the polydispersity was broader ($M_w = 144\,000$, $M_w/M_n = 1.8$). At −20 °C the polymerization also proceeded more

Scheme 2

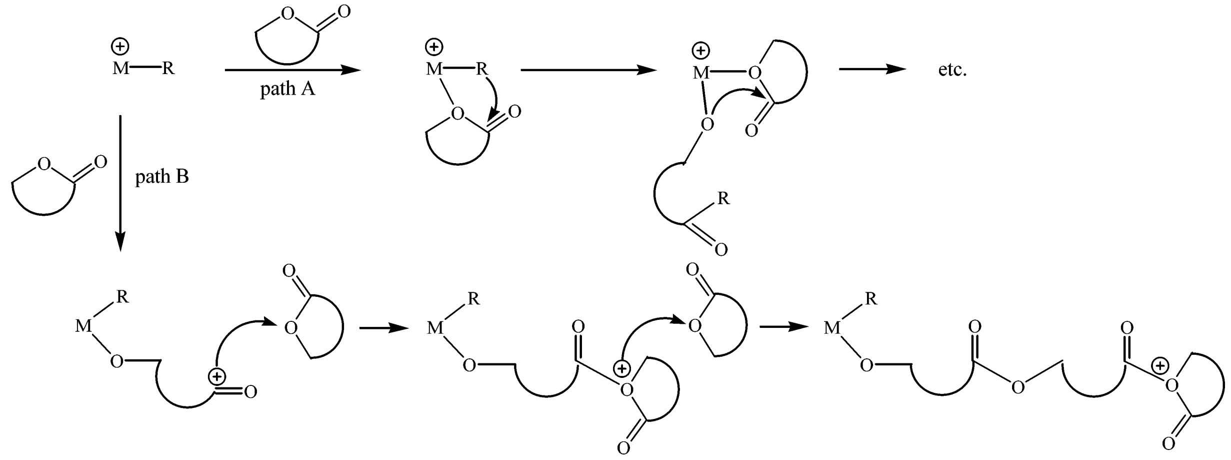


Table 3. Polymerization of ϵ-Caprolactone Catalyzed by Complexes 1−6[a]

entry	initiator	temp [°C]	time [min]	yield [g]	conv (%)[b]	prod[c]	M_w[d]	M_w/M_n[d]
1	Y(allyl)$_3$ **1**	20	1.3	1.23	61	615	38 000	1.3
2	**1**	0	2	0.74	36	246	25 000	1.2
3	**1**	−20	3.5	traces				
4	Sm(allyl)$_3$ **2**	20	1.5	2.03	99	902	51 000	1.4
5	**2**	−20	3.5	0.97	47	184	23 000	1.1
6	La(allyl)$_3$ [e]	20	0.3	2.06	99	4161	59 000	1.4
7	La(allyl)$_3$ [e]	−20	0.3	1.49	73	3010	28 000	1.1
8	La(allyl)$_2$(DBI) **3**	0	0.2	2.03	99	6766	144 000	1.8
9	**3**	−20	0.5	1.64	81	2186	52 500	1.2
10	**3**	−50	0.5	1.52	75	2026	53 000	1.2
11	**3**[f]	20	3	0.74	36	164	151 000	1.8
12	**3**[f]	20	20	1.90	94	63	141 000	2.0
13	Y(allyl)$_2$(DBI) **4**	0	1.5	1.49	73	662	72 000	1.2
14	Sm(allyl)$_2$(DBI) **5**	20	1.5	2.03	99	902	92 000	1.6
15	**5**	0	1.5	2.03	99	902	78 000	1.5
16	**5**	−50	1.5	0.46	23	204	20 500	1.2
17	Nd(allyl)$_2$(DBI) **6**	0	1	2.03	99	1353	29 500	1.8

[a] Polymerization conditions: 90 μmol of initiator, ϵ-CL/initiator = 200. [b] Percentage conversion of the monomer (weight polymer recovered × 100/weight of monomer). [c] kg polymer (mol Ln)$^{-1}$·h^{-1}. [d] Determined by GPC relative to polystyrene standards. [e] $[La(\eta^3\text{-}C_3H_5)_3(\eta^1\text{-}C_4H_8O_2)]_2(\mu\text{-}C_4H_8O_2)$. [f] 90 μmol of initiator, ϵ-CL/initiator = 5000.

slowly and led to a decrease in polydispersity (M_w = 52 500, M_w/M_n = 1.2). This catalyst was still active even at −50 °C.

In these tests the polymer molecular weights were limited by the monomer/initiator ratio of 200:1. Increasing this ratio 25-fold gave polymers with significantly higher molecular weights ($M_w > 10^5$) (entries 11 and 12). End group analysis showed that the polymer contained $-CH_2CH{=}CH_2$ termini, proof that the polymerization follows the nucleophilic route (Scheme 2, path A) and is initiated by the transfer of an allyl ligand to the monomer, with formation of a metal alkoxide-propagating species.[17]

The nature of the metal affects the catalytic activity, which under the present polymerization conditions decreases in the order **3** ≫ **6** > **5** > **4**, in agreement with the decrease in ionic radii (La > Nd > Sm > Y). A similar dependence was found in lanthanocene-based systems.[18] Although a number of organo-lanthanides[6,19] have been shown to polymerize ϵ-caprolactone, only few show good activity at very low temperatures as in this case (entries 10 and 16).

Complexes **1**−**6** were examined for the production of polylactide (PLA).[19b,20] Although a number of zinc and magnesium β-diketiminato complexes have been reported[21] to polymerize lactide with high stereocontrol and well-controlled living chain propagation, relatively few examples of organo-lanthanides[22] with related chelating ligands are available.

Complexes **1**−**6** proved to be very active catalysts for the polymerization of *rac*-lactide (LA) under mild conditions (20−40 °C) (Table 4). A variety of polymerization conditions were explored. The tris(η^3-allyl) complexes **1** and **2** initiate rapid polymerization of *rac*-lactide at

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Table 4. Polymerization of *rac*-Lactide Catalyzed by Complexes 1−6[a]

entry	initiator	temp [°C]	time [h]	yield [g]	conv[b]	prod[c]	M_w[d]	M_w/M_n[d]
1	**1**	20	1	traces				
2	**1**	40	1	0.16	16	2.28	18 000	1.1
3	**1**	40	2.3	0.40	40	2.48	19 000	1.2
4	**1**	40	3.5	0.58	58	2.36	20 000	1.2
5	**1**	40	4.7	0.76	76	2.31	20 000	1.2
6	**2**	20	1	traces				
7	**2**	20	2.5	0.05	5	0.28	22 500	1.2
8	**2**	20	4.5	0.64	64	2.03	27 500	1.3
9	**2**	20	6	0.79	79	1.88	29 000	1.3
10	**2**	20	7.5	0.86	86	1.63	30 000	1.4
11	**2**	40	1	0.23	23	3.28	29 000	1.4
12	*e*	20	1.5	0.56	56	5.33	25 000	1.3
13	*e*	40	1.1	0.63	63	8.18	25 500	1.3
14	**3**	40	1.1	0.58	58	7.53	21 500	1.2
15	**3**	40	2.3	0.70	70	4.34	25 500	1.3
16	**4**	40	1	0.16	16	2.28	18 500	1.2
17	**4**	40	2.3	0.35	35	2.17	19 000	1.2
18	**4**	40	3.5	0.51	51	2.08	21 000	1.3
19	**4**	40	4.7	0.65	65	1.97	24 500	1.3
20	**4**	40	5.8	0.77	77	1.89	27 000	1.4
21	**4**[f]	40	1	0.51	51	7.28	18 500	1.2
22	**5**	40	2.3	0.46	46	2.85	28 000	1.2
23	**6**	40	1.1	0.61	61	7.92	39 000	1.3
24	**6**	40	2.3	0.68	68	4.22	39 500	1.3
25	**6**	40	3.5	0.78	78	3.18	42 000	1.4

[a] Polymerization conditions: 70 μmol of initiator, *rac*-LA: initiator = 100. [b] Percentage conversion of the monomer (weight polymer recovered × 100/weight of monomer). [c] kg polymer (mol Ln)$^{-1}$·h^{-1}. [d] Determined by GPC relative to polystyrene standards. [e] $[\{La(\eta^3\text{-}C_3H_5)_3(\eta^1\text{-}C_4H_8O_2)\}_2(\mu\text{-}C_4H_8O_2)]$. [f] Addition of HO^{i}Pr to the precatalyst in a ratio of 1:1.

40 °C (entries 2 and 11); **1** gives 16% of conversion of 100 equiv of *rac*-lactide after 1 h, with a productivity of >2.3 × 10^3 g PLA (mol Y)$^{-1}$·h^{-1}. The product was a medium molecular weight polymer with very narrow polydispersity ($M_w = 18\,000$, $M_w/M_n = 1.1$). On the other hand, when **1** and **2** were tested at room temperature, no polymer was obtained after 1 h polymerization, whereas the analogous La complex $[La(\eta^3\text{-}C_3H_5)_3(\kappa^1\text{-}dioxane)]_2(\mu\text{-}dioxane)$ showed good activity (entry 12). Increasing the reaction time at 20 °C to several hours did, however, result in significant polymer formation. Evidently at that temperature there was an induction period of up to 2.5 h. No such induction period was observed at 40 °C, as is exemplified in Figure 4 for the yttrium BDI catalyst **4**.

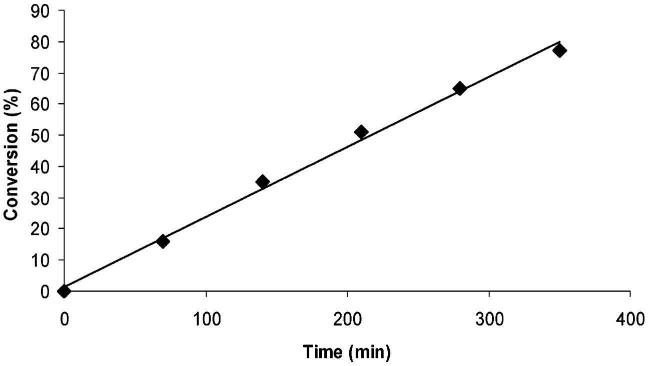

Figure 4. Conversion of *rac*-LA as a function of time, catalyzed by **4** at 40 °C (THF, [LA]/[Y] = 100).

These observations suggest the existence of a preactivation step, possibly due to the presence of traces of protic impurities. Consistent with that assumption, the addition of 1 equiv of HO^{i}Pr to the precatalyst resulted in a significant activity increase, with the conversion rising from 16 to 51% under otherwise identical conditions. The polymer characteristics were unchanged.

As seen in the case of ϵ-caprolactone polymerization, the effect of the metal radius on the catalytic activity can also be observed, La ≥ Nd > Sm > Y (entries 15, 17, 22, and 24). End group analysis of the polymers by ^{1}H NMR spectroscopy showed that, as for PCL, the polymerization was initiated by nucleophilic attack of allyl on lactide. The homonuclear decoupled ^{1}H NMR spectra in the methine region of the PLA (CDCl$_3$, 298 K, 500 MHz) revealed that, unlike zinc and magnesium BDI complexes, catalysts **3**−**6** are not stereoselective

Table 5. Crystal Data and Summary of Data Collection and Refinement Details for 1, 2, and 5

	1	**2**	**5**
formula	$C_{13}H_{23}O_2Y$	$C_{13}H_{23}O_2Sm$	$C_{35}H_{51}N_2Sm$
cryst size (mm)	0.28 × 0.07 × 0.05	0.14 × 0.05 × 0.02	0.16 × 0.14 × 0.12
fw	300.2	361.7	650.13
cryst syst	monoclinic	monoclinic	triclinic
space group	*C*2/*c* (no. 15)	*C*2/*c* (no. 15)	$P\bar{1}$ (no. 2)
a, Å	14.0919(5)	14.1965(3)	10.9089(3)
b, Å	7.7544(3)	7.8233(2)	12.3956(3)
c, Å	13.6632(6)	13.6478(4)	13.9731(4)
α, deg	90	90	65.0710(18)
β, deg	112.552(2)	111.5527(10)	78.7228(14)
γ, deg	90	90	73.3055(12)
V, Å^3	1378.87(9)	1409.79(6)	1635.17(8)
Z	4	4	2
D_{calcd}, Mg/m^3	1.446	1.704	1.320
μ, mm^{-1}	4.215	4.151	1.819
F(000)	624	716	674
no. of indep reflns	1576 (R_{int} = 0.075)	1621 (R_{int} = 0.052)	7428 (R_{int} = 0.0424)
no. of obsd reflns ($I > 2\sigma_i$)	1424	1488	6436
no. of data/restraints/parameters	1576/2/83	1621/0/79	7428/0/343
goodness of fit	1.073	1.078	1.076
final *R* indices (all data)	$R_1 = 0.068$, $wR_2 = 0.152$*	$R_1 = 0.034$, $wR_2 = 0.056$[b]	$R_1 = 0.0522$, $wR_2 = 0.0836$[c]
final *R* indices (obsd data)	$R_1 = 0.059$, $wR_2 = 0.146$[a]	$R_1 = 0.026$, $wR_2 = 0.054$	$R_1 = 0.0401$, $wR_2 = 0.0782$
weighting params *A*, *B*[a]	0.0808, 8.37	0.0184, 0.64	0.0154, 2.97
largest diff peak and hole (e·Å^{-3})	1.87, −1.36	0.88, −1.09	1.08, −0.56
location of largest diff peak(s)	close to Y atom	close to Sm atom	close to allyl group of C(30−32)

[a] Reflection weighting scheme: $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ with $P = (F_o^2 + 2F_c^2)/3$.

and give atactic PLA, most probably as the result of the larger ionic radius, which leads to more flexible and sterically less congested active centers. Similar behavior has been recently reported for calcium complexes of the type (BDI)Ca(N(SiMe$_3$)$_2$)$_2$·THF in comparison with the corresponding magnesium analogues.[23]

Conclusions

The tris(η^3-allyl) lanthanides [La(η^3-C$_3$H$_5$)$_3$(η^1-dioxane)]$_2$(μ-dioxane) and [Ln(η^3-C$_3$H$_5$)$_3$(μ-dioxane)]$_\infty$ (Ln = Y, **1**; Sm, **2**; Nd) are readily accessible in one-pot reactions from LnCl$_3$(THF)$_n$ with (allyl)MgCl, in almost quantitative yields. In the solid state, complexes **1** and **2** exist as linear coordination polymers containing distorted square-pyramidal lanthanide centers with alternating relative orientations. The reaction of the tris(η^3-allyl) lanthanides with BDI−H generates cleanly β-diketiminato compounds of the type Ln(η^3-C$_3$H$_5$)$_2$(BDI) (Ln = La, **3**; Y, **4**; Sm, **5**; Nd, **6**), the first such mixed-ligand lanthanide allyl compounds. The structure of **5** shows a distorted tetrahedral coordination geometry in the solid state. The allyl ligands are sufficiently nucleophilic for attack on cyclic esters, so that these compounds can act as highly effective single-component catalysts for the ring-opening polymerization of ϵ-caprolactone and *rac*-lactide and, with suitable precautions, without the need of an activator or scavenger. Not unexpectedly, the polymerization of LA is slower than that of CL but offers good control and gives polymers with polydispersities as narrow as M_w/M_n = 1.1 under mild conditions.

Experimental Section

General Procedures. All manipulations were performed under nitrogen, using standard Schlenk techniques. Solvents were predried over sodium wire (toluene, light petroleum, THF, diethyl ether) or calcium hydride (dichloromethane) and distilled under nitrogen from sodium (toluene), sodium−potassium alloy (light petroleum, bp 40−60 °C), sodium−benzophenone (THF, diethyl ether), or calcium hydride (dichloromethane). Deuterated solvents were stored over activated 4 Å molecular sieves and degassed by several freeze−thaw cycles. LnCl$_3$(H$_2$O)$_6$ and rare earth metal powders were purchased (Aldrich), and anhydrous LnCl$_3$[24] and β-diketimines[25] were prepared according to the literature procedures. LnCl$_3$(THF)$_n$ was prepared by Soxhlet extraction of LnCl$_3$ with THF for several days. ϵ-Caprolactone was dried by stirring over fresh CaH$_2$ for 48 h, distilled under reduced pressure, and stored over activated 4 Å molecular sieves. *rac*-Lactide was sublimed twice, recrystallized from THF, and finally sublimed again prior to use. NMR spectra were recorded using a Bruker Avance DPX-300 spectrometer. ^{1}H NMR spectra (300.1 MHz) were referenced to the residual solvent protons of the deuterated solvent used. ^{13}C NMR spectra (75.5 MHz) were referenced internally to the D-coupled ^{13}C resonances of the NMR solvent. Gel permeation chromatography (GPC) measurements were performed on a Polymer Laboratories PL-GPC-220 instrument equipped with a PLgel 5 Å Mixed-C column, a refractive index detector, and a PD2040 light-scattering detector. The GPC column was eluted with THF at 40 °C at 1 mL/min and was calibrated using eight monodisperse polystyrene standards in the range 580−483 000 Da.

Preparation of [Y(η^3-C$_3$H$_5$)$_3$(μ-C$_4$H$_8$O$_2$)]$_\infty$ (1). To a solution of YCl$_3$(THF)$_{3.5}$ (1 g, 2.43 mmol) in THF (100 mL) was added dropwise a solution of (allyl)MgCl in THF (16.2 mL, 0.45 M, 7.29 mmol) at room temperature, followed by 1,4-dioxane (25 mL). The initial pale orange solution became dark orange over time. The resulting suspension was stirred at room temperature for 15 h. Filtration and removal of the volatiles left an orange oil, which was extracted with 1,4-dioxane (10 mL). Finally, toluene was added (60 mL), and the mixture was left to crystallize at −26 °C to give **1** as an orange microcrystalline solid, yield 0.55 g (1.82 mmol, 82.2%). Anal. Calcd for C$_{13}$H$_{23}$O$_2$Y: C, 51.96; H, 7.66. Found: C, 51.88; H, 7.66. ^{1}H NMR (THF-d_8, 20 °C): δ 6.23 (m, 3 H, CH$_2$C*H*CH$_2$), 2.34 (d, J_{HH} = 9.6 Hz, 12 H$_{syn,anti}$, C*H*$_2$CHC*H*$_2$), 3.54 (s, 8 H, μ-C$_4$H$_8$O$_2$). ^{13}C NMR (THF-d_8, 20 °C): δ 149.5 (CH$_2$*C*HCH$_2$), 56.9 (*C*H$_2$CH*C*H$_2$), 67.9 (μ-C$_4$H$_8$O$_2$).

Preparation of [Sm(η^3-C$_3$H$_5$)$_3$(μ-C$_4$H$_8$O$_2$)]$_\infty$ (2). Following the procedure described for **1**, a solution of SmCl$_3$(THF)$_{3.5}$ (1 g, 2.11 mmol) in THF (100 mL) was treated with (allyl)MgCl (14.1 mL, 6.34 mmol) at room temperature, with addition of 1,4-dioxane (25 mL). The color changed from orange to red over time. Workup gave **2** as a red microcrystalline solid, yield 0.59 g (1.63 mmol, 82.9%). Anal. Calcd for C$_{13}$H$_{23}$O$_2$Sm: C, 43.17; H, 6.36. Found: C, 43.12; H, 6.44.

Preparation of La(η^3-C$_3$H$_5$)$_2${HC(MeCNC$_6$H$_3$^{i}Pr$_2$-2,6)$_2$} (3). To a yellow solution of [La(η^3-C$_3$H$_5$)$_3$(η^1-C$_4$H$_8$O$_2$)]$_2$(μ-C$_4$H$_8$O$_2$) (1 g, 1.26 mmol) in THF (60 mL) was added dropwise at room temperature a solution of the diketimine HC(MeC=NAr)(MeCNHAr) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (1.06 g, 2.53 mmol) in THF (20 mL). The mixture was warmed to 60 °C and stirred for 15 h, during which time the solution became pale yellow. After removing the volatiles, the residue was washed with cold petroleum (10 mL). Finally, adding THF (20 mL) and cooling to −26 °C afforded **3** as a pale yellow microcrystalline solid, yield 1.12 g (1.75 mmol, 69.1%). Anal. Calcd for C$_{35}$H$_{51}$N$_2$La: C, 65.84; H, 7.99; N, 4.38. Found: C, 65.68; H, 7.81; N, 4.41. ^{1}H NMR (benzene-d_6, 20 °C): δ 7.27 (s, 6 H, H$_{o,m,p}$), 6.41 (m, 2 H, CH$_2$C*H*CH$_2$), 4.91 (s, H, CH$_\beta$), 3.29 (d, $^3J_{HH}$ = 8.8 Hz, 4 H$_{syn}$, C*H*$_2$CHC*H*$_2$), 2.80 (sep, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 2.52 (d, $^3J_{HH}$ = 15.5 Hz, 4 H$_{anti}$, C*H*$_2$CHC*H*$_2$), 1.62 (s, 6 H, Me), 1.19 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.08 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6, 20 °C): δ 160.7 (CH$_2$*C*HCH$_2$), 142.4−123.6 (aryl), 118.3 (C$_\beta$), 93.5 (CH$_\beta$), 69.0 (*C*H$_2$CH*C*H$_2$), 28.1 *C*H(CH$_3$)$_2$, 27.3 (Me), 25.1−20.4 (CH(*C*H$_3$)$_2$).

Preparation of Y(η^3-C$_3$H$_5$)$_2${HC(MeCNC$_6$H$_3$^{i}Pr$_2$-2,6)$_2$} (4). Following the procedure described for **3**, an orange solution of **1** (1 g, 3.33 mmol) in THF (60 mL) was reacted with HC(MeC=NAr)(MeCNHAr) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (1.39 g, 3.33 mmol) in THF (20 mL) at room temperature. Suitable workup gave **4** as a pale orange microcrystalline solid, yield 1.23 g (2.09 mmol, 62.7%). Anal. Calcd for C$_{35}$H$_{51}$N$_2$Y: C, 71.44; H, 8.67; N, 4.76. Found: C, 71.23; H, 8.52; N, 4.78. ^{1}H NMR (benzene-d_6, 20 °C): δ 7.21 (s, 6 H, H$_{o,m,p}$), 6.80 (m, 2 H, CH$_2$C*H*CH$_2$), 4.97 (s, H, CH$_\beta$), 3.47 (d, $^3J_{HH}$ = 8.6 Hz, 4 H$_{syn}$, C*H*$_2$CHC*H*$_2$), 2.73 (sep, $^3J_{HH}$ = 6.8 Hz, 4 H, C*H*(CH$_3$)$_2$), 2.46 (d, $^3J_{HH}$ = 15.2 Hz, 4 H$_{anti}$, C*H*$_2$CHC*H*$_2$), 1.58 (s, 6 H, Me), 1.16 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.06 (d, $^3J_{HH}$ = 6.8 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C NMR (benzene-d_6, 20 °C): δ 163.6 (CH$_2$*C*HCH$_2$), 141.3−121.3 (aryl), 117.2 (C$_\beta$), 93.4 (CH$_\beta$), 68.7 (*C*H$_2$CH*C*H$_2$), 28.1 *C*H(CH$_3$)$_2$, 26.9 (Me), 24.1−19.9 (CH(*C*H$_3$)$_2$).

Preparation of Sm(η^3-C$_3$H$_5$)$_2${HC(MeCNC$_6$H$_3$^{i}Pr$_2$-2,6)$_2$} (5). Following the procedure described for **3**, a red solution of **2** (1 g, 2.76 mmol) in THF (60 mL) was reacted with HC(MeC=NAr)(MeCNHAr) (Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$) (1.15 g, 2.76 mmol) in THF (20 mL) at room temperature. After stirring for 15 h at 60 °C volatiles were removed and the residue was washed with cold light petroleum (10 mL). Finally, THF was added (20 mL) and the mixture left to crystallize at −26 °C to give **5** as a pale red microcrystalline solid, yield 1.23 g (2.09 mmol, 62.7%).

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Anal. Calcd for $C_{35}H_{51}N_2Sm$: C, 64.60; H, 7.84; N, 4.30. Found: C, 64.60; H, 7.84; N, 4.30.

Preparation of $Nd(\eta^3\text{-}C_3H_5)_2\{HC(MeCNC_6H_3{}^iPr_2\text{-}2,6)_2\}$ (6). The compound was made from $[Nd(\eta^3\text{-}C_3H_5)_3(\mu\text{-}C_4H_8O_2)]_\infty$ (1 g, 2.81 mmol) and HC(MeC=NAr)(MeCNHAr) (Ar = 2,6-${}^iPr_2C_6H_3$) (1.17 g, 2.81 mmol), to give **6** as a pale green microcrystalline solid, yield 1.09 g (1.69 mmol, 60.1%). Anal. Calcd for $C_{35}H_{51}N_2Nd$: C, 65.29; H, 7.92; N, 4.35. Found: C, 65.35; H, 7.87; N, 4.33.

X-ray Crystallography. Crystals coated with dry Nujol or perfluoropolyether were mounted on a glass fiber and fixed in the cold nitrogen steam (T = 180(2) K). Intensity data were collected on a Nonius Kappa CCD diffractometer equipped with a graphite monochromator (Mo Kα, λ = 0.71073 Å). Data were processed using the DENZO/SCALE PACK programs[26] and absorption corrections applied in SORTAV.[27] The structures were determined by direct methods in the SHELXS programs and refined by full-matrix least-squares methods, on F^2 values, in SHELXL.[28] Compounds **1** and **2** are isostructural and, in both, the allyl group of C(31−33) is disordered about a 2-fold symmetry axis, in overlapping sites; in **1**, C(31) was refined isotropically and both C−C bond lengths in this ligand were constrained; in **2**, C(31) and C(33′) are essentially superimposed and were refined as a single, anisotropic atom. The remaining non-hydrogen atoms (in all complexes) were refined with anisotropic thermal parameters. Hydrogen atoms were included in idealized positions, and their U_{iso} values set to ride on the U_{eq} values of the parent carbon atoms. Scattering factors for neutral atoms were taken from the literature.[29] Computer programs were run on a DEC-AlphaStation 200 4/100 in the Biological Chemistry Department, John Innes Centre.

Polymerization Procedures. Polymerizations of ϵ-caprolactone (CL) were carried out under nitrogen in flame-dried round-bottom flasks equipped with a magnetic stirrer. In a typical procedure, the initiator was dissolved in the appropriate amount of solvent, and the temperature equilibration was ensured by stirring the solution for 15 min on a water bath. ϵ-CL was injected, and polymerization times were measured from that point. Polymerizations were terminated by addition of acetic acid (5% vol) in methanol. The polymers were precipitated into excess methanol, filtered, dissolved in THF, reprecipitated with methanol, and dried in vacuo to constant weight.

Polymerizations of *rac*-lactide (LA) were performed under nitrogen in flame-dried round-bottom flasks. In the glovebox, the required amounts of *rac*-lactide and initiator were weighed out into separate Schlenk tubes. These were then attached to the vacuum line, and the initiator and the monomer were dissolved in the appropriate amounts of solvent. Temperature equilibration was ensured by stirring the flasks for 15 min on a water bath, followed by the injection of the initiator into the monomer solution. Polymerizations were stopped by injecting a solution of acetic acid (5% vol) in methanol. Polymers were precipitated in methanol, filtered, dissolved in THF, reprecipitated in methanol, and dried in vacuo to constant weight.

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Supporting Information Available: Full listing of crystallographic details for compounds **1**, **2**, and **5**. This material is available free of charge via the Internet at http:/pubs.acs.org.

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