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Bis[bis(oxazolinato)] Complexes of Yttrium and Lanthanum: Molecular Structure and Use in Polymerization of DL-Lactide and DL-β-Butyrolactone

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Bis[bis(oxazolinato)]lanthanide complexes of general type $[Box]_2Ln[N(SiHMe_2)_2]$ (Ln = Y, La; Box = deprotonated chiral and nonchiral 2,2′-methylene[bis(oxazoline)] ligands) have been prepared by amine elimination protocols. The complexes have been characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. The solid-state structure of the first bis[bis(oxazolinato)]-lanthanide complex, i.e. $\{2,2'$-(α-methylmethylene)bis(4,4-dimethyl-2-oxazolinato)$\}_2$-$Y[N(SiHMe_2)_2]$ (**1**), is reported. Complex **1** features a five-coordinate yttrium center in a distorted trigonal bipyramidal geometry, where the Box ligands adopts a conformation to minimize nonbonded interactions. The prepared complexes are among the most active initiators known in the ring-opening polymerization of DL-lactide and DL-β-butyrolactone, with TOF up to 31200 h^{-1} at room temperature, and are highly productive (TON up to 2400). The produced poly(lactide)s and poly(hydroxybutyrate)s have narrow polydispersities (M_w/M_n = 1.08–1.44) and controlled number-average molecular masses (M_n up to 182000 g mol^{-1}). However, whether chiral or nonchiral Box ligands are used, the polymers show an atactic microstructure.

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Introduction

Ring-opening polymerization (ROP) of lactides (LA) and related lactone monomers has become a quite topical research field in recent years.[1] A reason for this interest is that the resulting biodegradable/biocompatible polymers, in addition to their high-tech applications,[1a,1b] could replace conventional polyolefinic materials.[2] An interesting challenge in this chemistry is to control the stereoselective ROP of *racemic* monomers, to produce in turn either syndiotactic, heterotactic, or isotactic stereoblock polymers, which each have their own peculiar physico-chemical properties.[1] Group 3 metal complexes are among the best catalysts/initiators for such ROP reactions.[1b,1c] For instance, we have recently reported that discrete group 3 complexes having a tetradentate [amino-ether-bis(phenolate)] ligand are highly active single-site initiators in the synthesis of heterotactic and syndiotactic poly(lactide) (PLA) from *rac*-lactide and *meso*-lactide, respectively.[3] The same complexes are also very active and stereoselective initiators for the controlled polymerization of *rac*-β-butyrolactone (BBL), generating highly syndiotactic poly(3-hydroxybutyrate) (PHB).[4]

Bis(oxazoline) (Box) are some of the most effective transition-metal ligands for a variety of asymmetric catalytic transformations.[5] Although the synthesis of mono- and bis[bis(oxazolinato)] organogroup 3 metal complexes has been known since 1999,[6] their use in catalysis has been so far limited to asymmetric hydroamination.[7] In this study we synthesized chiral and nonchiral bis[bis(oxazolinato)]-lanthanide complexes for the ROP of *rac*-lactide and *rac*-BBL. Their activity and degree of control have been investigated. The first X-ray-characterized bis[bis(oxazolinato)]-lanthanide catalyst precursor is also presented.

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Results and Discussion

Synthesis of Complexes

Bis[bis(oxazolinato)]-lanthanide complexes **1**–**6** of the type $[Box]_2Ln[N(SiHMe_2)_2]$ (Ln = Y, La; Box = deprotonated ligand) were prepared following the general σ-bond metathesis procedure reported by Anwander et al.[6,7] The reaction between 2 equiv. of a neutral Box ligand and a homoleptic precursor $Ln[N(SiHMe_2)_2]_3(THF)_2$ in benzene or toluene resulted in the protonolysis of two of the bulky (dimethylsilyl)amido ligands by the relatively acidic methine (**1**–**3**) or methylene (**4**–**6**) protons (Scheme 1). Yttrium and lanthanum were chosen for this study because they are representative of small and large lanthanides, respectively, and allow straightforward NMR studies thanks to their diamagnetism. The reaction is readily monitored by ^1H NMR spectroscopy. For all the ligand/metal systems investigated, the resulting reaction mixture remains a clear, homogeneous

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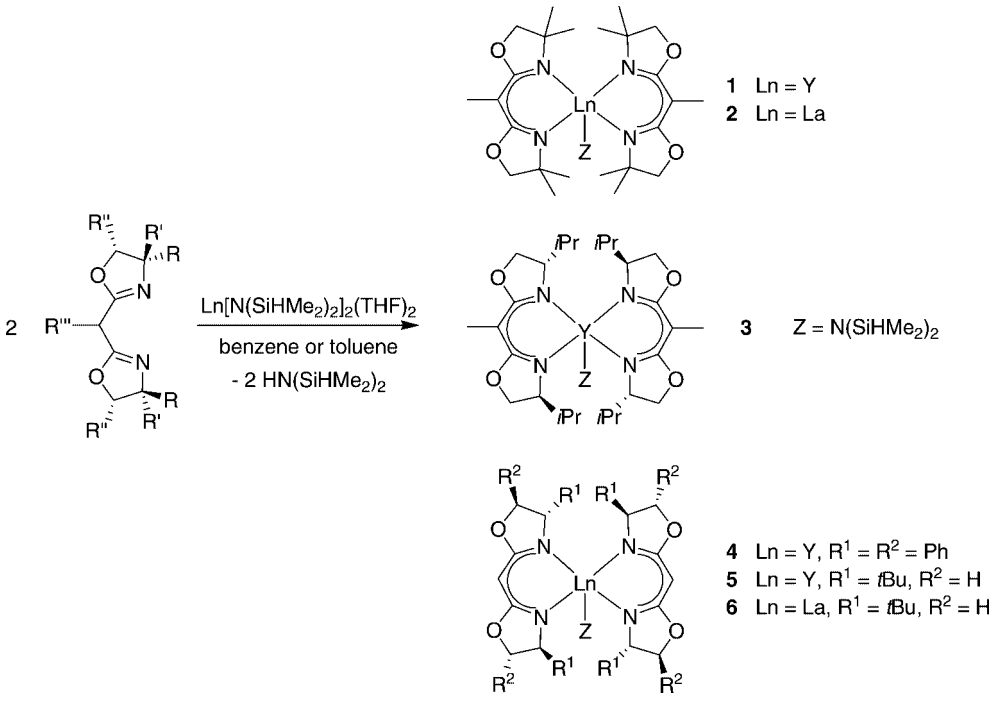

Scheme 1.

solution, and complete conversion of reagents is observed within 2 h at 20 °C. The resulting crude NMR shows clean release of 2 equiv. of $HN(SiHMe_2)_2$, with resonances for one major or exclusive (>95–99%) product $[Box]_2$-$Ln[N(SiHMe_2)_2]$. This good reactivity and selectivity allowed us to generate effectively in situ some of the complexes, and thus investigate the performances of a broad range of polymerization precursors (only a few of these are described in this report).

In addition to previously reported compounds **5** and **6**,[6] the identity of new complexes **1**–**4** was fully established by means of 1D and 2D $^1H/^{13}C$ NMR experiments and elemental analyses. Key NMR spectroscopic data include a single set of ^1H and ^{13}C resonances for two Box ligands equivalent on the NMR timescale at 20 °C. Also, two distinct ^{13}C resonances for inequivalent $SiH\mathit{Me}_2$ groups are observed in **1** (δ = 3.58, 3.29), **3** (δ = 3.71, 3.57) and **4** (δ = 3.51, 2.84); this is further confirmed by ^1H NMR spectroscopy in **3** (δ = 0.35, 0.32) and **4** (δ = 0.35, 0.18), but does not appear in the lower field ^1H NMR spectra (200–300 MHz) of **1**. The 300 MHz ^1H and 125 MHz ^{13}C NMR spectra of **2** show a single resonance for the $SiH\mathit{Me}_2$ groups, though incidental overlapping cannot be discarded.[6] Comparable to the case of **5** and **6**,[6] coordination of the chiral ligands in **3** and **4** renders the $SiHMe_2$ groups diastereotopic and inequivalent; however, this explanation cannot stand for the achiral complex **1**. On the other hand, the chemical shifts of the SiH protons (**1**, δ = 5.26; **2**, δ = 5.34; **3**, δ = 5.01; **4**, δ = 4.82 ppm) argue against any significant Si–H–Y β-agostic interaction.[8]

Molecular Structure of {1,1-Bis[4,4-dimethyl-1,3-oxazolin-2-yl]}$_2$Y[N(SiHMe$_2$)$_2$] (1)

To gain a better insight into the above-mentioned structural features, an X-ray diffraction study was conducted on **1**. This is the first molecular structure reported for a bis-[bis(oxazolinato)]-lanthanide compound[9] and it can be compared to the only two examples of mono[bis(oxazolinato)]-lanthanide complexes that have been characterized so far in the solid state.[6,7] Suitable crystals of **1** were grown at room temperature from a saturated benzene solution. The unit cell contains two independent molecules (**A** and **B**), which feature overall the same structural arrangement and coordination geometry, but noticeable differences in bond lengths and angles; nonetheless, structural trends remain comparable within both molecules and mostly data of molecule **A** will be discussed below. An ORTEP view of molecule **A** is presented in Figure 1 and a partial list of bond lengths and angles for both molecules **A** and **B** is given in Table 1; complete details of the crystallographic analysis are given in Table 3.

Compound **1** is monomeric in the solid state, with a five-coordinate yttrium center ligated by the four nitrogen atoms of the two Box ligands, and one $N(SiHMe_2)_2$ group. The geometry at the yttrium center is distorted trigonal bipyramidal, with the apical sites being occupied by two Box nitrogen atoms [N(101) and N(121) in molecule **A**]. An approximate [noncrystallographic] C_2 symmetry axis exists through the Y^{3+} and $N(SiHMe_2)_2$ centers. The Box ligands are oriented away from the $N(SiHMe_2)_2$ group in a horse

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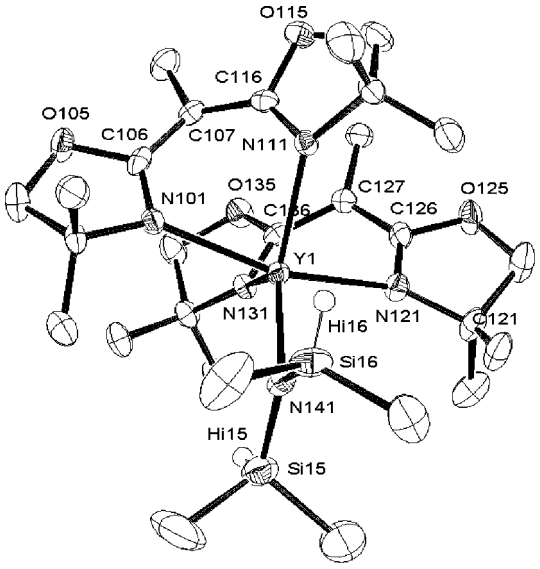

Figure 1. Molecular structure of $[Me_2Box]_2Y[N(SiHMe_2)_2]$ (**1**) (only molecule **A** is displayed). All hydrogen atoms, except those on Si atoms (Hi15 and Hi16), are omitted for reasons of clarity. Ellipsoids are drawn at the 50% probability level.

saddle fashion, thus minimizing steric hindrance. Comparable to that found in mono(Box)-lanthanide,[6,7] -copper,[10a] -rhodium,[10b] -aluminum,[11a] and -gallium[11b] complexes, significant delocalization of the ligand negative charge is suggested by the elongated N(101)–C(106) and N(111)–C(116) distances [1.321(3) and 1.322(3) Å, respectively] and the shortened C(106)–C(107) and C(116)–C(107) distances [1.401(4) and 1.406(4) Å, respectively]. The bis(oxazolinato) ligands in molecule **A** are somewhat dissymmetrically coordinated as apparent from the ca. 0.05–0.06 Å difference between the Y(1)–N(101)/Y(1)–N(111), and Y(1)–N(131)/Y(1)–N(131) distances, but the dissymmetry is less pronounced in molecule **B** (0.01–0.03 Å). Those Y–N(Box) distances in **1** [2.325(2)–2.389(2) Å] are longer than those in the four-coordinate mono[bis(oxazolinato)]-yttrium complex $[t\text{BuBox}]Y[N(SiHMe_2)_2]_2$ reported by Anwander et al. [2.288(5) Å],[6] reflecting the hindrance induced by the second Box ligand. Steric crowding in **1** is also reflected by the twisting angle between the two oxazoline ring planes relative to one another [mean plane N(101)/mean plane N(111), 32.7°; N(121)/N(131), 31.9°; N(201)/N(211), 32.4°; N(221)/N(231), 32.7°], values which are sig-

Table 1. Selected bond lengths [Å] and angles [°] for $[Me_2Box]_2Y[N(SiHMe_2)_2]$ (**1**).

Molecule A		Molecule B	
Bond lengths			
Y(1)–N(141)	2.253(2)	Y(2)–N(241)	2.241(2)
Y(1)–N(131)	2.325(2)	Y(2)–N(231)	2.355(2)
Y(1)–N(121)	2.389(2)	Y(2)–N(221)	2.366(2)
Y(1)–N(111)	2.336(2)	Y(2)–N(211)	2.365(2)
Y(1)–N(101)	2.388(2)	Y(2)–N(201)	2.332(2)
Y(1)–C(136)	3.008(3)	Y(2)–C(236)	3.041(3)
Y(1)–C(126)	3.077(3)	Y(2)–C(226)	3.088(3)
Y(1)–C(116)	3.023(3)	Y(2)–C(216)	3.087(3)
Y(1)–C(106)	3.099(3)	Y(2)–C(206)	3.039(3)
N(101)–C(106)	1.321(3)	N(201)–C(206)	1.326(3)
C(106)–C(107)	1.401(4)	C(206)–C(207)	1.408(3)
C(107)–C(116)	1.406(3)	C(207)–C(216)	1.407(3)
N(111)–C(116)	1.322(3)	N(211)–C(216)	1.317(3)
Si(15)–C(152)	1.839(4)	Si(26)–C(262)	1.864(3)
Si(15)–C(151)	1.854(4)	Si(26)–C(261)	1.872(3)
Si(16)–C(161)	1.859(3)	Si(27)–C(271)	1.856(3)
Si(16)–C(162)	1.869(3)	Si(27)–C(272)	1.868(3)
Bond angles			
N(141)–Y(1)–N(131)	119.32(8)	N(241)–Y(2)–N(201)	123.28(8)
N(141)–Y(1)–N(111)	128.74(7)	N(241)–Y(2)–N(231)	128.36(8)
N(131)–Y(1)–N(111)	111.94(7)	N(201)–Y(2)–N(231)	108.36(8)
N(141)–Y(1)–N(101)	99.83(7)	N(241)–Y(2)–N(221)	97.57(7)
N(131)–Y(1)–N(101)	92.57(7)	N(201)–Y(2)–N(221)	93.59(7)
N(111)–Y(1)–N(101)	77.01(7)	N(201)–Y(2)–N(211)	77.42(7)
N(141)–Y(1)–N(121)	99.35(7)	N(241)–Y(2)–N(211)	99.33(7)
N(131)–Y(1)–N(121)	77.62(7)	N(231)–Y(2)–N(221)	77.62(7)
N(111)–Y(1)–N(121)	91.26(7)	N(231)–Y(2)–N(211)	91.52(7)
N(101)–Y(1)–N(121)	160.81(7)	N(211)–Y(2)–N(221)	163.10(7)
C(106)–N(101)–Y(1)	109.98(16)	C(206)–N(201)–Y(2)	109.22(16)
N(101)–C(106)–C(107)	129.3(2)	N(201)–C(206)–C(207)	130.3(2)
C(106)–C(107)–C(116)	119.3(2)	C(206)–C(207)–C(216)	119.4(2)
N(111)–C(116)–C(107)	130.4(2)	N(211)–C(216)–C(207)	129.1(2)
C(116)–N(111)–Y(1)	108.25(15)	C(216)–N(211)–Y(2)	110.70(15)
Si(15)–N(141)–Y(1)	119.96(11)	Si(26)–N(241)–Y(2)	116.15(11)
Si(16)–N(141)–Y(1)	111.66(11)	Si(27)–N(241)–Y(2)	122.48(12)
Si(15)–N(141)–Si(16)	128.35(13)	Si(25)–N(241)–Si(26)	121.05(13)

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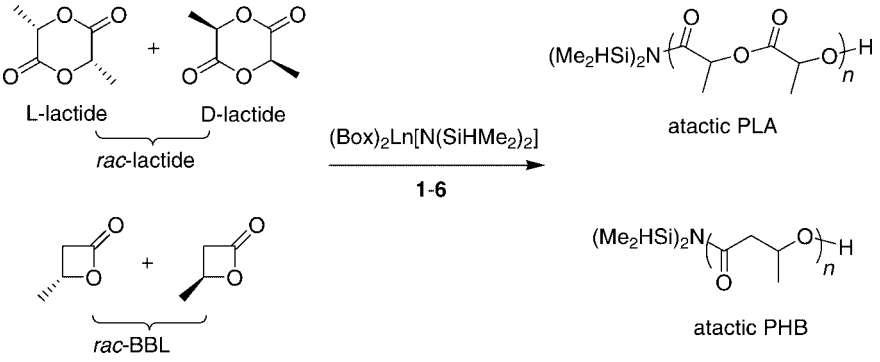
nificantly larger than those observed in mono[bis(oxazolinato)]-lanthanide complexes [12.4°, 15.7°].[6,7] On the other hand, the Y(1)–N(141) [2.253(2) Å] and Y(2)–N(241) [2.241(2) Å] silylamide bonds compare well to those in the four-coordinate [*t*BuBox]Y[N(SiHMe$_2$)$_2$]$_2$ [2.222(6) Å] and in the five-coordinate precursor amide complex [2.229(4)–2.276(4) Å].[12] The normal angles at the silylamide nitrogen atom and the long Y···H contact distances (>3.03 Å) argue against any significant β(Si–H)-Y agostic interaction, which is consistent with the NMR spectroscopic data (vide supra).

Ring-Opening Polymerization of *rac*-Lactide and *rac*-β-Butyrolactone

The prepared bis[bis(oxazolinato)]-lanthanide complexes are very active in the ROP of *rac*-lactide and *rac*-β-butyrolactone under mild conditions (Scheme 2, Table 2); polymerization experiments conducted with mono[bis(oxazolinato)]-yttrium complexes, e.g. [*t*BuBox]Y[N(SiHMe$_2$)$_2$]$_2$, gave poorly reproducible results. Complexes **1**–**4** allow complete conversion of 100 equiv. of lactide within 5–10 min at room temperature in either toluene or THF solutions at [*rac*-LA] = 0.5–1.0 mol/L. The yttrium complex **5** that bears bulky *tert*-butyl-substituted BOX ligands is inactive in toluene (entry 4), which possibly reflects the large steric crowding at the metal center. However, this complex shows good activity in THF (entry 5), stressing the crucial importance of solvent in these ROPs.[3,4,13] Disappointingly, the use of chiral Box ligands in the initiators does not lead to stereocontrol of the polymerization: all PLA and PHB polymers, including also those produced with the achiral initiators **1** and **2**, show atactic (or slightly isotactic-enriched) microstructures, as determined by NMR analysis.[4,14] Contrary to our previous observations with [amino-ether-bis-



Scheme 2.

Table 2. Polymerization of *rac*-lactide and *rac*-β-butyrolactone with bis[bis(oxazolinato)]-lanthanide complexes.[a]

Entry	M	[M]/[Ln]	Complex	Solvent	Time[b]	Conv.[c]	$M_{n,th}$[d]	$M_{n,exp}$[e]	M_w/M_n[e]
					[min]	[mol-%]	[g mol^{-1}]	[g mol^{-1}]	
1	*rac*-LA	100	**3**	toluene	5	>98	14400	18300	1.32
2	*rac*-LA	100	**3**	THF	5	>98	14400	36400	1.34
3	*rac*-LA	100	**4**	toluene	10	>98	14400	22400	1.29
4	*rac*-LA	100	**5**	toluene	20	0	14400	–	–
5	*rac*-LA	100	**5**	THF	20	>98	14400	37000	1.36
6	*rac*-LA	100	**6**	THF	10	95	13700	18000	1.18
7	*rac*-LA	500	**6**	THF	1	95	68400	63000	1.29
8	*rac*-LA	100	**1**	toluene	5	>98	14400	27600	1.25
9	*rac*-LA	100	**1**	THF	10	>98	14400	33000	1.27
10	*rac*-LA	100	**2**	THF	10	>98	14400	19000	1.22
11	(*S*)-LA	500	**1**	THF	5	>98	72000	89000	1.44
12	*rac*-LA	500	**1**	THF	5	95	68400	68300	1.14
13[f]	*rac*-LA	500	**1**	THF	10	>98	14400	6000	1.07
14	*rac*-LA	1000	**1**	THF	120	>98	144000	138000	1.24
15[g]	*rac*-LA	1000	**1**	THF	20	95	45600	33000	1.08
16	*rac*-LA	2000	**1**	THF	5	95	273600	182000	1.37
17	*rac*-LA	4000	**1**	THF	5	65	374400	ns[h]	ns[h]
8	*rac*-BBL	200	**1**	THF	2	60	9900	8000	1.21
19	*rac*-BBL	200	**5**	THF	2	>98	16800	17000	1.19
20	*rac*-BBL	200	**5**	toluene	2	>98	16800	19000	1.14

[a] General conditions: [M] = 0.5–1.0 mol L^{-1}, T = 20 °C. [b] Reaction time was not necessarily optimized. [c] Conversion of monomer M as determined by ^{1}H NMR spectroscopy. [d] M_n Value calculated from the relation: Molecular weight of M × conv. × [M]/[Ln]. [e] Experimental (uncorrected) M_n and M_w/M_n values determined by GPC in THF vs. polystyrene standards. [f] Reaction run in the presence of 5 equiv. (vs. Ln) of *i*PrOH. [g] Reaction run in the presence of 3 equiv. (vs. Ln) of *i*PrOH. [h] Polymer insoluble in hot THF.

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(phenolate)]-lanthanide systems,[3,4] decreasing the temperature down to –20 °C and changing the solvent (toluene, THF) resulted in no enhancement in stereoselectivity. Polymerization of L-lactide by **1** (entry 11) or **3** resulted in pure isotactic PLA; the decoupled ^{1}H NMR spectrum of the polymer showed one sharp resonance for the methine region. This observation supports the lack of base-promoted epimerization of L-lactide or PLA and argues against an anionic polymerization mechanism being operative.[15]

Because of the absence of stereocontrol with [Box]$_2$-Ln[N(SiHMe$_2$)$_2$] catalysts, further experiments aimed at investigating the degree of control of polymerization were carried out with the nonchiral systems **1** and **2** (entries 8–18). All the PLAs and PHBs obtained with amido complexes showed monomodal GPC traces with relatively narrow polydispersity values (M_w/M_n = 1.14–1.44). In most cases, the experimental (uncorrected) number-average molecular mass (M_n) values are close to the theoretical ones (calculated on the assumption that each silylamide group initiates the polymerization). As shown by the monotonous relationship between the monomer-to-metal ratio and M_n values (Figure 2), which is linear at least up to LA-to-Y = 1000, a good control of *rac*-LA polymerization is achieved with **1**. Even a catalyst loading of 0.05% yielded almost quantitatively PLA with M_n as high as 182000 g mol^{-1} (entry 16). The productivity of this system is remarkable, enabling high conversion for an unprecedented high *rac*-LA-to-Y ratio of 4000 within 5 min (TOF = 31200 h^{-1}) (entry 17). Very narrow polydispersities of 1.07–1.08 were obtained by pre-reacting the amido complex **1** with 2-propanol, to generate in situ the corresponding isopropoxide bis[bis(oxazolinato)] species (entries 13, 15). It is well known that isopropoxide is usually a better initiating group than amido [-N(SiMe$_3$)$_2$, -N(SiHMe$_2$)$_2$] for the ROP of *rac*-lactide at room temperature.[3b,16]

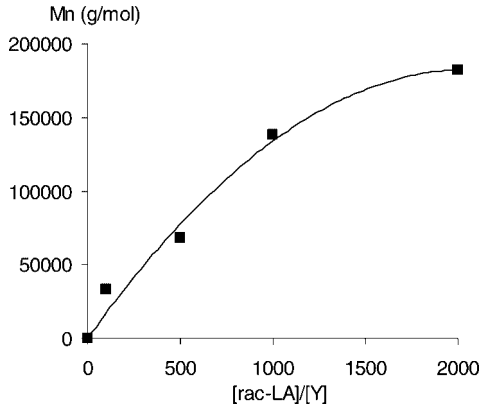

Figure 2. Variation of number-average molecular masses (M_n) with monomer-to-yttrium ratio in the polymerization of *rac*-lactide with complex **1** (see Table 2 for conditions).

The ROP of 200 equiv. of *rac*-BBL proceeded also in a controlled manner (entries 18–20). Surprisingly, the apparent rate is faster with **5** (TOF > 6000 h^{-1}) than **1** (TOF = 3600 h^{-1}). Even when the polymerization is conducted in toluene, **5** enables fast conversion of *rac*-BBL, i.e. the opposite trend to that observed for *rac*-lactide polymerization (entry 4). Reasons for this contradictory trend remain unclear to date, but concur with the peculiar behaviors of LA and BBL monomers in ROPs.

Conclusions

Amido-bis[bis(oxazolinato)] complexes of yttrium and lanthanum, readily prepared from a tris(amido) lanthanide precursor and a Box ligand, are very active single-site initiators for the ROP polymerization of *rac*-lactide and *rac*-β-butyrolactone. Their performances in terms of kinetics and productivity compare favorably with the best systems so far disclosed. The polymerizations proceed in a controlled fashion, leading to PLAs and PHBs with relatively narrow polydispersities and number-average molecular masses in good agreement with calculated values. However, such complexes based on well-known chiral Box ligands appear unable to control the microstructure of the polymer: only atactic PLAs and PHBs are produced, which can be achieved as well with a cheaper nonchiral bis[bis(oxazolinato)]-lanthanide complex.

Experimental Section

General Considerations: Synthesis of lanthanide complexes and polymerization experiments were carried out under purified argon using standard Schlenk techniques or in a high-performance (<1 ppm O_2, <2 ppm H_2O) glove box. Solvents (toluene, THF) and deuterated solvents ([D$_6$]benzene, [D$_8$]toluene, [D$_8$]THF/99.5% D, Eurisotop) were freshly distilled from Na/K alloy under nitrogen and degassed thoroughly by freeze-thaw-vacuum cycles prior to use. Bis(oxazoline) ligands were prepared following reported procedures[11a] or purchased from Aldrich and used as received. Lanthanide precursors Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ and La[N(SiHMe$_2$)$_2$]$_3$-(THF)$_2$,[17] and complexes **5** and **6**,[6] were prepared following literature procedures. Racemic lactide and *S*-lactide (Aldrich) were recrystallized twice from dry toluene and then sublimed under vacuum at 50 °C. Racemic β-butyrolactone (Aldrich) was freshly distilled from CaH_2 alloy under nitrogen and degassed thoroughly by freeze-thaw-vacuum cycles prior to use.

Instruments and Measurements: NMR spectra were recorded with Bruker AC-200, AC-300, and AC-500 spectrometers in Teflon valve NMR tubes. ^{1}H and ^{13}C chemical shifts are reported in ppm vs. SiMe$_4$ and were determined by reference to the residual solvent peaks. Assignment of signals was made from multinuclear 1D [^{1}H, ^{13}C{^{1}H}] and 2D (COSY, HMQC, HMBC) NMR experiments. Coupling constants are given in Hertz. Size exclusion chromatography (SEC) of PLAs and PHBs was performed in THF at 20 °C using a Waters SIS HPLC pump, a Waters 410 refractometer, a DAD-UV detector, and Waters styragel columns (HR2, HR3, HR4, HR5E) or PL-GEL Mixte B and 100A columns. The number average molecular masses (M_n) and polydispersity index (M_w/M_n) of the resultant polymers were calculated with reference to a polystyrene calibration. The microstructure of PLAs was measured by homodecoupling ^{1}H NMR spectroscopy at 20 °C in $CDCl_3$ with a Bruker AC-500 spectrometer. The microstructure of PHBs was measured by analyzing the carbonyl region of ^{13}C{^{1}H} NMR spectra at 40 °C in $CDCl_3$ with a Bruker AC-500 spectrometer operating at 125 MHz.

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{2,2′-(α-Methylmethylene)bis(4,4-dimethyl-2-oxazolinato)}$_2$Y[N(SiHMe$_2$)$_2$] (1): A solution of 2,2′-(α-methylmethylene)bis[4,4-dimethyl-2-oxazoline] (100 mg, 0.446 mmol) in toluene (5 mL) was added slowly under an inert atmosphere to a solution of Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (140 mg, 0.223 mmol) in toluene (5 mL) at room temperature. The mixture was warmed at 70 °C and then stirred for 12 h. Volatiles were removed in vacuo and the resulting white solid was washed with cold hexane (1.0 mL), and dried under vacuum to give **1** (95 mg, 62%). ^{1}H NMR (200 MHz, C_6D_6): δ = 5.26 (m, 2 H, Si*H*Me$_2$), 3.58 (d, J = 7.7, 4 H, C*H*$_2$O), 3.45 (d, J = 7.7, 4 H, C*H*$_2$O), 2.23 (s, 6 H, C*H*$_3$CCN), 1.43 (s, 12 H, C*H*$_3$), 1.04 (s, 12 H, C*H*$_3$), 0.45 (d, J = 2.8 Hz, 12 H, Si*H*Me$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 171.40 (N*C*O), 77.28 (*C*H$_2$O), 67.94 (Me*C*CN), 66.20 (*C*Me$_2$), 28.20 (C*Me*$_2$), 26.31 (C*Me*$_2$), 11.23 (*Me*CCN), 3.58 (SiH*Me*Me), 3.29 (SiHMe*Me*) ppm. $C_{28}H_{52}N_5O_4Si_2Y$ (667.82): calcd. C 50.36, H 7.85, N 10.49; found C 49.86, H 7.98, N 10.25.

{2,2′-(α-Methylmethylene)bis(4,4-dimethyl-2-oxazolinato)}$_2$La[N(SiHMe$_2$)$_2$] (2): Using the same procedure as used for synthesizing **1** (vide supra), compound **2** was obtained from La[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (26.0 mg, 0.038 mmol) as a white solid (15 mg, 54%). ^{1}H NMR (300 MHz, C_6D_6): δ = 5.34 [m, 2 H, Si*H*(CH$_3$)$_2$], 3.64 (m, 8 H, C*H*$_2$O), 2.35 (s, 6 H, C*H*$_3$CCN), 1.46 (s, 12 H, C*H*$_3$), 1.33 (s, 12 H, C*H*$_3$), 0.56 (d, J = 2.8, 12 H, Si*H*Me$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 169.90 (N*C*O), 77.39 (*C*H$_2$O), 64.57 (Me*C*CN), 62.21 (*C*Me$_2$), 29.99 (C*Me*Me), 27.62 (CMe*Me*), 11.62 (*Me*CCN), 2.81 (SiH*Me*$_2$) ppm. $C_{28}H_{52}LaN_5O_4Si_2$ (717.82): calcd. C 46.85, H 7.30, N 9.76; found C 46.12, H 7.68, N 9.65.

{2,2′-(α-Methylmethylene)bis[(4*S*)-4-isopropyl-2-oxazolinato]}$_2$Y[N(SiHMe$_2$)$_2$] (3): Using the same procedure as used for synthesizing **1** (vide supra), compound **3** was obtained from 2,2′-(α-methylmethylene)bis[(4*S*)-4-isopropyl-2-oxazoline] (100 mg, 0.400 mmol) and Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (165 mg, 0.200 mmol) in benzene (10 mL) at 20 °C, and recovered as a white solid (73 mg, 66%). ^{1}H NMR (500 MHz, C_6D_6): δ = 5.01 (m, 2 H, Si*H*Me$_2$), 3.92 (d, J = 10.2, 4 H, C*H*$_2$O), 3.86 (d, J = 10.2, 4 H, C*H*$_2$O), 3.65 (m, 2 H, NC*H*), 2.27 (s, 6 H, C*H*$_3$CCN + sept, 4 H, C*H*i Pr), 0.81 (d, J = 6.7, 12 H, C*H*$_3$ *i*Pr), 0.72 (d, J = 7.0, 12 H, C*H*$_3$ *i*Pr), 0.36 (d, J = 1.9, 6 H, SiH*Me*$_2$), 0.32 (d, J = 1.9, 6 H, SiH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (125 MHz, C_6D_6): δ = 173.25 (N*C*O), 68.77 (*C*HN), 66.16 (*C*H$_2$O), 64.90 (Me*C*CN), 32.80 (*C*H *i*Pr), 19.80 (*C*H$_3$ *i*Pr), 15.06 (*C*H$_3$ *i*Pr), 12.26 (*Me*CCN), 3.71 (SiH*Me*Me), 3.57 (SiHMe*Me*) ppm. $C_{20}H_{32}N_5O_4Si_2Y$ (551.58): calcd. C 43.55, H 5.85, N 12.70; found C 43.26, H 5.93, N 12.67.

NMR Scale Generation of {2,2′-Methylenebis[(4*S*,5*S*)-4,5-diphenyl-2-oxazolinato]}$_2$-Y[N(SiHMe$_2$)$_2$] (4): Using the same procedure as used for synthesizing **3** (vide supra), compound **4** was generated at the NMR scale from Y[N(SiHMe$_2$)$_2$]$_3$(THF)$_2$ (14.0 mg, 0.022 mmol) and 2 equiv. of 2,2′-methylenebis[(4*S*,5*S*)-4,5-diphenyl-2-oxazoline] (20.0 mg, 0.044 mmol). NMR spectroscopy revealed complete conversion of the reagents to **4** with release of 2 equiv. of HN(SiHMe$_2$)$_2$ (^{1}H NMR: δ = 4.71, 0.11 ppm. ^{13}C NMR: δ = 0.23 ppm). ^{1}H NMR (200 MHz, C_6D_6): δ = 6.89 (m, 40 H, *Ph*), 5.94 [d, J = 7.7, 4 H, C*H*Ph(O)], 5.56 [d, J = 7.6, 4 H, C*H*PhN], 5.32 (s, 2 H, C*H*CCN), 5.06 (m, 2 H, Si*H*Me$_2$), 0.35 (d, J = 2.8, 6 H, SiH*Me*$_2$), 0.18 (d, J = 1.9, 6 H, SiH*Me*$_2$) ppm. ^{13}C{^{1}H} NMR (75 MHz, C_6D_6): δ = 174.47 (N*C*O), 139.37 (C_q Ph), 135.83 (C_q Ph), 127.89 (*Ph*), 127.36 (*Ph*), 126.65 (*Ph*), 85.48 (*C*HPh), 71.77 (*C*HPh), 58.56 (*C*HCN), 3.51 (SiH*Me*Me), 2.84 (SiHMe*Me*) ppm.

Crystal Structure Determination of 1: A suitable single crystal of **1** was mounted onto a glass fiber using the "oil-drop" method. Diffraction data were collected at 100 K with an APEX 2 AXS-Bruker diffractometer with graphite monochromatized Mo-K_α radiation. The crystal structure was solved by means of direct methods, the remaining atoms were located from difference Fourier synthesis, followed by full-matrix least-squares refinement based on F^2 (program SIR-97).[18] Many hydrogen atoms could be found from the Fourier difference. Carbon-bound hydrogen atoms were placed at calculated positions and forced to ride on the attached carbon atom. The hydrogen atom contributions were calculated but not refined. All non-hydrogen atoms were refined with anisotropic displacement parameters. The unit cell of **1** was found to contain two independent molecules. The main crystallographic data are summarized in Table 3.

Table 3. Crystal data and structure refinement for **1**.

Empirical formula	$C_{28}H_{52}N_5O_4Si_2Y$
Formula weight	667.83
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	$P2_1/c$ (no. 14)
Unit cell dimensions	a = 11.762(3) Å
	b = 34.259(9) Å
	c = 17.378(5) Å
	β = 91.914(13)°
Volume	6999(3) Å^3
Z	8
Density (calculated)	1.268 Mg m^{-3}
Absorption coefficient	1.771 mm^{-1}
F(000)	2832
Crystal size	0.30 × 0.25 × 0.20 mm
Theta range for data collection	1.31 to 27.54°
Index ranges	$-12 \le h \le 15$, $-35 \le k \le 44$,
	$-22 \le l \le 22$
Reflections collected	73433
Independent reflections	15947
Max. and min. transmission	–0.465 and 0.632
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	15947/0/721
Goodness-of-fit on F^2	1.037
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0423, wR_2 = 0.0845

CCDC-603139 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General Procedure for Lactide Polymerization: In the glovebox, a Schlenk flask was charged with a solution of the initiator (typically 0.019 mmol, ca. 10 mg) in toluene (0.2 mL) or THF (0.2 mL). To this solution was added rapidly a solution of the monomer (*rac*-LA, S-LA, BBL) in the appropriate ratio in toluene or THF (3.0 mL). The mixture was immediately stirred with a magnetic stir bar at room temperature. Aliquots were periodically removed with a pipette for monitoring by ^{1}H NMR spectroscopy. After the desired time, the reaction was quenched with acidic methanol (0.5 mL of a 1.2 M HCl solution), and the polymer was precipitated with excess methanol (100 mL). The polymer was then dried under vacuum to constant weight.

General Procedure for *rac*-β-Butyrolactone Polymerization: In the glovebox, a Schlenk flask was charged with a solution of the initiator (typically 0.014 mmol, ca. 10 mg) in toluene (1.0 mL) or THF (1.0 mL). *rac*-β-Butyrolactone (typically 2.64 mmol, 216 μL) was then syringed in dropwise under vigorous stirring at room temperature. After a small sample of the crude material was removed with a pipette for characterization by ^{1}H NMR, the reaction was

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quenched with acidic methanol (0.5 mL of a 1.2-M HCl solution in MeOH), and the polymer was precipitated with excess methanol (ca. 100 mL). The polymer was then dried under vacuum to constant weight.

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