Synthetic and Mechanistic Aspects of the Immortal Ring-Opening Polymerization of Lactide and Trimethylene Carbonate with New Homo- and Heteroleptic Tin(II)-Phenolate Catalysts

ARTICLE *in* CHEMISTRY - A EUROPEAN JOURNAL · MARCH 2012

Impact Factor: 5.73 · DOI: 10.1002/chem.201102261 · Source: PubMed

CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201102261

Synthetic and Mechanistic Aspects of the Immortal Ring-Opening Polymerization of Lactide and Trimethylene Carbonate with New Homo- and Heteroleptic Tin(II)-Phenolate Catalysts

Valentin Poirier,[a] Thierry Roisnel,[a] Sourisak Sinbandhit,[b] Manfred Bochmann,[c] Jean-François Carpentier,*[a] and Yann Sarazin*[a]

Abstract: Several new heteroleptic Sn^{II} complexes supported by amino-ether phenolate ligands [Sn{LO^n}(Nu)] (LO^1 = 2-[(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl]-4,6-di-*tert*-butylphenolate, Nu = NMe_2 (**1**), $N(SiMe_3)_2$ (**3**), $OSiPh_3$ (**6**); LO^2 = 2,4-di-*tert*-butyl-6-(morpholinomethyl)phenolate, Nu = $N(SiMe_3)_2$ (**7**), $OSiPh_3$ (**8**)) and the homoleptic Sn{LO^1}$_2$ (**2**) have been synthesized. The alkoxy derivatives [Sn{LO^1}(OR)] (OR = O*i*Pr (**4**), (*S*)-OCH(CH_3)CO_2*i*Pr (**5**)), which were generated by alcoholysis of the parent amido precursor, were stable in solution but could not be isolated. [Sn{LO^1}]$^+$[$H_2N\{B(C_6F_5)_3\}_2$]$^-$ (**9**), a rare well-defined, solvent-free tin cation, was prepared in high yield. The X-ray crystal structures of compounds **3**, **6**, and **8** were elucidated, and compounds **3**, **6**, **8**, and **9** were further characterized by ^{119}Sn Mössbauer spectroscopy. In the presence of *i*PrOH, compounds **1**–**5**, **7**, and **9** catalyzed the well-controlled, immortal ring-opening polymerization (*i*ROP) of L-lactide (L-LA) with high activities (ca. 150–550 $mol_{L-LA}\,mol_{Sn}^{-1}\,h^{-1}$) for tin(II) complexes. The cationic compound **9** required a higher temperature (100 °C) than the neutral species (60 °C); monodisperse poly(L-LA)s were obtained in all cases. The activities of the heteroleptic pre-catalysts **1**, **3**, and **7** were virtually independent of the nature of the ancillary ligand, and, most strikingly, the homoleptic complex **2** was equally competent as a pre-catalyst. Polymerization of trimethylene carbonate (TMC) occurs much more slowly, and not at all in the presence of LA; therefore, the generation of PLA-PTMC copolymers is only possible if TMC is polymerized first. Mechanistic studies based on ^{1}H and ^{119}Sn{^{1}H} NMR spectroscopy showed that the addition of an excess of *i*PrOH to compound **3** yielded a mixture of compound **4**, compound [Sn(O*i*Pr)$_2$]$_n$ **10**, and free {LO^1}H in a dynamic temperature-dependent and concentration-dependent equilibrium. Upon further addition of L-LA, two active species were detected, [Sn{LO^1}(OPLLA)] (**12**) and [Sn(OPLLA)$_2$] (**14**), which were also in fast equilibrium. Based on assignment of the ^{119}Sn{^{1}H} NMR spectrum, all of the species present in the ROP reaction were identified; starting from either the heteroleptic (**1**, **3**, **7**) or homoleptic (**2**) pre-catalysts, both types of pre-catalysts yielded the same active species. The catalytic inactivity of the siloxy derivative **6** confirmed that ROP catalysts of the type **1**–**5** could not operate according to an activated-monomer mechanism. These mechanistic studies removed a number of ambiguities regarding the mechanism of the (*i*)ROPs of L-LA and TMC promoted by industrially relevant homoleptic or heteroleptic Sn^{II} species.

Keywords: lactide · NMR spectroscopy · phenolate ligands · ring-opening polymerization · tin

Introduction

Much effort is currently devoted to the tailoring of polyesters with controlled architectures.[1] The ring-opening polymerization (ROP) of cyclic esters, such as lactide (LA), yields biodegradable and/or biocompatible materials with attractive thermo-mechanical properties.[2] Whilst remarkable ROP organocatalysts are now emerging,[3] a plethora of well-defined metal complexes that allow for the living ROP of cyclic esters have already been discovered.[1,4] With the exception of actinides and the frowned-upon main-group heavy metals, discrete ROP initiators have been synthesized for virtually every metal. Of these, the most-prominent examples in terms of activity and degree of (stereo)control are aluminum,[5] zinc,[6] and rare-earth metals.[7]

[a] Dr. V. Poirier, Dr. T. Roisnel, Prof. J.-F. Carpentier, Dr. Y. Sarazin
Organometallics and catalysis
UMR 6226 Sciences Chimiques de Rennes
Université de Rennes 1 - CNRS
Campus de Beaulieu, 35042 Rennes Cedex (France)
E-mail: jean-francois.carpentier@univ-rennes1.fr
yann.sarazin@univ-rennes1.fr

[b] Dr. S. Sinbandhit
Centre Régional des Mesures Physiques de l'Ouest
Université de Rennes 1
Campus de Beaulieu, 35042 Rennes Cedex, (France)

[c] Prof. M. Bochmann
Wolfson Materials and Catalysis Centre
School of Chemistry, University of East Anglia
Norwich NR4 7TJ (UK)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102261.

Industrially, the catalyst of choice for the ROP of LA remains tin(II)(2-ethylhexanoate)$_2$ ("Sn(oct)$_2$"); Sn(oct)$_2$ is also still largely used in academia for other ROP reactions.[8] In fact, despite somewhat poor catalytic activities, Sn(oct)$_2$ enjoys enduring popularity owing very much to its low cost, robustness (being both rather insensitive to impurities and capable of polymerizing molten lactide to high-molecular-weight materials at temperatures as high as 180 °C), and versatility.[8] However, a clear understanding of the ROP mechanisms that are operative with this initiator is still lacking. When used by itself, it is often postulated that the Lewis acidic Sn(oct)$_2$ simply activates the monomer upon coordination to the metal center, whilst initiation results from attack on the activated monomer by protic impurities (e.g., H_2O, lactate, or lactic acid);[8d] cationic mechanisms have also been suggested.[8c,e] On the other hand, Duda and co-workers[8f] and Kricheldorf and co-workers[8d,g] have studied the polymerization of ε-caprolactone and LA catalyzed by Sn(oct)$_2$ in the presence of additional alcohol or water, and concluded that, under these conditions, polymerization most probably proceeded according to a coordination–insertion mechanism.[8f,g]

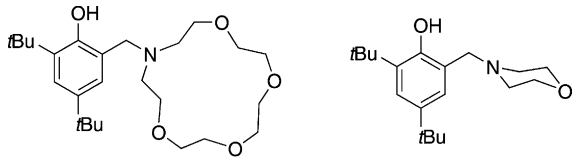
More recently, the groups of Tolman and Gibson have employed single-site tin(II) initiators supported by bulky amidinate,[9] salicylaldiminate,[10] or β-diketiminate[11] ancillary ligands for the living ROP of LA. These initiators were hampered by rather low activities (TOF = 10–100 $mol_{LA}\,mol_{Sn}^{-1}\,h^{-1}$) and productivities (TON = 100–500 $mol_{LA}\,mol_{Sn}^{-1}$), but allowed for an accurate control of the polymerization parameters ($M_w/M_n = 1.05$–1.60) and an improved comprehension of ROP mechanisms. During the polymerization of racemic lactide (*rac*-LA), all of these tin complexes yielded poly(lactide)s (PLA) with approximately the same level of heterotacticity (probability of racemic linkage, $P_r = 0.59$–0.67); this was a strong indication of the pivotal role played by the lone pair of electrons on the metal center in determining the stereochemistry of the reaction.

To address the issue of the viability of well-defined metal complexes for the large-scale (co)polymerization of cyclic esters, we[6f,12] and others[13] have embarked on the development of binary catalytic systems for the immortal ROP (*i*ROP) of *rac*-LA or L-LA and its related monomers. Introduced by Inoue and co-workers for the ROP of epoxides,[14] the *i*ROP concept relies on the use of an external protic co-catalyst (typically an alcohol) which acts as a transfer agent for a fast and reversible transfer between dormant and growing polymer chains.[12a] Upon addition of ROH, [M{L_nX}(Nu)] heteroleptic complexes of divalent metals (where M = Zn, Mg or Ca; $(L_nX)^-$ is a bulky ancillary monoanionic ligand; Nu^- is a reactive nucleophilic moiety) follow a coordination–insertion mechanism, whereas homoleptic [M{L_nX}$_2$] species are thought to induce ROP through an activated-monomer mechanism owing to the absence of a reactive group on the metal center.[6d,15] Although widely accepted for a variety of catalytic systems,[1e,6d,12a,15,16] this latter mechanism has never been truly demonstrated for [M{L_nX}$_2$] complexes.

Herein, we report the syntheses and catalytic activities of discrete [Sn^{II}{L_nO}(Nu)] complexes supported by bulky amino-ether phenolate ligands in the (*i*)ROP of LA. Kinetic and mechanistic studies performed by variable temperature (VT) ^1H and $^{119}Sn\{^1H\}$ NMR spectroscopy were conducted to determine the identities and roles of all of the metallic species involved in the *i*ROP of L-LA in the presence of *i*PrOH as a co-catalyst. In particular, these results demonstrate that a coordination–insertion mechanism is operative with both heteroleptic [Sn{L_nO}(Nu)] and, more surprisingly, homoleptic Sn{L_nO}$_2$ complexes, as the same active species are generated in both cases upon addition of an excess of alcohol. A rare example of a well-defined, solvent-free Sn^{II} cationic complex that is active for the controlled *i*ROP of L-LA is also presented.

Results and Discussion

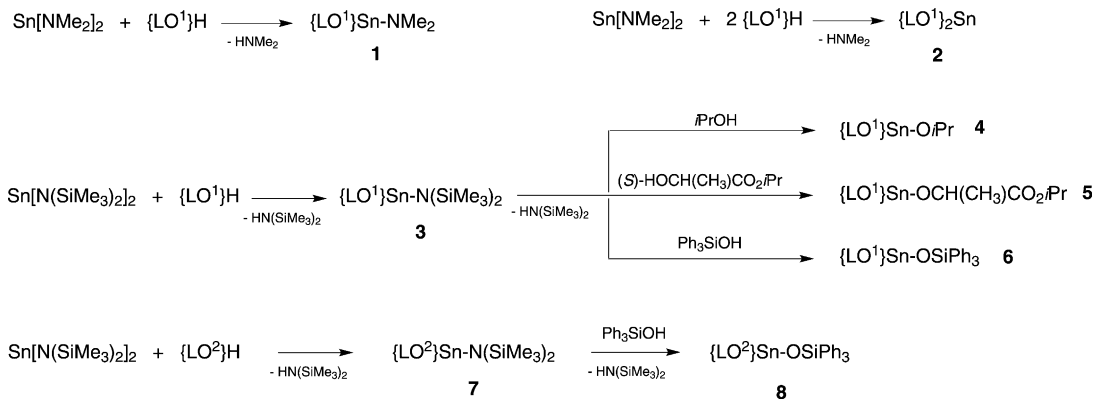
Syntheses and characterization: The multidentate amino-ether pro-ligands 2-[(1,4,7,10-tetraoxa-13-azacyclopentadecan-13-yl)methyl]-4,6-di-*tert*-butylphenol[17] {LO^1}H, and 2,4-di-*tert*-butyl-6-(morpholinomethyl)phenol, {LO^2}H (Scheme 1), which we have previously employed for the preparation of a variety of complexes of Zn and related divalent s-block metals,[6f,12b–e,16b] were selected for the synthesis of new heteroleptic Sn^{II} complexes. The rationale was that the steric encumbrance and the chelating ability of these monoanionic ligands would yield kinetically stable complexes that are capable of withstanding the large excess of protic co-catalyst required for the successful *i*ROP of cyclic esters.[12a]



{LO^1}H {LO^2}H

Scheme 1. Pro-ligands employed in this study.

The reaction of [Sn(NMe$_2$)$_2$] with 1.0 equivalent of {LO^1}H afforded the heteroleptic complex [Sn{LO^1}(NMe$_2$)] (**1**) in moderate yield (48 %; Scheme 2). Despite repeated attempts, we found that the crude product was systematically contaminated by a significant amount of the homoleptic derivative Sn{LO^1}$_2$ (**2**). As compound **1** is more soluble than compound **2** (which was also independently synthesized by the reaction of 2.0 equivalents of {LO^1}H with [Sn(NMe$_2$)$_2$] in aliphatic hydrocarbons), fairly pure samples of compound **1** (i.e. containing less than 5 % of compound **2**) could be obtained after repeated washing of the crude



Scheme 2. Syntheses of Sn^{II} complexes **1**–**8**.

sample with small amounts of *n*-pentane. The ^{1}H NMR spectra of both compounds in [D$_6$]benzene typically displayed very broad, poorly resolved signals for the amino-ether side-arm, which is indicative of a dynamic behavior in solution. Compounds **1** and **2** exhibited clearly separated ^{119}Sn{^{1}H} NMR chemical shifts: the resonance for compound **1** was found at $\delta = -147$ ppm whilst the signal for **2** was located at much higher field ($\delta = -566$ ppm).

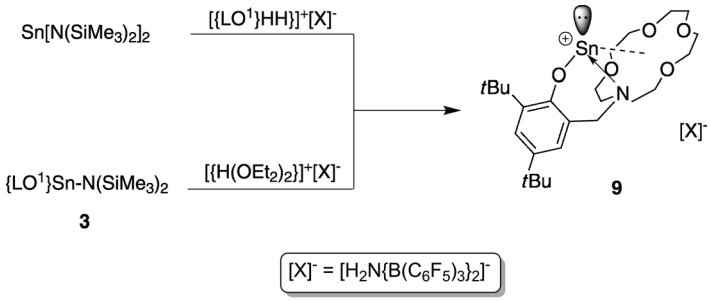
By contrast with compound **1**, the colorless [Sn{LO^1}{N(SiMe$_3$)$_2$}] (**3**) could be readily obtained free from impurity and in near-quantitative yield by the stoichiometric reaction of {LO^1}H with the bulky amido precursor [Sn{N(SiMe$_3$)$_2$}$_2$]. Whilst the signals in the ^{1}H NMR spectrum of compound **3** recorded at 25 °C in [D$_6$]benzene were broad owing to considerable fluxionality, they sharpened on cooling, and the identity of compound **3** was unambiguously established by recording the ^{1}H NMR spectrum at 0 °C (see the Supporting Information, S3). The ^{119}Sn{^{1}H} NMR spectrum of compound **3** at 25 °C displayed a single, sharp resonance at $\delta = -55$ ppm; the ^{29}Si{^{1}H} NMR signal at $\delta = -0.49$ ppm was in the expected area.[18] The solubility of compound **3** is very high, even in aliphatic hydrocarbons.

Treatment of compound **3** with 1.0 equivalent of *i*PrOH, enantiomerically pure (*S*)-HOCH(CH$_3$)CO$_2$*i*Pr, and Ph$_3$SiOH yielded the corresponding heteroleptic alkoxy complexes [Sn{LO^1}(O*i*Pr)] (**4**), [Sn{LO^1}{(*S*)-OCH(CH$_3$)CO$_2$*i*Pr}] (**5**), and [Sn{LO^1}(OSiPh$_3$)] (**6**). These three complexes are stable in solution and they were satisfactorily characterized by NMR spectroscopy at 25 °C. A sharp, high-field signal at $\delta = -22.2$ ppm was found in the ^{29}Si{^{1}H} NMR spectrum of compound **6**. The ^{119}Sn{^{1}H} NMR spectra of compounds **4** and **6** showed single resonances at $\delta = -351$ and -459 ppm, respectively. On the other hand, two signals of equal intensities were detected at $\delta = -409$ and -425 ppm in the ^{119}Sn{^{1}H} NMR spectrum of compound **5** (see the Supporting Information, S6). We attributed this phenomenon to the formation of a pair of configurationally stable diastereomers because the starting alcohol was enantiomerically pure; the tin center with its lone pair constitutes the second chiral center. Whilst compound **6** was isolated in high yield (88 %), all attempts to isolate complexes **4** and **5** were unsuccessful, with homoleptic compound **2** systematically recovered following removal of the volatile compounds under vacuum and washing of the solid residue with minimal amounts of *n*-pentane. Clearly, whilst compounds **4** and **5** were perfectly stable in benzene solution over the course of several days, at high concentrations, they suffered from solution–ligand redistribution reactions that eventually led to complete decomposition. This behavior was reminiscent of that observed with the analogous Zn complexes.[19] Complex **6** is fully soluble in ethers, aromatic- and chlorinated solvents, but sparingly so in aliphatic hydrocarbons.

By analogy with compound **3**, the less-hindered [Sn{LO^2}{N(SiMe$_3$)$_2$}] (**7**) was prepared by the stoichiometric reaction of {LO^2}H with [Sn{N(SiMe$_3$)$_2$}$_2$]. The reaction proceeded cleanly, as determined by ^{1}H NMR spectroscopy, but obtaining compound **7** free from HN(SiMe$_3$)$_2$ impurities was tedious: the released amine could not be removed under dynamic vacuum whilst the high solubility of compound **7** in *n*-pentane precluded efficient removal of the by-product with this solvent. Very small amounts of pure compound **7** were obtained by slow precipitation from cold *n*-pentane, and the complex was characterized by the full range of usual 1D and 2D NMR spectroscopic techniques. The dynamic behavior of the morpholine side-arm observed in the ^{1}H NMR spectrum of compound **7** (recorded at 25 °C in [D$_6$]benzene) could be suppressed at -20 °C, which allowed for the clear identification of the complex (see the Supporting Information, S8). The signals in the ^{29}Si{^{1}H} and ^{119}Sn{^{1}H} NMR spectra of compound **7** were located at $\delta = 0.14$ and -42 ppm, respectively.

[Sn{LO^2}(OSiPh$_3$)] (**8**) was prepared in moderate yield according to a one-pot procedure by the reaction of the in situ generated compound **7** with Ph$_3$SiOH. The solubility of compound **8** is similar to that of compound **6**. In the ^{29}Si{^{1}H} and ^{119}Sn{^{1}H} NMR spectra, compound **8** exhibited resonances ($\delta = -19.8$ and -353 ppm, respectively) shifted slightly downfield in comparison with those of compound **6**. This shift could be tentatively accounted for by a higher electron density on the metal center in the latter case where the ligand {LO^1}$^-$ is potentially more-strongly chelating and thus more-electron-donating.

Examples of low-coordinate, well-defined Sn^{II} cationic complexes are rare.[20–24] However, such species are attracting increasing attention, both for mechanistic purposes and because they display unusual and/or enhanced reactivities. Other than the seminal $C_5Me_5Sn^+$, reported by Jutzi et al.,[21] recent examples include the remarkable [Sn{BDI}]$^+X^-$ (where $X^- = B(C_6F_5)_4^-$, $AlCl_4^-$, or $MeB(C_6F_5)_3^-$) supported by the bulky β-diketiminate ligand ({BDI}$^-$ = [{N(2,6-*i*Pr$_2$C$_6$H$_3$)C(Me)}$_2$CH]$^-$) reported by Fulton and co-workers[22] and [Sn{ATI}]$^+$OTf$^-$ (where {ATI}$^-$ is a bulky aminotroponiminate ligand) reported by Ayers and Dias,[23] although in this last case interactions over long distances between the cationic metal and the neighboring anion were detected. In addition, Jambor and co-workers have just reported the solvent-containing heterobimetallic complexes [{2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}(H$_2$O)Sn–W(CO)$_5$]$^+$CB$_{11}$H$_{12}^-$ and [{2,6-(MeOCH$_2$)$_2$C$_6$H$_3$}(L)$_x$Sn–Cr(CO)$_5$]$^+X^-$ (where X^- = OTf$^-$, L = H$_2$O, and x = 1, or X^- = CB$_{11}$H$_{12}^-$, L = thf, and x = 2) that are further stabilized by metal pentacarbonyl moieties.[24] Inspired by the pioneering work by Kitagawa and co-workers,[17] we have already demonstrated the ability of the {LO^1}$^-$ framework to produce well-defined, solvent-free cationic complexes of the divalent alkaline-earth metals.[12d,e,16b] Naturally, we sought to extend these results to Sn^{II}. The protonolysis of compound **3** with a stoichiometric amount of [H(OEt$_2$)$_2$]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ afforded [Sn{LO^1}]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (**9**) in good yield (Scheme 3). Alternatively, compound **9** could also be conveniently prepared by the treatment of [Sn{N(SiMe$_3$)$_2$}$_2$] with the N-protonated form of the pro-ligand [{LO^1}HH]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (made quantitatively from the reaction of [H(OEt$_2$)$_2$]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ and {LO^1}H).[12d] It is noteworthy that compound **9** was available from various synthetic procedures, and that [Sn{N(SiMe$_3$)$_2$}$_2$] and compound **3** could be replaced, for instance, by [Sn(NMe$_2$)$_2$] and compound **1**, respectively.



Scheme 3. Synthesis of the solvent-free [Sn{LO^1}]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (**9**).

The identity and purity of the solvent-free ion-pair **9** were established by NMR spectroscopy and combustion analysis. The integrity of the weakly-coordinating anion was further attested to by ^{11}B ($\delta = -8.4$ ppm) and ^{19}F{^{1}H} NMR spectroscopy ($\delta = -132.9$, -160.2, and -165.7 ppm).[25] The high-field resonance at $\delta = -753$ ppm found in the ^{119}Sn{^{1}H} NMR spectrum of compound **9** compares well with that of [Sn{BDI}]$^+$AlCl$_4^-$ ($\delta = -626.7$ ppm), but is much more shielded than that of [Sn{BDI}]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ ($\delta = -139.5$ ppm) and especially [Sn{BDI}]$^+$[B(C$_6$F$_5$)$_4$]$^-$ ($\delta = +197.0$ ppm).[22] Considering the very similar, non-coordinating nature of the [H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ and [B(C$_6$F$_5$)$_4$]$^-$ ions and the ^{119}Sn NMR chemical shifts of the corresponding cations,[26] these values confirm that {LO^1}$^-$ is much more electron-donating than {BDI}$^-$. However, the comparable data for compound **9** and [Sn{BDI}]$^+$AlCl$_4^-$ (where the counterion is at best a weak π-donor) suggests that not all heteroatoms of the amino-ether macrocycle in {LO^1}$^-$ are coordinated onto the metal center in compound **9**. Unfortunately, despite repeated attempts, no X-ray data could be obtained for compound **9** to corroborate this assumption. The NMR-scale reaction of [{LO^2}HH]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ with [Sn{N(SiMe$_3$)$_2$}$_2$] (1:1) also yielded a compound with a ^{1}H NMR spectrum consistent with the formulation [Sn{LO^2}]$^+$ [H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$. Compared to compound **9**, its ^{119}Sn{^{1}H} NMR chemical shift ($\delta = -436$ ppm) was at a substantially lower field.

Finally, [Sn(O*i*Pr)$_2$]$_n$ (**10**) and [Sn{(*S*)-OCH(CH$_3$)CO$_2$*i*Pr}$_2$] (**11**) were synthesized in quantitative yield by the reaction of [Sn{N(SiMe$_3$)$_2$}$_2$] with two equivalents of *i*PrOH and enantiomerically pure (*S*)-HOCH(CH$_3$)CO$_2$*i*Pr, respectively. The former product was isolated as a soluble, air-sensitive, white powder, whilst the latter was a viscous colorless oil.[27] In their respective ^{119}Sn{^{1}H} NMR spectra, a single resonance was found at $\delta = -190$ (for compound **10**) and -347 ppm (for compound **11**). All relevant spectroscopic data for compounds **1**–**11** are collected in Table 1 (see the Supporting Information, S1–S13). Apart from compound **10** (which was clearly oligomeric at room temperature in solution) and compound **5** (which showed the presence of two diastereoisomers in equal proportions), the ^{119}Sn{^{1}H} NMR data of these complexes consisted of a single, well-defined signal which is consistent with the formation of monomeric structures in solution.

Compounds **3**, **6**, **8**, and **9** were further characterized by ^{119}Sn Mössbauer spectroscopy. All of the spectra were recorded at 77 K (see the Supporting Information, S20 and S21). Representative hyperfine parameters are given in Table 1. All of the signals consisted of doublets where both the isomer shift (I.S.) and quadrupole splitting (Q.S.) were at the lower end of the characteristic range of Sn^{II} species. For compounds **6**, **8**, and **9**, there was only a single peak in each spectrum. In the spectrum of compound **3**, an additional minor contribution (ca. 4%) was detected; both the I.S. and Q.S. of this minor species were typical of Sn^{4+} ions surrounded by oxygen atoms, and could most-probably be attributed to tin oxide and/or tin oxide hydroxides resulting from slight hydrolytic decomposition of the parent complex **3** during sample preparation. Compounds **6** and **8**, which only differ in the nature of the ancillary ligand, displayed rigorously the same Q.S., which suggested similar ligation modes in both cases; this similarity was in agreement with the crystallographic data (see below). The cationic complex **9** was characterized by a larger I.S. (3.37(5) mm s^{-1}) and a lower Q.S. (1.91(7) mm s^{-1}) than the neutral compounds (I.S.

Table 1. Summary of spectroscopic data for compounds **1**–**11**.

Complex	^{119}Sn{^{1}H} NMR[a] δ [ppm][d]	^{29}Si{^{1}H} NMR[b] δ [ppm][d]	^{119}Sn Mössbauer[c] I.S. [mm s^{-1}][e]	Q.S. [mm s^{-1}][f]
[Sn{LO^1}(NMe$_2$)] (**1**)	−147	--	--	--
Sn{LO^1}$_2$ (**2**)	−566	--	--	--
[Sn{LO^1}{N(SiMe$_3$)$_2$}](**3**)	−55[g]	−0.49	2.810 (5), 0.1 (1)	2.290 (8), 0.3 (2)
[Sn{LO^1}(O*i*Pr)] (**4**)	−351[g]	--	--	--
[Sn{LO^1}{(*S*)-OCH(CH$_3$)CO$_2$*i*Pr}] (**5**)	−409, −425	--	--	--
[Sn{LO^1}(OSiPh$_3$)] (**6**)	−459	−22.2	2.849 (8)	2.09 (1)
[Sn{LO^2}{N(SiMe$_3$)$_2$}] (**7**)	−42[h]	+0.14	--	--
[Sn{LO^2}(OSiPh$_3$)] (**8**)	−353	−19.8	2.77 (1)	2.09 (2)
[Sn{LO^1}]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (**9**)	−753[i]	--	3.37 (5)	1.91 (7)
[Sn(O*i*Pr)$_2$]$_n$ (**10**)	−190[j]	--	--	--
[Sn{(*S*)-OCH(CH$_3$)CO$_2$*i*Pr}$_2$] (**11**)	−347	--	--	--

[a] Recorded at 298 K in [D$_6$]benzene (149.20 MHz) unless otherwise stated and referenced against [SnMe$_4$]. [b] Recorded at 298 K in [D$_8$]toluene (79.49 MHz) unless otherwise stated and referenced against [SiMe$_4$]. [c] Recorded at 77 K in a $BaSnO_3$ absorber and referenced against $BaSnO_3$. [d] Chemical shift. [e] I.S. = isomer shift. [f] Q.S. = quadrupole splitting. [g] Recorded at 111.88 MHz. [h] Recorded in [D$_8$]toluene. [i] Recorded in [D$_2$]dichloromethane. [j] Recorded at 333 K.

in the range 2.77(1)–2.85(8) mm s^{-1}). Moreover, the absorption for compound **9** (0.58%) was smaller than that of compounds **3** (18.7%), **6** (11.2%), or **8** (2.21%), whilst the signal width for the cationic compound **9** (1.2(1) mm s^{-1}) was larger than that of the neutral complexes (0.83(1)–0.95(1) mm s^{-1}). Although these values may be specific to molecular cationic Sn^{II} compounds, no comparative data were available in the literature.

Crystallographic studies: Single-crystals of compound **3**, **6**, and **8** suitable for X-ray diffraction studies were obtained by recrystallization from cold, concentrated *n*-pentane solutions. In the solid state, the molecular structure of [Sn{LO^1}{N(SiMe$_3$)$_2$}] (**3**) features a trigonal-pyramidal geometry, with the {LO^1}$^-$ ligand coordinated in a κ^2 fashion (Figure 1). The Sn1–O21 (2.07 Å), Sn1–N1 (2.44 Å), and Sn1–N40 (2.11 Å) bond lengths are comparable to those already reported for similar compounds.[10] The O21-Sn1-N40 (94.1°), N1-Sn1-N40 (96.8°), and N1-Sn1-O21 (86.1°) angles suggest the absence of sp hybridization and that the tin–

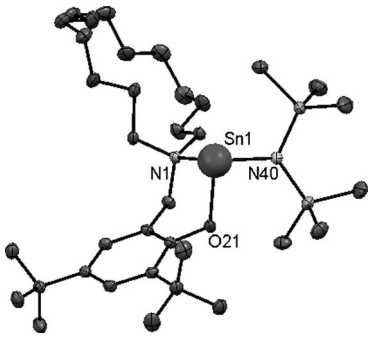


Figure 1. Molecular structure of [Sn{LO^1}{N(SiMe$_3$)$_2$}] (**3**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–O21 2.074(1), Sn1–N1 2.437(1), Sn1–N40 2.112(1); O21-Sn1-N40 94.06(4), N1-Sn1-N40 96.78(4), N1-Sn1-O21 86.08(4).

ligand bonds involve the p orbitals almost exclusively; therefore, the nature of the electron lone pair in compound **3** is essentially 5s^2 and is non-directional. In contrast to compound **3**, in [Zn{LO^1}{N(SiMe$_3$)$_2$}] (the zinc analogue of compound **3**), the {LO^1}$^-$ ligand is κ^3-coordinated and the geometry around the metal is tetrahedral.[12c] There is no geometric distortion of the macrocycle in compound **3**, as the N,O,O,O,O core remains essentially planar.

The structure of [Sn{LO^1}(OSiPh$_3$)] (**6**) resembles that of compound **3** (Figure 2), with

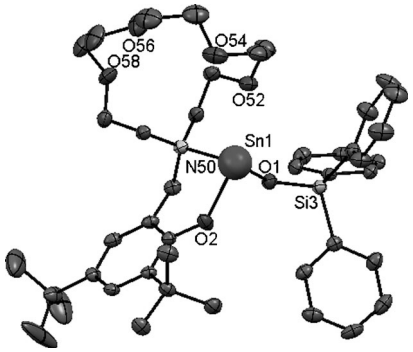


Figure 2. Molecular structure of [Sn{LO^1}(OSiPh$_3$)] (**6**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.028(2), Sn1–O2 2.089(2), Sn1–N50 2.344(2), Sn1–O52 2.745(2); O2-Sn1-N50 84.28(7), O2-Sn1-O1 90.54(7), O1-Sn1-N50 85.45(7).

narrow O2-Sn1-N50 (84.3°), O2-Sn1-O1 (90.5°), and O1-Sn1-N50 (85.4°) angles. However, unlike in this latter complex, the macrocycle side-arm is considerably distorted in compound **6**. Indeed, the nitrogen atom sits 1.83 Å above the mean plane formed by the O52, O54, O56, and O58 atoms. The Sn1–O52 distance (2.74 Å) is rather short for non-interacting atoms and it could possibly be considered as a long-range contact.

The geometry around the metal center in [Sn{LO^2}(OSiPh$_3$)] (**8**) (Figure 3) is very similar to that of compound **6**. The morpholine side-arm retains the chair conformation originally displayed in the pro-ligand {LO^2}H,[12c] and hence the ligand is only κ^2-coordinated to the metal. The striking similarity between the geometric arrangements around the central Sn atom of compound **6** (where none of the O atoms of the aza-crown-ether are tightly coordinated to the metal) and compound **8** in the solid state is in agreement with the similar Mössbauer data recorded for these two complexes (see above).

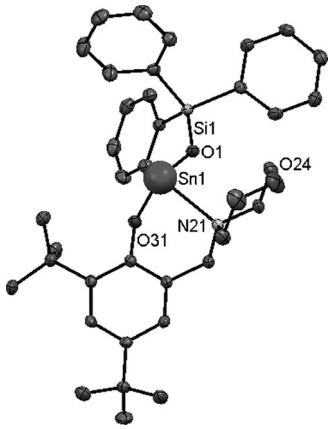


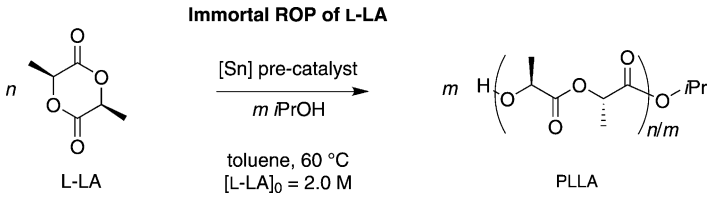
Figure 3. Molecular structure of [Sn{LO^2}(OSiPh$_3$)] (**8**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn1–O1 2.020(2), Sn1–O31 2.062(2), Sn1–N21 2.382(2); O1-Sn1-O31 91.53(6), O1-Sn1-N21 87.05(6), N21-Sn1-O31 86.40(6).

Table 2. Data for the *i*ROP of L-LA using the [Sn{LO^x}(X)]/*i*PrOH binary catalytic systems.[a]

Entry	Pre-catalyst	T [°C]	t [min]	Yield[b] [%]	TOF[c] [h^{-1}]	$M_{n,calcd}$[d] [g mol^{-1}]	$M_{n,SEC}$[e] [g mol^{-1}]	M_w/M_n[e]
1	**2**	60	180	88	293	12700	14000	1.17
2	**1**	60	90	82	547	11800	10600	1.09
3	**1**	60	180	89	297	12800	11400	1.11
4	**3**	60	120	84	420	12100	13000	1.11
5	**3**	60	180	87	290	12500	11900	1.11
6[f]	**3**	60	180	92	307	13300	10300	1.13
7[g]	**6**	60	300	0	--	--	--	--
8	**7**	60	180	83	277	11900	13000	1.11
9	**9**	60	360	0	--	--	--	--
10	**9**	100	120	43	215	6200	7000	1.08
11	**9**	100	300	94	188	13500	16100	1.29
12	**10**	60	180	90	300	13000	15000	1.14

[a] Polymerization conditions: [L-LA]/[Sn]/[*i*PrOH] = 1000:1:10, toluene, [L-LA]$_0$ = 2.0 M. [b] Yield of isolated PLLA. [c] Turnover frequency (mol$_{L-LA}$ mol$_{Sn}^{-1}$ h^{-1}) calculated at the given conversion. [d] Calculated from [L-LA]$_0$/[*i*PrOH]$_0$ × monomer conversion × M_{L-LA} + M_{iPrOH}, with M_{L-LA} = 144 g mol^{-1} and M_{iPrOH} = 60 g mol^{-1}. [e] Determined by size-exclusion chromatography (SEC) versus polystyrene standards and corrected by a factor of 0.58.[42] [f] Used *rac*-LA. [g] Carried out with 500 equivalents of L-LA.

Polymerization studies: To assess the potential of these new Sn^{II} complexes as *i*ROP pre-catalysts and to investigate potential operative mechanistic pathways,[28] these new compounds were first tested in the polymerization of 1000 equivalents of enantiomerically pure L-LA in toluene in the presence of 10 equivalents of *i*PrOH as a co-initiator (Scheme 4 and Table 2).



Scheme 4. Immortal ROP of L-LA catalyzed by the binary catalytic systems [Sn^{II}]/*i*PrOH.

With the exception of the siloxy derivative **6**, which was totally inactive (most probably as a consequence of the poor reactivity of the OSiPh$_3$ moiety) under the given experimental conditions (Table 2, entry 7), nearly full conversion of 1000 equivalents of L-LA was achieved within 3 h for all neutral complexes (Table 2, entries 1–8). The three tin–amide complexes (**1**, **3**, and **7**) exhibited similar turnover frequencies (yet calculated at nearly full conversion), in the range 270–550 mol$_{L-LA}$ mol$_{Sn}^{-1}$ h^{-1}. This result represents a slight improvement over heteroleptic systems reported by the groups of Gibson and Tolman, for which activities in the range 10–100 mol$_{L-LA}$ mol$_{Sn}^{-1}$ h^{-1} were reported.[9–11] Therefore, rather surprisingly, the nature of the ligand in our systems ({LO^1}$^-$ vs. {LO^2}$^-$) seems to have little influence over the activity of the catalytic system.

The cationic compound **9** was not active at 60 °C (Table 2, entry 9) and required higher temperatures (100 °C) to afford complete conversion of the monomer with satisfactory activities (188–215 mol$_{L-LA}$ mol$_{Sn}^{-1}$ h^{-1}) and good control over the polymerization parameters (Table 2, entries 10 and 11). This need for higher temperature was hardly surprising. Indeed, the use of amido complexes **1**, **3**, or **7** in combination with an alcohol induced polymerization of L-LA through a conventional bimolecular coordination–insertion mechanism in which acyl cleavage of the monomer coordinated to the metal center resulted from the attack of the nucleophilic alkoxide group on the coordinated monomer.[4–7,29] On the other hand, cations such as compound **9**, which do not possess any internal reactive nucleophilic groups, necessarily operate via an activated-monomer mechanism in the presence of an external nucleophile (alcohol): the monomer is activated by the electrophilic cation and is then opened upon nucleophilic attack by the alcohol. This latter process is possibly tri-molecular, or involves a bimolecular reaction with an unfavorable pre-equilibrium.[12d,e,16b,30]

The homoleptic compound **2** demonstrated almost identical *i*ROP catalytic behavior (Table 2, entry 1) to the heteroleptic tin amides **1**, **3**, and **7** (Table 2, entries 3, 5 and 7), both in terms of activity and in the nature of the resulting poly(L-LA) (PLLA). This observation was unexpected, as unlike heteroleptic (pre-)catalysts, homoleptic complexes such as **2** normally require the addition of an external alcohol to promote (*i*)ROP reactions, which are generally considered to follow the aforementioned activated-monomer mechanism.[4–7,15]

All of the catalytically active complexes demonstrated satisfactory control over the polymerization parameters. The agreement between theoretical and experimental molecular weights and the narrow molecular-weight distributions (with values of M_w/M_n typically around 1.10) are indicative of fast and reversible chain-transfer between dormant and growing

(macro)alcohols. Analysis of the polymer termini by NMR spectroscopy and MALDI-ToF MS attested that all of the PLLA samples were capped with the expected $CH(CH_3)OH$ and $(CH_3)_2CHOC(O)$ end-groups (see the Supporting Information, S23 and S24). No epimerization of the chiral centers was detected in the *i*ROP of L-LA,[31] as all the resulting polymers were purely isotactic. When the reaction was carried out with *rac*-LA (Table 2, entry 6), slightly heterotactic-enriched PLA was obtained, with a P_r value (0.60) that in the characteristic range for related Sn^{II} species.[9–11] MALDI-ToF MS analysis revealed that intermolecular transesterification reactions occurred to a significant extent, but did not show the presence of cyclic polymers (i.e. the products of intramolecular transesterification). These side-reactions could explain the difficulty encountered in reaching full conversion (Table 2, entries 2 vs. 3 and 4 vs. 5), but they did not significantly modify the molecular-weight distributions of the resulting polymers.

The good control over macromolecular features and the "immortal" nature of the catalytic systems were further illustrated in the cases of the neutral (**3**) and cationic (**9**) pre-catalysts by varying the monomer-to-alcohol ratio at fixed pre-catalyst loadings ($[L\text{-}LA]_0/[Sn]_0 = 1000{:}1$). The experimentally determined molecular weights matched their theoretical values (Figure 4). The living character of the **3**/*i*PrOH catalytic system was also demonstrated by successful conversion of two batches of 500 equivalents of L-LA added sequentially in a "double-feed" experiment, the second batch being introduced after full conversion of the first one. The final material had a molecular weight twice that of the intermediate PLLA ($M_{n,SEC} = 13100$ and $7700\ g\,mol^{-1}$, respectively) and exhibited a monomodal distribution ($M_w/M_n = 1.28$).

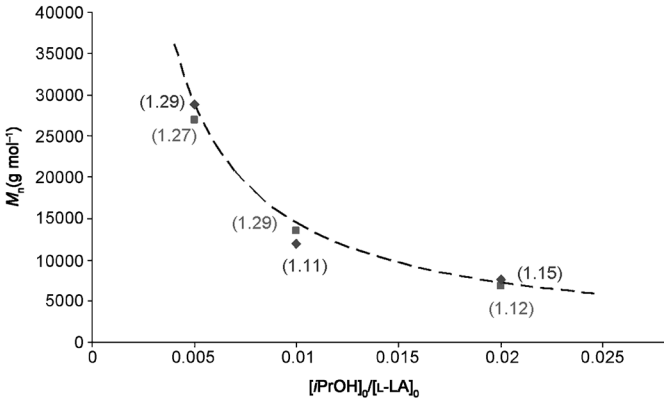


Figure 4. Plot of experimental $M_{n,SEC}$ versus the monomer-to-alcohol ratio for the *i*ROP of L-LA with compound **3**/*i*PrOH (◆) or compound **9**/*i*PrOH (■) using $[L\text{-}LA]_0/[Sn]_0 = 1000{:}1$ at $[L\text{-}LA]_0 = 2.0$ M; all experiments were run to full conversion. M_w/M_n values determined by SEC are given into brackets; the dashed line represents the theoretical curve.

Mechanistic investigations: To address the issues of 1) the nature of the active species in the binary catalytic system **3**/*i*PrOH and the role of these two components, 2) the troubling similarity between the catalytic activity of systems based on the homoleptic compound **2** and the heteroleptic complexes **1** and **3**, 3) the moderate influence of the nature of the ancillary ligand on the catalytic activity of the complex, and 4) the different reactivity of L-LA and trimethylene carbonate (TMC) in *i*ROP reactions promoted by these discrete organometallic catalysts,[32] mechanistic studies were performed using $^{119}Sn\{^1H\}$ and ^1H NMR analysis. Unless otherwise specified, all NMR experiments described hereafter were carried out in [D_6]benzene at 25 °C.

Living ring-opening polymerization: First, the living ROP (i.e. in the presence of 1 equivalent of *i*PrOH vs. compound **3**) of L-LA and TMC catalyzed by **3**/*i*PrOH was investigated. In the absence of alcohol, compound **3** was inert towards both cyclic esters (5 equiv), and in both cases a unique signal at $\delta = -57$ ppm (i.e. virtually identical to that of compound **3**) was detected in the $^{119}Sn\{^1H\}$ NMR spectra of the reaction mixtures. Even upon heating to 60 °C overnight, L-LA was not polymerized by compound **3** alone; on the other hand, TMC polymerized under these conditions, but most likely as the result of an impurity or thermal initiation because both of the ^1H and $^{119}Sn\{^1H\}$ NMR spectra revealed that the complex **3** had remained unreacted.

Upon addition of one equivalent of *i*PrOH, compound **3** catalyzed the polymerization of L-LA.[33] As noted earlier, the stoichiometric reaction of compound **3** and *i*PrOH led to the clean formation of [Sn{LO^1}(O*i*Pr)] (**4**), with a characteristic $^{119}Sn\{^1H\}$ NMR chemical shift of −351 ppm (Table 1). Upon further addition of five equivalents of L-LA, compound **4** could not be detected any longer as the instantaneous opening and insertion of one monomer unit was observed by ^1H NMR spectroscopy (Figure 5), leading to the formation of a new compound assumed to be the catalytically active species (named [{Sn{LO^1}(OPLLA)] (**12**) hereafter). This formation was confirmed by $^{119}Sn\{^1H\}$ NMR spectroscopy: the resonances of this newly formed species (**12**) were located at $\delta = -432$ (major) and −409 ppm (minor; Figure 5), that is, extremely close to those of the in situ generated [Sn{LO^1}{(*S*)-OCH(CH_3)CO_2*i*Pr}] (**5**; $\delta = -425$ and −409 ppm, see Table 1). As earlier, the presence of two resonances in the $^{119}Sn\{^1H\}$ NMR spectrum of [Sn{LO^1}(OPLLA)] (**12**) was tentatively attributed to the formation of a pair of diastereoisomers; in this case, one configuration was favored over the other. Gibson and co-workers demonstrated that the rate-determining step of the ROP of *rac*-LA catalyzed by [Sn{BDI}(Nu)] complexes was the insertion of the second monomer unit.[11b] Our spectroscopic observations are in agreement with those results, as the first insertion of L-LA was almost instantaneous (or at least it was achieved within the first point of analysis), whilst the subsequent insertions were much slower and could be readily monitored. The polymerization reaction continued to progress without further changes in the $^{119}Sn\{^1H\}$ NMR spectrum (i.e. with a main resonance at $\delta = -432$ ppm), even when full conversion of L-LA was reached; this result attest-

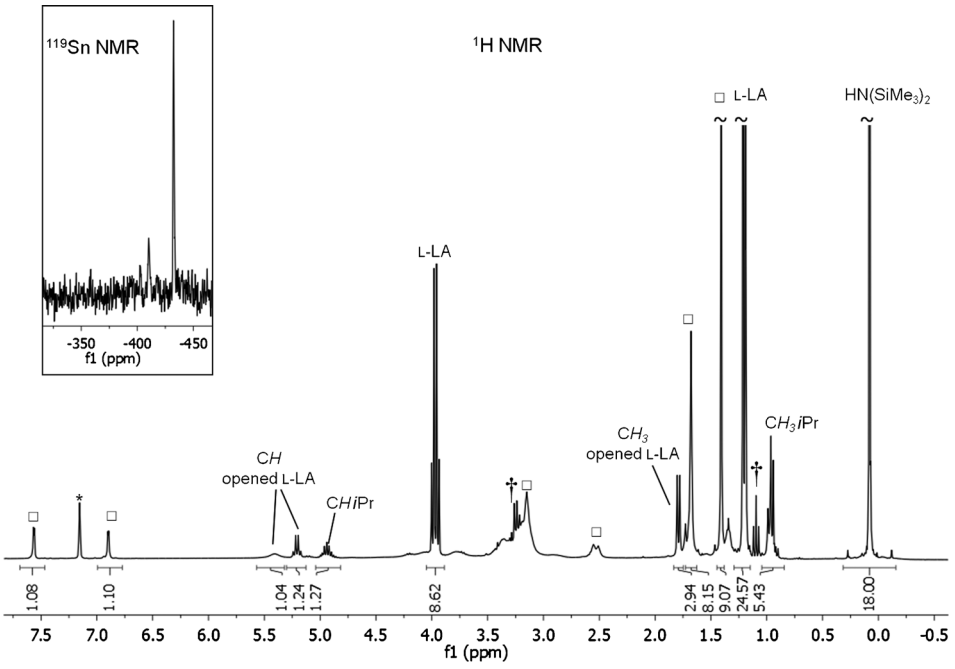


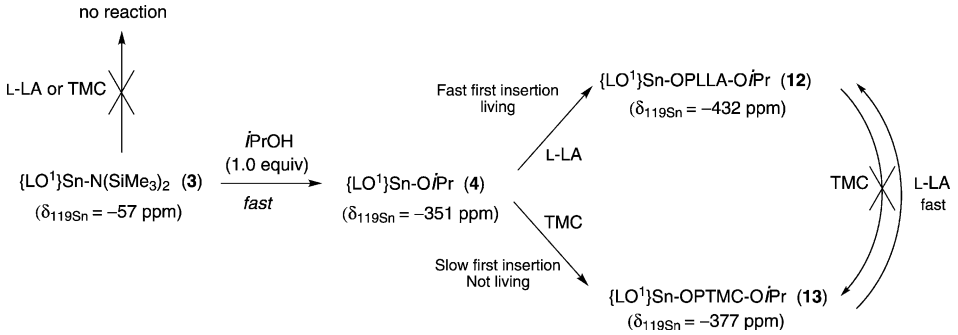
Figure 5. ^{1}H (300.13 MHz) and ^{119}Sn{^{1}H} NMR (111.88 MHz) spectra ([D$_6$]benzene, 25 °C) of the reaction of compound **3** with one equivalent of *i*PrOH and five equivalents of L-LA. Data acquisition was started 5 min after the addition of *i*PrOH. *, □, and † indicate signals corresponding to [D$_6$]benzene, {LO^1}$^-$, and residual Et$_2$O, respectively.

ed to the stability of the propagating [Sn{LO^1}(OPLLA)] (**12**) species. The consumption of L-LA, as monitored by ^{1}H NMR spectroscopy, exhibited first-order dependence on monomer concentration (see the Supporting Information, S25).

A parallel study was conducted with TMC. In striking contrast with L-LA, the first insertion of TMC was slow, and even after ca. 30 min the main organometallic species was still the in situ generated [Sn{LO^1}(O*i*Pr)] (**4**; $\delta_{119Sn} = -351$ ppm). The conversion of this complex into the catalytically active [Sn{LO^1}(OPTMC)] (**13**; $\delta_{119Sn} = -377$ ppm) was very slow (typically 4–5 h) and the two tin species **4** and **13** co-existed for almost the whole course of the reaction (observed by both ^{1}H and ^{119}Sn{^{1}H} NMR spectroscopy). Complete transformation of compound **4** into compound **13** was ultimately observed when nearly full conversion of the monomer was reached. Unlike with L-LA, the initiation of the ROP of TMC with compound **4** was slower than the propagation and the rate of consumption of TMC was apparently zero-order in monomer concentration under these conditions (see the Supporting Information, S26).

The slowly formed [Sn{LO^1}(OPTMC)] species (**13**) could very rapidly initiate the ROP of L-LA. Indeed, when the previous experiment was repeated until complete conversion of TMC, the single resonance in the ^{119}Sn{^{1}H} NMR spectrum was found at $\delta = -377$ ppm, as mentioned above. L-LA was then added to the reaction mixture and its polymerization began immediately: in the ^{119}Sn{^{1}H} NMR spectrum of the resulting solution, the resonance at $\delta = -377$ ppm disappeared before the first point of analysis and was replaced by a singlet at $\delta = -432$ ppm, which is the chemical shift corresponding to the species identified during the ROP of L-LA alone ([Sn{LO^1}(OPLLA)], **12**). Thus, as observed for other related Zn-based *i*ROP systems,[19] the sequential polymerization of L-LA after that of TMC could be achieved without any detrimental effects. However, the reverse was not true. L-LA completely inhibited the catalytic systems for the (*i*)ROP of TMC. When five equivalents of both monomers were reacted together with compound **3** and *i*PrOH ([TMC]$_0$/[L-LA]$_0$/[**3**]$_0$/[*i*PrOH]$_0$ = 5:5:1:1), only L-LA was polymerized whilst TMC remained unreacted, even after the complete conversion of L-LA (see the Supporting Information, S27). The ^{1}H and ^{119}Sn{^{1}H} NMR spectra indicated that during the whole course of this reaction, a single tin species existed in solution, which corresponded to that observed for the (*i*)ROP of L-LA alone, namely [Sn{LO^1}(OPLLA)] (**12**; $\delta_{119Sn} = -432$ ppm). In addition, unlike compound **4**, complex **5**—a close mimic of the active species (**12**) for the (*i*)ROP of L-LA—showed no reactivity towards TMC.[34] Inhibition of the catalytic activity of these tin-based systems for the ROP of TMC by L-LA probably resulted from different coordination environments in the respective catalytically active species, as suggested by the 50 ppm difference in the ^{119}Sn{^{1}H} NMR chemical shifts of [Sn{LO^1}(OPLLA)] (**12**) and [Sn{LO^1}(OPTMC)] (**13**). As yet, accurate mechanisms that identify the rate-limiting steps and transition states for the ROP of these two monomers with discrete Sn^{II} complexes have not been elucidated. Our experimental findings are summarized in Scheme 5.

Immortal ring-opening polymerization: Next, the immortal ROP of L-LA, that is, in the presence of excess *i*PrOH, was studied. The addition of three equivalents of alcohol to compound **3** (without monomer) resulted in the formation of the desired [Sn{LO^1}(O*i*Pr)] (**4**) but was unexpectedly[35] accompanied by the important release of free {LO^1}H, as revealed by ^{1}H NMR spectroscopy (Figure 6). However, despite using an excess of *i*PrOH, the protonolysis of compound **4** with concomitant release of {LO^1}H was not quantitative. Furthermore, the ^{1}H NMR resonances of the metal-bound isopropoxide and free-*i*PrOH groups merged as broad singlets. These observations were diagnostic of a relatively fast equilibrium on the NMR time-scale. We clearly



Scheme 5. Summary of the identified species (with their $^{119}Sn\{^1H\}$ NMR chemical shifts) in the ROPs of L-LA and TMC promoted by compounds **3** and **4** in [D_6]benzene at 25 °C.

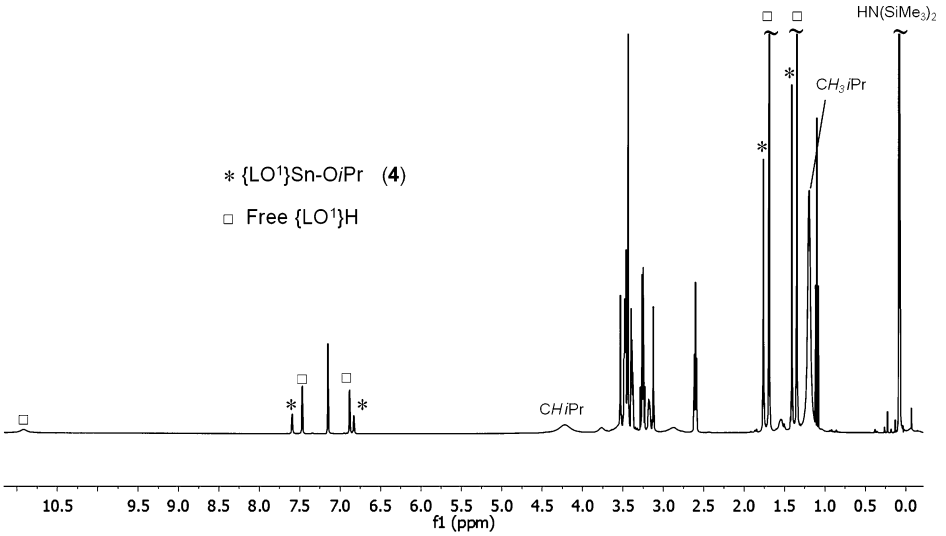


Figure 6. ^1H NMR spectrum (400.13 MHz, [D_6]benzene, 25 °C) of the reaction of compound **3** and three equivalents of *i*PrOH in the absence of lactide. □ and ∗ indicate signals corresponding to free {LO^1}H and compound **4**, respectively.

demonstrated that the ratio between free {LO^1}H and compound **4** in solution varied reversibly with the temperature and also depended on the initial loading of alcohol versus compound **3** (see the Supporting Information, S28 and S29). With an initial 3–16 equivalents of *i*PrOH versus compound **3**, the presence of compound **4** could still be detected (for instance, a **4**/{LO^1}H ratio of about 1:10 was found when 16 equivalents of *i*PrOH were used), and after the initial reaction, the mixtures showed no sign of evolution over the course of several days.

The surprising[36] release of {LO^1}H implied that another tin species was necessarily co-generated, most probably a homoleptic tin(II) bis-alkoxide complex of the type [Sn(O*i*Pr)$_2$]$_n$ (**10**). However, in our previous experiments, all of the room temperature $^{119}Sn\{^1H\}$ NMR spectra seemingly exhibited only one resonance at $\delta = -351$ ppm, which corresponded to that of compound **4**. Variable-temperature NMR spectroscopy demonstrated that this result was due to a dynamic behavior, and at 60 °C or above, an additional, broad singlet assigned to compound **10** appeared at approximately $\delta = -190$ ppm (see the Supporting Information, S16). This assignment was confirmed by the deliberate synthesis of compound **10** by reaction of [Sn{N(SiMe$_3$)$_2$}$_2$] with two equivalents of *i*PrOH.[27] The identity of this compound was established by ^1H NMR spectroscopy at 25 °C; on the other hand, no resonance was visible in its $^{119}Sn\{^1H\}$ NMR spectrum recorded at 25 °C, and the signal for this complex ($\delta = -190$ ppm) was only localized by $^{119}Sn\{^1H\}$ NMR at 60 °C. Finally, a solution equilibrium between compounds **4** and **10** was further supported by the reaction of one equivalent of {LO^1}H with compound **10**: the pro-ligand partially displaced one of the isopropoxide moieties in compound **10**, because the formation of a similar equilibrated mixture of compounds **4** and **10** was unequivocally observed in both the resulting ^1H and $^{119}Sn\{^1H\}$ NMR spectra.

A preliminary experiment confirmed that {LO^1}H is unable to promote the polymerization of L-LA by itself. The behavior of the **3**/*i*PrOH binary system in the presence of L-LA was investigated spectroscopically. Upon addition of three equivalents of *i*PrOH to a solution of compound **6** and L-LA (15 equiv) in [D_6]benzene, polymerization occurred readily and it could be monitored by NMR spectroscopy (Figure 7). The ^1H NMR resonances for the propagating species [Sn{LO^1}(OPLLA)] (**12**) were identified, together with signals corresponding to a large quantity of free {LO^1}H. Again, this observation confirmed that more than one tin-based compound was present in solution at any given stage of the reaction. Still, consumption of L-LA started without any induction period and followed perfect first-order kinetics in monomer concentration, with an apparent rate constant of $2.2(1)\cdot10^{-4}$ s^{-1} (see the Supporting Information, S30).

The presence of two tin species in solution was confirmed by ^{119}Sn NMR spectroscopy, which exhibited two resonances at $\delta = -336$ and -432 ppm (Figure 7). As previously discussed, the latter resonance was diagnostic of the [Sn{LO^1}(OPLLA)] species (**12**), whereas, on the basis of our hypothesis regarding the equilibrium generated upon addition of excess *i*PrOH to compound **3**, the new resonance at $\delta = -336$ ppm was assigned to a [Sn(OPLLA)$_2$] species (**14**). This assumption was confirmed by two independent experi-

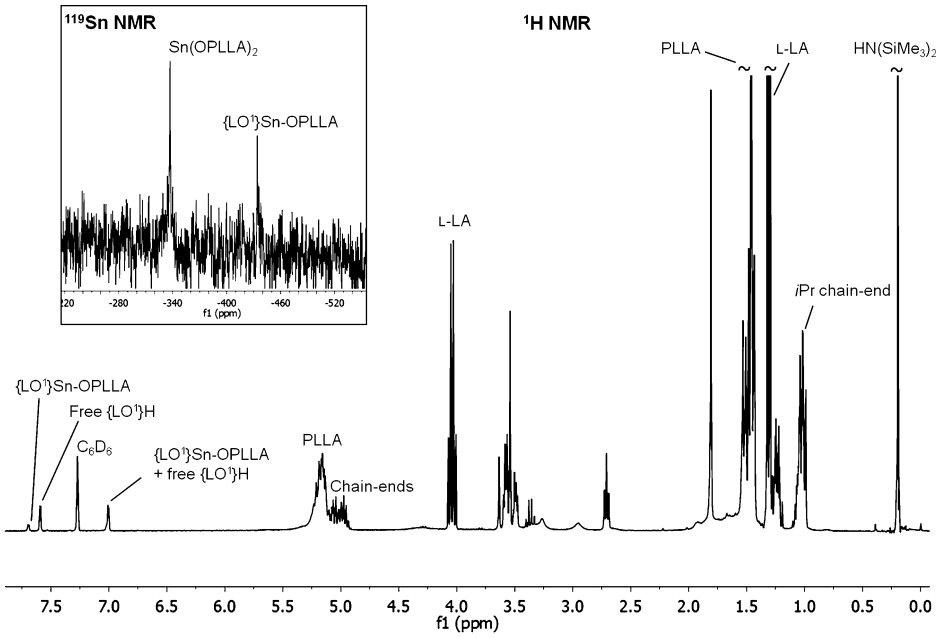
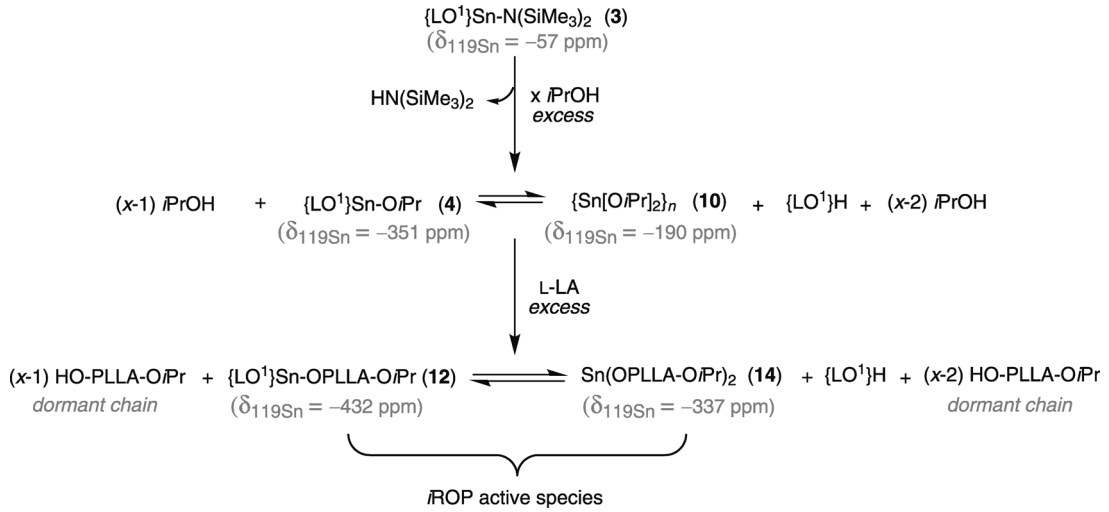


Figure 7. ^{1}H (300.13 MHz) and $^{119}Sn\{^{1}H\}$ NMR (111.88 MHz) spectra ([D_6]benzene, 25 °C) of the reaction of compound **3** with three equivalents of *i*PrOH and 15 equivalents of L-LA, recorded 80 min after the addition of the alcohol.

ments. Firstly, compound **10** ($\delta_{119Sn} = -190$ ppm) was generated in situ by the reaction of $[Sn\{N(SiMe_3)\}_2]$ ($\delta_{119Sn} = +769$ ppm) with two equivalents of *i*PrOH, and then two equivalents of L-LA were added. The resulting ^{1}H NMR spectrum was consistent with the insertion of monomer units into the two Sn–O*i*Pr bonds in compound **10**, and the ^{119}Sn NMR spectrum exhibited a single resonance at $\delta = -344$ ppm, that is, very close to that of compound **14**. Secondly, the addition of two equivalents of enantiomerically pure (*S*)-isopropyllactate to $[Sn\{N(SiMe_3)\}_2]$ afforded the desired compound $[Sn\{(S)\text{-}OCH(CH_3)CO_2iPr\}_2]$ (**11**). The $^{119}Sn\{^{1}H\}$ NMR spectrum of compound **11** exhibited a single resonance at $\delta = -347$ ppm, which was in the same region as in the two previous cases. Therefore, the simultaneous presence of two potentially propagating species (namely $[Sn\{LO^1\}(OPLLA)]$ (**12**) and $[Sn(OPLLA)_2]$ (**14**)) in solution under *i*ROP conditions was established. These observations were intriguing because the kinetic data measured by NMR spectroscopy and the narrow molecular-weight distributions observed in larger-scale reactions (conducted in Schlenk flasks) for the *i*ROP of L-LA were typical of catalytic systems with a single active species. Nevertheless, they were not incompatible with a well-controlled, more-complex mechanism. Indeed, under immortal conditions, the polymer chains are in fast and reversible equilibrium between their resting and propagating states, and they can be readily transferred onto any of the two (and in principal, more than two) active species. Moreover, we have shown that the two potentially active catalysts, compounds **4** and **11**, were in dynamic equilibrium, and the same is actually true of $[Sn\{LO^1\}(OPLLA)]$ (**12**) and $[Sn(OPLLA)_2]$ (**14**). In the reaction of one equivalent of $\{LO^1\}H$ with compound **11**, one of the $OCH(CH_3)CO_2iPr$ moieties was partially displaced by the proligand, and the non-quantitative formation of $[Sn\{LO^1\}\{(S)\text{-}OCH(CH_3)CO_2iPr\}]$ (**5**) was detected at $\delta = -409$ and -425 ppm along with $[Sn\{(S)\text{-}OCH(CH_3)CO_2iPr\}_2]$ ($\delta = -347$ ppm) in the $^{119}Sn\{^{1}H\}$ NMR spectrum of the reaction mixture (see the Supporting Information, S18). As a result of these two concomitant equilibria under *i*ROP conditions, all of the resulting PLLA chains presented the same averaged macromolecular features, just as if they had been formed by a single species. A summary of the results on the mechanism of the *i*ROP of L-LA catalyzed by the binary system **3**/*i*PrOH is displayed in Scheme 6.

In light of the above results, the synthesis of well-defined heteroleptic complexes might seem to be not strictly necessary to achieve the *i*ROP of L-LA in the presence of a protic co-catalyst. Indeed, against all previous assumptions, the simple compounds $[Sn(OR)_2]_n$ (OR = O*i*Pr or $OCH(CH_3)CO_2iPr$) constitute the preponderant species in solution with comparable catalytic activity. Duda and co-workers have shown that $[Sn(OnBu)_2]$ is a competent initiator for the living ROP of L-LA.[36] Yet, in our systems, the presence of a small proportion of heteroleptic species in the reaction medium still had a beneficial role on polymerization kinetics. In fact, monitoring the *i*ROPs of L-LA catalyzed by $[Sn\{N(SiMe_3)_2\}_2]$ and by compound **3** in the presence of *i*PrOH (see the Supporting Information, S31) showed that the catalytic system **3**/*i*PrOH ($k_{app} = 1.0(1) \times 10^{-3}\ s^{-1}$) was moderately faster than $[Sn\{N(SiMe_3)_2\}_2]$/*i*PrOH ($5.9(3) \times 10^{-4}\ s^{-1}$).[37] The same study revealed that the homoleptic compound **2** also showed very similar behavior ($k_{app} = 8.4(4) \cdot 10^{-3}\ s^{-1}$), an observation that had already been made during large-scale reactions. To investigate the reason for this, compound **2** was reacted with 2 equivalents of *i*PrOH, which led to the formation of exactly the same species as those produced by **3**/*i*PrOH, namely compounds **4** and **10**, along with free $\{LO^1\}H$; no trace of the homoleptic compound **2** was found. The ability of *i*PrOH to exchange a proton with tin phenolate species explains the near-identical *i*ROP catalytic activities of compounds **2** and **3**. Moreover, when compound **2** was reacted immediately with 5 equivalents of *i*PrOH and 15 equivalents of L-LA, the ^{1}H NMR spectra recorded during the monitoring of the reaction closely matched those recorded under similar conditions when **3**/*i*PrOH was used; only two resonances were found in the $^{119}Sn\{^{1}H\}$ NMR spectrum ($\delta = -337$ and -432 ppm; see



Scheme 6. Identified Sn^{II} species (and their respective $^{119}Sn\{^1H\}$ NMR chemical shifts) during the *i*ROP of L-LA catalyzed by compound **3**/*i*PrOH.

the Supporting Information, S19), which corresponded to the two species [Sn(OPLLA)$_2$] (**14**) and [Sn{LO^1}(OPLLA)] (**12**) as identified previously. Therefore, the various equilibria established for the catalytic system **3**/*i*PrOH (Scheme 6) could also be directly applied to compound **2**.

Finally, under large-scale conditions, the heteroleptic siloxy derivative **6** was unable to catalyze the *i*ROP of L-LA. Monitoring the reaction between *i*PrOH and compound **6** by NMR spectroscopy showed that only a partial release of free {LO^1}H occurred, whereas the siloxide Ph_3SiO[Sn] moiety remained unreacted. Although the formation of a putative "[Sn(*i*PrO)($OSiPh_3$)]" species could not be clearly assessed, the formation of the catalytically active [Sn{(*S*)-$OCH(CH_3)CO_2$*i*Pr}$_2$] (**11**) was never detected. Consequently, no species able to catalyze the *i*ROP of L-LA was generated, thereby explaining the inefficiency of the **6**/*i*PrOH catalyst. One must emphasize that, even if compound **6** does not possess the efficient nucleophilic group required for a coordination–insertion mechanism, catalytic activity could potentially occur through an activated-monomer process (promoted directly by compound **6** or by the undefined species formed after its treatment with *i*PrOH). Therefore, the absence of any catalytic activity from species **6**/*i*PrOH provides a strong indication that neutral (as opposed to cationic species such as compound **9**) tin(II) complexes (both homo- and heteroleptic) of the type **1**–**5** pre-catalysts cannot catalyze the *i*ROP of L-LA through an activated-monomer mechanism; instead, the *i*ROP of cyclic esters most-probably occurs exclusively by a coordination–insertion mechanism.[36b]

Conclusion

We have prepared several well-defined complexes of tin(II) which constitute efficient pre-catalysts and model intermediates for the (*i*)ROP of cyclic esters in the presence of a protic, nucleophilic co-catalyst, such as the archetypal *i*PrOH. Detailed spectroscopic studies have been conducted to investigate the polymerization mechanisms, and we have been able to establish that two catalytically active species, [Sn{LO^1}(OPLLA)] (**12**) and [Sn(OPPLA)$_2$] (**14**), are in equilibrium in the reaction medium at any given time during the polymerization reaction. Because the growing chains (PLLAO–[Sn]) are in rapid and reversible equilibrium with dormant ones (PLLAO–H), and because the two active species (**12** and **14**) are also in fast equilibrium with one another, the resulting polymers display monomodal and very narrow molecular weight distributions that are usually characteristic of single, discrete initiators.

Moreover, these ^1H and $^{119}Sn\{^1H\}$ NMR mechanistic studies have shown that in the presence of one or more equivalents of a protic co-catalyst, both homo- and heteroleptic complexes promoted the (*i*)ROP of L-LA through a single coordination–insertion mechanism. Therefore, any potential ambiguity concerning the nature of the mechanism (coordination–insertion versus activated-monomer) was removed as further evidence was provided by the complete inactivity of the siloxy complex [Sn{LO^1}($OSiPh_3$)] (**6**) towards L-LA, which only reacted with *i*PrOH to yield catalytically inactive metal species.

From a mechanistic point-of-view, a direct comparison between these new tin(II) complexes and other, analogous complexes of divalent oxophilic metals (Zn, Mg, Ca) cannot be drawn easily. The latter metals yield more active (but also much more sensitive) binary catalyst systems by at least one order of magnitude (Ca catalysts exhibit TOF numbers up to 28000 $mol_{L-LA}\,mol_{Ca}^{-1}\,h^{-1}$).[6f,12c,f] Thus, Zn and Ca complexes are much too fast for NMR kinetic measurements. On the other hand, we have observed several similarities between the catalytic behavior of many of these pre-catalysts, and a reappraisal of the effective *i*ROP mechanisms involving Zn, Mg, and Ca may be necessary. Crucially, these results show that equally competent catalysts are pro-

duced from heteroleptic and homoleptic Sn^{II} complexes. Given the importance of tin(II) catalysts for the polymerization of cyclic esters in industry, and the scope offered by immortal catalytic systems for the large-scale ROP of these monomers, the results described here will be of direct relevance to both industrial and academic research groups with an interest in this area.

Experimental Section

General procedures: All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry, solvent-free glove-box (Jacomex; $O_2 < 1$ ppm, $H_2O < 5$ ppm) for catalyst loading. Anhydrous $SnCl_2$ (Acros, 98%), $LiNMe_2$ (Aldrich, 95%), isopropyl-(*S*)-lactate (Aldrich), and Ph_3SiOH (Acros) were used as received. $HN(SiMe_3)_2$ (Acros) was dried over activated 3 Å molecular sieves and distilled prior to use. Propan-2-ol was dried and distilled over magnesium turnings and stored over 3 Å molecular sieves. The synthetic precursors $[Sn\{N(SiMe_3)_2\}_2]$,[38] $[Sn(NMe_2)_2]$,[39] $[H(OEt_2)_2]^+[H_2N\{B(C_6F_5)_3\}_2]^-$,[25a] $[\{LO^1\}HH]^+[H_2N\{B(C_6F_5)_3\}_2]^-$,[12c] and the pro-ligands $\{LO^1\}H$[12c,17] and $\{LO^2\}H$[12c] were prepared as described in the literature. Toluene was pre-dried over sodium and distilled under argon over molten sodium prior to use. THF was first pre-dried over sodium hydroxide and distilled under argon over CaH_2, and then freshly distilled a second time under argon over sodium mirror/benzophenone ketyl prior to use. All deuterated solvents (Eurisotop, Saclay, France) were stored in sealed ampoules over activated 3 Å molecular sieves and were thoroughly degassed by several freeze-thaw-vacuum cycles. Technical grade L-LA was provided by Total Petrochemicals and purified by recrystallization from a hot (80 °C) solution of concentrated *i*PrOH, followed by two subsequent recrystallizations in hot toluene (105 °C). After purification, L-LA was stored at all times at a temperature of −30 °C in the inert atmosphere of the glove-box.

NMR spectra were recorded on Bruker AC-300, Avance DPX-300, AM-400, and AM-500 spectrometers. All chemicals shifts were determined using residual signals of the deuterated solvents and were calibrated versus $SiMe_4$. Assignment of the signals was carried out using 1D (^1H, $^{13}C\{^1H\}$) and 2D NMR experiments (COSY, HMBC, HMQC). Coupling constants are given in Hertz. $^{19}F\{^1H\}$ NMR chemical shifts were determined by external reference to an aqueous solution of $NaBF_4$. ^{119}Sn NMR spectra were externally calibrated versus $[SnMe_4]$.

Low-temperature ^{119}Sn Mössbauer spectra were recorded in transmission geometry in the constant acceleration mode, using equipment supplied by Ortec and Wissel, by placing the sample in a liquid-nitrogen-flow cryostat. The nominal activity of the $Ba^{119m}SnO_3$ source was 10 mCi. The hyperfine parameters (isomer shift and quadrupole splitting) were determined by fitting Lorentzian lines to the experimental data by using the ISO program.[40] Isomer shifts of samples studied in the present work are given with respect to the spectrum of $BaSnO_3$ at 77 K. The error in the determination of the hyperfine parameters is (± 0.06) mm s^{-1}.

Elemental analyses were performed on a Carlo Erba 1108 Elemental Analyzer instrument at the London Metropolitan University by Stephen Boyer and were the average of a minimum of two independent measurements. Repeated attempts to obtain satisfactory data in a reproducible fashion for the Sn^{II}–amide complexes were unsuccessful.[41]

Size-exclusion chromatography (SEC) measurements were performed on a Polymer Laboratories PL-GPC 50 instrument equipped with a PLgel 5 Å MIXED-C column and a refractive-index detector. The column was eluted with THF at RT at a rate of 1 mL min^{-1} and was calibrated using 11 monodisperse polystyrene standards in the range of 580–380000 g mol^{-1}. According to literature recommendations,[42] the molecular weights of all PLAs were corrected by a factor of 0.58.

MALDI-ToF mass spectra were recorded with a Bruker Daltonic MicroFlex LT apparatus, using a nitrogen laser source (337 nm, 3 ns) in linear mode with a positive acceleration voltage of 20 kV. Samples were prepared as follows: 1 μL of a 2:1 mixture of a saturated solution of α-cyano-4-hydroxycinnamic acid (Bruker Care) in HPLC quality acetonitrile and a 0.1% solution of trifluoroacetic acid in ultrapure water was deposited onto the sample plate. After total evaporation, 1 μL of a solution of the polymers in HPLC-purity THF (5 to 10 mg mL^{-1}) was deposited. Bruker Care Peptide Calibration Standards and Protein Calibration Standard I were used for external calibration.

$[Sn\{LO^1\}(NMe_2)]$ (1): A solution of $\{LO^1\}H$ (0.43 g, 0.98 mmol) in *n*-pentane (15 mL) was added at −80 °C over a period of 10 min to a solution of $[Sn(NMe_2)_2]$ (0.21 g 1.01 mmol) in *n*-pentane (30 mL). The temperature was raised to −30 °C and the resulting mixture was stirred for 2 h at this temperature; the formation of a white precipitate was observed. The volatile compounds were then removed under vacuum at RT. The resulting white solid was washed with *n*-pentane (3×3 mL) and dried in vacuo to give compound **1** which was contaminated by ca. 5% of the homoleptic derivative **2**. Yield 0.28 g (48%); ^1H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta = 7.63$ (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 6.91 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 4.20–2.50 (br, 22H; O−C*H*$_2$, N−C*H*$_2$−CH$_2$, and N−C*H*$_2$−Ar), 3.26 (s, 6H; N−C*H*$_3$), 1.77 (s, 9H; C(C*H*$_3$)$_3$), 1.44 ppm (s, 9H; C(C*H*$_3$)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 °C): $\delta = 159.3$, 139.1, 137.5, 125.9, 124.0, 122.6 (all C_{Ar}), 71.4, 69.9, 65.8 (O−*C*H$_2$ and N−*C*H$_2$−CH$_2$), 57.3 (Ar−*C*H$_2$−N), 40.9 (N−*C*H$_3$), 35.2 (*C*(CH$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 31.9 (C(*C*H$_3$)$_3$), 30.2 ppm (C(*C*H$_3$)$_3$); $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149.20 MHz, 25 °C): $\delta = -147$ ppm. Attempts to obtain satisfactory and reproducible elemental analysis calcd (%) for $C_{27}H_{48}N_2O_5Sn$: 599.38 were unsuccessful.

$Sn\{LO^1\}_2$ (2): A solution of $\{LO^1\}H$ (1.43 g, 3.28 mmol) in *n*-pentane (30 mL) was added to a solution of $[Sn(NMe_2)_2]$ (0.329 g, 1.59 mmol) in *n*-pentane (30 mL). The resulting mixture was stirred for 3 h at RT; rapid formation of a white precipitate was observed. After concentration of the solution under vacuum, the supernatant was removed by filtration and the isolated solid was washed with *n*-pentane (2×10 mL). Drying under vacuum afforded the homoleptic complex **2** as a colorless crystalline powder. Yield 1.40 g (89%); ^1H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta =$ 7.64 (d, $^4J_{HH} = 2.7$ Hz, 2H; Ar−*H*), 6.94 (d, $^4J_{HH} = 2.7$ Hz, 2H; Ar−*H*), 4.80 (br s, 2H; Ar−C*H*$_2$−N), 3.95–3.70 (br, 8H; O−C*H*$_2$, N−C*H*$_2$−CH$_2$, and N−C*H*$_2$−Ar), 3.45–3.25 (br, 30H; O−C*H*$_2$, N−C*H*$_2$−CH$_2$, and N−C*H*$_2$−Ar), 3.04 (br s, 4H; N−C*H*$_2$−CH$_2$), 1.75 (s, 18H; C(C*H*$_3$)$_3$), 1.46 ppm (s, 18H; C(C*H*$_3$)$_3$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 °C): $\delta = 159.2$, 137.5, 137.2, 127.1, 123.7, 123.0 (all C_{Ar}), 71.0, 70.3, 70.2, 66.4 (all O−*C*H$_2$), 56.0 (Ar−*C*H$_2$−N), 50.2 (N−*C*H$_2$−CH$_2$), 35.2 (*C*(CH$_3$)$_3$), 33.8 (*C*(CH$_3$)$_3$), 31.8 (C(*C*H$_3$)$_3$), 30.2 ppm (C(*C*H$_3$)$_3$); $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149.20 MHz, 25 °C): $\delta = -566$ ppm; elemental analysis calcd (%) for $C_{50}H_{84}N_2O_{10}Sn$ (991.92): C 60.5, H 8.5, N 2.8; found: C 60.6, H 8.4, N 2.7.

$[Sn\{LO^1\}\{N(SiMe_3)_2\}]$ (3): A solution of $\{LO^1\}H$ (2.77 g, 6.32 mmol) in Et_2O (30 mL) was added at −80 °C over a period of 60 min to a solution of $[Sn\{N(SiMe_3)_2\}_2]$ (2.92 g, 6.64 mmol) in Et_2O (50 mL). The solution rapidly turned from a deep-orange to a pale-yellow color. The resulting mixture was stirred for 90 min, whilst allowing the temperature to warm to −40 °C, and the volatile compounds were then removed under vacuum. The resulting solid was washed with cold *n*-pentane (3×10 mL) at −20 °C and dried in vacuo to give compound **3** as a white powder. Yield 4.10 g (91%). Single-crystals suitable for X-ray diffraction studies were obtained by recrystallization from a cold *n*-pentane solution. ^1H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta = 7.63$ (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 7.00 (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 4.18 (br s, 1H; Ar−C*H*$_2$−N), 3.88 (br s, 1H; N−CH$_2$−C*H*$_2$), 3.79 (br s, 1H; N−CH$_2$−C*H*$_2$), 3.64 (br s, 1H; N−CH$_2$−C*H*$_2$), 3.64 (br s, 1H; N−CH$_2$−C*H*$_2$), 3.47–3.17 (br m, 15H; O−C*H*$_2$, N−C*H*$_2$−CH$_2$, and Ar−C*H*$_2$−N), 2.88 (br s, 2H; N−C*H*$_2$−CH$_2$), 1.70 (s, 9H; C(C*H*$_3$)$_3$), 1.39 (s, 9H; C(C*H*$_3$)$_3$), 0.50 ppm (s, 18H; N[Si(C*H*$_3$)$_3$]$_2$); ^1H NMR (C_7D_8, 400.13 MHz, −20 °C): $\delta = 7.66$ (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 7.0 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 4.18 (d, $^2J_{HH} = 11.8$ Hz, 1H; Ar−C*H*$_2$−N), 3.91 (m, 1H; N−CH$_2$−C*H*$_2$), 3.83 (m, 1H; N−CH$_2$−C*H*$_2$), 3.62 (m, 1H; N−CH$_2$−C*H*$_2$), 3.55 (m, 1H; N−C*H*$_2$−CH$_2$), 3.38 (m, 1H; N−CH$_2$−C*H*$_2$), 3.32 (m, 1H; N−C*H*$_2$−CH$_2$), 3.30 (d, $^2J_{HH} = 11.8$ Hz, 1H; Ar−C*H*$_2$−N), 3.45–3.20 (br, 12H; O−C*H*$_2$), 2.88 (m, 2H; N−C*H*$_2$−CH$_2$), 1.76 (s, 9H; C(C*H*$_3$)$_3$), 1.45 (s, 9H; C(C*H*$_3$)$_3$), 0.56 ppm (s, 18H; N[Si(C*H*$_3$)$_3$]$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25 °C): $\delta = 158.4$, 140.33, 139.13, 126.6,

124.5, 124.3 (all C_{Ar}), 71.0, 70.2, 65.5 (all O−CH_2), 65.2 (N−CH_2−CH_2), 57.2 (Ar−CH_2−N), 53.1, 51.8 (N−CH_2−CH_2), 34.9 ($C(CH_3)_3$), 33.9 ($C(CH_3)_3$), 31.7 ($C(CH_3)_3$), 30.3 ($C(CH_3)_3$), 6.5 ppm (N[Si(CH_3)$_3$]$_2$); ^{29}Si{^{1}H} NMR (C_7D_8, 79.49 MHz, 25 °C): $\delta = -0.49$ ppm; ^{119}Sn{^{1}H} NMR (C_6D_6, 111.88 MHz, 25 °C): $\delta = -55$ ppm; repeated attempts to obtain satisfactory elemental analysis calcd (%) for $C_{31}H_{60}N_2O_5Si_2Sn$ (715.69) were unsuccessful.

In situ generation of [Sn{LO^1}(O*i*Pr)] (4): Under an inert atmosphere, compound **3** (27 mg, 38 μmol) was loaded into an NMR tube. Dry C_6D_6 (0.6 mL) was then added via syringe followed by *i*PrOH (2.9 μL, 38 μmol). The ^{1}H NMR spectrum of the resulting solution was consistent with the proposed formulation of compound **4**. No sign of further evolution was detected over the course of several days. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta = 7.60$ (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 6.95 (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 4.77 (br m, 1H; C*H*(CH_3)$_2$), 4.10–3.70 and 3.55–2.95 (br m, 20H; O−CH_2, N−CH_2−CH_2, and N−CH_2−Ar), 1.80 (s, 9H; C(CH_3)$_3$), 1.48 (br d, 6H; CH(CH_3)$_2$), 1.43 ppm (s, 9H; C(CH_3)$_3$); ^{119}Sn{^{1}H} NMR (C_6D_6, 111.88 MHz, 25 °C): $\delta = -351$ ppm.

In situ generation of [Sn{LO^1}{(*S*)-OCH(CH_3)CO_2*i*Pr}] (5): Under an inert atmosphere, compound **3** (43 mg, 60 μmol) was loaded into an NMR tube. Dry C_6D_6 (0.6 mL) was then added via syringe followed by isopropyl-(*S*)-lactate (7.9 μL, 60 μmol). The ^{1}H NMR spectrum of the resulting solution was in agreement with the expected formulation of compound **5**. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta = 7.61$ (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 6.96 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 5.14 (br m, 2H; C*H*(CH_3)$_2$ and C*H*(CH_3)), 4.10–2.60 (br, 20H; O−CH_2, N−CH_2−CH_2 and N−CH_2−Ar), 1.77 (s, 9H, C(CH_3)$_3$), 1.65 (br d, 3H, CH(CH_3)), 1.44 (s, 9H, C(CH_3)$_3$), 1.04 ppm (br m, 6H, CH(CH_3)$_2$); ^{119}Sn{^{1}H} NMR (C_6D_6, 149.20 MHz, 25 °C): $\delta = -409$, -425 ppm (approx. 1:1 ratio).

[Sn{LO^1}(OSiPh$_3$)] (6): A solution of {LO^1}H (0.63 g, 1.44 mmol) in Et_2O (10 mL) was added to a solution of [Sn{N(SiMe$_3$)$_2$}$_2$] (0.64 g, 1.46 mmol) in Et_2O (20 mL) at −50 °C over a period of 20 min. The resulting mixture was stirred for a further 20 min at −50 °C before a solution of $HOSiPh_3$ (0.41 g, 1.39 mmol) in Et_2O (10 mL) was added dropwise. The solution was stirred for another 20 min at −30 °C and the volatile compounds were then removed under vacuum to yield compound **6** as a white solid which was washed with *n*-pentane (3×10 mL) and dried in vacuo. Yield 1.00 g (88 %). Single-crystals suitable for X-ray diffraction were obtained by recrystallization from *n*-pentane. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta = 8.06$ (m, 6H; Ar−*H*), 7.66 (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 7.24 (m, 6H; Ar−*H*), 7.29 (m, 3H; Ar−*H*), 6.80 (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 4.63 (m, 1H; Ar−CH_2−N), 3.91 (br m, 1H; N−CH_2−CH_2), 3.64 (br m, 1H; N−CH_2−CH_2), 3.57 (br m, 1H; N−CH_2−CH_2), 3.27–2.92 (br m, 14H; O−CH_2 and N−CH_2−CH_2), 2.82 (br m, 2H; Ar−CH_2−N and N−CH_2−CH_2), 2.43 (br s, 1H; N−CH_2−CH_2), 2.09 (br s, 1H; N−CH_2−CH_2), 1.81 (s, 9H, C(CH_3)$_3$), 1.44 ppm (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): $\delta = 158.9$, 140.7, 138.5, 137.0, 135.6, 128.7, 128.0 (overlapped with C_6D_6), 128.5, 124.1, 122.0 (all C_{Ar}), 70.8, 70.6, 69.5, 69.0 (O−*C*H_2), 66.2, 64.5 (N−CH_2−*C*H_2), 58.9 (Ar−*C*H_2−N), 53.8, 48.6 (N−*C*H_2−CH_2), 35.2 (*C*(CH_3)$_3$), 33.9 (*C*(CH_3)$_3$), 31.9 (C(*C*H_3)$_3$), 30.1 ppm (C(*C*H_3)$_3$); ^{29}Si{^{1}H} NMR (C_6D_6, 79.49 MHz, 25 °C): $\delta = -22.2$ ppm; ^{119}Sn{^{1}H} NMR (C_6D_6, 149.20 MHz, 25 °C): $\delta = -459$ ppm; elemental analysis calcd (%) for $C_{43}H_{57}NO_6SiSn$ (830.91): C 62.2, H 6.9, N 1.7; found: C 62.3, H 6.8, N 1.6.

[Sn{LO^2}{N(SiMe$_3$)$_2$}] (7): A solution of {LO^2}H (0.25 g, 0.81 mmol) in Et_2O (20 mL) was added at −45 °C over a period of 15 min to a solution of [Sn{N(SiMe$_3$)$_2$}$_2$] (0.37 g, 0.84 mmol) in Et_2O (20 mL). The resulting mixture was stirred for another 15 min at −45 °C and the volatile compounds was then removed under vacuum. The sticky solid was stripped repeatedly with *n*-pentane (6×5 mL), but complete removal of the released amine could not be achieved. A small quantity of pure compound **7** (ca. 30 mg) could be obtained by precipitation from a concentrated solution in *n*-pentane at −50 °C over a period of several weeks. ^{1}H NMR (C_6D_6, 400.13 MHz, 25 °C): $\delta = 7.68$ (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 6.80 (d, $^4J_{HH} = 2.6$ Hz, 1H; Ar−*H*), 4.3–1.8 (br m, 10H; Ar−CH_2−N and CH_2−CH_2−O), 1.68 (s, 9H; C(CH_3)$_3$), 1.41 (s, 9H; C(CH_3)$_3$), 0.45 ppm (s, 18H; N[Si(CH_3)$_3$]$_2$); ^{1}H NMR (C_7D_8, 400.13 MHz, −20 °C): $\delta = 7.63$ (d, $^4J_{HH} = 2.4$ Hz, 1H; Ar−*H*), 6.80 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 4.08 (d, $^2J_{HH} = 11.8$ Hz, 1H; Ar−CH_2−N), 3.74 (m, 1H; O−CH_2), 3.54 (m, 1H; O−CH_2), 3.35 (m, 1H; O−CH_2), 3.22 (m, 1H; O−CH_2), 3.08 (m, 1H; N−CH_2−CH_2), 2.39 (m, 2H; N−CH_2−CH_2 and Ar−CH_2−N), 2.14 (m, 1H; N−CH_2−CH_2), 1.80 (m, 1H; N−CH_2−CH_2), 1.72 (s, 9H; C(CH_3)$_3$), 1.47 (s, 9H, C(CH_3)$_3$), 0.47 ppm (s, 18H, N[Si(CH_3)$_3$]$_2$); ^{13}C{^{1}H} NMR (C_6D_6, 100.62 MHz, 25 °C): $\delta = 157.8$, 139.8, 138.8, 125.6, 124.1, 122.3 (all C_{Ar}), 64.0 (O−*C*H_2), 60.1 (Ar−*C*H_2−N), 52.4 (N−*C*H_2−CH_2), 34.3 (*C*(CH_3)$_3$), 33.4 (*C*(CH_3)$_3$), 31.1 (C(*C*H_3)$_3$), 29.7 (C(*C*H_3)$_3$), 5.8 ppm (N[Si(*C*H_3)$_3$]$_2$); ^{29}Si{^{1}H} NMR (C_7D_8, 79.49 MHz, 25 °C): $\delta = 0.14$ ppm; ^{119}Sn{^{1}H} NMR (C_7D_8, 149.20 MHz, 25 °C): $\delta = -42$ ppm. Satisfactory elemental analysis calcd (%) for $C_{25}H_{48}N_2O_2Si_2Sn$ (583.53) could not be obtained.

[Sn{LO^2}(OSiPh$_3$)] (8): A solution of {LO^2}H (0.58 g, 1.90 mmol) in Et_2O (20 mL) was added to a solution of [Sn{N(SiMe$_3$)$_2$}$_2$] (0.84 g, 1.91 mmol) in Et_2O (20 mL) at −30 °C over a period of 10 min. The resulting mixture was stirred for a further 15 min at −30 °C before a solution of $HOSiPh_3$ (0.52 g, 1.88 mmol) in Et_2O (15 mL) was added dropwise. The solution was stirred for another 15 min and allowed to warm to RT. The volatile compounds were then removed under vacuum. Addition of cold *n*-pentane provoked the formation of a solid precipitate, which was isolated and washed with small amounts of *n*-pentane (2×5 mL). Following drying in vacuo, analytically pure compound **8** was obtained as a colorless powder. Yield 0.68 g (52 %). Single-crystals suitable for X-ray diffraction studies were obtained by recrystallization from *n*-pentane. ^{1}H NMR (C_6D_6, 500.13 MHz, 25 °C): $\delta = 7.95$ (m, 6H; Ar−*H*), 7.64 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 7.28 (m, 6H; Ar−*H*), 7.23 (m, 3H; Ar−*H*), 6.71 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 4.03 (d, $^2J_{HH} = 11.8$ Hz, 1H; Ar−CH_2−N), 3.52 (m, 1H; O−CH_2), 3.42 (m, 1H; N−CH_2−CH_2), 3.30 (m, 1H; O−CH_2), 3.19 (m, 1H; O−CH_2), 3.03 (m, 1H; O−CH_2), 2.34 (d, $^2J_{HH} = 11.8$ Hz, 1H; Ar−CH_2−N), 2.05 (m, 1H; N−CH_2−CH_2), 1.90 (m, 1H; N−CH_2−CH_2), 1.69 (m, 1H; N−CH_2−CH_2), 1.67 (s, 9H, C(CH_3)$_3$), 1.42 ppm (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (C_6D_6, 125.76 MHz, 25 °C): $\delta = 157.0$, 139.6, 139.5, 139.0, 135.3, 129.2, 127.7 (overlapped with C_6D_6), 125.9, 124.8, 121.8 (all C_{Ar}), 65.2, 64.2 (O−*C*H_2), 61.0 (Ar−*C*H_2−N), 53.8, 52.0 (N−*C*H_2−CH_2), 35.0 (*C*(CH_3)$_3$), 34.0 (*C*(CH_3)$_3$), 31.8 ppm (C(*C*H_3)$_3$), 30.1 (C(*C*H_3)$_3$); ^{29}Si{^{1}H} NMR (C_6D_6, 79.49 MHz, 25 °C): $\delta = -19.8$ ppm; ^{119}Sn{^{1}H} NMR (C_6D_6, 149.20 MHz, 25 °C): $\delta = -353$ ppm; elemental analysis calcd (%) for $C_{37}H_{45}NO_3SiSn$ (698.55): C 63.6, H 6.5, N 2.0; found: C 63.7, H 6.5, N 1.9.

[Sn{LO^1}]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (9): *Route A*: A solution of [Sn{N(SiMe$_3$)$_2$}$_2$] (0.17 g, 0.39 mmol) in Et_2O (10 mL) was added at RT via cannula to a solution of [{LO^1}HH]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (0.57 g, 0.37 mmol) in Et_2O (20 mL). The solution was stirred for 1 h before the volatile compounds were evaporated under vacuum. The resulting oil was purified by three successive dissolution/precipitation cycles using CH_2Cl_2 and *n*-pentane, to afford pure compound **9** as a white powder after drying under vacuum. Yield 0.42 g (72 %).

Route B: [H(OEt$_2$)$_2$]$^+$[H$_2$N{B(C$_6$F$_5$)$_3$}$_2$]$^-$ (0.85 g, 0.71 mmol) was added with a bent finger to a solution of **3** (0.52 g, 0.73 mmol) in Et_2O (20 mL) at RT. The solution was stirred for 1 h before the solvent was evaporated under vacuum. The resulting oil was purified by three successive dissolution/precipitation cycles using CH_2Cl_2 and *n*-pentane, to afford analytically pure compound **9** as a colorless powder after drying under vacuum. Yield 0.90 g (79 %).

^{1}H NMR (CD_2Cl_2, 500.13 MHz, 25 °C): $\delta = 7.45$ (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 6.96 (d, $^4J_{HH} = 2.5$ Hz, 1H; Ar−*H*), 5.71 (br s, 2H; NH_2), 4.00–3.85 (m, 14H; O−CH_2 and Ar−CH_2−N), 3.75–3.65 (m, 4H; O−CH_2), 3.32 (m, 2H; N−CH_2−CH_2), 3.02 (m, 2H, N−CH_2−CH_2), 1.45 (s, 9H, C(CH_3)$_3$), 1.31 ppm (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (CD_2Cl_2, 125.76 MHz, 25 °C): $\delta = 156.4$ (C_{Ar}–H), 148.8, 146.9 (C_{Ar}–F), 141.0 (C_{Ar}–H), 140.1 (C_{Ar}–F), 139.4 (C_{Ar}–H), 138.1, 137.7, 135.6 (all C_{Ar}–F), 126.1 (two overlapped signals), 121.3 (C_{Ar}–H), 70.9, 68.6, 68.4, 67,6 (all O−*C*H_2), 59.6 (Ar −*C*H_2–N), 54.0 (overlapped with CD_2Cl_2, N−*C*H_2−CH_2), 34.8 (*C*(CH_3)$_3$), 34.1 (*C*(CH_3)$_3$), 31.2 (C(*C*H_3)$_3$), 29.7 ppm (C(*C*H_3)$_3$); ^{19}F{^{1}H} NMR (CD_2Cl_2, 376.46 MHz, 25 °C): $\delta = -132.9$ (d, $^3J_{FF} = 19$ Hz, 12F; *o-F*), −160.2 (t, $^3J_{FF} = 19$ Hz, 6F; *p-F*), −165.7 ppm (t, $^3J_{FF} = 19$ Hz, 12F; *m-F*); ^{11}B{^{1}H} NMR (CD_2Cl_2, 128.38 MHz, 25 °C): $\delta = -8.4$ ppm; ^{119}Sn{^{1}H} NMR (CD_2Cl_2, 149.20 MHz, 25 °C): $\delta = -753$ ppm; elemental

analysis calcd (%) for $C_{61}H_{44}B_2F_{30}N_2O_5Sn$ (1595.28): C 45.9, H 2.8, N 1.8; found: C 46.1, H 2.6, N 1.7.

$[Sn(OiPr)_2]_n$ (10): To a solution of $[Sn\{N(SiMe_3)_2\}_2]$ (0.45 g, 1.03 mmol) in Et_2O (10 mL) was added dropwise a solution of *i*PrOH (0.15 g, 2.58 mmol) in Et_2O (10 mL) at RT. After complete addition, the solution was stirred for a further 10 min before the volatile compounds were evaporated under vacuum. The desired product was recovered from the resulting oily mixture by extraction with *n*-pentane (3×10 mL), yielding compound **10** in high purity. Yield 0.20 g (81%); ^{1}H NMR (C_6D_6, 300.13 MHz, 25°C): $\delta = 4.59$ (m, 2H; C*H*), 1.34 ppm (d, $^3J_{HH=}6.1$ Hz; CH_3); $^{13}C\{^1H\}$ NMR (C_6D_6, 75.47 MHz, 25°C): $\delta = 65.6$ (*C*H), 28.2 ppm (*C*H_3); $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149 MHz, 90°C): $\delta = -190$ ppm. This synthesis is analogous to that described by Caulton and co-workers.[27]

$[Sn\{(S)\text{-}OCH(CH_3)CO_2iPr\}_2]$ (11): Isopropyl-(*S*)-lactate (0.25 g, 1.89 mmol) was added at RT via syringe to a solution of $[Sn\{N(SiMe_3)_2\}_2]$ (0.42 g, 0.95 mmol) in Et_2O (10 mL). The solution was stirred for 10 min before the volatile compounds were evaporated under vacuum. The resulting viscous oil was stripped with Et_2O (2×5 mL) and then with *n*-pentane (2×10 mL), but the final material remained oily. NMR analysis indicated that the desired compound had been obtained in satisfactory purity. Yield 0.32 g (88%). ^{1}H NMR (C_6D_6, 500.13 MHz, 25°C): $\delta = 5.10$ (q, $^3J_{HH=}6.8$ Hz, 2H; C*H*(CH_3)), 4.92 (sept, $^3J_{HH=}6.3$ Hz, 2H; C*H*(CH_3)$_2$), 1.67 (d, $^3J_{HH=}6.8$ Hz, 6H; CH(C*H*$_3$)), 0.98 ppm (dd, $^3J_{HH=}6.3$ Hz, 12H; CH(C*H*$_3$)$_2$); $^{13}C\{^1H\}$ NMR (C_6D_6, 125.76 MHz, 25°C): $\delta = 181.3$ (*C*O_2R), 69.3, 68.7 (*C*H(CH_3) and *C*H(CH_3)$_2$), 23.8, 21.3 ppm (CH(*C*H_3) and CH(*C*H_3)$_2$); $^{119}Sn\{^1H\}$ NMR (C_6D_6, 149 MHz, 25°C): $\delta = -347$ ppm.

Typical polymerization procedure: In the glove-box, the metal catalyst was placed in a Schlenk flask together with the monomer. The Schlenk flask was then sealed and removed from the glove box. All subsequent operations were carried out on a vacuum manifold using Schlenk techniques. The required amount of solvent was added via syringe to the catalyst and the monomer, followed by addition of the co-catalyst (*i*PrOH). The resulting mixture was immerged in an oil bath that had been pre-set to the desired temperature and the polymerization time was measured from this point. The reaction was terminated by addition of acidified MeOH (HCl, 10 wt%) and the polymer was precipitated in MeOH and washed thoroughly. The polymer was then dried to a constant weight in a vacuum oven at 55°C under dynamic vacuum ($< 5\times10^{-2}$ mbar).

NMR kinetic measurements: In a typical experiment, the catalyst and monomer were loaded into an NMR tube in the glove-box. The NMR tube was placed in a Schlenk flask, which was then removed from the glove-box and connected to the vacuum manifold. All subsequent operations were performed using Schlenk techniques. The appropriate amounts of solvent ([D_8]toluene) and co-catalyst (*i*PrOH) were added to the NMR tube in that order at RT. The NMR tube was then sealed, heated gently and briefly to ensure complete dissolution of the monomer (time measurement started from this point), and introduced in the spectrometer that was pre-set to the desired temperature. Data points were collected at regular intervals (typically 15–60 s, with D1 = 0.5 s and NS = 4 scans) until conversion of the monomer stopped (which usually coincided with full conversion). The conversion was reliably determined by integrating the methine region of PLLA (δ_{1H} 5.00 ppm at 60°C in [D_8]toluene) vs. that of the monomer (δ_{1H} 4.08 ppm at 60°C in [D_8]toluene). The accuracy of the measurements was corroborated by the good agreement between theoretical (based on the conversion, $M_{n,theo} = 144.13\times[\text{L-LA}]_0/[i\text{PrOH}]_0\times\text{conversion}$) and experimental molecular weights ($M_{n,NMR}$ determined by integration of the resonance of the methine hydrogen atoms vs. those of the chain-ends).

X-ray diffraction crystallography: Diffraction data were collected using a Bruker APEX CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). A combination of ω and Φ scans was carried out to obtain a unique data set. The crystal structures were solved by direct methods, remaining atoms were located by difference Fourier synthesis followed by full-matrix least-squares refinement based on F2 (programs SIR97 and SHELXL-97).[43] A summary of crystal and refinement data for compounds **3, 6**, and **8** is given in the Supporting Information (S22). CCDC-831186 (**3**), CCDC-831187 (**6**), and CCDC-831188) (**8**) contain 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.

Acknowledgements

This work was sponsored by Total Petrochemicals (research grant to V.P.). The authors gratefully thank Dr. Sabine Sirol and Dr. Martine Slawinski (Total Petrochemicals) for fruitful discussions. The authors gratefully acknowledge the CNRS (Y.S., J.-F.C.) and the Institut Universitaire de France (J.-F.C.) for their financial support. We thank Dr. Mark Schormann (UEA) for solving the crystal structure of compound **8**. We are also thankful to Stephen Boyer (London Metropolitan University) for carrying out all of the elemental analyses.

[1] a) K. E. Uhrich, S. M. Cannizzaro, R. S. Langer, K. M. Shakesheff, *Chem. Rev.* **1999**, *99*, 3181–3198; b) R. E. Drumright, P. R. Gruber, D. E. Henton, *Adv. Mater.* **2000**, *12*, 1841–1846; c) A.-C. Albertsson, I. K. Varma, *Biomacromolecules* **2003**, *4*, 1466–1486; d) S. Mecking, *Angew. Chem.* **2004**, *116*, 1096–1104; *Angew. Chem. Int. Ed.* **2004**, *43*, 1078–1085; e) O. Dechy-Cabaret, B. Martin-Vaca, D. Bourissou, *Chem. Rev.* **2004**, *104*, 6147–6176; f) J. M. Becker, R. J. Pounder, A. P. Dove, *Macromol. Rapid Commun.* **2010**, *31*, 1923–1937; g) C. M. Thomas, *Chem. Soc. Rev.* **2010**, *39*, 165–173.

[2] a) *Biopolymers from Renewable Resources* (Ed.: D. L. Kaplan), Springer, Berlin, **1998**; b) M. J. Stanford, A. P. Dove, *Chem. Soc. Rev.* **2010**, *39*, 486–494.

[3] For reviews on ROP organocatalysts, see: a) N. E. Kamber, W. Jeong, R. M. Waymouth, R. C. Pratt, B. G. G. Lohmeijer, J. L. Hedrick, *Chem. Rev.* **2007**, *107*, 5813–5840; b) M. K. Kiesewetter, E. Ji Shin, J. L. Hedrick, R. M. Waymouth, *Macromolecules* **2010**, *43*, 2093–2107.

[4] a) B. J. O'Keefe, M. A. Hillmyer, W. B. Tolman, *J. Chem. Soc. Dalton Trans.* **2001**, 2215–2224; b) J. Wu, T.-L. Yu, C.-T. Chen, C.-C. Lin, *Coord. Chem. Rev.* **2006**, *250*, 602–626; c) C. A. Wheaton, P. G. Hayes, B. J. Ireland, *Dalton Trans.* **2009**, 4832–4846; d) P. J. Dijkstra, H. Du, J. Feijen, *Polym. Chem.* **2011**, *2*, 520–527.

[5] For key references on Al initiators, see: a) A. Le Borgne, V. Vincens, M. Jouglard, N. Spassky, *Makromol. Chem. Macromol. Symp.* **1993**, *73*, 37–46; b) M. Wisniewski, A. Le Borgne, N. Spassky, *Macromol. Chem. Phys.* **1997**, *198*, 1227–1238; c) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **2002**, *124*, 1316–1326; d) N. Nomura, R. Ishii, M. Akakura, K. Aoi, *J. Am. Chem. Soc.* **2002**, *124*, 5938–5939; e) A. Amgoune, L. Lavanant, C. M. Thomas, Y. Chi, R. Welter, S. Dagorne, J.-F. Carpentier, *Organometallics* **2005**, *24*, 6279–6282; f) N. Nomura, R. Ishii, Y. Yamamoto, T. Kondo, *Chem. Eur. J.* **2007**, *13*, 4433–4451; g) M. Bouyahyi, E. Grunova, N. Marquet, E. Kirillov, C. M. Thomas, T. Roisnel, J.-F. Carpentier, *Organometallics* **2008**, *27*, 5815–5825; h) H. Du, A. H. Velders, P. J. Dijkstra, Z. Zhong, X. Chen, J. Feijen, *Macromolecules* **2009**, *42*, 1058–1066; i) H. Du, A. H. Velders, P. J. Dijkstra, J. Sun, Z. Zhong, X. Chen, J. Feijen, *Chem. Eur. J.* **2009**, *15*, 9836–9845; j) N. Nomura, A. Akita, R. Ishii, M. Mizuno, *J. Am. Chem. Soc.* **2010**, *132*, 1750–1751; k) A. D. Schwarz, Z. Chu, P. Mountford, *Organometallics* **2010**, *29*, 1246–1260; l) M. Bouyahyi, T. Roisnel, J.-F. Carpentier, *Organometallics* **2010**, *29*, 491–500; m) A. Otero, A. Lara-Sánchez, J. Fernández-Baeza, C. Alonso-Moreno, J. A. Castro-Osma, I. Márquez-Segovia, L. F. Sánchez-Barba, A. M. Rodríguez, J. C. Garcia-Martinez, *Organometallics* **2011**, *30*, 1507–1522; n) D. J. Darensbourg, O. Karroonnirun, S. J. Wilson, *Inorg. Chem.* **2011**, *50*, 6775–6787. For examples of related indium initiators, see: o) I. Peckermann, A. Kapelski, T. P. Spaniol, J. Okuda, *Inorg. Chem.* **2009**, *48*, 5526–5534; p) J.-C. Buffet, J. Okuda, P. L. Arnold, *Inorg. Chem.* **2010**, *49*, 419–426; q) A. Pietrangelo, S. C. Knight, A. K. Gupta, L. J. Yao, M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2010**, *132*, 11649–11657.

[6] For key references on Zn initiators, see: a) M. Cheng, A. B. Attygalle, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*,

11583–11584; b) B. M. Chamberlain, M. Cheng, D. R. Moore, T. M. Ovitt, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238; c) C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, Jr., M. A. Hillmyer, W. B. Tolman, *J. Am. Chem. Soc.* **2003**, *125*, 11350–11359; d) C. M. Silvernail, L. J. Yao, L. M. R. Hill, M. A. Hillmyer, W. B. Tolman, *Inorg. Chem.* **2007**, *46*, 6565–6574; e) J. Börner, U. Flörke, K. Huber, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem. Eur. J.* **2009**, *15*, 2362–2376; f) V. Poirier, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* **2009**, 9820–9827; g) F. Drouin, P. O. Oguadinma, T. J. J. Whitehorne, R. E. Prud′homme, F. Schaper, *Organometallics* **2010**, *29*, 2139–2147; h) D. J. Darensbourg, O. Karroonnirun, *Inorg. Chem.* **2010**, *49*, 2360–2371; i) D. J. Darensbourg, O. Karroonnirun, *Macromolecules* **2010**, *43*, 8880–8886; j) L. Wang, H. Ma, *Dalton Trans.* **2010**, *39*, 7897–7910; k) L.-C. Liang, W.-Y. Lee, T.-L. Tsai, Y.-L. Hsua, T.-Y. Lee, *Dalton Trans.* **2010**, *39*, 8748–8758; l) J. Börner, I. dos Santos Vieira, A. Pawlis, A. Döring, D. Kuckling, S. Herres-Pawlis, *Chem. Eur. J.* **2011**, *17*, 4507–4512.

[7] For key references on Group III and lanthanide initiators, see: a) S. J. McLain, T. M. Ford, N. E. Drysdale, *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1992**, *33*, 463–464; b) T. M. Ovitt, G. W. Coates, *J. Am. Chem. Soc.* **1999**, *121*, 4072–4073; c) C.-X. Cai, A. Amgoune, C. W. Lehmann, J.-F. Carpentier, *Chem. Commun.* **2004**, 330–331; d) A. Amgoune, C. M. Thomas, T. Roisnel, J.-F. Carpentier, *Chem. Eur. J.* **2006**, *12*, 169–179; e) H. Ma, T. P. Spaniol, J. Okuda, *Angew. Chem.* **2006**, *118*, 7982–7985; *Angew. Chem. Int. Ed.* **2006**, *45*, 7818–7821; f) H. E. Dyer, S. Huijser, A. D. Schwarz, C. Wang, R. Duchateau, P. Mountford, *Dalton Trans.* **2008**, 32–35; g) N. Ajellal, D. M. Lyubov, M. A. Sinenkov, G. K. Fukin, A. V. Cherkasov, C. M. Thomas, J.-F. Carpentier, A. A. Trifonov, *Chem. Eur. J.* **2008**, *14*, 5440–5448; h) A. Otero, J. Fernández-Baeza, A. Lara-Sánchez, C. Alonso-Moreno, I. Márquez-Segovia, L. F. Sánchez-Barba, A. M. Rodríguez, *Angew. Chem.* **2009**, *121*, 2210–2213; *Angew. Chem. Int. Ed.* **2009**, *48*, 2176–2179; i) J. W. Kramer, D. S. Treitler, E. W. Dunn, P. M. Castro, T. Roisnel, C. M. Thomas, G. W. Coates, *J. Am. Chem. Soc.* **2009**, *131*, 16042–16044; j) Z. Zhang, X. Xu, S. Sun, Y. Yao, Y. Zhang, Q. Shen, *Chem. Commun.* **2009**, 7414–7416; k) Z. Zhang, X. Xu, W. Li, Y. Yao, Y. Zhang, Q. Shen, Y. Luo, *Inorg. Chem.* **2009**, *48*, 5715–5724; l) R. H. Platel, A. J. P. White, C. K. Williams, *Chem. Commun.* **2009**, 4115–4117; m) Y. Luo, W. Li, D. Lin, Y. Yao, Y. Zhang, Q. Shen, *Organometallics* **2010**, *29*, 3507–3514; n) H. E. Dyer, S. Huijser, N. Susperregui, F. Bonnet, A. D. Schwarz, R. Duchateau, L. Maron, P. Mountford, *Organometallics* **2010**, *29*, 3602–3621; o) J.-C. Buffet, A. Kapelski, J. Okuda, *Macromolecules* **2010**, *43*, 10201–10203; p) M. Bouyahyi, N. Ajellal, E. Kirillov, C. M. Thomas J.-F. Carpentier, *Chem. Eur. J.* **2011**, *17*, 1872–1883; q) N. Susperregui, M. U. Kramer, J. Okuda, L. Maron, *Organometallics* **2011**, *30*, 1326–1333.

[8] For key references on the use of $Sn(oct)_2$ for the ROP of cyclic esters, see: a) H. Takayanagi, T. Kobayashi, T. Masuda, H. Shinoda, Eur. Pat. 88-306393 19880713, **1989**; *Chem. Abstr.* **1989**, *110*, 135964; b) A. Duda, S. Penczek, *Macromolecules* **1990**, *23*, 1636–1639; c) A. J. Nijenhuis, D. W. Grijpma, A. J. Pennings, *Macromolecules* **1992**, *25*, 6419–6424; d) H. R. Kricheldorf, I. Kreiser-Saunders, C. Boettcher, *Polymer* **1995**, *36*, 1253–1259; e) G. Schwach, J. Coudane, R. Engel, M. Vert, *J. Polym. Sci. Part A* **1997**, *35*, 3431–3440; f) A. Kowalski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 689–695; g) H. R. Kricheldorf, I. Kreiser-Saunders, A. Stricker, *Macromolecules* **2000**, *33*, 702–709.

[9] a) K. B. Aubrecht, M. A. Hillmyer, W. B. Tolman, *Macromolecules* **2002**, *35*, 644–650; b) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall, A. J. P. White, S. H. Dale, M. R. J. Elsegood, *Dalton Trans.* **2007**, 4464–4471.

[10] a) N. Nimitsiriwat, E. L. Marshall, V. C. Gibson, M. R. J. Elsegood, S. H. Dale, *J. Am. Chem. Soc.* **2004**, *126*, 13598–13599; b) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall, M. R. J. Elsegood, *Inorg. Chem.* **2008**, *47*, 5417–5424; c) N. Nimitsiriwat, V. C. Gibson, E. L. Marshall, M. R. J. Elsegood, *Dalton Trans.* **2009**, 3710–3715.

[11] a) A. P. Dove, V. C. Gibson, E. L. Marshall, A. J. P. White, D. J. Williams, *Chem. Commun.* **2001**, 283–284; b) A. P. Dove, V. C. Gibson, E. L. Marshall, H. S. Rzepa, A. J. P. White, D. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 9834–9843.

[12] For a review, see: a) N. Ajellal, J.-F. Carpentier, C. Guillaume, S. M. Guillaume, M. Hélou, V. Poirier, Y. Sarazin, A. Trifonov, *Dalton Trans.* **2010**, *39*, 8363–8376. For our more-recent work on the *i*ROP of lactide, see: b) Y. Sarazin, D. Roşca, V. Poirier, T. Roisnel, A. Silvestru, L. Maron, J.-F. Carpentier, *Organometallics* **2010**, *29*, 6569–6577; c) V. Poirier, T. Roisnel, J.-F. Carpentier, Y. Sarazin, *Dalton Trans.* **2011**, *40*, 523–534; d) Y. Sarazin, B. Liu, T. Roisnel, L. Maron, J.-F. Carpentier, *J. Am. Chem. Soc.* **2011**, *133*, 9069–9087; e) B. Liu, T. Roisnel, Y. Sarazin, *Inorg. Chim. Acta* **2011**, DOI: 10.1016/j.ica.2011.09.020. For our more-recent work on the *i*ROP of cyclic carbonates, see: f) M. Hélou, O. Miserque, J.-M. Brusson, J.-F. Carpentier, S. M. Guillaume, *Chem. Eur. J.* **2010**, *16*, 13805–13813.

[13] a) E. Martin, P. Dubois, R. Jérôme, *Macromolecules* **2000**, *33*, 1530–1535; b) Y.-C. Liu, B.-T. Ko, C.-C. Lin, *Macromolecules* **2001**, *34*, 6196–6201; c) M.-L. Hsueh, B.-H. Huang, C.-C. Lin, *Macromolecules* **2002**, *35*, 5763–5768; d) M.-L. Shueh, Y.-S. Wang, B.-H. Huang, C.-Y. Kuo, C.-C. Lin, *Macromolecules* **2004**, *37*, 5155–5162; e) W. Zhao, D. Cui, X. Liu, X. Chen, *Macromolecules* **2010**, *43*, 6678–6684.

[14] a) S. Asano, T. Aida, S. Inoue, *J. Chem. Soc. Chem. Commun.* **1985**, 1148–1149; b) T. Aida, Y. Maekawa, S. Asano, S. Inoue, *Macromolecules* **1988**, *21*, 1195–1202; c) H. Sugimoto, T. Aida, S. Inoue, *Macromolecules* **1990**, *23*, 2869–2875; d) T. Aida, S. Inoue, *Acc. Chem. Res.* **1996**, *29*, 39–48; e) S. Inoue, *J. Polym. Sci. Part A* **2000**, *38*, 2861–2871.

[15] E. Grunova, T. Roisnel, J.-F. Carpentier, *Dalton Trans.* **2009**, 9010–9019.

[16] a) Y. Shibasaki, H. Sanada, M. Yokoi, F. Sanda, T. Endo, *Macromolecules* **2000**, *33*, 4316–4320; b) Y. Sarazin, V. Poirier, T. Roisnel, J.-F. Carpentier, *Eur. J. Inorg. Chem.* **2010**, 3423–3428.

[17] S. Itoh, H. Kumei, S. Nagatomo, T. Kitagawa, S. Fukuzumi, *J. Am. Chem. Soc.* **2001**, *123*, 2165–2175.

[18] *The Chemistry of Organic Silicon Compounds, Vol. 3* (Eds.: Z. Z. Rappoport, Y. Apeloig), Wiley, New York, **2001**.

[19] V. Poirier, J.-F. Carpentier, Y. Sarazin, unpublished results.

[20] For selected reviews, see: a) P. Jutzi, *Adv. Organomet. Chem.* **1986**, *26*, 217–295; b) P. Jutzi, *J. Organomet. Chem.* **1990**, *400*, 1–17.

[21] a) P. Jutzi, F. Kohl, C. Krüger, *Angew. Chem.* **1979**, *91*, 81–82; *Angew. Chem. Int. Ed. Engl.* **1979**, *18*, 59–60; b) F. Kohl, P. Jutzi, *Chem. Ber.* **1981**, *114*, 488–494; c) B. Rhodes, J. C. W. Chien, M. D. Rausch, *Organometallics* **1998**, *17*, 1931–1933; d) Y. Sarazin, D. L. Hughes, N. Kaltsoyannis, J. A. Wright, M. Bochmann, *J. Am. Chem. Soc.* **2007**, *129*, 881–894.

[22] M. J. Taylor, A. J. Saunders, M. P. Coles, J. R. Fulton, *Organometallics* **2011**, *30*, 1334–1339.

[23] A. E. Ayers, H. V. R. Dias, *Inorg. Chem.* **2002**, *41*, 3259–3268.

[24] a) R. Jambor, B. Kašná, S. G. Koller, C. Strohmann, M. Schürmann, K. Jurkschat, *Eur. J. Inorg. Chem.* **2010**, 902–908; b) R. Dostálová, L. Dostál, A. Růžička, R. Jambor, *Organometallics* **2011**, *30*, 2405–2410.

[25] a) S. J. Lancaster, A. Rodriguez, A. Lara-Sanchez, M. D. Hannant, D. A. Walker, D. L. Hughes, M. Bochmann, *Organometallics* **2002**, *21*, 451–453; b) M. Bochmann, *Coord. Chem. Rev.* **2009**, *253*, 2000–2014.

[26] M. H. Hannant, J. A. Wright, S. J. Lancaster, D. L. Hughes, P. N. Horton, M. Bochmann, *Dalton Trans.* **2006**, 2415–2426.

[27] For the synthesis of $[Sn^{II}Sn^{IV}(OiPr)_6]$ by reaction of in situ generated $[Sn(OiPr)_2]_n$ with $[Sn(OiPr)_4]_n$, see: D. J. Teff, C. D. Minear, D. V. Baxter, K. G. Caulton, *Inorg. Chem.* **1998**, *37*, 2547–2553.

[28] The term "pre-catalyst" for the Sn complexes is preferred here ahead of the more common "catalyst", as they do not display significant catalytic activity in the controlled ROP of L-LA in the absence of *i*PrOH. Hence, *i*PrOH is labeled "co-catalyst"; note that the alcohol takes the role of both the initiating group and transfer agent in these systems.

[29] a) H. Ma, J. Okuda, *Macromolecules* **2005**, *38*, 2665–2673; b) L. F. Sánchez-Barba, A. Garcés, J. Fernández-Baeza, A. Otero, C. Alonso-Moreno, A. Lara-Sánchez, A. M. Rodríguez, *Organometallics* **2011**, *30*, 2775–2789.

[30] L. Clark, M. G. Cushion, H. E. Dyer, A. D. Schwarz, R. Duchateau, P. Mountford, *Chem. Commun.* **2010**, *46*, 273–275.

[31] M. H. Chisholm, S. S. Iyer, M. E. Matison, D. G. McCollum, M. Pagel, *Chem. Commun.* **1997**, 1999–2000.

[32] With these Sn^{II} complexes, as well as their related Zn-based complexes such as those given in reference [12c], kinetic measurements by ^1H NMR spectroscopy have shown that the polymerization of L-LA is fast, proceeds without an induction period, and is characterized by a rapid first insertion followed by a comparatively slow second insertion of the monomer, whilst the polymerization of TMC presents a small induction period where the first insertion of the monomer is very slow compared to the following insertion.

[33] We are aware that the conversion of as low as 5–10 equivalents of monomer per metal center should only yield oligomers, but the term "polymerization" is consistently used throughout the manuscript instead of "oligomerization" for ease of reading.

[34] The polymerization of TMC with $[TMC]_0/[\mathbf{3}]_0/[i\text{PrOH}]_0 = 5:1:1$ required 3 h to reach full conversion of the monomer in $[D_6]$benzene at 25 °C; on the other hand, no reaction took place with $[TMC]_0/[\mathbf{3}]_0/[HOCH(CH_3)CO_2i\text{Pr}]_0 = 5:1:1$ under otherwise identical conditions.

[35] On the basis of the respective pK_a values of phenols (ca. 9.90) and *i*PrOH (16.5), the release of $\{LO^1\}H$ upon treatment of compound **3** with even a slight excess of *i*PrOH is counterintuitive on thermodynamic grounds.

[36] a) A. Kowalski, J. Libiszowski, A. Duda, S. Penczek, *Macromolecules* **2000**, *33*, 1964–1971; b) For related studies on Zn and Al systems, see: A. Kowalski, J. Libiszowski, K. Majerska, A. Duda, S. Penczek, *Polymer* **2007**, *48*, 3952–3960.

[37] Polymerizations carried out in $[D_8]$toluene at 60 °C with $[\text{L-LA}]_0 = 1.0$ M and $[\text{L-LA}]_0/[Sn]_0/[i\text{PrOH}]_0 = 100:1:10$.

[38] C. D. Schaeffer, J. J. Zuckerman, *J. Am. Chem. Soc.* **1974**, *96*, 7160–7162.

[39] P. Foley, M. Zeldin, *Inorg. Chem.* **1975**, *14*, 2264–2267.

[40] W. Kündig, *Nucl. Instrum. Methods* **1969**, *75*, 336–340.

[41] The identities and purities of the (micro)crystalline samples submitted for combustion analysis were established by X-ray diffraction and NMR spectroscopic studies (see the Supporting Information). We are unaware of similar problems with the elemental analysis of tin–amide complexes; however, note that siloxy complexes **6** and **8**, which were formed directly from the treatment of compounds **3** and **7** with Ph_3SiOH, respectively, presented satisfactory elemental analyses.

[42] M. Save, M. Schappacher, A. Soum, *Macromol. Chem. Phys.* **2002**, *203*, 889–899.

[43] a) G. M. Sheldrick, SHELXS-97, Program for the Determination of Crystal Structures, University of Göttingen, Germany, **1997**; b) G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, **1997**.

Received: July 22, 2011
Revised: October 11, 2011
Published online: January 20, 2012

