Mono-guanidinate complexes of lanthanum: synthesis, structure and their use in lactide polymerization

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La[N(SiMe₃)₂]₃ reacted with 1,3-dicyclohexylcarbodiimide in refluxing toluene to yield the mono-guanidinate complex La[CyNC(N(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ **1**. Compound **1** is monomeric in solution; X-ray structural analysis reveals an unassociated complex in the solid state, with a four-coordinate lanthanum center. Complex **1** reacts with 2,6-di-*tert*-butylphenol (2 equivalents) in cold pentane to yield the bis(phenoxide) complex La[CyNC(N(SiMe₃)₂)NCy]-(OC₆H₃ᵗBu₂-2,6)₂. X-Ray analysis indicates a similar structure to that of **1**, with a four-coordinate lanthanum center coordinated by a single guanidinate ligand and two phenoxide groups. This compound catalyses the ring-opening polymerization of D,L-lactide to polylactide. Although high molecular weight polymer is obtained, polydispersities are broad and no control over the stereochemistry of the polymer is observed.

Introduction

In recent years there has been renewed interest in the development of biodegradable polymers as alternatives to traditional plastics derived from the polymerization of α-olefins.[1] Lactic acid-based polyesters have been explored for use in several applications, including packaging materials, food containers, medical sutures and drug delivery systems.[2–4] Polylactide (PLA) is derived from ring-opening polymerization of lactic acid dimers (D-lactide, L-lactide) that are generated from renewable


L-lactide   D-lactide   polylactide
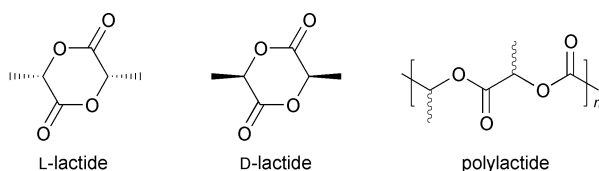
resources (*e.g.* corn fermentation, agricultural starch waste),[5,6] thus avoiding some of the ecological problems associated with the production of polymers dependent on crude oil and natural gas feedstocks. A second attractive feature of these types of polymers is the presence of an asymmetric carbon atom in the repeating unit. It is the sequence of these stereocenters that determines the mechanical properties of the resultant polymer. Thus, in contrast to α-olefin polymerization, which relies on sophisticated ligand design to control tacticity, the stereochemistry of the monomers plays an equally important role in the ultimate physicochemical properties of polymers prepared by ring-opening polymerization of lactide.

Rare-earth metal alkoxides polymerize lactide,[7–10] although knowledge of the active site has often been limited. Many early systems utilized metal–oxo clusters as initiators which did not allow the stereochemical properties of the polymer to be controlled by systematic variation of the ligand environment.[10–12] Only recently discrete, well defined systems have been employed as initiators,[13–16] allowing for the production of polymers with new and unusual structures and properties.[17–20] It has been shown that metal alkoxide complexes supported by bulky ligands can promote the synthesis of PLA with various tacticities *via* a chain-end control mechanism.[21] We have been investigating a class of C_s symmetric metal alkoxides, and were interested in determining if these complexes could impart

similar control over the sequence of stereocenters in PLA. Here we describe the synthesis of some lanthanide guanidinate complexes and the use of these compounds as initiators for the polymerization of D,L-lactide.
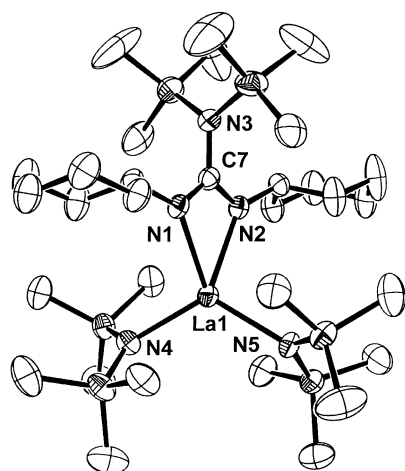
Results and discussion

Reaction of La[N(SiMe₃)₂]₃ with 1,3-dicyclohexylcarbodiimide (1 equivalent) in refluxing toluene for 48 h results in insertion of the carbodiimide into the lanthanum–amide bond to yield predominantly the mono-guanidinate species La[CyNC(N-(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ **1**.[22] The bis-guanidinate complex La[CyNC(N(SiMe₃)₂)NCy]₂(N(SiMe₃)₂) **2** is also formed in the reaction but the two are separated by fractional crystallization (Scheme 1). Both are isolable as yellow powders that are soluble

Scheme 1

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J. Chem. Soc., Dalton Trans., 2001, 923–927   **923**
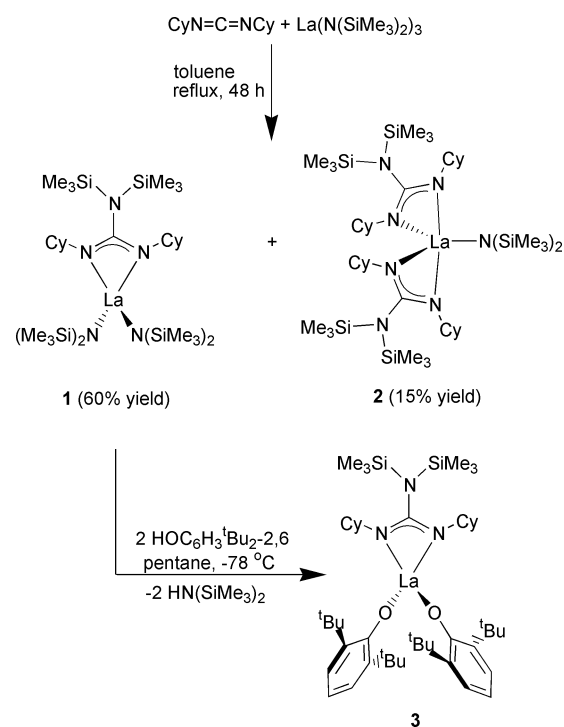
Table 1 Selected bond distances (Å) and angles (°) for La[CyNC-(N(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ **1**

La1–N1	2.486(3)	La1–N2	2.475(3)
La1–N4	2.382(3)	La1–N5	2.377(3)
N1–C7	1.333(4)	N2–C7	1.328(4)
N1–La1–N2	53.86(9)	N1–La1–N4	106.0(1)
N1–La1–N5	128.01(9)	N2–La1–N4	126.4(1)
N2–La1–N5	107.1(1)	N4–La1–N5	120.2(1)
N1–C7–N2	115.3(3)	N1–C7–N3	122.5(3)
N2–C7–N3	122.2(3)		

Table 2 Selected bond distances (Å) and angles (°) for La[CyNC-(N(SiMe₃)₂)NCy](OC₆H₃ᵗBu₂-2,6)₂ **3**

La1–N1	2.467(5)	La1–N2	2.448(5)
La1–O1	2.178(4)	La1–O2	2.186(4)
N1–C7	1.340(8)	N2–C7	1.322(8)
N1–La1–N2	54.5(2)	N1–La1–O1	108.4(2)
N1–La1–O2	131.2(2)	N2–La1–O1	126.5(2)
N2–La1–O2	113.5(2)	O1–La1–O2	112.8(2)
N1–C7–N2	115.6(5)	N1–C7–N3	121.3(6)
N2–C7–N3	123.1(6)	La1–O1–C20	174.8(4)
La1–O2–C34	174.3(4)		

Fig. 1 ORTEP[23] view of La[CyNC(N(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ **1** drawn with 50% probability ellipsoids.
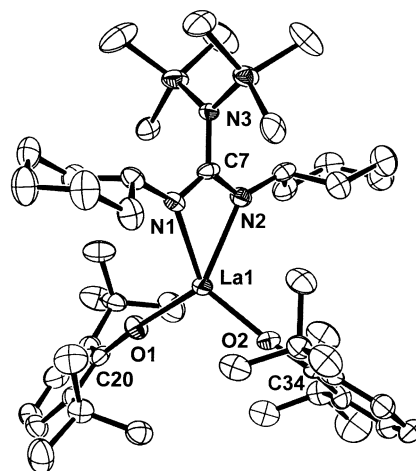

Fig. 2 ORTEP view of [CyNC(N(SiMe₃)₂)NCy]La(OC₆H₃ᵗBu₂-2,6)₂ **3** drawn with 50% probability ellipsoids.

in aliphatic and aromatic solvents. Their ¹H and ¹³C NMR spectra are highly symmetric; for each compound, two singlets are observed for the two types of SiMe₃ groups present in the molecule. Additionally, the unique cyclohexyl proton appears downfield of the other protons of the ring. The formulation of these complexes as guanidinate species is also supported by elemental analysis and IR spectroscopy, which exhibits a C=N stretch at approx. 1610 cm⁻¹ consistent with the delocalized double bond of the N–C–N linkage.

Crystals of complex **1** suitable for X-ray diffraction were grown by cooling a saturated pentane solution to −30 °C. The molecular structure of **1** is presented in Fig. 1 and a partial list of bond lengths and angles is given in Table 1; complete details of the crystallographic analyses of **1** and **3** are given in Table 4. Compound **1** is monomeric in the solid state, with a four-coordinate lanthanum center ligated by both nitrogens of the guanidinate ligand, and two N(SiMe₃)₂ groups. In spite of the low coordination number for lanthanum, once compound **1** is formed we see no evidence for redistribution to di- and un-substituted products. Bulky amido groups have been employed previously in the isolation of mono-ligand yttrium complexes,[24–27] although the lanthanum analogues are less common. It is evident that the combination of two amido groups and a sterically bulky guanidinate ligand are sufficient to stabilize a coordinatively and electronically unsaturated lanthanum center. The structure of **1** also illustrates that a formally 12-electron, four-coordinate lanthanide center can be synthesized free from interaction with salt or solvent molecules. The geometry about the metal is best described as distorted tetrahedral, with N–La–N bond angles ranging from 53.86(9) to 128.01(9)°. The La–N(guan) bond lengths (2.486(3) Å, 2.475(3) Å) are slightly shorter than those reported for the bis-amidinate complex La[2-NC₅H₄(CH₂)₂NC(p-MeC₆H₄)NPh]₂[N(SiMe₃)₂] (2.491(4)–2.609(4) Å),[28] as are the La–N(amide) bond lengths of 2.382(3) and 2.377(3) Å (vs. 2.453(4) Å in La[2-NC₅H₄-(CH₂)₂NC(p-MeC₆H₄)NPh]₂[N(SiMe₃)₂]). Although three-coordinate alkyl,[29] amide[30] and aryloxide[31] complexes of

lanthanum are known, compound **1** represents a rare example of a neutral, four-coordinate lanthanum complex. Related all-nitrogen coordination spheres have recently been described for yttrium.[24,26]

La[CyNC(N(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ **1** reacts cleanly with 2,6-di-tert-butylphenol (2 equivalents) in cold pentane to yield the bis(phenoxide) complex La[CyNC(N(SiMe₃)₂)NCy]-(OC₆H₃ᵗBu₂-2,6)₂ **3** (Scheme 1). Protonolysis of the guanidinate ligand by HOC₆H₃ᵗBu₂-2,6 to give the known complex La(OC₆-H₃ᵗBu₂-2,6)₃[31] was not observed provided only two equivalents of the phenol were used. However, use of a less sterically demanding phenol such as 2,4,6-trimethylphenol (2 equiv-alents) resulted in mixtures of products with the formation of [CyNC(N(SiMe₃)₂)NCy]H.[32] We were also unable to synthesize the mono-phenoxide species La[CyNC(N(SiMe₃)₂)NCy]₂-La(OC₆H₃ᵗBu₂-2,6); La[CyNC(N(SiMe₃)₂)NCy]₂(N(SiMe₃)₂) **2** was unreactive with HOC₆H₃ᵗBu₂-2,6 (1 equivalent) under a variety of conditions. Compound **3** was isolated as an extremely air- and moisture-sensitive yellow powder. As for **1** and **2**, NMR spectra of **3** indicate a single, symmetric species in solution.

Crystals of the bis(phenoxide) complex were grown by cool-ing a saturated pentane solution of **3** to −30 °C. An ORTEP view is shown in Fig. 2; selected bond lengths and angles are presented in Table 2. The structure of **3** is similar to that of **1** with a four-coordinate lanthanum center bound by a single guanidinate ligand and two phenoxide groups. As for **1**, the metal center displays a distorted tetrahedral geometry, with the smallest N–La–N angle corresponding to the bite of the ancillary guanidinate ligand (54.5(2)°). The La–N(guan) bond lengths are equal to those determined for the bis-amido deriv-ative (2.467(5) and 2.448(5) Å), suggesting that the silylamide and phenoxide groups are electronically and sterically analo-gous. The La–O bond lengths of 2.178(4) and 2.186(4) Å are somewhat shorter than those found in lanthanum trisphenoxide species such as [La(OC₆H₃Ph₂-2,6)₃(THF)₂]·THF (2.234(9)–2.25(1) Å),[33] [La(OC₆H₃Ph₂-2,6)₃(THF)₂]·2THF (2.229(6)–

Table 3 Polymerization of D,L-lactide with La[CyNC(N(SiMe$_3$)$_2$)-NCy](OC$_6$H$_3$^{t}Bu$_2$-2,6)$_2$ **3** in CH$_2$Cl$_2$ at 25 °C

Entry	[M] : [C]	t/h	Yield (%)	M_n ($\times 10^3$)	M_n/M_w
1	50	24	80	11.1	1.60
2	100	24	68	18.5	1.56
3	300	24	78	48.0	2.25
4	500	24	60	102.0	2.02
5	600	24	100	49.0	1.48
6	700	24	78	5.3	1.85
7	1000	24	45	1.1	1.19
8	500	0.5	73	29.6	2.05
9	500	1	64	115.0	1.66
10	500	8	100	122.0	1.57

2.253(6) Å[34] and [La(OC$_6$H$_3$Me$_2$-2,6)$_3$(MeO(CH$_2$CH$_2$O)$_4$Me)] (2.28(2)–2.30(2) Å),[35] but similar to those reported for La$_2$(OC$_6$H$_3$^{i}Pr$_2$-2,6)$_6$ (2.187(5)–2.273(5) Å).[36] Interesting features of the structure of **3** are the almost linear La–O–C$_{aryl}$ linkages (La1–O1–C20 174.8(4), La1–O2–C34 174.3(4)°). Although homoleptic lanthanide aryloxide compounds are known to display M–O–C$_{aryl}$ bond angles that approach 180°,[31,37,38] substitution of one of the phenoxides by a C$_5$Me$_5$ group results in complexes with one linear and one bent M–O–C$_{aryl}$ unit (Y(C$_5$Me$_5$)-(OC$_6$H$_3$^{t}Bu$_2$-2,6)$_2$ Y–O–C$_{aryl}$ 168.0(3), 128.6(3)°;[39] Ce(C$_5$Me$_5$)-(OC$_6$H$_3$^{t}Bu$_2$-2,6)$_2$ Ce–O–C$_{aryl}$ 158.6(2), 105.0(2)°[40,41]). The almost linear La–O–C bonds in **3** reflect the large steric bulk of the guanidinate ligand, and the lower formal electron count of the ancillary ligand compared to the C$_5$Me$_5$ group.

Complex **3** is active for the polymerization of lactide under mild conditions (Table 3). Moderate control of the polymer molecular weight was observed with changes in the [M] : [C] ratio (M = monomer, C = catalyst) with the highest molecular weight observed at a ratio of 500 : 1 (M_n = 102,000; entry 4). At higher monomer loadings the molecular weight decreased sharply, with only oligomers isolated at the highest monomer : catalyst ratio (entry 7). The polymerization was complete within hours with little change in the molecular weight after the first hour of polymerization (entries 8–10). There was no correlation between molecular weight and polydispersity, with M_n/M_w values ranging from 1.19 to 2.25. These observations argue against a living polymerization of lactide, and point towards a significant degree of transesterification (see later). The molecular weights of the polymers produced are greater than predicted from the assumption that every phenoxide ligand initiates polymerization ($M_{n,calc}$ = 36,000; $M_{n,found}$ = 102,000 g mol^{-1}). Similar results using Y(OC$_6$H$_3$^{t}Bu$_2$-2,6)$_3$ as a catalyst were attributed to an anionic polymerization mechanism, due to proton transfer from monomer, solvent or trace impurities to the initiator.[10] However, polymerization of L-lactide by **3** ([M] : [C] = 500 : 1, 25 °C; 16 h) resulted in pure isotactic PLA; the ^{13}C-{^{1}H} NMR spectrum of the polymer showed one sharp resonance for each of the ketonic, methyl and methine carbons. Our inability to detect any syndiotactic linkages supports the lack of base-promoted epimerization of L-lactide or PLA and argues against an anionic polymerization mechanism being operative.[13,15] The higher than expected molecular weights may be due to a faster rate of propagation than initiation, or not all of the lanthanum–oxygen bonds are actively involved in polymerization. The observation that **3** does not utilize all of its possible active sites has precedent in related lanthanide alkoxide chemistry.[8,14]

NMR analysis[6,42] revealed no stereoselectivity in the polymerization of D,L-lactide by complex **3**; *i.e.* upon insertion of an (R,R) monomer into the polymer chain the complex has no preference for reaction with either a second (R,R) monomer, forming isotactic PLA, or an (S,S) unit, generating heterotactic PLA. Polymerizations run at 0 °C resulted in low molecular weight oligomers with no enhancement in stereoregularity ([M] : [C] = 500 : 1; 4 h; M_n = 1100). ^{13}C-{^{1}H} NMR spectro-

scopy also indicated that a significant amount of transesterification had occurred; methine peaks due to *iss*, *sss* and *ssi* tetrads were evident. From the intensities of these tetrads the contribution of transesterification to the chain structure can be estimated to be ≈70%.[43] This was also supported by the observation of bimodal GPC traces for some of the samples reported here, a result of efficient transesterification in competition with ring-opening polymerization.[44] The high degree of chain transfer is likely due to the presence of two phenoxide groups per metal center; a recently reported yttrium bisphenoxide complex is also an effective transesterification catalyst.[14]

Conclusion

Mono-guanidinate complexes of lanthanum, an unexplored class of compounds, are easily prepared in good yield by the reaction of lanthanum tris-amide with carbodiimide; this approach circumvents the incorporation of salt and solvent molecules into the metal coordination sphere, which is often observed when ancillary ligands are introduced to lanthanide metals *via* salt metathesis reactions.[45–50] This problem is often compounded when the syntheses of mono-ligand compounds are attempted due to the high degree of steric and electronic unsaturation at the metal center.[51–55] We have shown that by utilizing bulky ligands, and avoiding halide reagents, these problems can be avoided. Although the lanthanum bis-phenoxide species **3** catalyses the ring-opening polymerization of lactide, significant transesterification is observed due to the presence of two adjacent aryloxide groups, resulting in little control of the stereochemistry, and in turn the mechanical properties of the resultant polymer. This study shows that guanidinates and the related amidinate class of ligands are suitable spectator ligands for the production of PLA and suggests that systematic variation of the steric properties of the guanidinate or amidinate ancillary ligands may allow for more control over the microstructure of the polylactide produced.

Experimental

General considerations

Table 4 Crystallographic data

	La[CyNC(N(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ **1**	La[CyNC(N(SiMe₃)₂)NCy](OC₆H₃ᵗBu₂-2,6)₂ **3**
Formula	$C_{31}H_{76}LaN_5Si_6$	$C_{47}H_{82}LaN_3O_2Si_2$
M	826.39	916.26
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$
a/Å	9.5129(2)	10.3424(5)
b/Å	24.1821(1)	19.440(1)
c/Å	20.3228(3)	25.212(1)
β/°	91.340(1)	93.241(1)
V/Å³	4673.82(9)	5060.9(4)
Z	4	4
Total reflections	22292	24671
Independent reflections	8409	9340
μ(Mo-Kα)/cm⁻¹	10.88	11.55
R_{int}	0.039	0.039
R	0.030	0.036
R_w	0.040	0.032
T/°C	−83	−112

Preparations

La[CyNC(N(SiMe₃)₂)NCy](N(SiMe₃)₂)₂ 1. 1,3-Dicyclohexyl-carbodiimide (3.80 g, 18.4 mmol) and La[N(SiMe₃)₂]₃ (11.4 g, 18.4 mmol) were combined in a large Schlenk tube and toluene (200 mL) was added. The yellow solution was heated to reflux for 2 d, after which time the solvent was removed under vacuum. The resultant solid was extracted into the minimum amount of pentane, and the solution cooled to −30 °C. The product was isolated as large yellow plates (9.12 g, 60% yield). The less soluble bis-ligand complex La[CyNC(N(SiMe₃)₂)-NCy]₂(N(SiMe₃)₂) **2** was isolated by fractional crystallization (2.85 g, 15% yield). For **1**: mp 210–213 °C (Found: C, 45.44; H, 9.16; N, 8.03%. $C_{31}H_{76}LaN_5Si_6$ requires C, 45.06; H, 9.27; N, 8.47%); ν_{max}/cm⁻¹ 1612w, 1302m, 1243s, 1182m, 1135m, 1014s, 964w, 939w, 861s, 827s, 753s and 662m (Nujol); δ_H(C₆D₆) 3.37 (mult, 2H, unique Cy H), 1.95–1.15 (mult, 20H, C₆H₁₀), 0.38 (s, 18H, ligand SiMe₃) and 0.22 (s, 36H, amide SiMe₃); δ_C(C₆D₆) 166.7 (NCN), 55.5, 39.2, 26.7 and 26.6 (C₆H₁₁), 4.7 and 3.1 (SiMe₃). For **2**: mp 213–215 °C (Found: C, 50.97; H, 9.38; N, 9.10%. $C_{44}H_{98}LaN_7Si_6$ requires C, 51.17; H, 9.56; N, 9.49%); ν_{max}/cm⁻¹ 1610w, 1345m, 1300w, 1252s, 1173m, 1132m, 1070w, 1015s, 961m, 943s, 862m, 839s, 764w, 665w and 640w (Nujol); δ_H(C₆D₆) 3.45 (mult, 4H, unique Cy H), 2.00–1.20 (mult, 40H, C₆H₁₀), 0.50 (s, 18H, amide SiMe₃) and 0.29 (s, 36H, ligand SiMe₃); δ_C(C₆D₆) 167.3 (NCN), 55.7, 38.9, 26.8 and 26.7 (C₆H₁₁), 5.3 and 3.4 (SiMe₃).

La[CyNC(N(SiMe₃)₂)NCy](OC₆H₃ᵗBu₂-2,6)₂ 3. To a pentane solution (100 mL) of complex **1** (3.50 g, 4.06 mmol) cooled to −78 °C was added a pentane solution (50 mL) of 2,6-di-*tert*-butylphenol *via* cannula. The pale yellow solution was left to stir overnight and warm to room temperature. The volume was then reduced, and the contents of the flask were cooled to −30 °C. The product was isolated as yellow rods (3.47 g, 93% yield). mp 251–253 °C (Found: C, 61.79; H, 8.86; N, 4.71%. $C_{47}H_{82}LaN_3O_2Si_2$ requires C, 61.61; H, 9.02; N, 4.59%); ν_{max}/cm⁻¹ 1582w, 1404s, 1348s, 1304m, 1253s, 1188s, 1136m, 1098m, 1070w, 1002m, 964m, 939s, 863s, 834s, 820s, 745s, 652s and 642s (Nujol); δ_H(C₆D₆) 7.28 (d, 4H, *m*-H, $^3J_{H-H}$ = 7.7), 6.83 (t, 2H, *p*-H, $^3J_{H-H}$ = 7.7 Hz), 3.40 (mult, 2H, unique Cy H), 1.95–1.05 (mult, 20H, C₆H₁₀), 1.59 (s, 36H, CMe₃) and 0.21 (s, 18H, SiMe₃); δ_C(C₆D₆) 168.0 (NCN), 163.4, 137.3, 125.4, 117.5 (di-*tert*-butyl phenyl), 55.7, 38.7, 35.0 and 26.6 (C₆H₁₁), 32.5 (C*Me₃*), 26.4 (*C*Me₃) and 2.4 (SiMe₃).

Lactide polymerization

Compound **3** (15 mg, 0.016 mmol) and 50–1000 equivalents of lactide (≈0.1–2.3 g) were combined in a Schlenk tube and 10 mL of CH₂Cl₂ added. The contents of the flask were then stirred for a pre-determined period, after which time the reaction was quenched by the addition of 5 drops of 1 M HCl solution. The reaction mixture was then poured into cold heptane to precipitate the polymer, which was collected and dried under vacuum for 24 h. ¹H and ¹³C-{¹H} NMR spectra of polylactide were recorded in CDCl₃.

General procedures for X-ray crystallography

Pertinent details for the individual compounds can be found in Table 4. The data were corrected for Lorentz and polarization effects, but no correction for crystal decay was applied. All non-hydrogen atoms were refined anisotropically, unless stated otherwise. Hydrogen atoms were assigned idealized positions and included in structure factor calculations, but not refined, unless stated otherwise.

CCDC reference number 186/2333.

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