This article is published as part of the Dalton Transactions themed issue entitled:

New Horizons in Organo-f-element Chemistry

Guest Editor: Geoff Cloke University of Sussex, UK

Published in issue 29, 2010 of Dalton Transactions



Image reproduced with the permission of Tobin Marks

Articles in the issue include:

PERSPECTIVES:

Organo-f-element catalysts for efficient and highly selective hydroalkoxylation and hydrothiolation Charles J. Weiss and Tobin J. Marks, *Dalton Trans.*, 2010, DOI: 10.1039/c003089a

Non-classical divalent lanthanide complexes François Nief, *Dalton Trans.,* 2010, DOI: 10.1039/c001280g

COMMUNICATIONS:

<u>A bimetallic uranium μ -dicarbide complex: synthesis, X-ray crystal structure, and bonding</u> Alexander R. Fox, Sidney E. Creutz and Christopher C. Cummins *Dalton Trans.*, 2010, DOI: 10.1039/c0dt00419g

PAPERS:

Coordination polymerization of renewable butyrolactone-based vinyl monomers by lanthanide and early metal catalysts

Garret M. Miyake, Stacie E. Newton, Wesley R. Mariott and Eugene Y.-X. Chen, *Dalton Trans.*, 2010, DOI: 10.1039/c001909g

Visit the Dalton Transactions website for more cutting-edge inorganic and organometallic chemistry research www.rsc.org/dalton

Synthesis and characterization of amine bridged bis(phenolate) lanthanide aryloxides and their application in the polymerization of lactide[†]

Kun Nie, Xiangyong Gu, Yingming Yao,* Yong Zhang and Qi Shen

Received 28th January 2010, Accepted 5th May 2010 First published as an Advance Article on the web 3rd June 2010 DOI: 10.1039/c001888k

A series of neutral lanthanide aryloxides supported by an amine bridged bis(phenolate) ligand were synthesized, and their catalytic behavior for the polymerization of L-lactide was explored. The reactions of $(C_5H_5)_3Ln(THF)$ with amine bridged bis(phenol)LH₂ [L = Me₂NCH₂CH₂N{CH₂-(2-*O*-C₆H₂-Bu^t₂-3,5)}₂] in a 1 : 1 molar ratio, and then with 1 equivalent of 2,6-diisopropylphenol, *p*-cresol or 4-methoxyphenol, respectively, *in situ* in THF gave the neutral lanthanide aryloxides LLn(OC₆H₃-2,6-Prⁱ₂)(THF) [Ln = Nd (1), Sm (2), Yb (3)], LLn(OC₆H₄-4-CH₃)(THF)_n [Ln = Nd (4), Sm (5), *n* = 2; Ln = Y (6), *n* = 1] and LLn(OC₆H₄-4-OCH₃)(THF)_n [Ln = Nd (7), Sm (8), *n* = 2; Ln = Yb (9), *n* = 1] in high isolated yields. These complexes were well characterized by elemental analyses, IR spectra and NMR spectroscopy in the case of complex 6. The definitive molecular structures of complexes 1–8 were determined by single-crystal X-ray analyses, which revealed that both the substituents of the aryloxo groups and the ionic radii of the lanthanide metals affect the solid-state structures of the bis(phenolate) lanthanide aryloxides. It was found that complexes 1–9 are efficient initiators for the ring-opening polymerization of L-lactide, and the structures of the aryloxo groups have no obvious effect on the catalytic activity and controllability. A further study revealed that complex 6 can initiate the highly heteroselective ring-opening polymerization of *rac*-lactide.

Introduction

Amine bridged bis(phenol)s, as a type of dianionic chelate ligands, have received considerable attention in organolanthanide chemistry in recent years, and some of these complexes have been found to be efficient initiators for the ring-opening polymerization of cyclic esters.¹⁻¹⁴ These ligand systems have attractive features, such as easily available and tunable, which allows it to be possible for the systematic study on the effect of the steric and electronic properties of the ligand on the reactivity of the corresponding lanthanide complexes.¹⁵⁻¹⁹ It has been found that the presence of heteroatom(s) on the bridged bis(phenolate) ligands has significant influence on the reactivity of the corresponding lanthanide complexes, and the coordination of the electron-donating heteroatoms to the lanthanide ions improves their catalytic activity for the polymerization of cyclic esters in most cases.²⁰ On the other hand, the initiating groups in bridged bis(phenolate) lanthanide complexes also have profound effect on their catalytic behavior for the polymerization of cyclic esters.²¹ For example, amine bridged bis(phenolate) lanthanide alkoxides showed better controllability for cyclic ester polymerizations in comparison with the corresponding lanthanide amides and alkyls, giving the polymers with high molecular weight and narrow molecular weight distributions. However, almost all of the amine bridged bis(phenolate) lanthanide alkoxides are generated *in situ* by the alcoholysis reactions of lanthanide amido and alkyl complexes with alcohols.^{6,9,12} To our knowledge, there is only one example of structurally characterized amine bridged bis(phenolate) lanthanide alkoxide in the literature.¹⁴ Furthermore, the effect of the structures of the alkoxo groups on the catalytic behavior has seldom been studied up to date.

Recently, we became interested in studying the synthesis and reactivity of lanthanide complexes that are supported by the bulky bridged bis(phenolate) ligands.^{15-18,22-27} It was found that the carbon-bridged bis(phenolate) lanthanide alkoxo complexes can be conveniently synthesized by the protolytic exchange reactions using $(C_5H_5)_3$ Ln(THF) as the starting materials,^{24,25} but attempts were unsuccessful to synthesize the desired amine bridged bis(phenolate) lanthanide alkoxides through the same method.²⁸ A further study revealed that the lanthanide aryloxides stabilized by the amine bridged bis(phenolate) ligand can be prepared in high yields by the sequential protolytic exchange reactions using $(C_5H_5)_3Ln(THF)$ as the precursors, and a series of neutral amine bridged bis(phenolate) lanthanide aryloxo complexes were synthesized and well characterized. Furthermore, the catalytic behavior of these lanthanide aryloxides for the ring-opening polymerization of lactide was elucidated. Herein we report these results.

Experimental

General

All of the manipulations were performed in a purified argon atmosphere using standard Schlenk techniques. The solvents were degassed and distilled from sodium benzophenone ketyl

Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Dushu Lake Campus, Soochow University, Suzhou, 215123, People's Republic of China. E-mail: yaoym@suda.edu.cn; Fax: (86)512-65880305; Tel: (86)512-65882806

[†] CCDC reference numbers 763744–763751. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c001888k

under argon prior to use. (C5H5)3Ln(THF)29 and ligand LH2 $[L = Me_2NCH_2CH_2N\{CH_2-(2-O-C_6H_2-Bu_2^t-3,5)\}_2]^{30}$ were prepared according to the procedures that are recommended in the literatures. All phenols were pre-dried, and recrystallized, or distilled before use. L-Lactide and rac-lactide were recrystallized twice from dry toluene and was then sublimed under vacuum at 50 °C. Lanthanide analyses were performed by EDTA titration with an xylenol orange indicator and a hexamine buffer.³¹ Carbon, hydrogen, and nitrogen analyses were performed by direct combustion with a Carlo-Erba EA-1110 instrument. The IR spectra were recorded with a Nicolet-550 FTIR spectrometer as KBr pellets. The ¹H and ¹³C NMR spectra were recorded in a C_6D_6 solution for complex 6 with a Unity Varian spectrometer. Because of their paramagnetism, no resolvable NMR spectrum for other complexes was obtained. The uncorrected melting points of crystalline samples in sealed capillaries (under argon) are reported as ranges. Molecular weight and molecular weight distribution (PDI) were determined against a polystyrene standard by gel permeation chromatography (GPC) on a PL 50 apparatus, and THF was used as an eluent at a flow rate of 1.0 mL min⁻¹ at 40 °C. Microstructures of PLAs were measured by homodecoupling ¹H NMR spectroscopy at 20 °C in CDCl₃ on a Bruker AC 500.

Syntheses

LNd(OC₆H₃-2,6-Prⁱ₂)(THF) (1). To a THF solution of $(C_5H_5)_3$ Nd(THF) (1.46 g, 3.55 mmol) was added a THF solution of LH₂ (1.86 g, 3.55 mmol). The reaction mixture was stirred for 1 h at room temperature, and then 2,6-diisopropylphenol (0.66 mL, 3.55 mmol) was added by a syringe. The mixture was stirred overnight at 50 °C, and then the solvent was evaporated under vacuum. Toluene (10 mL) was added to the residue, blue crystals were obtained at room temperature in a few days (2.09 g, 72%), mp 207–209 °C; (Found: C, 65.75; H, 8.75; N, 2.94; Nd, 15.89. $C_{50}H_{79}N_2O_4Nd$ (916.39) requires C, 65.53; H, 8.69; N, 3.06; Nd, 15.74); v_{max}/cm^{-1} 2956 s, 2905 s, 2868 s, 1601 m, 1587 m, 1478 s, 1414 m, 1388 w, 1360 w, 1301 m, 1272 m, 1204 m, 1165 m, 1131 m, 1117 m, 1042 m, 911 m, 857 m, 837 m, 760 m, 743 m (KBr pellet).

LSm(**OC**₆**H**₃-**2**,**6**-**Pr**ⁱ₂)(**THF**) (2). The synthesis of complex 2 was carried out in the same way as that described for complex 1, but $(C_5H_5)_3$ Sm(THF) (1.32 g, 3.16 mmol) was used instead of $(C_5H_5)_3$ Nd(THF). Colorless crystals were obtained in the toluene–THF solution (2.16 g, 74%), mp 231–233 °C; (Found: C, 64.82; H, 8.55; N, 2.83; Sm, 16.06. $C_{s0}H_{79}$ N₂O₄Sm (922.50) requires C, 65.10; H, 8.63; N, 3.04; Sm, 16.30); v_{max} /cm⁻¹ 2955 s, 2905 s, 2864 s, 1601 m, 1588 m, 1476 s, 1414 m, 1388 w, 1359 w, 1302 m, 1271 m, 1204 m, 1165 m, 1131 m, 1116 m, 1042 m, 911 m, 859 m, 838 m, 760 m, 743 m (KBr pellet).

LYb(OC₆H₃-2,6-Prⁱ₂)(THF) (3). The synthesis of complex **3** was carried out in the same way as that described for complex **1**, but $(C_5H_5)_3$ Yb(THF) (1.35 g, 3.07 mmol) was used instead of $(C_5H_5)_3$ Nd(THF). Yellow crystals were obtained in the toluene–THF solution (2.32 g, 80%), mp 208–210 °C; (Found: C, 62.95; H, 8.19; N, 2.80; Yb, 18.05. $C_{50}H_{79}N_2O_4$ Yb (945.19) requires C, 63.54; H, 8.42; N, 2.96; Yb, 18.31); v_{max}/cm^{-1} 2956 s, 2905 s, 2865 s, 1602 m, 1588 s, 1479 s, 1415 m, 1388 w, 1359 w, 1305 m, 1274 m, 1204 m, 1165 m, 1132 m, 1113 m, 1042 m, 911 m, 862 m, 840 m, 765 m, 745 m (KBr pellet).

LNd(OC₆H₄-4-CH₃)(THF)₂ (4). The synthesis of complex 4 was carried out in the same way as that described for complex 1, but *p*-cresol (0.51 mL, 4.91 mmol) was used instead of 2,6diisopropylphenol. Blue crystals were obtained at -5 °C in a few days (3.65 g, 81%), mp 171–173 °C; (Found: C, 63.73; H, 8.58; N, 2.94; Nd, 15.65. C₄₉H₇₇N₂O₅Nd (918.37) requires C, 64.09; H, 8.45; N, 3.05; Nd, 15.71); v_{max}/cm^{-1} 2953 s, 2905 s, 2867 s, 1603 s, 1500 s, 1476 s, 1436 w, 1414 w, 1359 s, 1328 w, 1280 s, 1238 m, 1203 w, 1165 m, 1132 w, 1042 m, 879 m, 859 m, 763 m, 742 m (KBr pellet).

LSm(**OC**₆**H**₄-**4**-**CH**₃)(**THF**)₂ (**5**). The synthesis of complex **5** was carried out in the same way as that described for complex **4**, but $(C_5H_5)_3$ Sm(THF) (2.02 g, 4.84 mmol) was used instead of $(C_5H_5)_3$ Nd(THF). Colorless crystals were obtained in the toluene solution at -5 °C (3.71 g, 83%), mp 167–168 °C; (Found: C, 63.19; H, 8.52; N, 2.91; Sm, 16.49. C₄₉H₇₇N₂O₅Sm (924.48) requires C, 63.66; H, 8.39; N, 3.03; Sm, 16.26); v_{max} /cm⁻¹ 2953 s, 2905 s, 2868 s, 1603 s, 1505 s, 1476 s, 1437 w, 1414 w, 1359 s, 1329 w, 1278 s, 1239 m, 1202 w, 1165 m, 1132 w, 1042 m, 879 m, 833 m, 763 m, 742 m (KBr pellet).

 $LY(OC_6H_4-4-CH_3)(THF)$ (6). The synthesis of complex 6 was carried out in the same way as that described for complex 4, but (C5H5)3Y(THF) (1.70 g, 4.77 mmol) was used instead of (C5H5)3Nd(THF). Colorless crystals were obtained in the hexane-THF solution (3.13 g, 83%), mp 148-150 °C; (Found: C, 68.22; H, 8.97; N, 3.13; Y, 11.35. C45H69N2O4Y (790.93) requires C, 68.34; H, 8.79; N, 3.54; Y, 11.24); v_{max}/cm^{-1} 2954 s, 2905 s, 2868 s, 1608 s, 1507 s, 1478 s, 1437 w, 1415 w, 1359 s, 1329 w, 1282 s, 1238 m, 1202 w, 1166 m, 1132 w, 1044 m, 874 m, 837 m, 772 m, 739 m (KBr pellet). ¹H NMR (300 MHz, C_6D_6 , 25 °C): δ 7.65 (d, ⁴J(H, H) = 2.2 Hz, 2H, ArH), 7.19 (s, 2H, ArH), 7.06 (m, 4H, ArH), 4.03 (d, 2 J(H, H) = 12.4 Hz, 2H, ArCH₂N), 3.92 (br, 4H, α -CH₂ THF), $2.99 (d, {}^{2}J(H, H) = 12.5 Hz, 2H, ArCH_{2}N), 2.31 (s, 3H, ArCH_{3}),$ 2.15 (br, 2H, NCH₂CH₂N), 1.86 (s, 18H, C(CH₃)₃), 1.76 (s, 6H, N(CH₃)₂), 1.50 (s, 18H, C(CH₃)₃), 1.42 (br, 2H, NCH₂CH₂N), 1.25 (br, 4H, β-CH₂ THF). ¹³C{1H} NMR (300 MHz, C₆D₆, 25 °C): δ 163.5, 162.1, 138.2, 137.0, 136.6, 130.5, 129.6, 128,9, 128.7, 128.3, 126.1, 126.0, 125.0, 124.9, 120.1 (Ar-C), 71.0 (α-CH₂ THF), 65.6 (ArCH₂N), 59.1 (N(CH₂)₂N), 49.3 (N(CH₂)₂N), 45.9 (ArCH₃), 36.0 (N(CH₃)₂), 34.6 (N(CH₃)₂), 32.6 (C(CH₃)₃), 31.0 (C(CH₃)₃), 25.6 (β-CH₂ THF), 21.8 (C(CH₃)₃), 21.2 (C(CH₃)₃).

LNd(OC₆H₄-4-OCH₃)(THF)₂ (7). The synthesis of complex 7 was carried out in the same way as that described for complex 1, but 4-methoxyphenol (0.58 g, 4.64 mmol) was used instead of 2,6-diisopropylphenol. Blue crystals were obtained at room temperature in a few days (3.29 g, 76%), mp 203–205 °C; (Found: C, 62.61; H, 8.44; N, 2.90; Nd, 15.58. C₄₉H₇₇N₂O₆Nd (934.37) requires C, 62.99; H, 8.31; N, 3.00; Nd, 15.44); v_{max}/cm^{-1} 2952 s, 2905 s, 2867 s, 1603 m, 1499 s, 1477 s, 1436 m, 1413 m, 1384 w, 1359 w, 1328 m, 1290 m, 1261 m, 1227 m, 1167 m, 1042 m, 912 m, 879 m, 831 m, 753 m, 743 m (KBr pellet).

LSm[OC₆H₄(OCH₃)](THF)₂ (8). The synthesis of complex 8 was carried out in the same way as that described for complex 7, but $(C_5H_5)_3$ Sm(THF) (1.84 g, 4.41 mmol) was used instead of $(C_5H_5)_3$ Nd(THF). Colorless crystals were obtained in the toluene–THF solution (3.28 g, 79%), mp 206–208 °C; (Found: C, 62.17; H, 8.37; N, 2.87; Sm, 15.31. $C_{49}H_{77}N_2O_6$ Sm (940.48) requires C,

Table 1 Crystallographic data for complexes 1-4

Compound	1	2	3	4
Formula	$C_{50}H_{79}N_2O_4Nd$	$C_{50}H_{79}N_2O_4Sm$	$C_{50}H_{79}N_2O_4Yb$	$C_{49}H_{77}N_{2}O_{5}Nd$
Fw	916.39	922.50	945.19	918.37
T/K	223(2)	223(2)	223(2)	223(2)
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Crystal size/mm	$0.60 \times 0.45 \times 0.20$	$0.30 \times 0.30 \times 0.20$	$0.22 \times 0.20 \times 0.20$	$0.40 \times 0.35 \times 0.28$
Space group	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$	Pnma
a/Å	15.2696(6)	15.3534(14)	15.604(3)	21.889(2)
b/Å	16.8752(7)	16.8680(15)	16.456(3)	20.6138(18)
c/Å	19.2287(8)	19.187(2)	19.273(3)	10.7149(9)
$V/\text{\AA}^3$	4954.8(4)	4968.9(8)	4948.9(15)	4834.8(7)
Z	4	4	4	4
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.228	1.233	1.269	1.262
μ/mm^{-1}	1.089	1.223	1.931	1.118
F(000)	1940	1948	1980	1940
$\theta_{\rm max}/^{\circ}$	25.50	25.50	25.50	25.50
Collected	14970	16070	14662	20198
Unique reflns	8503	8999	8865	4607
Obsd refins $[I > 2.0\sigma(I)]$	7930	6447	8018	4255
No. of variables	495	454	478	276
GOF	1.033	1.091	1.056	1.119
R	0.0381	0.1032	0.0512	0.0489
wR	0.0902	0.2604	0.1097	0.1240
$R_{ m int}$	0.0246	0.0930	0.0410	0.0349
Absolute structure parameter	-0.005(14)	0.04(3)	0.006(12)	
Largest diff. peak, hole/e Å-3	0.601, -0.780	2.391, -1.202	1.731, -1.247	1.333, -0.697

62.58; H, 8.25; N, 2.98; Sm, 15.99); v_{max}/cm^{-1} 2951 s, 2905 s, 2865 s, 1603 m, 1500 s, 1479 s, 1437 m, 1413 m, 1384 w, 1359 w, 1328 m, 1290 m, 1276 m, 1238 m, 1167 m, 1042 m, 912 m, 879 m, 832 m, 778 m, 742 m (KBr pellet).

LYb[OC₆H₄(OCH₃)](THF)₂ (9). The synthesis of complex **9** was carried out in the same way as that described for complex **7**, but $(C_5H_5)_3$ Yb(THF) (2.14 g, 4.86 mmol) was used instead of $(C_5H_5)_3$ Nd(THF). Yellow crystals were obtained in the toluene–THF solution (3.29 g, 76%), mp 215–217 °C; (Found: C, 60.92; H, 7.72; N, 2.88; Yb, 19.02. $C_{45}H_{69}N_2O_5$ Yb (891.08) requires C, 60.66; H, 7.80; N, 3.14; Yb, 19.42); v_{max} /cm⁻¹ 2951 s, 2898 s, 2866 s, 1604 m, 1503 s, 1476 s, 1441 m, 1415 m, 1384 w, 1359 w, 1326 m, 1291 m, 1263 m, 1226 m, 1169 m, 1043 m, 913 m, 877 m, 829 m, 777 m, 743 m (KBr pellet).

Typical procedure for the polymerization reactions

The procedures for the polymerization of L-lactide initiated by complexes 1–9 were similar, and a typical polymerization procedure is given below. A 50 mL Schlenk flask, equipped with a magnetic stirring bar, was charged with the desired amount of L-lactide and toluene. The contents of the flask were then stirred at 70 °C until L-lactide was dissolved, and then a solution of the initiator in toluene was added to this solution by syringe. The mixture was stirred vigorously at 70 °C for the desired time, during which time an increase in the viscosity was observed. The reaction mixture was quenched by the addition of methanol and then poured into methanol to precipitate the polymer, which was dried under vacuum and weighed.

X-Ray crystallographic structure determinations⁺

Suitable single crystals of complexes 1-8 were sealed in a thin-walled glass capillary for determination the single-crystal

structures. Intensity data were collected with a Rigaku Mercury CCD area detector in ω scan mode using Mo-K α radiation ($\lambda = 0.71070$ Å). The diffracted intensities were corrected for Lorentz/polarization effects and empirical absorption corrections. Details of the intensity data collection and crystal data are given in Tables 1 and 2.

The structures were solved by direct methods and refined by full-matrix least-squares procedures based on $|F|^2$. During refinement, constraints are used in some cases because of the presence of disordered atoms. In complex 6, the methyl groups (C24-C26) are disordered, and were refined isotropically. In complexes 7 and 8, the benzene rings (C20–C25) and the methoxyl groups (O3 and C26) are disordered, and were refined isotropically. The other nonhydrogen atoms, including disordered carbon atoms (C32-C34, C42, C43 in complexes 1-3; C9-C11 and C17-C19 in complexes 4, 5, 7, and 8) were refined anisotropically. The hydrogen atoms on the disordered carbon atoms and C8 in complexes 7 and 8 were not generated. The other hydrogen atoms in these complexes were generated geometrically, assigned appropriate isotropic thermal parameters, and allowed to ride on their parent carbon atoms. All of the hydrogen atoms were held stationary and included in the structure factor calculation in the final stage of full-matrix leastsquares refinement. The structures were solved and refined using SHELEXL-97 programs.

Results and discussion

Synthesis of amine bis(phenolate) lanthanide aryloxides

We previously found that the reactions of $(C_5H_5)_3Ln(THF)$ with amine bridged bis(phenol) in THF gave the amine bis(phenolate) cyclopentadienyl lanthanide complexes, but these lanthanide complexes can not further react with methanol or isopropanol even in refluxed THF or toluene to generate the desired amine

Table 2 Crystallographic data for complexes 5-8

Compound	5	6-toluene	7	8
Formula	$C_{49}H_{77}$ N ₂ O ₅ Sm	$C_{52}H_{77}N_2O_4Y$	C49H77N2O6Nd	$C_{49}H_{77}N_2O_6Sm$
Fw	924.48	883.07	934.37	940.48
T/K	223(2)	223(2)	223(2)	223(2)
Crystal system	Orthorhombic	Monoclinic	Orthorhombic	Orthorhombic
Crystal size/mm	$0.20 \times 0.20 \times 0.20$	$0.30 \times 0.20 \times 0.18$	$0.26 \times 0.18 \times 0.14$	$0.55 \times 0.30 \times 0.26$
Space group	Pnma	$P2_1/n$	Pnma	Pnma
a/Å	21.8277(13)	14.5340(12)	21.9718(14)	21.9170(12)
b/Å	20.6671(13)	21.4857(15)	20.6271(13)	20.6367(10)
c/Å	10.6996(6)	16.2519(13)	10.7530(8)	10.7274(5)
$\beta/^{\circ}$		98.143(2)		
$V/Å^3$	4826.8(5)	5023.9(7)	4873.4(6)	4851.9(4)
Z	4	4	4	4
$D_{\rm c}/{\rm g}~{\rm cm}^{-3}$	1.272	1.168	1.273	1.287
μ/mm^{-1}	1.261	1.203	1.112	1.257
F(000)	1948	1896	1972	1980
$\theta_{\rm max}/^{\circ}$	25.50	25.50	25.50	25.50
Collected	17609	25721	15115	16286
Unique reflns	4578	9314	4645	4610
Obsd reflns $[I > 2.0\sigma(I)]$	4093	6470	4142	4259
No. of variables	276	490	266	265
GOF	1.106	1.101	1.166	1.132
R	0.0449	0.0923	0.0570	0.0526
wR	0.1157	0.2127	0.1460	0.1260
$R_{\rm int}$	0.0411	0.0720	0.0362	0.0331
Largest diff. peak, hole/e Å ⁻³	1.004, -0.672	0.866, -0.732	0.964, -0.722	1.065, -0.995

bis(phenolate) lanthanide alkoxides.²⁸ Now, a further study revealed that the amine bis(phenolate) cyclopentadienyl lanthanide complexes generated in situ can react smoothly with phenols under mild conditions to give the amine bridged bis(phenolate) lanthanide aryloxo complexes in high isolated yields. Thus, a series of lanthanide aryloxides were prepared using (C5H5)3Ln(THF) as the starting materials. The reactions of $(C_5H_5)_3Ln(THF)$ with amine bridged bis(phenol) LH₂ in a 1:1 molar ratio, and then with 1 equivalent of 2,6-diisopropylphenol, p-cresol or 4methoxyphenol, respectively, in situ in THF at 50 °C, after workup, gave the desired neutral lanthanide aryloxides LLn(OC₆H₃-2,6- Pr_{2}^{i})(THF) [Ln = Nd (1), Sm (2), Yb (3)], LLn(OC₆H₄-4- CH_3)(THF)_n [Ln = Nd (4), Sm (5), n = 2; Ln = Y (6), n = 1] and $LLn(OC_6H_4-4-OCH_3)(THF)_n$ [Ln = Nd (7), Sm (8), n = 2; Ln = Yb (9), n = 1] in high isolated yields (72–83%) as shown in Scheme 1. The compositions of complexes 1-9 were confirmed by elemental analysis and NMR spectroscopy in the case of complex 6. The definitive molecular structures of complexes 1-8 were determined by single-crystal structure analysis. It was found that both the ionic radii of the lanthanide metals and the bulkiness of the aryloxo groups have effect on the solid state structures of these complexes. When the aryloxo group is diisopropylphenolate, complexes (1-3) have similar structures, and only one THF molecule is coordinated to the metal center. For the less bulky 4-methylphenolate and 4-methoxyphenolate, there are two THF molecules to coordinate to the larger neodymium and samarium ions (complexes 4, 5, 7 and 8); whereas there is one THF molecule to coordinate to the small yttrium and ytterbium ions (complexes 6 and 9). Complexes 1-9 are moderately sensitive to air and moisture. The crystals decompose in a few minutes when they are exposed to air, but both the crystals and the solution are rather stable when stored under argon. All of the lanthanide

aryloxo complexes are freely soluble in THF and toluene, and slightly soluble in hexane.

Crystal structures

To provide complete structural information for these new amine bridged bis(phenolate) lanthanide species, single-crystal X-ray structural analyses were carried out for complexes 1 to 8. X-Ray diffraction analyses displayed that all of these complexes have monomeric structures, and the difference in overall structures among these complexes is the number of the coordinated THF molecules.

The crystals suitable for an X-ray structure determination of complexes 1 to 3 were obtained from concentrated toluene solution at room temperature. Complexes 1 to 3 are isomorphous, and only the ORTEP diagram of complex 3 is shown in Fig. 1. The selected bond lengths and angles for these molecules are provided in Table 3. Like other amine bridged bis(phenolate) lanthanide complexes,3,8 the sidearm amido group was found to bind to the metal center in the solid state. Each metal ion is sixcoordinated to two oxygen atoms and two nitrogen atoms from the dianionic amine bridged bis(phenolate) ligand, one oxygen atom from diisopropylphenoxo group, and one oxygen atom from one THF molecule. The coordination geometry around the metal center can be best described as a slightly distorted octahedron, in which O(1), O(2), O(4) and N(2) can be considered to occupy equatorial positions within the octahedron. O(3) and N(1) occupy axial positions, and the O(3)-Ln-N(1) angle is slightly distorted away from the idealized position of 180° to about 169° for these complexes. The overall coordination geometries of complexes 1-3 are similar to those of LYbCl(THF), LYbNPh₂(THF) and LYbMe(THF).3 The average Ln–O(Ar) bond lengths range from



Scheme 1 Synthesis of amine bridged bis(phenolate) lanthanide aryloxides.

Table 3 Selected bond lengths (Å) and bond angles (°) for complexes 1–3 and 6

Bond lengths	1	2	3	6
Ln1–O1	2.224(3)	2.175(9)	2.096(5)	2.144(4)
Ln1–O2	2.232(4)	2.200(11)	2.120(5)	2.159(4)
Ln1–O3	2.212(4)	2.170(11)	2.084(6)	2.098(4)
Ln1–O4	2.498(4)	2.449(12)	2.358(5)	2.365(4)
Ln1–N1	2.676(4)	2.618(11)	2.519(7)	2.526(5)
Ln1–N2	2.687(4)	2.820(16)	2.500(6)	2.514(5)
Bond angles		· · · ·		
O3-Ln1-N1	168.80(13)	168.7(4)	168.76(19)	160.03(16)
O1-Ln1-N2	86.19(14)	88.0(5)	94.0(2)	92.66(16)
N2–Ln1–O2	94.48(14)	93.5(4)	90.7(3)	91.99(16)
O2–Ln1–O4	84.10(15)	82.9(5)	85.09(19)	85.37(15)
O4-Ln1-O1	82.46(13)	83.7(4)	82.43(19)	84.66(15)
N1–Ln1–O4	88.58(14)	90.2(4)	89.1(2)	96.38(16)
O1–Ln1–O2	148.79(13)	149.7(4)	155.4(2)	153.70(15)

2.228(3) (for Nd) to 2.108(5) Å (for Yb, see Table 3), which reflected the usual lanthanide contraction from Nd³⁺ to Yb³⁺.³² Similar consequences of the decrease of the ionic radii of the Ln³⁺ ions from Nd³⁺ to Yb³⁺ are also observed from the Ln–O(Ph) and Ln–O(THF) bond lengths in these complexes.

In complex 1, the average Nd–O(Ar) bond length of 2.228(3) Å is comparable to the corresponding bond lengths in bridged bis(phenolate) neodymium complexes, such as $[(MBMP)Nd(\mu - OPr_2^i)(THF)_2]_2$ (2.215(6) Å, $MBMP^{2-} = 2,2'$ -methylenebis(6-*tert*-butyl-4-methylphenoxo),²⁴ (MBMP)Nd[N(TMS)_2](THF)_2 (2.200(2) Å, TMS = SiMe₃),²⁶ and [ONNO]Nd[N(TMS)_2](THF) {2.229(5) Å, H₂[ONNO] = 1,4-bis(2-hydroxy-3,5-di-*tert*-butyl-benzyl)-imidazolidine}.¹² The Nd–O(Ph) bond length of



Fig. 1 ORTEP diagram of complex 3 showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Disordered carbon atoms of methyl groups and hydrogen atoms are omitted for clarity. Complexes 1 and 2 are isomorphous with complex 3.

2.212(4) Å, is comparable with the Nd–O(Ar) bond lengths observed in the aforementioned complexes, and $(ArO)_3Nd(THF)$ (ArO = 2,6-di-*tert*-butyl-4-methylphenolate) (2.176 Å).³³ In complexes **2** and **3**, the average Sm–O(Ar) and Yb–O(Ar) bond length are 2.189(10) and 2.108(5) Å, respectively, which are comparable to the corresponding bond lengths in complex **1**, when the difference in ionic radii is considered, and other amine

Table 4 Selected bond lengths (Å) and bond angles (°) for complexes 4, 5, 7 and 8

	4	5	7	8
Ln1–O1	2.239(3)	2.212(3)	2.246(3)	2.219(3)
Ln1–O2	2.232(5)	2.202(4)	2.223(6)	2.189(5)
Ln1–O3	2.568(5)	2.595(4)		
Ln1–O4	2.622(4)	2.663(4)	2.580(6)	2.560(6)
Ln1–O5			2.616(5)	2.590(5)
Ln1–N1	2.688(4)	2.663(4)	2.695(6)	2.656(6)
Ln1–N2	2.721(5)	2.684(5)	2.722(7)	2.691(7)
Ol-Lnl-O2	105.70(7)	105.25(7)	105.32(9)	105.02(9)
O2–Ln1–O1A	105.70(7)	105.25(7)	105.32(9)	105.02(9)
Ol-Lnl-OlA	148.02(15)	149.08(15)	148.66(18)	149.49(18)
O2–Ln1–N1	141.73(17)	141.94(17)	141.2(2)	141.6(2)
Ol-Lnl-Nl	75.86(7)	76.47(7)	76.06(9)	76.63(9)
O2–Ln1–N2	76.15(18)	75.83(17)	75.9(2)	75.9(2)
O1-Ln1-N2	90.85(8)	91.27(8)	90.59(10)	91.10(10)
N1-Ln1-N2	65.58(15)	66.11(15)	65.29(19)	65.74(19)

bridged bis(phenolate) samarium¹⁰ and ytterbium complexes.³ The Sm–O(Ph) and Yb–O(Ph) bond lengths of 2.170(11) and 2.084(6) Å, respectively, are in agreement with the corresponding values in (ArO)₃Sm(THF) (2.155 Å)³⁴ and (ArO)₂YbCl(THF) (2.080(1) Å).³⁵

The definitive molecular structures of complexes **4–6** were determined. All of these complexes have monomeric structures, and their selected bond parameters are listed in Tables 3 and 4, respectively. Complexes **4** and **5** are isomorphous, and only the ORTEP diagram of complex **4** is shown in Fig. 2. In complexes **4** and **5**, each metal ion is coordinated to two oxygen atoms and two nitrogen atoms from the amine bridged bis(phenolate) ligand, one oxygen atom from 4-methylphenoxo group, and two oxygen atoms from two THF molecules. The coordination geometry around the metal center can be best described as a slightly distorted capped trigonal prism, with the capping atom being the oxygen atom of 4-methylphenoxo group. The overall coordination geometry is similar to that of amine bridged bis(phenolate) yttrium chloride,¹⁹ but different from those of complexes **1–3**. This difference can



Fig. 2 ORTEP diagram of complex 4 showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Disordered carbon atoms and hydrogen atoms are omitted for clarity. Complex 5 is isomorphous with complex 4.

be attributed to the less bulkiness of 4-methylphenoxo group than 2,6-diisopropylphenoxo group. The Ln-O(Ar) and Ln-O(Ph) bond lengths in complexes 4 and 5 are comparable with the corresponding values in complexes 1 and 2. The molecular structure of complex 6 is shown in Fig. 3. In complex 6, only one THF molecule is coordinated to yttrium ion. Thus, the yttrium ion is six-coordinated to form a slightly distorted octahedral geometry, which is different from those of complexes 4 and 5. The overall coordination geometry of complex 6 is similar to those of complexes 1-3. The Y-O(Ar) bond length of 2.152(4) Å accords with the values in amine bridged bis(phenolate) yttrium complexes LY(CH₂SiMe₃)(THF) [2.147(2) Å],⁸ LY(CH₂C₆H₄NMe₂o)[2.141(3) Å],³⁶ [ONOO]Y(CH₂SiMe₃)(THF) [ONOO = $MeOCH_2CH_2N\{CH_2-(2-O-C_6H_2-Bu_2-3,5)\}_2$ [2.129(4) Å], and [ONOO]YN(SiHMe₂)₂(THF) [2.151(2) Å].³⁷ The Y–O(Ph) bond length is comparable with those values in complexes 1–5, when the difference in ionic radii is considered.



Fig. 3 ORTEP diagram of complex 6 showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Disordered carbon atoms of methyl groups and hydrogen atoms are omitted for clarity.

Complexes 7 and 8 are isomorphous, and only the ORTEP diagram of complex 7 is shown in Fig. 4. In complexes 7 and 8, each metal ion is surrounded by one amine bridged bis(phenolate) ligand, one 4-methoxyphenoxo group and two THF molecules. The overall coordination geometries of complexes 7 and 8 are identical with those of complexes 4 and 5. As expected, the Ln–O(Ar) and Ln–O(Ph) bond lengths in complexes 7 and 8 are comparable with the corresponding values in complexes 4 and 5.

Ring-opening polymerization of lactide

Biodegradable polymers, such as poly(*e*-caprolactone) (PCL) and poly(lactide) (PLA), have recently gained great attention as a replacement for conventional synthetic materials because of their biodegradable, biocompatible, and permeable properties.^{38,39} Ring-opening polymerization of cyclic esters initiated by organometallic complexes is a convenient method for the synthesis of these polymers with high molecular weights.⁴⁰⁻⁴⁶ To understand the effect of initiating groups on the polymerization activity and controllability of amine bridged bis(phenolate)



Fig. 4 ORTEP diagram of complex 7 showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level. Disordered carbon and oxygen atoms and hydrogen atoms are omitted for clarity. Complex 8 is isomorphous with complex 7.

lanthanide complexes, the catalytic behavior of complexes **1–9** for the ring-opening polymerization of L-lactide was examined.

As expected, the amine bridged bis(phenolate) lanthanide aryloxides are efficient initiators for the ring-opening polymerization of L-lactide. The representative L-lactide polymerization data are summarized in Table 5. It can be seen that all of these lanthanide aryloxides can initiate L-lactide polymerization in toluene to

 Table 5
 Polymerization of L-lactide initiated by complexes 1–9°

give the polymers with high molecular weights and relatively narrow molecular weight distributions ($M_w/M_n = 1.10-1.59$). For example, using complex **1** as the initiator, the polymerization gives 88% yield in 2 h even for $[M]_0/[1]_0 = 1000$ (entry 2), and produced PLA with a molecular weight of 13.90×10^4 and a PDI of 1.47. The polymerization temperature affects the activity. As expected, the higher the temperature was, the faster the polymerization proceeded. For instance, using complex **6** as the initiator, almost complete yield could reach at 70 °C in 1 h when the molar ratio of monomer to initiator ([M]/[I]) is 400 (entry 17), whereas the yield was 45% at 50 °C in 1 h (entry 18) under the same polymerization conditions.

The ionic radii of the lanthanide metals have a significant effect on the catalytic activity for L-lactide polymerization. Upon a decrease of the ionic radii, the catalytic activity decreased. Using neodymium complex 1 as the initiator, the yield was 92% when the molar ratio of monomer to initiator is 800 in 1 h (entry 1), whereas it was 24% using an ytterbium complex 3 as the initiator in 2 h, even when the molar ratio of monomer to initiator decreases to 600 under the same polymerization conditions (entry 7). The observed activity decreasing order, $Nd > Sm > Yb \approx Y$, is in agreement with the order of ionic radii, which is consistent with the active trend observed in the methylene-linked bis(phenolate) lanthanide systems for the polymerization of *e*-caprolactone,²⁴ imidazolidinebridged bis(phenolate) rare-earth metal amides¹² and the bis(allyl) diketiminatolanthanide complexes for lactide polymerization.47 On the other hand, using the yttrium aryloxo complex as the initiator (entries 16–19), the polymerizations give the polymers with apparently small PDI values, which indicated that the central metal ions also affect the polymerization controllability.

In comparison with the amine bridged bis(phenolate) lanthanide alkyl^{6,8} and amido complexes,⁴⁸ these aryloxo complexes

Entry	Initiator	$[M]_0/[I]_0$	T∕°C	t	Yield (%) ^b	$M_{\rm c}{}^{c}(\times 10^{4})$	$M_n^{d}(\times 10^4)$	PDI^{d}
1	1	800	70	1 h	92	10.60	11.34	1.38
2	1	1000	70	2 h	88	12.67	13.90	1.47
3	2	400	70	1 h	98	5.64	10.37	1.59
4	2	600	70	2 h	96	8.29	10.64	1.54
5	2	800	70	2 h	95	10.94	12.06	1.59
6	3	400	70	1 h	98	5.64	9.81	1.58
7	3	600	70	2 h	24	2.51	4.31	1.21
8	4	600	70	1 h	99	8.55	7.22	1.54
9	4	800	70	1 h	96	11.06	8.80	1.55
10	4	1000	70	2 h	86	12.38	8.02	1.42
11	5	400	70	1 h	98	5.64	6.32	1.59
12	5	600	70	2 h	98	8.47	8.53	1.51
13	5	800	70	2 h	98	11.29	8.77	1.44
14	5	1000	70	3 h	27	3.89	3.21	1.37
15	5	800	70	1 h	48	5.53	4.69	1.42
16	6	200	70	1 h	99	2.85	4.09	1.30
17	6	400	70	1 h	99	5.70	4.56	1.29
18	6	400	50	1 h	45	2.59	2.53	1.10
19	6	600	70	3 h	22	1.73	1.51	1.14
20	7	800	70	1 h	94	10.83	9.77	1.45
21	7	1000	70	2 h	83	11.95	8.74	1.54
22	8	600	70	2 h	98	8.47	9.86	1.45
23	8	800	70	2 h	98	11.29	10.34	1.43
24	9	400	70	1 h	98	5.64	5.09	1.22
25	9	600	70	2 h	20			

^{*a*} General polymerization conditions: toluene as the solvent, [L-LA] = 1 mol L⁻¹. ^{*b*} Yield: weight of polymer obtained/weight of monomer used. ^{*c*} $M_c = (144.13) \times [M]_0 / [I]_0 \times (polymer yield)$ (%). ^{*d*} Measured by GPC calibrated with standard polystyrene samples.

Table 6	Polymerization	of L-lactide initiate	ed by complexes 2 and	5
---------	----------------	-----------------------	-----------------------	---

Entry	Initiator	$[M]_0/[I]_0$	T∕°C	t	Yield (%) ^b	$M_{\rm c} {}^{c}(\times 10^4)$	$M_{\rm n}$ ^d (× 10 ⁴)	PDI ^d
1	2	800	70	10 min	17	1.96	3.06	1.22
2	2	800	70	20 min	20	2.30	3.13	1.20
3	2	800	70	30 min	28	3.23	4.98	1.24
4	2	800	70	1 h	75	8.64	9.12	1.38
5	2	800	70	1.5 h	88	10.14	10.86	1.44
6	2	800	70	2 h	95	10.94	12.06	1.59
7	5	800	70	10 min	40	4.61	4.39	1.12
8	5	800	70	20 min	55	6.34	5.02	1.22
9	5	800	70	30 min	68	7.83	6.01	1.25
10	5	800	70	1 h	93	10.71	7.71	1.36
11	5	800	70	1.5 h	98	11.29	9.42	1.43
12	5	800	70	2 h	98	11.29	8.77	1.44

^{*a*} General polymerization conditions: toluene as the solvent, [L-LA] = 1 mol L⁻¹. ^{*b*} Yield: weight of polymer obtained/weight of monomer used. ^{*c*} $M_c = (144.13) \times [M]_0/[I]_0 \times (\text{polymer yield})$ (%). ^{*a*} Measured by GPC calibrated with standard polystyrene samples.

Table 7	Polym	erization	of rac-l	actide	initiated	by	complex	6
---------	-------	-----------	----------	--------	-----------	----	---------	---

Entry	$[M]_0/[I]_0$	T∕°C	t	Yield (%) ^b	$M_{\rm c} {}^{c}(\times 10^4)$	$M_n^{\ a}(\times 10^4)$	PDI^d	P_r^{e}
1	100	20	10 min	93	1.34	2.99	1.12	0.98
2	100	20	1 h	100	1.44	3.50	1.17	0.95
3	200	20	1 h	100	2.88	4.34	1.14	0.97
4	300	20	1 h	100	4.32	5.25	1.15	0.95
5	400	20	1 h	100	5.76	5.29	1.16	0.96
6	500	20	1 h	100	7.20	6.75	1.11	0.98
7	600	20	2 h	88	7.60	7.03	1.09	0.98
8	700	20	3 h	66	6.65	4.24	1.14	0.97
9	700	20	4 h	100	10.08	7.46	1.14	0.98
10	1000	20	5 h	82	11.81	7.65	1.11	0.97

^{*a*} General polymerization conditions: THF as the solvent, $[L-LA] = 1 \mod L^{-1}$. ^{*b*} Yield: weight of polymer obtained/weight of monomer used. ^{*c*} $M_c = (144.13) \times [M]_0 / [I]_0 \times (polymer yield)$ (%). ^{*a*} Measured by GPC calibrated with standard polystyrene samples. ^{*c*} Measured by homodecoupling ¹H NMR spectroscopy at 20 °C in CDCl₃.

exhibit similar activity for lactide polymerization. The amine bridged bis(phenolate) yttrium alkyl and amido complexes can initiate the complete polymerization of lactide when the molar ratio of the monomer to the initiator is 500 within 1 h or 80 min, respectively; The yield is 99% using the amine bridged bis(phenolate) yttrium aryloxide 3 as the initiator at 70 °C in 1 h (entry 6). However, compared with the bridged bis(phenolate) lanthanide alkoxo complexes generated in situ,^{6,12} complexes 1-9 show relatively poor controllability for L-lactide polymerization, and give the resultant polymers with relatively broad molecular weight distributions. These results indicated that the electronic properties of the Ln-O bonds have profound effect on the controllability of lactide polymerization. A comparative study revealed that the structures of the aryloxo groups in these complexes have no obvious effect on the activity and controllability for Llactide polymerization. The activity and controllability initiated by the complexes with the same central metal ion is very similar (entries 4, 12 and 22). However, the measured molecular weights of the polymers initiated by complexes 1-3 are all superior from the theoretical values, whereas the measured molecular weights of the polymers initiated by complexes 4-9 are near to the calculated ones. These results indicated that the initiation efficiency is low for the former. To further understand this phenomenon, the polymerization kinetics was measured using complexes 2 and 5 as the initiators, respectively, and the results are summarized in Table 6. It can be seen that the polymerization initiated by complex 5 is apparently faster than that initiated by complex 2 under the

same polymerization conditions. The yield is 40% after 10 min using complex **5** as the initiator (entry 7), whereas the yield is only 17% using complex **2** as the initiator (entry 1). In addition, the molecule weight distributions of the resultant polymers broadened as prolonging the polymerization time using both complexes as the initiators, which indicated the presence of transesterification under the current polymerization conditions. Based on these results, we postulated that the coordination of the bulky 2,6diisopropylphenoxo group to lanthanide ion increases the steric hindrance around the metal center, which blocks the coordination of the monomer at initiation step. Thus, the polymerization kinetics initiated by complexes **1–3** are slow initiation and fast propagation in comparison with those initiated by complexes **4–9**, which decreases the initiation efficiency.

Because complex **6** showed relatively good controllability for the ring-opening polymerization of L-lactide, its catalytic behavior for *rac*-lactide polymerization was also tested, and the preliminary results are listed in Table 7. It can be seen that complex **6** can initiate the controlled highly heteroselective ring-opening polymerization of *rac*-lactide. The polymerizations proceed smoothly in THF at 20 °C, and give the polymers with high molecular weights and narrow molecular weight distributions ($M_w/M_n = 1.09$ – 1.17). The catalytic activity of complex **6** is similar to that of the amine bridged bis(phenolate) yttrium alkyl complexes,⁸ but is lower than that of the methoxyl-amino bridged bis(phenolate) yttrium alkoxide.⁶ For example, complex **6** and the yttrium alkyl complex can polymerize completely 500 equivalents of *rac*-lactide in 1 h, whereas the yttium alkoxide complex can polymerize 1000 equivalents of *rac*-lactide within 40 min under the same polymerization conditions. However, the controllability of complex **6** for this polymerization is as good as that of the yttrium alkoxide,⁶ and is better than the yttrium alkyl complexes⁸ mentioned above, which is consistent with the general rule suggested by Okuda *et al.*²¹ It is worthy to note that complex **6** showed high stereoselectivity for *rac*-lactide polymerization to give heterotactic polymers with P_r over 0.95. The stereocontrol ability of complex **6** is similar to that of the amine bridged bis(phenolate) yttrium alkyl complexes (P_r over 0.94), but is better than that of the methoxyl-amino bridged bis(phenolate) that the initiating group has no obvious effect on the stereoselectivity, whereas the ancillary ligand plays a crucial role.

Conclusion

In summary, a series of neutral amine bridged bis(phenolate) lanthanide aryloxo complexes were successfully synthesized via protolytic ligand exchange reactions using the readily available $(C_{5}H_{5})_{3}Ln(THF)$ as the precursors, and their structure features have been provided by X-ray diffraction study. These complexes represent the first structurally characterized examples of amine bridged bis(phenolate) lanthanide aryloxo complexes. These results indicated that the acidity of the phenols has a profound influence on the reactivity of amine bridged bis(phenolate) cyclopentadienyl lanthanide complexes, because the amine bridged bis(phenolate) lanthanide alkoxides cannot be prepared by this method. These lanthanide aryloxo complexes can initiate efficiently the ring-opening polymerization of L-lactide, and the observed activity increasing order is in agreement with the order of the ionic radii. In comparison with the amine bridged bis(phenolate) lanthanide alkoxides, these lanthanide aryloxides show inferior controllability for L-lactide polymerization. The structures of the aryloxo groups have no obvious effect on the catalytic activity and controllability of L-lactide polymerization, but the steric bulkiness of the aryloxo group can affect the initiation step.

Acknowledgements

Financial support from the National Natural Science Foundation of China (Grants 20771078, 20972108 and 20632040), the Major Basic Research Project of the Natural Science Foundation of the Jiangsu Higher Education Institutions (Project 07KJA15014), and the Qing Lan Project is gratefully acknowledged.

References

- C. X. Cai, C. W. Lehmann and J. F. Carpentier, *Chem. Commun.*, 2004, 330.
- 2 F. M. Kerton, A. C. Whitwood and C. E. Willans, *Dalton Trans.*, 2004, 2237.
- 3 Y. M. Yao, M. M. Ma, X. P. Xu, Y. Zhang, Q. Shen and W. T. Wong, Organometallics, 2005, 24, 4014.
- 4 F. Bonnet, A. R. Cowley and P. Mountford, Inorg. Chem., 2005, 44, 9046.
- 5 A. Amgoune, C. M. Thomas, S. Ilinca, T. Roisnel and J. F. Carpentier, Angew. Chem., Int. Ed., 2006, 45, 2782.
- 6 A. Amgoune, C. M. Thomas, T. Roisnel and J. F. Carpentier, *Chem.-Eur. J.*, 2006, **12**, 169.

- 7 E. E. Delbridge, D. T. Dugah, C. R. Nelson, B. W. Skelton and A. H. White, *Dalton Trans.*, 2007, 143.
- 8 X. L. Liu, X. M. Shang, T. Tang, N. H. Hu, F. K. Pei, D. M. Cui, X. S. Chen and X. B. Jing, *Organometallics*, 2007, 26, 2747.
- 9 A. Amgoune, C. M. Thomas and J. F. Carpentier, *Macromol. Rapid Commun.*, 2007, 28, 693.
- 10 H. E. Dyer, S. Huijser, A. D. Schwarz, C. Wang, R. Duchateau and P. Mountford, *Dalton Trans.*, 2008, 32.
- 11 C. E. Willans, C. E. Sinenkov, G. K. Fukin, K. Sheridan, J. M. Lynam, A. A. Trifonov and F. M. Kerton, *Dalton Trans.*, 2008, 3592.
- 12 Z. Z. Zhang, X. P. Xu, W. Y. Li, Y. M. Yao, Y. Zhang, Q. Shen and Y. Y. Luo, *Inorg. Chem.*, 2009, 48, 5715.
- 13 N. Ajellal, M. Bouyahyi, A. Amgoune, C. M. Thomas, A. Bondon, I. Pillin, Y. Grohens and J. F. Carpentier, *Macromolecules*, 2009, 42, 987.
- 14 J. W. Kramer, D. S. Treitler, E. W. Dunn, P. M. Castro, T. Roisnel, C. M. Thomas and G. W. Coates, *J. Am. Chem. Soc.*, 2009, **131**, 16042.
- 15 H. Zhou, H. D. Guo, Y. M. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, 46, 958.
- 16 H. D. Guo, H. Zhou, Y. M. Yao, Y. Zhang and Q. Shen, *Dalton Trans.*, 2007, 3555.
- 17 X. P. Xu, Y. M. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, 46, 3743.
- 18 Z. J. Zhang, X. P. Xu, S. Sun, Y. M. Yao, Y. Zhang and Q. Shen, *Chem. Commun.*, 2009, 7414.
- 19 C. L. Boyd, T. Toupance, B. R. Tyrrell, B. D. Ward, C. R. Wilson, A. R. Cowley and P. Mountford, *Organometallics*, 2005, 24, 309.
- 20 H. Y. Ma, T. P. Spaniol and J. Okuda, Dalton Trans., 2003, 4770.
- 21 H. Y. Ma and J. Okuda, Macromolecules, 2005, 38, 2665.
- 22 M. Y. Deng, Y. M. Yao, Q. Shen, Y. Zhang and J. Sun, *Dalton Trans.*, 2004, 944.
- 23 X. P. Xu, M. T. Ma, Y. M. Yao, Y. Zhang and Q. Shen, Eur. J. Inorg. Chem., 2005, 676.
- 24 Y. M. Yao, X. P. Xu, B. Liu, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2005, 44, 5133.
- 25 X. P. Xu, Y. M. Yao, M. Y. Hu, Y. Zhang and Q. Shen, J. Polym. Sci., Part A: Polym. Chem., 2006, 44, 4409.
- 26 X. P. Xu, Z. J. Zhang, Y. M. Yao, Y. Zhang and Q. Shen, *Inorg. Chem.*, 2007, 46, 9379.
- 27 R. P. Qi, B. Liu, X. P. Xu, Z. J. Yang, Y. M. Yao, Y. Zhang and Q. Shen, *Dalton Trans.*, 2008, 5016.
- 28 L. Z. Zhou, Y. M. Yao, Y. Zhang and Q. Shen, J. Rare Earths, 2007, 25, 544.
- 29 J. M. Birmingham and G. Wilkinson, J. Am. Chem. Soc., 1956, 78, 42.
- 30 E. Y. Tshuva, I. Goldberg and M. Kol, Organometallics, 2001, 20, 3017.
- 31 J. L. Atwood, W. E. Hunter, A. L. Wayda and W. J. Evans, *Inorg. Chem.*, 1981, 20, 4115.
- 32 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, 32, 751.
- 33 L. L. Zhang, Y. M. Yao, Y. J. Luo, Q. Shen and J. Sun, *Polyhedron*, 2000, **19**, 2243.
- 34 Q. Z. Qi, Y. H. Lin, J. Y. Hu and Q. Shen, Polyhedron, 1995, 14, 413.
- 35 Y. M. Yao, Q. Shen, Y. Zhang, M. Q. Xue and J. Sun, *Polyhedron*, 2001, 20, 3201.
- 36 M. L. Pang, Y. M. Yao, Y. Zhang and Q. Shen, *Chin. Sci. Bull.*, 2008, 53, 1978.
- 37 C. X. Cai, L. Toupet, C. W. Lehmann and J. F. Carpentier, J. Organomet. Chem., 2003, 683, 131.
- 38 E. Chiellini and R. Solaro, Adv. Mater., 1996, 8, 305.
- 39 S. Mecking, Angew. Chem., Int. Ed., 2004, 43, 1078.
- 40 B. J. O'Keefe, M. A. Hillmyer and W. B. Tolman, J. Chem. Soc., Dalton Trans., 2001, 2215.
- 41 G. W. Coates, J. Chem. Soc., Dalton Trans., 2002, 467.
- 42 O. D. Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147.
- 43 M. Chisholm and Z. J. Zhou, J. Mater. Chem., 2004, 14, 3081.
- 44 J. C. Wu, T. L. Yu, C. T. Chen and C. C. Lin, *Coord. Chem. Rev.*, 2006, **250**, 602.
- 45 S. Agarwal, C. Mast, K. Dehnicke and A. Greiner, *Macromol. Rapid Commun.*, 2000, 21, 195.
- 46 R. E. Drumright, P. R. Gruber and D. E. Henton, *Adv. Mater.*, 2000, 12, 1841.
- 47 L. F. Sachez-Barba, D. L. Hughes, S. M. Humphrey and M. Bochmann, Organometallics, 2005, 24, 3792.
- 48 F. K. Song, C. H. Yan, H. M. Sun, Y. M. Yao, Q. Shen and Y. Zhang, *Chin. Sci. Bull.*, 2009, **54**, 3231.