7176 *Inorg. Chem.* **2010**, *49*, 7176–7181
DOI: 10.1021/ic1010488

Inorganic Chemistry
Article

Group 4 Salalen Complexes and Their Application for the Ring-Opening Polymerization of *rac*-Lactide

Emma L. Whitelaw, Matthew D. Jones,* and Mary F. Mahon

Department of Chemistry, University of Bath, Claverton Down, Bath, BA2 7AY United Kingdom

Received May 24, 2010

In this paper, we report the preparation and characterization of a series of unsymmetrical group 4 metal complexes based on ONNO salalen-type ligands. In these examples, the ligand is unsymmetrical with an amine and an imine nitrogen center. All complexes {except Hf(**3**)(O^iPr)$_2$} adopt a β-cis configuration in the solid state, which is also in agreement with solution-state NMR spectroscopic measurements. The complexes have been tested for the ROP of *rac*-lactide (both in solution and under melt conditions). Narrow polydispersities have been seen (1.07−1.82). The Ti(IV) complexes produce atactic PLA, whereas the Zr(IV) complexes form PLA with a heterotactic bias. Hf(IV) complexes have been shown to produce isotactic PLA with a P_m of 0.75. The kinetics for all initiators have been investigated and are discussed.

Introduction

Due to the ever increasing demands on the world's natural resources, now is the time to develop new products from sustainable resources. One such example of this is the production of polylactide (PLA) *via* the ring-opening polymerization (ROP) of the cyclic ester monomer lactide (LA). The monomer can be prepared from lactic acid which is derived from corn starch. The polymer itself is utilized in many applications from drug delivery systems, surgical sutures, food packaging, to clothing products.[1,2] These polymers have also been extensively utilized as scaffolds for tissue engineering applications.[3] Therefore, the development of novel and controllable initiators is of vital importance, as polymers with different properties are required for each application. Initiators are often based on Lewis acidic metal centers[4−6] (although organocatalyzed processes are known)[7−9] such as group 3 elements,[10−14] group 4 elements,[15−20] Zn(II),[21−25]

---

*To whom correspondence should be addressed. E-mail: mj205@bath.ac.uk.

(1) Albertsson, A. C.; Varma, I. K. *Biomacromolecules* **2003**, *4*, 1466.
(2) Sinclair, R. G. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33*, 585.
(3) Rezwan, K.; Chen, Q. Z.; Blaker, J. J.; Boccaccini, A. R. *Biomaterials* **2006**, *27*, 3413.
(4) O'Keefe, B. J.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2002**, *124*, 4384.
(5) Ovitt, T. M.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 1316.
(6) O'Keefe, B. J.; Hillmyer, M. A.; Tolman, W. B. *J. Chem. Soc., Dalton Trans.* **2001**, 2215.
(7) Jensen, T. R.; Breyfogle, L. E.; Hillmyer, M. A.; Tolman, W. B. *Chem. Commun.* **2004**, 2504.
(8) Lohmeijer, B. G. G.; Pratt, R. C.; Leibfarth, F.; Logan, J. W.; Long, D. A.; Dove, A. P.; Nederberg, F.; Choi, J.; Wade, C.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 8574.
(9) Pratt, R. C.; Lohmeijer, B. G. G.; Long, D. A.; Lundberg, P. N. P.; Dove, A. P.; Li, H. B.; Wade, C. G.; Waymouth, R. M.; Hedrick, J. L. *Macromolecules* **2006**, *39*, 7863.
(10) Amgoune, A.; Thomas, C. M.; Roisnel, T.; Carpentier, J. F. *Chem.—Eur. J.* **2006**, *12*, 169.
(11) Cai, C. X.; Amgoune, A.; Lehmann, C. W.; Carpentier, J. F. *Chem. Commun.* **2004**, 330.
(12) Grunova, E.; Kirillov, E.; Roisnel, T.; Carpentier, J. F. *Organometallics* **2008**, *27*, 5691.
(13) Platel, R. H.; Hodgson, L. M.; White, A. J. P.; Williams, C. K. *Organometallics* **2007**, *26*, 4955.
(14) Platel, R. H.; White, A. J. P.; Williams, C. K. *Chem. Commun.* **2009**, 4115.
(15) Chmura, A. J.; Cousins, D. M.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2008**, 1437.
(16) Chmura, A. J.; Davidson, M. G.; Frankis, C. J.; Jones, M. D.; Lunn, M. D. *Chem. Commun.* **2008**, 1293.
(17) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F.; Johnson, A. F.; Khunkamchoo, P.; Roberts, S. L.; Wong, S. S. F. *Macromolecules* **2006**, *39*, 7250.
(18) Gendler, S.; Segal, S.; Goldberg, I.; Goldschmidt, Z.; Kol, M. *Inorg. Chem.* **2006**, *45*, 4783.
(19) Jones, M. D.; Davidson, M. G.; Kociok-Kohn, G. *Polyhedron* **2010**, *29*, 697.
(20) Gregson, C. K. A.; Blackmore, I. J.; Gibson, V. C.; Long, N. J.; Marshall, E. L.; White, A. J. P. *Dalton Trans.* **2006**, 3134.
(21) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2001**, *123*, 3229.
(22) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2005**, *44*, 8004.
(23) Jones, M. D.; Davidson, M. G.; Keir, C. G.; Hughes, L. M.; Mahon, M. F.; Apperley, D. C. *Eur. J. Inorg. Chem.* **2009**, 635.
(24) Rieth, L. R.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2002**, *124*, 15239.
(25) Williams, C. K.; Breyfogle, L. E.; Choi, S. K.; Nam, W.; Young, V. G.; Hillmyer, M. A.; Tolman, W. B. *J. Am. Chem. Soc.* **2003**, *125*, 11350.
(26) Ma, H. Y.; Spaniol, T. P.; Okuda, J. *Dalton Trans.* **2003**, 4770.
(27) Skvortsov, G. G.; Yakovenko, M. V.; Castro, P. M.; Fukin, G. K.; Cherkasov, A. V.; Carpentier, J. F.; Trifonov, A. A. *Eur. J. Inorg. Chem.* **2007**, 3260.
(28) Du, H. Z.; Velders, A. H.; Dijkstra, P. J.; Sun, J. R.; Zhong, Z. Y.; Chen, X. S.; Feijen, J. *Chem.—Eur. J.* **2009**, *15*, 9836.
(29) Ma, H. Y.; Melillo, G.; Oliva, L.; Spaniol, T. P.; Englert, U.; Okuda, J. *Dalton Trans.* **2005**, 721.

lanthanides,[26,27] Al(III),[28−34] Ca(II),[35] Mg(II),[21,22] and Ba(II).[36] Most pertinent to this study are those produced with group 4 metals.[15−20,37−45] It has been observed that it is possible to produce highly heterotactic PLA from Zr(IV) and Hf(IV) C_3 symmetric amine tris(phenolate) complexes under the industrially preferred melt conditions.[16] However, we have recently shown that subtle changes to the ligand mean that atactic PLA is produced.[46] Recently, Kol and co-workers observed that amine bis(phenolate) Ti(IV) and Zr(IV) complexes are extremely active for the polymerization of *rac*-lactide and L-lactide.[47] In the case of *rac*-lactide, Kol's catalysts produced heterotactic PLA.[47] One of us has demonstrated that Zr(IV) and Hf(IV) amine bis(phenolate) complexes can also afford isotactic PLA under melt conditions.[17]

In this paper, we report the preparation and characterization of a series of unsymmetrical amine/imine bis(phenolate) (salalen) complexes and their exploitation for the ROP of *rac*-lactide. To the best of our knowledge, this is the first example of the use of salalen ligands for the ROP of *rac*-lactide. Examples of X-ray structures of Hf(IV)−salalen complexes are also presented. To date, the vast majority of ONNO-type ligands in the literature are based on symmetrical amine bis(phenolate), salan, or salen-type systems.[4,6,28,34,48,49]

Results and Discussion

Synthesis and Characterization of Ligands and Complexes. The ligands prepared in this study are shown in Scheme 1, and adapted literature procedures were followed for their preparation.[15,46] The complexes were prepared from a 1:1 reaction of the appropriate ligand with the group 4 alkoxide, as shown in Scheme 1.[46] All complexes were characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy and single-crystal X-ray diffraction, Figure 1. In the solid state, the metal center is seen to adopt a pseudo-octahedral geometry, Table 1. This is exemplified by a O(1)−M−N(1) bond angle of approximately 170° in all cases. As expected, the M−N(imine) distance is considerably shorter than the M−N(amine). The bond distances and angles are in agreement with those in the literature for similar species.[17,18,20,37,46,47] For such salalen ligands, it is possible to produce *fac*−*fac*, *mer*−*mer*, *fac*−*mer*, or *mer*−*fac* isomers.[50] In these examples, a *fac*−*mer* geometry is observed in the solid state, with the salan fragment *fac* and the salen *mer*.[50] The two isopropoxides are *cis*-oriented, one being *trans* to the imine with the other *trans* to a phenoxy oxygen, and overall the complexes have C_1 symmetry. The complexes are not fluxional on the NMR time-scale, and the ^{1}H NMR spectra for the compounds {except Hf(**3**)(O^{i}Pr)$_2$}, in CDCl$_3$, contain only one imine resonance and two septet isopropoxide

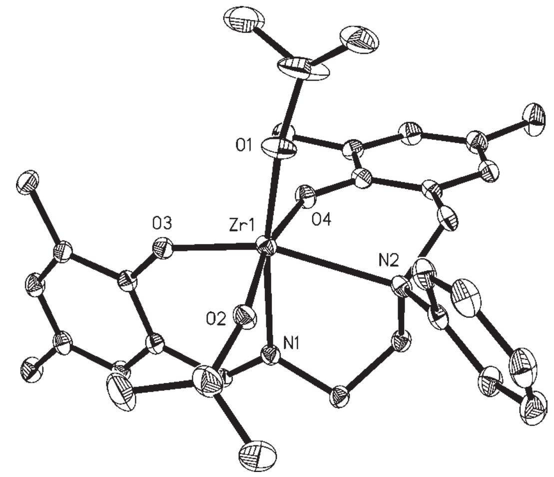
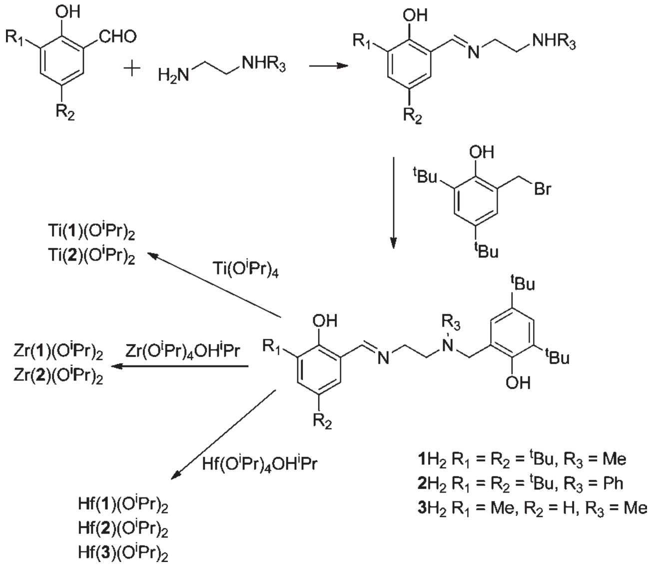


Figure 1. Solid-state structure of Zr(**2**)(O^{i}Pr)$_2$. The methyl groups of the ^{t}Bu moieties have been removed for clarity, as have all hydrogen atoms. The ellipsoids are shown at the 30% probability level.

Scheme 1. Ligands and Complexes Prepared in This Study



---

(30) Nomura, N.; Akita, A.; Ishii, R.; Mizuno, M. *J. Am. Chem. Soc.* **2010**, *132*, 1750.

(31) Nomura, N.; Ishii, R.; Akakura, M.; Aoi, K. *J. Am. Chem. Soc.* **2002**, *124*, 5938.

(32) Nomura, N.; Ishii, R.; Yamamoto, Y.; Kondo, T. *Chem.—Eur. J.* **2007**, *13*, 4433.

(33) Schwarz, A. D.; Chu, Z. Y.; Mountford, P. *Organometallics* **2010**, *29*, 1246.

(34) Zhong, Z. Y.; Dijkstra, P. J.; Feijen, J. *Angew. Chem., Int. Ed. Engl.* **2002**, *41*, 4510.

(35) Chisholm, M. H.; Gallucci, J. C.; Phomphrai, K. *Inorg. Chem.* **2004**, *43*, 6717.

(36) Davidson, M. G.; O'Hara, C. T.; Jones, M. D.; Keir, C. G.; Mahon, M. F.; Kociok-Kohn, G. *Inorg. Chem.* **2007**, *46*, 7686.

(37) Sarazin, Y.; Howard, R. H.; Hughes, D. L.; Humphrey, S. M.; Bochmann, M. *Dalton Trans.* **2006**, 340.

(38) Schwarz, A. D.; Thompson, A. L.; Mountford, P. *Inorg. Chem.* **2009**, *48*, 10442.

(39) Chen, H. Y.; Liu, M. Y.; Sutar, A. K.; Lin, C. C. *Inorg. Chem.* **2010**, *49*, 665.

(40) Sergeeva, E.; Kopilov, J.; Goldberg, I.; Kol, M. *Inorg. Chem.* **2010**, *49*, 3977.

(41) Hsieh, K. C.; Lee, W. Y.; Hsueh, L. F.; Lee, H. M.; Huang, J. H. *Eur. J. Inorg. Chem.* **2006**, 2306.

(42) Hu, M. G.; Wang, M.; Zhu, H. J.; Zhang, L.; Zhang, H.; Sun, L. C. *Dalton Trans.* **2010**, *39*, 4440.

(43) Kim, S. H.; Lee, J.; Kim, D. J.; Moon, J. H.; Yoon, S.; Oh, H. J.; Do, Y.; Ko, Y. S.; Yim, J. H.; Kim, Y. *J. Organomet. Chem.* **2009**, *694*, 3409.

(44) Krauzy-Dziedzic, K.; Ejfler, J.; Szafert, S.; Sobota, P. *Dalton Trans.* **2008**, 2620.

(45) Romain, C.; Brelot, L.; Bellemin-Laponnaz, S.; Dagorne, S. *Organometallics* **2010**, *29*, 1191.

(46) Whitelaw, E. L.; Jones, M. D.; Mahon, M. F.; Kociok-Kohn, G. *Dalton Trans.* **2009**, 9020.

(47) Zelikoff, A. L.; Kopilov, J.; Goldberg, I.; Coates, G. W.; Kol, M. *Chem. Commun.* **2009**, 6804.

(48) Chmura, A. J.; Davidson, M. G.; Jones, M. D.; Lunn, M. D.; Mahon, M. F. *Dalton Trans.* **2006**, 887.

(49) Kleij, A. W. *Eur. J. Inorg. Chem.* **2009**, 193.

(50) Yeori, A.; Gendler, S.; Groysman, S.; Goldberg, I.; Kol, M. *Inorg. Chem. Commun.* **2004**, *7*, 280.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes Ti(**1**)(O^{i}Pr)$_2$, Ti(**2**)(O^{i}Pr)$_2$, Zr(**1**)(O^{i}Pr)$_2$, Zr(**2**)(O^{i}Pr)$_2$, Hf(**1**)(O^{i}Pr)$_2$, Hf(**2**)(O^{i}Pr)$_2$, and Hf(**3**)(O^{i}Pr)$_2$

	Ti(**1**)(O^{i}Pr)$_2$	Ti(**2**)(O^{i}Pr)$_2$	Zr(**1**)(O^{i}Pr)$_2$	Zr(**2**)(O^{i}Pr)$_2$	Hf(**1**)(O^{i}Pr)$_2$	Hf(**2**)(O^{i}Pr)$_2$	Hf(**3**)(O^{i}Pr)$_2$
M−O1	1.8410(13)	1.8269(10)	1.9788(12)	1.963(2)	1.9739(16)	1.962(2)	1.964(2)
M−O2	1.8274(13)	1.8284(10)	1.9567(12)	1.949(2)	1.9521(17)	1.944(2)	1.954(2)
M−O3	1.9032(12)	1.8952(10)	2.0268(11)	2.016(2)	2.0168(16)	2.007(2)	2.008(2)
M−O4	1.9405(13)	1.9369(10)	2.0534(11)	2.062(2)	2.0471(16)	2.048(2)	2.041(2)
M−N1	2.1972(16)	2.1966(12)	2.3385(14)	2.340(2)	2.3087(19)	2.308(3)	2.327(3)
M−N2	2.3053(16)	2.3932(12)	2.4335(14)	2.487(3)	2.399(2)	2.452(3)	2.379(3)
O1−M−N1	168.43(6)	170.62(5)	168.59(5)	171.71(10)	169.24(7)	171.58(10)	176.44(10)
N1−M−N2	74.87(6)	75.39(4)	71.94(5)	72.74(9)	72.74(7)	73.45(8)	74.19(10)

resonances and are consistent with the solid state structures being maintained in solution. In the ^{13}C{^{1}H} NMR spectra, three CH$_2$ peaks are observed, and four resonances for the methyl groups of the ^{t}Bu are seen, again indicating that the solid-state structure is maintained in solution. When ligand **3**H$_2$ was reacted with Hf(O^{i}Pr)$_4$(OH^{i}Pr), the desired 1:1 complex was isolated, as indicated by the single-crystal X-ray diffraction, which again showed the *fac*−*mer* isomer was present in the solid state. However, the ^{1}H and ^{13}C{^{1}H} NMR spectra indicate that there are two structural isomers present in solution, in equal proportions; this is exemplified by the fact there are two imine resonances at 7.92 and 6.87 ppm in the ^{1}H spectrum and consequently two imine resonances in the ^{13}C{^{1}H} NMR spectrum together with 24 aromatic resonances. This is presumably facilitated by the decrease in steric bulk of the ligand. A low-temperature NMR spectrum (CDCl$_3$ 243 K) was equivalent to that at room temperature.

Polymerization of *rac*-Lactide. All complexes prepared were trialed for the polymerization of *rac*-LA, both under solution for 2 and 24 h and under the industrially preferred melt conditions at 130 °C in the absence of a solvent (Tables 2 and 3). All initiators were active for the ROP of *rac*-LA in solution at 80 °C for 24 h.

In general, the Zr(IV) and Hf(IV) complexes appear to offer a greater degree of control, as observed by the lower polydispersity indexes of the resulting polymers, Table 2. Although Hf(**1**)(O^{i}Pr)$_2$ as an initiator was unsuccessful for the production of polymeric material after 2 h, an isotactic oligomeric product was obtained (P_r = 0.2 *via* ^{1}H homonuclear decoupled NMR, which showed an increase in the intensity of the *iii* tetrad). When Hf(**1**)(O^{i}Pr)$_2$ was used for the same reaction over a longer period of time, M_n increased, but the isotactic content had decreased and a P_r value of 0.3 was obtained. (See the Supporting Information for the spectra of the methine region of the ^{1}H homonuclear decoupled NMR and the ^{13}C{^{1}H} NMR spectra, which confirm the presence of isotactic PLA.) Interestingly, with Hf(**2**)(O^{i}Pr)$_2$, atactic PLA was produced under solution conditions. The Zr(IV) complexes produced PLA with a slight heterotactic bias. This illustrates the subtle effect that the ligand−metal combination has on the stereoselectivity for the polymerization of *rac*-lactide. Analysis of the polymers produced with Ti(**1**)(O^{i}Pr)$_2$, Zr(**1**)(O^{i}Pr)$_2$, and Hf(**1**)(O^{i}Pr)$_2$ at 80 °C in solution *via* MALDI-TOF mass spectrometry indicated the presence of the isopropoxide end group, which suggests that the expected coordination−insertion mechanism is in operation. The Ti(IV) and Zr(IV) complexes formed with **1**H$_2$ were shown to be more active than those from **2**H$_2$, as higher conversions were achieved. In the melt, the Zr(IV) complex was shown to be fast with almost a quantitative yield after 15 min for Zr(**1**)(O^{i}Pr)$_2$. Hf(**1**)(O^{i}Pr)$_2$ was much slower than either the Ti(IV) or Zr(IV) analogue but, interestingly, showed a preference for isotactic PLA. It has been shown for a series of amine bis(phenolate) ligands that reduction in the steric bulk of the ortho substituent from a ^{t}Bu to a Me changed the selectivity of the polymerization from atactic to isotactic.[17] Therefore, ligand **3**H$_2$ was prepared and complexed to Hf(IV) in an attempt to increase the isotactic enrichment in the polymer shown by Hf(**1**)(O^{i}Pr)$_2$. Unfortunately, there was no significant increase in the isotacticity of the resulting polymer under melt conditions; however, the rate of the reaction was significantly enhanced with near quantitative conversion in the melt after only 15 min, c.f. 48 h for Hf(**1**)(O^{i}Pr)$_2$. Presumably, the reduction in steric bulk facilitates the coordination of the lactide monomer to the metal center. For Hf(**3**)(O^{i}Pr)$_2$,

Table 2. Solution Polymerization of *rac*-Lactide[a]

initiator	time/h	conv/%[b]	M_n[c]	PDI[c]	P_r[d]
Ti(**1**)(O^{i}Pr)$_2$	2	98	11600	1.45	0.5
Ti(**1**)(O^{i}Pr)$_2$	24	98	9900	1.62	0.5
Ti(**2**)(O^{i}Pr)$_2$	2	69	8500	1.18	0.55
Ti(**2**)(O^{i}Pr)$_2$	24	97	10100	1.82	0.5
Zr(**1**)(O^{i}Pr)$_2$	2	91	10500	1.13	0.6
Zr(**1**)(O^{i}Pr)$_2$	24	99	15800	1.44	0.56
Zr(**2**)(O^{i}Pr)$_2$	24	96	10500	1.09	0.57
Hf(**1**)(O^{i}Pr)$_2$	24	98	8100	1.08	0.30
Hf(**2**)(O^{i}Pr)$_2$	24	96	14300	1.07	0.5
Hf(**3**)(O^{i}Pr)$_2$	24	99	1000	1.43	0.30
Hf(**3**)(O^{i}Pr)$_2$[e]	6	99	8250	1.25	0.25

[a] In all cases, a 100:1 monomer-to-initiator ratio was employed; 0.72 g of monomer was used in all cases, with toluene (10 mL) as the solvent and at 80 °C. [b] Conversion as determined from ^{1}H NMR spectroscopy. [c] Determined from GPC analysis using THF as the solvent. The theoretical molecular weight = (conversion/100) × 100 × 144 + 60. [d] Determined from ^{1}H NMR homonuclear decoupled NMR spectroscopy. Nota bene, Zr(**2**)(O^{i}Pr)$_2$, Hf(**1**)(O^{i}Pr)$_2$, and Hf(**2**)(O^{i}Pr)$_2$ were tested for 2 h but failed to produced any polymer. [e] In this case, the solvent was CH$_2$Cl$_2$ and the temperature = 20 °C.

Table 3. Melt Polymerization of *rac*-Lactide[a]

initiator	time/h	conv/%[b]	M_n[c]	PDI	P_r[d]
Ti(**1**)(O^{i}Pr)$_2$	0.25	89	38000	1.44	0.5
Ti(**2**)(O^{i}Pr)$_2$	0.25	95	43200	1.51	0.5
Zr(**1**)(O^{i}Pr)$_2$	0.25	98	42400	1.19	0.57
Zr(**2**)(O^{i}Pr)$_2$	0.25	52	8700	1.07	0.56
Hf(**1**)(O^{i}Pr)$_2$	48	75	24400	1.32	0.30
Hf(**2**)(O^{i}Pr)$_2$	24	96	46600	1.49	0.5
Hf(**3**)(O^{i}Pr)$_2$	0.25	99	7700	1.45	0.30

[a] In all cases, a 300:1 monomer-to-initiator ratio was employed; 2.0 g of monomer was used, with the temperature = 130 °C. [b] Conversion as determined from ^{1}H NMR spectroscopy. [c] Determined from GPC analysis using THF as the solvent. The theoretical molecular weight = (conversion/100) × 300 × 144 + 60. [d] Determined from ^{1}H NMR homonuclear decoupled NMR spectroscopy.

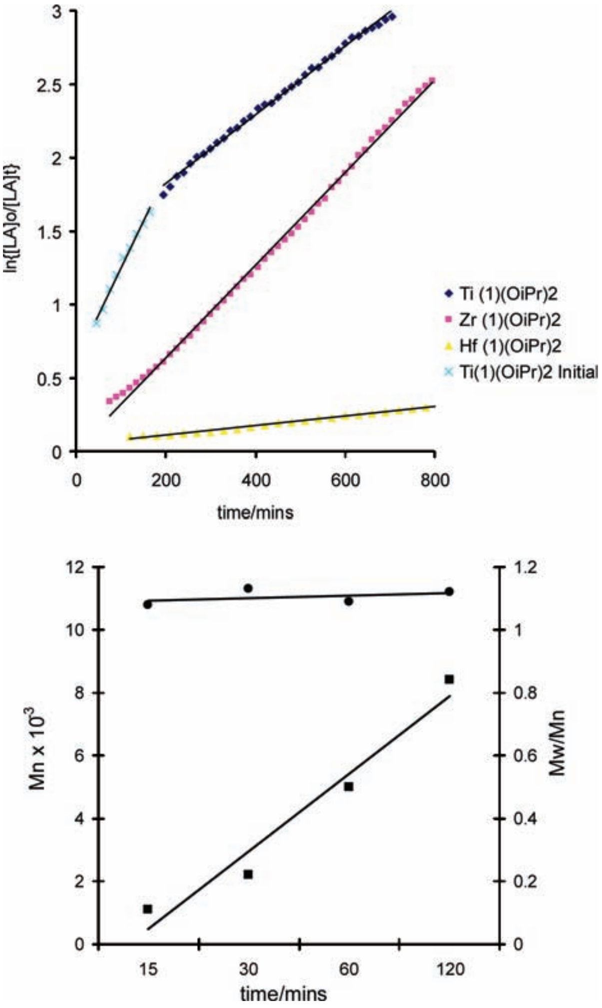


Figure 2. (Top) Kinetic measurements for the solution polymerization of *rac*-LA with Ti(**1**)(O^{i}Pr)$_2$, Zr(**1**)(O^{i}Pr)$_2$, and Hf(**1**)(O^{i}Pr)$_2$ at 80 °C. The equations of the lines are Ti(**1**)(O^{i}Pr)$_2$ initial $y = 0.0064x + 0.6117$, $R^2 = 0.99$; Ti(**1**)(O^{i}Pr)$_2$ $y = 0.0022x + 1.4024$, $R^2 = 0.9906$; Zr(**1**)(O^{i}Pr)$_2$ $y = 0.0031x + 0.0101$, $R^2 = 0.9978$; Hf(**1**)(O^{i}Pr)$_2$ $y = 0.0003x + 0.0391$, $R^2 = 0.9969$. (Bottom) A plot of M_n (squares) and M_w/M_n (circles) versus time for Zr(**1**)(O^{i}Pr)$_2$.

the molecular weights of the polymers (both in solution and under melt conditions) were lower than expected for one polymer chain growing per metal center. In this case, due to the reduction in steric bulk of the ligand, the lower molecular weights may be due to more than one polymer chain growing per metal center. Due to the high activity of Hf(**3**)(O^{i}Pr)$_2$, transesterification processes maybe prevalent, reducing the control the initiator provides for the molecular weight.[47] To achieve a controlled molecular weight, the polymerization was carried out at room temperature for 6 h in CH_2Cl_2. In this case, a M_n of 8250 was observed, and a polymer had a $P_r = 0.25$.

To study the polymerization further, Zr(**1**)(O^{i}Pr)$_2$ was employed as an initiator in a time study to investigate the living character of the polymerization, Figure 2. It can be seen that as time increased, M_w/M_n remained constant while M_n increased linearly, supporting the idea that the polymerization is well-controlled. The kinetics for the polymerization using Ti(**1**)(O^{i}Pr)$_2$, Zr(**1**)(O^{i}Pr)$_2$, and Hf(**1**)(O^{i}Pr)$_2$ as the initiators were investigated at 80 °C by ^{1}H NMR spectroscopy in $C_6D_5CD_3$, Figure 2; see the Supporting Information for data for Ti/Zr/Hf(**2**)(O^{i}Pr)$_2$ and Hf(**3**)(O^{i}Pr)$_2$. The apparent rate of propagation (k_{app}) can be determined by analysis of a semilogarithmic plot of $\ln\{[LA]_o/[LA]_t\}$ vs time, where $[LA]_o = 0.578$ mol dm^{-3} with a monomer/initiator ratio of 100:1. The pseudo-first-order rate constant for Hf(**1**)(O^{i}Pr)$_2$ was 3.0×10^{-4} min^{-1}, and Zr(**1**)(O^{i}Pr)$_2$ was found to be 10 times faster with $k_{app} = 3.2 \times 10^{-3}$ min^{-1},[20] the latter being similar in magnitude to Ti(salen)(O^{i}Pr)$_2$ complexes prepared by Gibson et al.,[20] whose fastest initiator afforded a k_{app} of 3.7×10^{-3} min^{-1}, albeit at 70 °C. Interestingly, the Ti(**1**)(O^{i}Pr)$_2$ initiated system revealed two reaction regimes. Initially, the polymerization proceeds with a k_{app} of 6.4×10^{-3} min^{-1}, which is significantly faster than literature values. However, after ca. 3 h, the polymerization slows significantly, to afford a k_{app} of 2.2×10^{-3} min^{-1}. This could be due to the mass transport limitations in the NMR tube as the viscosity of the polymerization increases, or alternatively the polymer could wrap around the metal center, hindering the approach of the monomer to the active center. A similar trend was observed with complexes Ti(**2**)(O^{i}Pr)$_2$ (5.5×10^{-3} min^{-1} initial and 3.0×10^{-3} min^{-1} in the second regime), Zr(**2**)(O^{i}Pr)$_2$ (2.6×10^{-3} min^{-1}), and Hf(**2**)(O^{i}Pr)$_2$ (0.7×10^{-3} min^{-1}). When the kinetics were investigated for Hf(**3**)(O^{i}Pr)$_2$ at 80 °C in C_6D_5-CD_3, a rate of 1.2×10^{-2} min^{-1} was observed; however, it was clear under these conditions that the catalysis was proceeding too fast for this to be a reliable method to determine k_{app}, as a conversion of 60% was observed after the first 15 min. It was decided to perform the same experiment at room temperature (for lactide solubility reasons, it was necessary to perform this in $CDCl_3$), and in this experiment, a k_{app} of 4.6×10^{-3} min^{-1} was obtained (see the Supporting Information). For L-lactide, Hf(**3**)(O^{i}Pr)$_2$ affords a k_{app} of 7.5×10^{-3} min^{-1}. For comparison, the fastest titanium complex {Ti(**1**)(O^{i}Pr)$_2$} was tested in $CDCl_3$ at room temperature, and in this case, no polymer was detected. Hf(**3**)(O^{i}Pr)$_2$ is complementary to the previously reported Zr(IV) amine tris(phenolate)[16] complex, which has a k_{app} of 4.2×10^{-3} min^{-1} for *rac*-lactide, but in this case, isotactic PLA is formed.

Conclusion

In conclusion, seven new group 4 metal complexes have been prepared with salalen ligands, and all complexes have been characterized *via* single-crystal X-ray diffraction. These complexes were shown to initiate the ring-opening polymerization of *rac*-lactide in a controlled manner, and several systems were also able to control the tacticity of the resulting polymer. Further experiments are on-going to probe the kinetics of the polymerizations.

Experimental Section

General Procedures. For the preparation and characterization of metal complexes, all reactions and manipulations were performed under an inert atmosphere of argon using standard Schlenk or glovebox techniques. Ti(O^{i}Pr)$_4$ (97% Aldrich) was purified by vacuum distillation prior to use; Zr(O^{i}Pr)$_4$^{i}PrOH (99.9%, Aldrich) and Hf(O^{i}Pr)$_4$^{i}PrOH (99.9%, Strem) were used without further purification. *rac*-LA (Aldrich) was recrystallized from toluene and sublimed twice prior to use. All other chemicals were purchased from Aldrich. All solvents used in the preparation of metal complexes and polymerization reactions

Table 4. Crystallographic Details for Ti(**1**)(O^{i}Pr)$_2$, Ti(**2**)(O^{i}Pr)$_2$, Zr(**1**)(O^{i}Pr)$_2$, Zr(**2**)(O^{i}Pr)$_2$, Hf(**1**)(O^{i}Pr)$_2$, Hf(**2**)(O^{i}Pr)$_2$, and Hf(**3**)(O^{i}Pr)$_2$

complex	Ti(**1**)(O^{i}Pr)$_2$	Ti(**2**)(O^{i}Pr)$_2$	Zr(**1**)(O^{i}Pr)$_2$	Zr(**2**)(O^{i}Pr)$_2$
empirical formula	$C_{39}H_{64}N_2O_4Ti_1$	$C_{44}H_{66}N_2O_4Ti_1$	$C_{39}H_{64}N_2O_4Zr_1$	$C_{44}H_{66}N_2O_2Zr_1$
formula weight	672.82	734.89	716.14	778.21
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$	$C2/c$
a/Å	14.5370(3)	24.0590(3)	14.6670(2	24.3950(3)
b/Å	20.9780(4)	18.0360(3)	21.1850(4)	17.9500(3)
c/Å	14.0970(2)	20.0870(3)	14.0480(3)	20.0070(3)
α/deg	90	90	90	90
β/deg	114.437(1)	102.740(1)	114.037(1)	102.602(1)
γ/deg	90	90	90	90
volume/Å^3	3913.86(12)	8501.7(2)	3986.5(1)	8549.8(2)
Z	4	8	4	8
Dcalc/gcm^{-3}	1.142	1.148	1.193	1.209
μ/mm^{-1}	0.257	0.242	0.314	0.298
reflns collected	51088	18758	84036	82109
θ range/deg	3.72−26.01	3.85−27.47	3.52−27.50	3.61−27.48
indep. reflns (R_{int})	7670, 0.0767	9698, 0.0265	9117, 0.0638	9779, 0.1021
goodness-of-fit	1.000	1.024	1.051	1.131
R_1, wR_2 [$I > 2\sigma(I)$]	0.0408, 0.0960	0.0398, 0.0930	0.0333, 0.0767	0.0599, 0.1115
R_1, wR_2 [all data]	0.0651, 0.1105	0.0587, 0.1030	0.0474, 0.0829	0.0953, 0.1229
max, min difference/e Å^{-3}	0.237, −0.379	0.294, −0.395	0.593, −0.599	0.832, −0.835

complex	Hf(**1**)(O^{i}Pr)$_2$	Hf(**2**)(O^{i}Pr)$_2$	Hf(**3**)(O^{i}Pr)$_2$
empirical formula	$C_{39}H_{64}N_2O_4Hf_1$	$C_{44}H_{66}N_2O_4Hf_1$	$C_{38}H_{64}N_2O_4Hf_1$
formula weight	803.41	865.48	791.40
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$C2/c$	$P2_1/c$
a/Å	14.0610(1)	24.3640(2)	11.0520(1)
b/Å	21.1280(2)	17.9370(2)	24.7750(3)
c/Å	14.6510(1)	20.0680(2)	14.5020(2)
α/deg	90	90	90
β/deg	114.080(2)	102.801(1)	97.668(1)
γ/deg	90	90	90
volume/Å^3	3973.8(5)	8552.1(2)	3935.33(8)
Z	4	8	4
Dcalc/gcm^{-3}	1.342	1.344	1.336
μ/mm^{-1}	2.662	2.480	2.688
reflns collected	73379	65155	56183
θ range/deg	3.52−27.48	3.86−27.49	2.91−27.48
indep. reflns (R_{int})	9085, 0.0462	9780, 0.0730	8956, 0.0972
Goodness-of-fit	1.073	1.076	1.063
R_1, wR_2 [$I > 2\sigma(I)$]	0.0246, 0.0563	0.0327, 0.0715	0.0347, 0.0679
R_1, wR_2 [all data]	0.0312, 0.0592	0.0444, 0.0798	0.0544, 0.0743
max, min difference/e Å^{-3}	1.504, −0.947	0.973, −1.762	0.955, −1.466

were dry and obtained *via* SPS (solvent purification system). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker 250, 300, or 400 MHz instrument and referenced to residual solvent peaks. Coupling constants are given in hertz. Elemental analyses were performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath. The ligands were prepared according to standard literature procedures and the purity confirmed *via* ^{1}H/^{13}C{^{1}H} NMR and HR-MS prior to use.

Synthesis of Ligands. A typical ligand synthesis is as follows. **1**H$_2$: A solution of 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.23 g, 0.01 mol) and N-methyl-ethylenediamine (1.02 g, 1.2 mL, 0.01 mol) in methanol (20 mL) was prepared. The solution was stirred until a clear solution was observed and left to stand for 24 h to yield a yellow oil, which was collected and dried (2.68 g, 66%). The oil (1 g, 3.44 mmol) was dissolved in THF (20 cm^3), to which a solution of 3,5-di-*tert*-2-hydroxybenzyl bromide (1.03 g, 3.44 mmol) in THF (20 cm^3) was added. Triethylamine (0.35 g, 0.48 mL, 3.44 mmol) was added and the mixture stirred at 80 °C for 3 h. The white precipitate was filtered and the solvent removed under reduced pressure. The product was isolated *via* flash chromatography (CH_2Cl_2) to obtain the product (1.33 g, 76%). ^{1}H NMR ($CDCl_3$): 1.29 (9H, s, C(CH_3)$_3$), 1.32 (9H, s, C(CH_3)$_3$), 1.39 (9H, s, C(CH_3)$_3$), 1.46 (9H, s, C(CH_3)$_3$), 2.40 (3H, s, CH_3), 2.85 (2H, t J = 6.5 Hz, CH_2), 3.76 (2H, s, CH_2), 3.78 (2H, t J = 6.5 Hz, CH_2), 6.84 (1H, d J = 2.5 Hz, Ar−H), 7.09 (1H, d J = 2.5 Hz, Ar−H), 7.22 (1H, d J = 2.5 Hz, Ar−H), 7.40 (1H, d J = 2.5 Hz, Ar−H), 8.39 (1H, s, CH). m/z calcd for $C_{33}H_{53}N_2O_2$ = 509.4107. Found: 509.4145

Synthesis and Characterization of the Complexes. A typical example for the preparation of a complex is as follows. Zr(**2**)(O^{i}Pr)$_2$: Zr(O^{i}Pr)$_4$^{i}PrOH (0.5 g, 1.28 mmol) was dissolved in toluene (20 cm^3), to which **2**H$_2$ (0.731 g, 1.28 mmol) was added. This was stirred for 2 h, after which time the solvent was removed *in vacuo*, and the product was recrystallized in hexane. After 4 days at −20 °C, a crop of crystals was obtained, which were filtered and dried. ^{1}H ($CDCl_3$): 0.43 (3H, d J = 5 Hz, CH_3 isopropoxide), 0.51 (3H, d J = 5 Hz, CH_3 isopropoxide), 1.19 (9H, s, C(CH_3)$_3$), 1.25−1.30 (18H, m, C(CH_3)$_3$), 1.30−1.35 (6H, m, CH_3 isopropoxide), 1.53 (9H, s, C(CH_3)$_3$), 3.26 (1H, sept J = 5.5 Hz, CH isopropoxide), 3.38 (1H, t J = 11 Hz, CH_2), 3.44 (1H, m, CH_2), 3.64 (1H, d J = 13 Hz, CH_2), 3.79 (1H, t J = 11 Hz, CH_2), 4.60 (1H, sept J = 5.5 Hz, CH isopropoxide), 5.09 (1H, d J = 13 Hz, CH_2), 6.83 (1H, s, Ar−H), 6.95 (1H, s, Ar−H), 7.19−7.24 (2H, m, Ar−H), 7.40−7.49 (3H, m, Ar−H), 7.72 (2H, d J = 8 Hz, Ar−H), 7.97 (1H, s, CH). ^{13}C{^{1}H} ($CDCl_3$): 26.3, 27.3 (CH_3 isopropoxide), 29.3, 29.6, 31.5, 31.8 (C(CH_3)$_3$), 33.9, 34.0, 34.8, 35.3 (C(CH_3)$_3$), 52.2, 58.2, 68.6 (CH_2), 69.6, 70.8 (CH isopropoxide), 121.5 (Ar−C), 122.0 (Ar−CH), 123.1 (Ar−C), 123.9, 124.0, 125.2, 127.8, 128.9, 129.2 (Ar−CH), 136.7, 137.6, 138.4, 138.6, 152.3 (Ar−C), 159.4, 159.8 (Ar−O), 165.2 (CH). Anal Calcd for $C_{44}H_{66}N_2O_4Zr$: C, 67.90; H, 8.55; N, 3.60. Found: C, 67.1; H, 8.57; N, 3.56.

X-Ray Crystallography. Crystallographic data are summarized in Table 4. All data were collected on a Nonius Kappa CCD area detector diffractometer using Mo Kα radiation (λ = 0.71073 Å) at a temperature of 150(2) K, and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs.[51] Refinement was straightforward with the following noteworthy points: For Ti(**1**)(O^{i}Pr)$_2$, two ^{t}Bu groups showed disorder over two positions in an 70:30 ratio, and in Ti(**2**)(O^{i}Pr)$_2$, a ^{t}Bu group showed disorder over two positions in a 60:40 ratio. For Zr(**1**)(O^{i}Pr)$_2$, ^{t}Bu groups showed disorder over two positions in a 70:30 ratio, and for Zr(**2**)(O^{i}Pr)$_2$, a ^{t}Bu group showed disorder over two positions in a 50:50 ratio. For Hf(**1**)(O^{i}Pr)$_2$, a ^{t}Bu group showed disorder over two positions in a 65:35 ratio. For Hf(**2**)(O^{i}Pr)$_2$, two ^{t}Bu groups were disordered over two positions in a 60:40 ratio. Hydrogen atoms were included in idealized positions and refined using the riding model. Data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Polymerization Procedure. For solvent-free polymerizations, the monomer/initiator ratio employed was 300:1 at a temperature of 130 °C. In all cases, 2 g of *rac*-lactide were used. After the reaction time, methanol (20 mL) was added to quench the reaction, and the resulting solid was dissolved in dichloromethane. The solvents were removed *in vacuo*, and the resulting solid was washed with copious amounts of methanol to remove any unreacted monomer. ^{1}H NMR spectroscopy ($CDCl_3$) and GPC (THF) were used to determine tacticity and molecular weights (M_n and M_w) of the polymers produced; P_r values (the probability of heterotactic linkages) were determined by analysis of the methine region of the homonuclear decoupled ^{1}H NMR spectra. The equations used to calculate P_r and P_m are given by Coates et al.[21] ^{1}H homonuclear decoupled spectra are given in the Supporting Information. Gel permeation chromatography (GPC) analyses were performed on a Polymer Laboratories PL-GPC 50 integrated system using a PLgel 5 μm MIXED-D 300 × 7.5 mm column at 35 °C, with THF solvent (flow rate, 1.0 mL/min). The polydispersity index (PDI) was determined from M_w/M_n, where M_n is the number average molecular weight and M_w the weight average molecular weight. The polymers were referenced to 11 narrow molecular weight polystyrene standards with a range of M_w 615−568 ,000 Da.

Acknowledgment. We gratefully acknowledge the EPSRC (National mass spectrometry service center Swansea), the University of Bath, and Johnson Matthey for funding.

Supporting Information Available: ^{1}H homonuclear decoupled NMR spectra, crystal data in .cif format, full experimental procedures, and further kinetic details. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(51) Sheldrick, G. M. *SHELXL-97*; Institute for Anorganische University of Göttingen: Göttingen, Germany, 1998.