Group 4 Complexes with Aminebisphenolate Ligands and Their Application for the Ring Opening Polymerization of Cyclic Esters

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ABSTRACT: A series of tetradentate amine(bisphenolate) ligands have been synthesized and complexed to Ti(IV), Zr(IV), and Hf(IV) centers. Two distinct ligand sets have been synthesized both exhibiting ONNO coordination. The steric bulk of the ligands was varied to assess the impact of sterics on the catalytic performance in the ring-opening-polymerization (ROP) of cyclic esters. In all cases the metal centers are pseudo octahedral in geometry. Several group 4 amine(bisphenolate) complexes have been characterized by single-crystal X-ray diffraction. The complexes were tested for the ROP of ϵ-caprolactone and L/*rac*-lactide, with significant activity seen for complexes of all group 4 metals. For Ti(IV), complexes of sterically demanding ligands were more effective initiators, whereas sterically less demanding ligands were more successful for Zr(IV) complexes. Copolymers of poly(ϵ-caprolactone) and poly-L-lactide were produced utilizing the Zr(IV) initiators. The polymerization of *rac*-lactide was also studied allowing stereoselectivity of a range of metal−ligand combinations to be assessed. Isotactic polymer was produced with both Zr(IV) and Hf(IV) centers whereas Ti(IV) produced an atactic polymer.

Introduction

Several reports detail the utilization of titanium compounds as initiators for the ring-opening-polymerization (ROP) of cyclic esters.[1−8] However, comparatively few studies have hitherto been published utilizing the heavier group 4 metals zirconium and hafnium, and to the best of our knowledge a comparison of all three group 4 metals using the same ligand sets has not been undertaken.[9−13] There is an exigent need to form high molecular weight aliphatic polyesters since these biodegradable[14] polymers are available from renewable resources and are therefore promising as environmentally friendly alternatives for a range of current commodity polymers.[15] For polyester production the catalysis needs to be controlled with, for example, the ability to achieve a narrow molecular weight distribution and stereo-regularity.[16] These prerequisites for the polymer should be achievable using well characterized, discrete single site catalytic centers. To this end, several groups have reported the formation of both heterotactic ($(SSRR)_n = isi/sis$) and isotactic stereoblock ($(RR)_n(SS)_n = (i)_ns(i)_n$ polymers by the well-controlled metal alkoxide-catalyzed ROP of *rac*-lactide. Chisholm et al utilized chiral aluminum complexes[17,18] and formed predominantly isotactic polymer. The same group also utilized calcium, magnesium and zinc catalysts to form heterotactic PLA;[19] Gibson et al.[20−22] used aminophenoxide ligands bound to aluminum and found that subtle changes in the ligand periphery dramatically influenced the stereochemistry of the resulting polymer; Coates et al.[23−25] used magnesium, aluminum, yttrium, zinc and magnesium based systems to induce stereoselectivity in the polymer. Feijen et al.[26,27] reported aluminum salen complexes and formed predominantly isotactic stereoblock PLA.

Herein, we report the synthesis and structural characterization of a series of group 4 metal complexes of aminebisphenolate ligands[28,29] and their use in the ROP of cyclic esters (ϵ-caprolactone and L/*rac*-lactide). Previous investigations based on Ti(IV) complexes of bis(phenolate)s have shown that bulky ligands are more effective than sterically unhindered ligands[4] and our results support these conclusions. However, in contrast, we also show that sterically *less* demanding ligands are more effective initiators in combination with Zr(IV) centers, and that the use of these Zr(IV) (and Hf(IV)) complexes result in significant stereoselective polymerization of *rac*-lactide. Finally, we demonstrate the utility of one of our initiators for the one-pot copolymerization of ϵ-caprolactone and L-lactide, a copolymer that is of importance for drug delivery systems as it combines the rapid biodegradation of polylactide (PLA) with the greater permeability of polycaprolactone (PCL).[30−34]

Experimental Section

General Considerations. The ligands **1aH$_2$** and **1bH$_2$**,[35,36] **1cH$_2$**,[37,38] **2aH$_2$**,[39] and **2bH$_2$**[36] were prepared according to standard literature procedures. Ligand **2cH$_2$** was prepared by a similar procedure (see Supporting Information for details). 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. All solvents were freshly distilled from suitable drying agents and degassed prior to use (toluene over sodium/benzophenone and dichloromethane over calcium hydride, hexane was eluted over activated alumina columns and stored under argon). $Ti(O^iPr)_4$ (97%, Aldrich) was purified by vacuum distillation prior to use, $Zr(O^iPr)_4{}^iPrOH$ (99.9%, Aldrich)

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Table 1. Crystal Data for the Structures Reported

	Ti(O^{i}Pr)$_2$**1c**	Ti(O^{i}Pr)$_2$**2a**	Ti(O^{i}Pr)$_2$**2b**	Zr(O^{i}Pr)$_2$**2a**	Zr(O^{i}Pr)$_2$**2b**	Hf(O^{i}Pr)$_2$**2b**	ligand **2aH$_2$**
formula	$C_{25}H_{36}Cl_2N_4O_8Ti$	$C_{30}H_{40}N_2O_4Ti$	$C_{87}H_{135}N_4O_8Ti_2$	$C_{30}H_{42}N_2O_4Zr$	$C_{42}H_{64}N_2O_4Zr$	$C_{42}H_{64}HfN_2O_4$	$C_{24}H_{28}N_2O_2$
fw	639.38	540.54	1460.7	583.86	752.17	839.44	376.48
cryst syst	monoclinic	tetragonal	triclinic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	$P2_1/n$	$I4_1/a$	$P\bar{1}$	$P2_1/c$	$P2_1/n$	$P2_1/c$	$Pna2_1$
a (Å)	11.804(1)	25.548(1)	13.330(3)	14.585(2)	11.079(1)	11.1038(2)	12.593(2)
b (Å)	12.783(1)	25.548(1)	18.809(4)	14.293(2)	20.281(2)	20.2199(3)	9.041(1)
c (Å)	19.755(2)	18.319(1)	18.947(4)	15.668(2)	18.947(2)	18.9272(3)	36.256(6)
α (deg)	90	90	102.409(1)	90	90	90	90
β (deg)	90.974(1)	90	101.825(1)	109.707(1)	97.383(1)	97.343(1)	90
γ (deg)	90	90	105.297(1)	90	90	90	90
vol (Å^3)	2980.41(5)	11956.82(9)	4299.08(16)	3074.90(7)	4221.97(7)	4214.64(1)	4127.87(1)
Z	4	16	2	4	4	4	8
D_{calc} (g cm^{-3})	1.425	1.201	1.128	1.261	1.183	1.323	1.212
no. of reflcns collcd	32 260	83 000	68 617	34 306	62 147	97 741	49 469
no. of indep reflcns (R_{int})	6817 (0.0362)	6796 (0.0487)	19543 (0.1020)	8071 (0.1370)	6614 (0.1176)	12300 (0.0748)	5226 (0.0777)
goodness-of-fit	1.051	1.045	1.173	1.155	1.047	1.013	0.983
R_1, wR_2 [$I > 2\sigma(I)$]^a	0.0472, 0.1265	0.0484, 0.1287	0.0992, 0.1708	0.0745, 0.2173	0.0501, 0.0905	0.0323, 0.0620	0.0495, 0.1044
R_1, wR_2 (all data)^a	0.0536, 0.1313	0.0621, 0.1476	0.1444, 0.1861	0.0915, 0.2343	0.0728, 0.0976	0.0649, 0.0695	0.1141, 0.1247
Flack param	−	−	−	−	−	−	−0.2(12)^b

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR_2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$. [b] Flack, H. D. *Acta. Crystallogr.* **1983**, *A39*, 876−881.

and Hf(O^{i}Pr)$_4$^{i}PrOH (99%, Strem) were used without further purification. ε-Caprolactone (99% Aldrich) was purified via vacuum distillation and degassed prior to use. L-lactide (98%, Aldrich) and *rac*-lactide (98%, Aldrich) were recrystallized from dry toluene and sublimed twice. ^{1}H/^{13}C NMR spectra were recorded on a Bruker 300 or 400 MHz spectrometer and referenced to residual protio and ^{13}C solvent peaks. Coupling constants are given in hertz. Elemental analysis was performed by Mr. A. K. Carver at the Department of Chemistry, University of Bath, on an Exeter Analytical CE440 Elemental analyzer. Thermal analyses were performed using Differential Scanning Calorimetry (DSC; Perkin-Elmer Pyris 1) using helium as the purge gas and indium (T_m 156.6 °C) and octane (T_m −56 °C) as calibrations standards. The reported melting temperature (T_m) and crystallization temperature (T_c) were obtained from the peak maxima obtained from a second heating cycle of the materials. The glass transition temperature (T_g) was taken as the midpoint of the transition determined for the second heating cycle. The protocol employed is detailed 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, 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 615−5680000 Da.

Crystallography. Data were collected at 150 K on a Nonius KappaCCD area detector diffractometer using Mo−Kα radiation ($\lambda = 0.71073$ Å), and all structures were solved by direct methods and refined on all F^2 data using SHELXL-97 suite of programs, with hydrogen atoms included in idealized positions and refined using the riding model; see Table 1 for the crystallographic parameters.[40]

Synthesis of Metal Complexes. An exemplary synthetic procedure for Ti(O^{i}Pr)$_2$**1a** is given below. Full details of synthesis and characterization of all new ligands and metal complexes are given in the Supporting Information.

Ti(O^{i}Pr)$_4$ (0.50 mL, 1.7 mmol) was added to dichloromethane (20 mL), to which the ligand (603 mg, 1.7 mmol) was added with vigorous stirring. After 1 h the solvent was removed in-vacuo and the resulting solid was washed with hexane (2 × 20 mL) and dried in vacuo. The complex was recrystallized from a hexane/dichloromethane mixture. Yield: 0.71 g, 80%. Anal. Calcd for $C_{28}H_{44}N_2O_4$-Ti: C, 64.62; H, 8.46; N, 5.38. Found: C, 64.97; H, 8.02; N 5.12. ^{1}H NMR (CDCl$_3$): 1.21 (d, J = 6 Hz, 6H, CH(CH_3)$_2$), 1.30 (d, J = 6 Hz, 6H, CH(CH_3)$_2$), 1.73 (d, J = 9.5 Hz, 2H, N−CH$_2$), 2.22 (s, 6H, CH$_3$), 2.25 (s, 6H, CH$_3$), 2.41 (s, 6H, NCH$_3$), 3.05 (d, J = 9.5 Hz, 2H, N−CH$_2$), 3.06 (d, J = 13 Hz, 2H, N−CH$_2$), 4.70 (d, J = 13 Hz, 2H, N−CH$_2$), 5.19 (sept, J = 6 Hz, 2H, CH(CH$_3$)$_2$), 6.64 (d, J = 1.5 Hz, 2H, Ar), 6.90 (d, J = 1.5 Hz, 2H, Ar). ^{13}C NMR (CDCl$_3$): 17.2 (CH$_3$), 20.5 (CH$_3$), 26.2 (C(CH_3)$_2$), 26.5 (C(CH_3)$_2$), 46.9 (N−CH$_3$), 51.5, 64.6 (N−CH$_2$), 77.2 (CH(CH$_3$)$_2$), 123.6, 125.0, 125.9, 127.6, 130.8, (Ar), 158.2 (Ar−O).

Polymerization of Cyclic Esters. Solution Polymerization of ε-Caprolactone: In a typical run, the initiator (0.1 mmol) was dissolved in toluene (10 mL) to which ε-caprolactone (10.0 mmol, 1.11 mL) was added. This was left to stir at room temperature for 24 h, after which time the catalysis was quenched using a 30% acetic acid aqueous solution. The polymer was then precipitated using hexane, filtered, washed with copious amounts of hexane and dried in-vacuo. For example with Zr(O^{i}Pr)$_2$**1a**: the initiator (56.3 mg, 0.1 mmol) was dissolved in toluene (10 mL) to which ε-caprolactone (1.11 mL, 10.0 mmol) was added. This was allowed to stir at room temperature for 24 h. The polymerization was quenched with a 30% acetic acid(aq) (20 mL) and filtered, the resulting white solid was washed with hexane (3 × 50 mL) and dried in-vacuo, to yield polycaprolactone (1.1 g, 99%). GPC results M_n = 12 000, M_w = 18800, PDI = 1.59. Typical ^{1}H NMR analysis of PCL: 1.15 (d, J = 6 Hz, CH(CH_3)$_2$ end group), 1.3 (m, 2H, CH_2 backbone), 1.6 (m, 4H, CH_2 backbone), 2.2 (m, 2H, CH_2 backbone), 3.6 (t, −CH_2OH end group), 4.0 (m, 2H, OCH_2 backbone), 4.9 (sept, J = 6 Hz CH(CH$_3$)$_2$ end group).

Solution Polymerization of L-Lactide. In a typical run the initiator (0.1 mmol) was dissolved in toluene (10 mL) to which L-lactide (10.0 mmol, 1.44 g) was added and the vessel was heated to 110 °C for 2 h. The vessel was then exposed to air to terminate the polymerization. The polymer was precipitated with pentane and washed with copious amounts of pentane and dried in vacuo. The conversion was determined via ^{1}H NMR (C_6D_6) by integration of the monomer methine region at 3.8 ppm and the polymer methine at 5.1 ppm.

Solution Copolymerization of L-Lactide and ε-Caprolactone. The initiator (0.1 mmol) was dissolved in toluene (10 mL) to which ε-caprolactone (10.0 mmol, 1.11 mL) was added, this was left to stir at room temperature for 24 h, after which time L-lactide (10.0 mmol, 1.44 g) was added and the mixture heated to 110 °C for 2 h. The catalysis was quenched using a 30% acetic acid(aq) solution and the polymer precipitated using hexane, filtered, washed with copious amounts of hexane and dried in vacuo.

Solventless Polymerization of *rac*-Lactide. For solventless 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 (2 or 24 h) 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$_3$ or C_6D_6) and GPC (THF) were used to determine conversions and

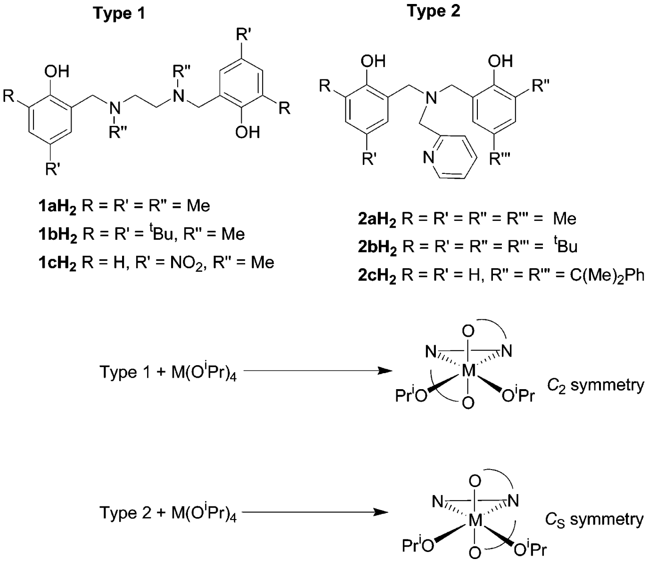

Figure 1. Ligands used in this study, which fall into two general structural motifs.

molecular weights (M_n and M_w) of the polymers produced; P_r and P_m (the probability of hetero and isotactic 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.[24] For example, with Zr(O^{i}Pr)$_2$**1a**: the initiator (25.9 mg, 0.046 mmol) was added to the reaction vessel together with *rac*-lactide (2.0 g, 14 mmol) and heated at 130 °C for 2 h. Methanol (20 mL) was then added and dichloromethane (50 mL) was added to dissolve the mixture. The volatiles were removed in vacuo and the white solid was washed with methanol (3 × 100 mL) and dried, to afford polylactide as a white solid (1.1 g, 55%). GPC results $M_n = 6050$, $M_w = 8900$, PDI = 1.47, the ^{1}H homonuclear decoupled NMR showed this to be isotactic PLA with $P_m = 0.7$.

Results and Discussion

Synthesis and Characterization of Metal Complexes: The ligands utilized in this study fall into two general types (Figure 1) and were chosen for their ease of synthesis employing standard literature preparations, allowing facile variation of steric factors and coordination geometry.[29,35−38,41] These were complexed to titanium, zirconium and hafnium by reaction with 1 equiv of Ti(O^{i}Pr)$_4$ or Zr/Hf(O^{i}Pr)$_4$^{i}PrOH, respectively.[29,35,42] The range of complexes synthesized permits comparisons in structure and reactivity to be drawn between (i) different metals (Ti vs Zr vs Hf), (ii) differing steric demand of ligands (e.g., **1a** vs **1b** vs **1c**), and (iii) the effect of different *N,N'*-ligand binding modes (e.g., **1a** vs **2a**).

All complexes were characterized by ^{1}H, ^{13}C NMR spectroscopy, elemental analysis and Ti(O^{i}Pr)$_2$**1c**, Ti(O^{i}Pr)$_2$**2a**, Ti(O^{i}Pr)$_2$**2b**, Zr(O^{i}Pr)$_2$**2a**, Zr(O^{i}Pr)$_2$**2b**, and Hf(O^{i}Pr)$_2$**2b** were characterized by single-crystal X-ray diffraction together with ligand **2aH$_2$**. Taken together, this structural study represents the first structural characterization of a homologous series of group 4 complexes for these ligand types. Representative crystal structures for Ti(O^{i}Pr)$_2$**1c** and Ti(O^{i}Pr)$_2$**2a** are shown in Figure 2. In all solid-state structures the metal center adopts a pseudo octahedral geometry in which the phenoxide oxygen atoms assume a trans configuration. The ligand geometries favor mutually cis N atoms which results in the two isopropoxide ligands being cis with respect to each other and trans to nitrogen. Selected bond angles and distances are given in Table 2, and are normal for group 4 amino(phenolates).[39,43−46] For Zr(O^{i}Pr)$_2$**2b** and Hf(O^{i}Pr)$_2$**2b**, the M−O bond lengths are very similar; however, there is a slight but significant shortening of the M−N bond lengths on moving from Zr to Hf. A similar trend was observed in the only other series of group 4 metal amino(phenolates) to be reported.[5] Figure 3 shows a overlay of the Ti(IV) and Hf(IV) complexes of ligand **2b** highlighting their similarity.

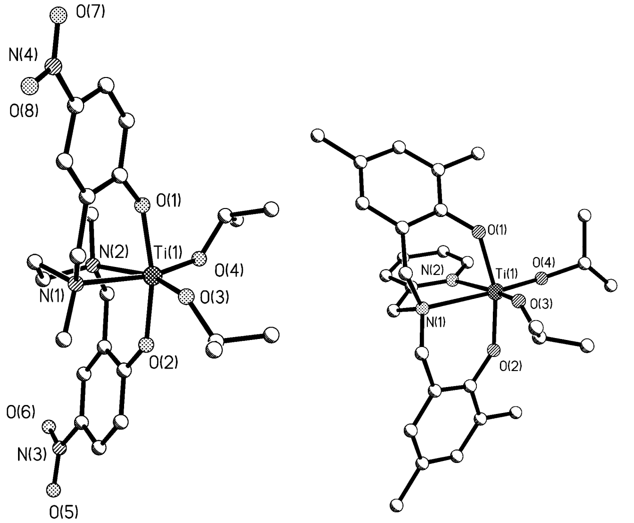

Figure 2. Molecular structure of complexes Ti(O^{i}Pr)$_2$**1c** and Ti(O^{i}Pr)$_2$**2a**. All hydrogen atoms are omitted for clarity, as are lattice solvent molecules. The numbering system employed is that used for the other complexes. For Ti(O^{i}Pr)$_2$**2a**, one isopropoxide is disordered over two sites; only one is shown in the figure.

The ^{1}H and ^{13}C NMR spectra for all complexes are consistent with the solid-state structures and no fluxional processes were apparent at room temperature. For example, the methylene groups appear as discrete doublets, in agreement with rigid chelates on the NMR time scale, as shown previously in the literature for similar complexes.[35,42]

Solution Polymerization of ϵ-Caprolactone. The Ti(IV) and Zr(IV) complexes were screened for the ROP of ϵ-caprolactone at room temperature (initiator-to-monomer ratio 1:100, time 24 h). Of the nine complexes four were active for the polymerization and the results are given in Table 3.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes Ti(O^{i}Pr)$_2$1c, Ti(O^{i}Pr)$_2$2a, Ti(O^{i}Pr)$_2$2b, Zr(O^{i}Pr)$_2$2a, Zr(O^{i}Pr)$_2$2b, and Hf(O^{i}Pr)$_2$2b

	Ti(O^{i}Pr)$_2$**1c**	Ti(O^{i}Pr)$_2$**2a**	Ti(O^{i}Pr)$_2$**2b**	Zr(O^{i}Pr)$_2$**2a**	Zr(O^{i}Pr)$_2$**2b**	Hf(O^{i}Pr)$_2$**2b**
M1−O1	1.921(1)	1.918(2)	1.896(2)	2.049(3)	2.033(2)	2.025(2)
M1−O2	1.939(1)	1.876(2)	1.923(2)	2.029(3)	2.036(2)	2.025(2)
M1−O3	1.806(1)	1.811(2)	1.805(2)	1.966(3)	1.939(2)	1.925(2)
M1−O4	1.819(1)	1.809(1)	1.817(2)	1.927(3)	1.937(2)	1.928(2)
M1−N1	2.309(2)	2.368(2)	2.340(3)	2.425(3)	2.446(2)	2.418(2)
M1−N2	2.325(2)	2.285(2)	2.280(3)	2.458(3)	2.431(3)	2.394(2)
O1−M1−O2	166.53(6)	162.56(6)	162.11(1)	156.49(1)	156.72(8)	158.03(7)
N1−M1−N2	75.83(5)	72.20(6)	72.93(9)	69.57(11)	69.33(8)	70.17(6)
M1−O3−C^{i}Pr	137.25(1)	139.5(2)	135.7(3)	151.3(4)	174.1(2)	174.8(2)

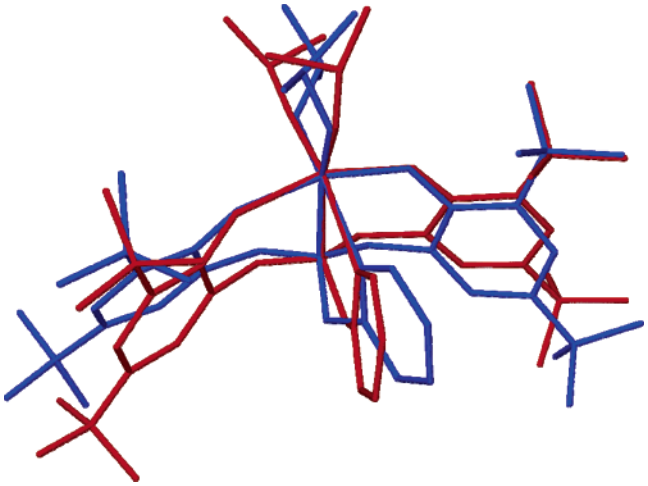

Figure 3. Overlay of Hf(O^{i}Pr)$_2$**2b** (blue) and Ti(O^{i}Pr)$_2$**2b** (red) illustrating their structural similarities.

Table 3. Results for Solution Polymerization of ε-Caprolactone (CL)[a]

initiator	% yield[b]	M_w[c]	M_n[c]	PDI[c]	M_n(NMR)[d]
Ti(O^{i}Pr)$_2$**1b**	>99	9700	3800	2.60	8500[e]
Zr(O^{i}Pr)$_2$**1a**	>99	18 800	12 000	1.59	6000
Zr(O^{i}Pr)$_2$**1b**	10	1150	900	1.27	1000
Zr(O^{i}Pr)$_2$**2a**	>99	18 600	13 800	1.35	7500
Zr(O^{i}Pr)$_2$**2a**[f]	>99	34 000	23 000	1.48	11 500

[a] Conditions [CL]/[Init] = 100:1, 10 mL toluene, time 24 h, and room temperature (20 °C), where all the Ti(IV) and Zr(IV) complexes were tested for polymerization and only the positive results are given in the table. [b] Isolated yield. [c] Determined from GPC using polystyrene as the reference. [d] Calculated from ^{1}H NMR (CDCl$_3$) analysis by integration of the end group of the isopropoxide at 4.9 ppm and the backbone resonance at 4.0 ppm. [e] The high M_n (NMR) is consistent with the formation of cyclic oligomers through intramolecular transesterification. [f] A further 100 equiv of ε-caprolactone was added and the polymerization allowed to proceed for a further 24 h.

For Ti(IV) complexes of type 1 ligands the only active initiator is Ti(O^{i}Pr)$_2$**1b**, for which the ligand has the bulkiest group ortho to the phenoxide. The relatively high polydispersity (2.60) suggests that the polymerization is poorly controlled and that transesterification may be prevalent. Both the Ti(IV) complexes with type 2 ligands proved to be inactive. For Zr(IV) complexes, the opposite trend is observed with Zr(O^{i}Pr)$_2$**1a** proving to be highly active and exhibiting controlled polymerization (PDI = 1.59). Under the experimental conditions employed Zr(O^{i}Pr)$_2$**1b** is much less active. These results highlight that an established trend for the effect of ligand variation on reactivity for one metal (Ti) cannot be transferred intuitively to a heavier congener (Zr). They also reinforce previous observations that minor differences in the steric and electronic environment around the metal center can have a significant impact on the reactivity (and selectivity) of an initiator.[6,21] A similar trend is found for Zr(IV) complexes containing type 2 ligands with the more bulky Zr(O^{i}Pr)$_2$**2b** being inactive but Zr(O^{i}Pr)$_2$**2a** showing high activity and well-controlled polymerization (PDI = 1.35). In contrast to titanium alkoxide-based initiators whose ability to polymerize ε-caprolactone is well established,[1−7,15] few examples for the ROP of ε-caprolactone with well-defined zirconium alkoxide initiators are known[9−13] and to our knowledge, room-temperature ROP of ε-caprolactone using Zr(IV) has not previously been reported [for example, Zr(O^{n}Pr)$_4$ was reported to polymerize ε-caprolactone only at 100 °C[47]].

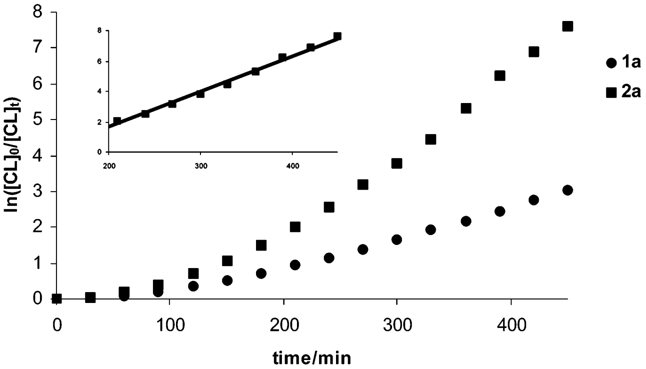

Figure 4. Kinetics of ε-caprolactone polymerization initiated with Zr(O^{i}Pr)$_2$**1a** (circles) and Zr(O^{i}Pr)$_2$**2a** (squares). Solvent C$_6$D$_6$, the relative concentrations were determined by ^{1}H NMR spectroscopy, temperature = 25 °C. [CL]$_0$ is the initial concentration of ε-caprolactone and [CL]$_t$ the concentration at time *t*. Full conversion for Zr(O^{i}Pr)$_2$**1a** was reached after 15 h and Zr(O^{i}Pr)$_2$**2a** after 7 h, respectively. Inset shows linear fit (r^2 = 0.9931) for the first-order region after initiation period for Zr(O^{i}Pr)$_2$**2a**. The linear region for Zr(O^{i}Pr)$_2$**1a** has r^2 = 0.998 and is given as Supporting Information.

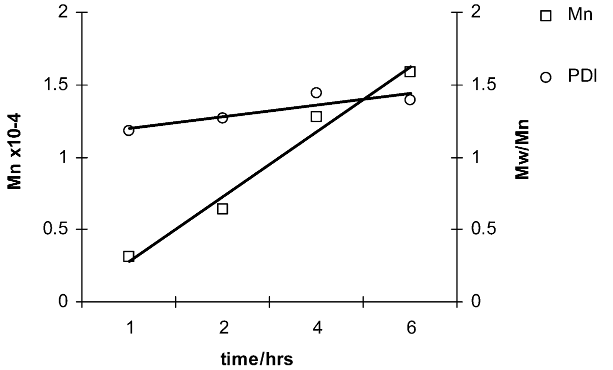

Figure 5. Plot of M_n and PDI (determined from GPC analysis) vs time for the polymerization of ε-caprolactone using Zr(O^{i}Pr)$_2$**2a** as the initiator. See Table 3 for polymerization conditions.

In all cases, end group analysis of the isolated PCL by ^{1}H NMR spectroscopy suggests initiation via an isopropoxide group, consistent with previous results for metal alkoxide initiators.[15] For complexes Zr(O^{i}Pr)$_2$**1a** and Zr(O^{i}Pr)$_2$**2a** polymerization was monitored by ^{1}H NMR spectroscopy (Figure 4). A short induction period is followed by polymerization that is first order with respect to the monomer, as indicated by the linear relationship between ln([CL]$_0$/[Cl]$_t$) and time. The induction period is similar to that previously reported for polymerizations initiated by aluminum isopropoxides (and attributed to the coordination step in the coordination−insertion mechanism)[48,49] but contrasts with the lack of induction observed for calcium alkoxides initiated polymerization.[49] The type 2 complex, containing a pyridyl group, is significantly more active, 50% conversion is reached after 2 h whereas for Zr(O^{i}Pr)$_2$**1a** 50% conversion is achieved after 6 h, in both cases full conversion is achieved in 15 h. This can be rationalized in terms of the structural differences between type 1 and type 2 complexes. For the latter, one N-donor atom is part of a potentially labile sidearm whereas for type 1, both N-donors are part of the ligand backbone and are consequently less labile.

The linear correlation between M_n and time and constant PDI (Figure 5) indicates that the polymerization is well controlled. This was further exemplified by a polymerization resumption experiment (the last two entries in Table 3). In this experiment a further 100 equiv of ε-caprolactone was added once the initial 100 equiv had been used. As expected for “living” polymerization the molecular weight of the final polymer doubled.

Solution Polymerization of L-Lactide. The same Ti(IV) and Zr(IV) complexes were also screened for the polymerization of

Table 4. Results for Solution Polymerization of L-Lactide[a]

initiator	% yield[b]	M_w[c]	M_n[c]	PDI[c]
Ti(O^{i}Pr)$_2$**1b**	20	800	550	1.43
Zr(O^{i}Pr)$_2$**1a**	>99	11 500	10 800	1.08
Zr(O^{i}Pr)$_2$**2a**	>99	12 200	10 800	1.13

[a] Conditions [LA]/[Init] = 100:1, 10 mL toluene, time 2 h, and temperature 110 °C. [b] Determined from ^{1}H NMR analysis (C_6D_6), by integration of the monomer methine region at 3.8 ppm and the polymer methine at 5.1 ppm. [c] Determined from GPC using polystyrene as the reference. All the Ti(IV) and Zr(IV) complexes were tested for the polymerization, and only the positive results are given in the table.

Table 5. Results for the Solution Copolymerization of ϵ-Caprolactone and L-Lactide[a]

initiator	% yield[b]	M_w[c]	M_n[c]	PDI[c]
Zr(O^{i}Pr)$_2$**1a**	90	28 800	21 800	1.32
Zr(O^{i}Pr)$_2$**2a**	98	34 500	28 300	1.22

[a] See Experimental section for the conditions. [b] Determined from ^{1}H NMR analysis (C_6D_6) (see Table 4). [c] Determined from GPC using polystyrene as the reference.

L-lactide in solution (Table 4). Similar trends in reactivity are observed as for ϵ-caprolactone. Titanium-based complexes are inactive with the exception of the bulkiest complex Ti(O^{i}Pr)$_2$**1b** and even in this case only modest conversion was achieved. For zirconium, whereas complexes containing bulky ligands Zr(O^{i}Pr)$_2$**1b** and Zr(O^{i}Pr)$_2$**2b** are inactive, reducing the steric demand of the ligand results in high initiator activity and well-controlled polymerization for Zr(O^{i}Pr)$_2$**1a** and Zr(O^{i}Pr)$_2$**2a**.

Solution Copolymerization of ϵ-Caprolactone and L-Lactide. The PCL−PLA copolymer was prepared using the Zr(IV) catalysts based on ligands **1aH$_2$** and **2aH$_2$**. To form the copolymer, the order of addition was critical; no copolymer was produced if the L-lactide was polymerized first,[30,31] so that attempts to form PCL−PLA−PCL were unsuccessful.[31] The GPC plots (Table 5) are unimodal and show that the molecular weight of the block copolymer has increased relative to that expected for pure polymers; see the Supporting Information. ^{13}C NMR spectroscopic analysis of the copolymer afforded two carbonyl resonances at 173.5 ppm (PCL block) and 169.6 ppm (PLA block) respectively indicating that little transesterification occurred during the polymerization sequence;[50] see the Supporting Information.

The thermal analysis (DSC) of the homopolymers PCL and PLA exhibit sharp endothermic peaks at 53 and 158 °C (second heating cycle) and sharp exothermic peaks at 33 and 105 °C (cooling cycle) corresponding to the melting temperature (T_m) and the crystallization temperature (T_c), respectively. These results indicate crystallinity consistent with precedents in the literature.[27,34,51,52] For the homopolymers, glass transition temperatures (T_g) of −47 (PCL) and +51 (PLA) °C were obtained, consistent with literature precedent.[53−56] For the copolymer the endothermic peaks are at 46 and 146 °C (corresponding to the PCL and PLA block) which are lower by 7 and 12 °C than for the respective homopolymers. For the copolymer the exothermic peaks are at 27 and 99 °C (for the PCL and PLA block), i.e., 6 °C lower than those for homopolymers. The two melting endotherms and crystallization exotherms which occur at slightly lower T_m and T_c than observed for the pure homopolymers suggests two different crystal domains in the material of the type to be expected for a block copolymer and certainly not that expected for a random copolymer. Full analysis of the DSC data is given in the Supporting Information.

Stereoselective Polymerization of *rac*-Lactide. The complexes were further tested for the polymerization of *rac*-lactide both in solution and under melt conditions in order to assess stereocontrol of the initiators (Table 6). As with L-lactide the only initiators that showed significant conversions in solution were Zr(O^{i}Pr)$_2$**1a** and Zr(O^{i}Pr)$_2$**2a** (Table 6, entries 5 and 8). However initiators that proved inactive under solution conditions were found to be active under melt conditions. Thus, all titanium complexes, with the exception of Ti(O^{i}Pr)$_2$**2b**, were active for the polymerization of *rac*-lactide under melt conditions and all produced atactic PLA (Table 6, entries 1−4). Entries 1 and 13 in Table 6 provide a comparison between Ti and Hf initiators which lead to similar conversions and which contain the same non bulky ligand (**1a**). The molecular weight of the Hf-initiated polymer is approximately half that yielded using the Ti initiator which is consistent with initiation and propagation of polymer chains occurring at both isopropoxide sites for Hf but at only one site for Ti. The use of more bulky aminebisphenolate ligands with Zr and Hf initiators leads to low conversions even after 24 h (Table 6, entries 7, 10 and 14). The observation of higher molecular weights for these polymers relative to those obtained with non-bulky ligands (e.g., Table 6, entries 6, 9 and 13) implies that bulky ligands may restrict polymerization to one isopropoxide site for Zr and Hf initiators.

In contrast to the atactic polymers yielded by titanium initiators, zirconium and hafnium complexes exhibited varying degrees of stereocontrol over the polymerization. The zirconium complexes of ligands **1a** and **2a** both formed isotactically enriched PLA under melt and solution conditions (Table 6, entries 5, 6, 8, and 9), with type 1 showing greater stereoselectivity than type 2 ligands. ^{1}H homonuclear decoupled NMR spectra (Figure 6) show that in both cases the *iii* tetrad, indicative

Table 6. Results for the Polymerization of *rac*-Lactide

entry	initiator	time/h	mon:init	% yield	M_w[c]	M_n[c]	PDI[c]	P_r/P_m[d]
1	Ti(O^{i}Pr)$_2$**1a**[a]	2	300:1	74	54 000	33 000	1.64	0.5/0.5
2	Ti(O^{i}Pr)$_2$**1b**[a]	2	300:1	68	54 200	36 000	1.51	0.5/0.5
3	Ti(O^{i}Pr)$_2$**1c**[a]	2	300:1	62	54 500	41 000	1.34	0.5/0.5
4	Ti(O^{i}Pr)$_2$**2a**[a]	2	300:1	75	45 100	32 700	1.38	0.5/0.5
5	Zr(O^{i}Pr)$_2$**1a**[b]	2	100:1	> 99	10 700	9150	1.17	0.25/0.75
6	Zr(O^{i}Pr)$_2$**1a**[a]	2	300:1	55	8900	6050	1.47	0.3/0.7
7	Zr(O^{i}Pr)$_2$**1b**[a]	24	300:1	21	15 200	13 500	1.13	-
8	Zr(O^{i}Pr)$_2$**2a**[b]	2	100:1	> 99	7900	7100	1.11	0.4/0.6
9	Zr(O^{i}Pr)$_2$**2a**[a]	2	300:1	45	5600	4400	1.27	0.45/0.55
10	Zr(O^{i}Pr)$_2$**2b**[a]	24	300:1	13	11 600	10 250	1.14	0.5/0.5
11	Zr(O^{i}Pr)$_2$**2c**[a]	2	300:1	10	2900	1700	1.42	0.35/0.65
12	Zr(O^{i}Pr)$_2$**2c**[b]	2	100:1	75	9450	8650	1.10	0.4/0.6
13	Hf(O^{i}Pr)$_2$**1a**[a]	2	300:1	68	21 700	14 100	1.54	0.3/0.7
14	Hf(O^{i}Pr)$_2$**2b**[a]	24	300:1	30	10 100	7800	1.29	0.5/0.5

[a] [*rac*-lactide]/[init] 300:1 temperature 130 °C, solvent free. [b] [*rac*-lactide]/[init] = 100:1, 10 mL toluene, temperature 110 °C. [c] Determined from GPC using polystyrene as the reference. [d] Calculated from the ^{1}H homonuclear decoupled NMR ($CDCl_3$) analysis.

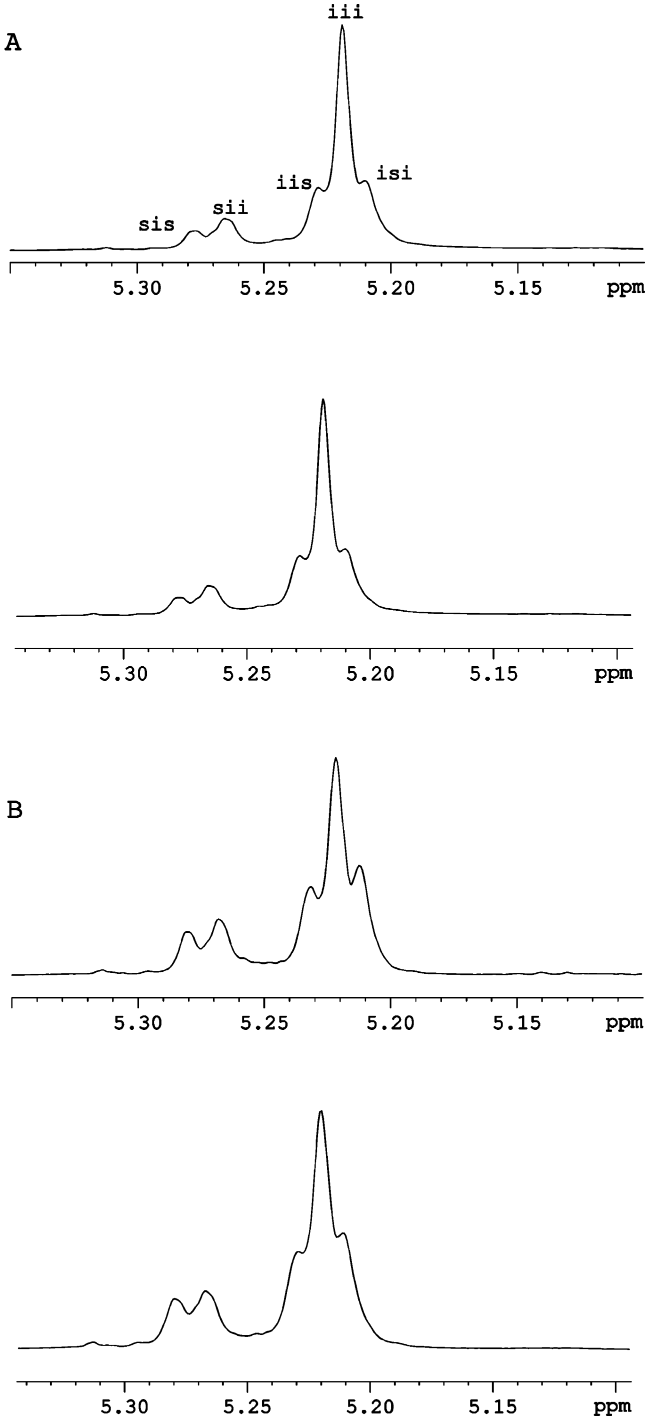

Figure 6. ^{1}H homonuclear decoupled NMR for the methine region of the polymer formed with **A** Zr(O^{i}Pr)$_2$(**1a**) and **B** Zr(O^{i}Pr)$_2$(**2a**). Top polymer produced using toluene as solvent, bottom polymer produced from melt reaction.

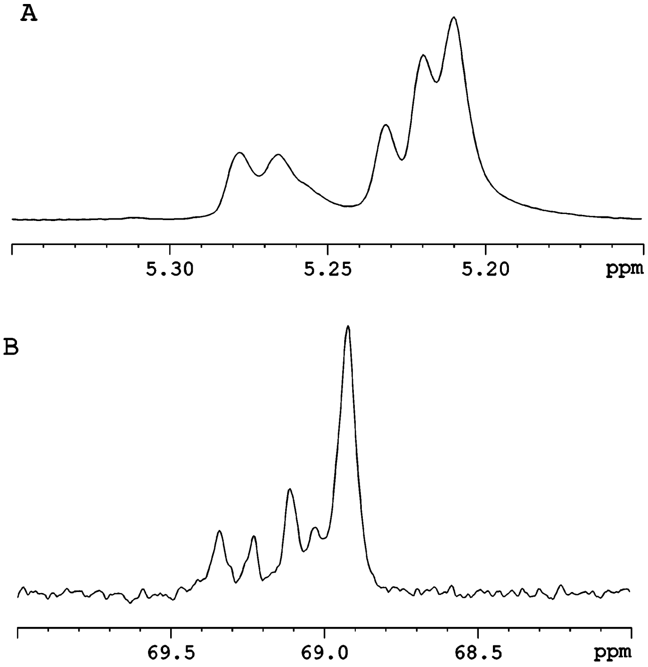

Figure 7. (A) ^{1}H homonuclear decoupled NMR for the methine region of the polymer formed with Zr(O^{i}Pr)$_2$(**1b**). (B**)** ^{13}C NMR region of the same polymer. See Supporting Information for the carbonyl region.

of isotactic PLA, is the main resonance. The *sii*, *iis* and *isi* tetrads are present in approximately equal intensity, with a small *sis* peak, indicative of isotactic stereoblock PLA.[30] The ^{13}C NMR spectra (see Supporting Information) also shows the resonance due to the *iii* tetrad is significantly enhanced, compared to atactic PLA.

A possible explanation for the enhancement in stereocontrol of type 1 over type 2 ligands can be traced to structural differences in their metal complexes (discussed above and Figure 1). The favored coordination mode of *achiral* ligands of type 1 around octahedral Zr(IV) centers is *fac*−*fac*, leading to pseudo C_2 symmetric chiral complexes (Δ or Λ forms).[57] For type 2 ligands, complexes have pseudo C_s symmetry, and are therefore nonchiral. This subtle difference between the two ligand systems may account for the difference in selectivity by a chain end controlled mechanism. In such a process the coordinated ligand influences the stereocenter of the last inserted monomer, which governs the microstructure of the resulting polymer.[24] Within the subset of type 1 ligands, a further distinction is that Ti complexes lead to atactic PLA whereas Zr and Hf both exhibit stereoselectivity. Again, the origin of this difference can be traced to minor variations in the coordination chemistry of group 4 metals. In a recent DFT study Rzepa et al. investigated the origin of stereocontrol in single-site magnesium alkoxide-catalyzed ROP of *rac*-lactide.[22] This study highlighted the significance of chelation of lactate units of the growing polymer chain in determining the stereoselectivity of subsequent insertions.[22] Given that Zr and Hf metal centers favor higher coordination numbers than Ti,[58] it is possible that chelation of the growing polymer chain occurs to a greater extent in Zr- and Hf-initiated polymerizations which, in turn favors approach of either *R,R*- or *S,S*-lactide in the rate-determining transition state. In contrast, if chelation within Ti complexes is less favored, stereoselectivity of subsequent monomer insertions will be reduced. Experiments performed under melt and solution conditions yield remarkably similar results, although in both cases for which analogous polymerization were performed, the melt conditions produced a polymer with a slightly lower isotactic enrichment. For Zr(O^{i}Pr)**1b** the ^{1}H homonuclear decoupled NMR spectrum of the polymer reproducibly exhibits an unusual enhancement of the resonance assigned to the *isi* tetrad (5.21 ppm, Figure 7). The ^{13}C{^{1}H} NMR spectrum reveals the presence of *iss*, *sss* and *ssi* tetrads which is consistent with approximately 80% stereorandom transesterification taking place.[59] These tetrads have an analogous chemical shift to the *isi* tetrad and therefore lead to an enhancement of the resonance at 5.21 ppm in the ^{1}H homonuclear decoupled spectrum.[60,61]

For Zr(O^{i}Pr)**2b** a typical NMR for atactic polymer was observed, which was mirrored by the Hf(IV) complex of the same ligand. There was no appreciable increase in the stereoselectivity using the Zr(IV) complex of the unsymmetrical ligand **$2cH_2$**, which was similar in reactivity to $Zr(O^iPr)_2$**2a**.

Conclusions

A series of titanium, zirconium, and hafnium alkoxides supported by two types of aminebisphenolate ligands were prepared. Structural characterization by single-crystal X-ray diffraction revealed two classes of six-coordinate complexes, depending on the ligand type (pseudo-C_s or pseudo-C_2) but only minor structural differences due to the identity of the metal. A number of these complexes were shown to be active as initiators for the ROP of cyclic esters with good control over molecular weights and low molecular weight distributions. The well-controlled nature of the ROP was also demonstrated by synthesis of a PCL–PLA block copolymer and through polymerization resumption experiments.

Good control of polymer microstructure through stereoselective polymerization of *rac*-lactide was demonstrated for Zr and Hf complexes of less bulky ligands, which yielded predominantly isotactic PLA, even in solventless reactions at 130 °C. The use of either Ti or bulky ligands, however, resulted in the loss of stereocontol and the formation of atactic PLA.

Zr and Hf aminebisphenolates provide promising alternatives to some of the more extensively studied metal alkoxide systems (e.g., Mg, Zn, Al, Sn) as initiators for the stereoselective ROP of cyclic esters although (as with other systems) the precise molecular origin of control over activity and stereoselectivity in ROP of cyclic esters remains to be elucidated and requires further investigation.

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Supporting Information Available: Text detailing the preparation, characterization, and analysis of the complexes, figure showing the crystal structure of $Zr(O^iPr)_2$ **1a**, tables of DSC data, figures showing the DSC anaysis, plot $\ln([CL]_0/[CL]_t)$ vs time, ^1H and ^{13}C NMR spectra, and GPC plot, and a .cif file containing the crystal structure analysis. This material is available free of charge via the Internet at http://pubs.acs.org. The crystallographic information may also be obtained from the Cambridge Crystallographic Data Centre, CCDC Nos: 604481–604487.

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