# PAPER

Cite this: New J. Chem., 2013, 37, 949

Received (in Victoria, Australia) 11th October 2012, Accepted 8th January 2013

DOI: 10.1039/c3nj40916c

www.rsc.org/njc

# 1 Introduction

In the modern era, there has been a continuous decrease in research based on commodity polymers owing to the rapid consumption of non-renewable petroleum resources. Non-biodegradability of these polymers is also an important issue that has posed a key threat to the ultimate fate of such polymers.<sup>1,2</sup> Currently, scientists are more focused on studying biodegradable polymers due to growing environmental awareness of the harmful effects of non-biodegradable materials.<sup>1,3-6</sup> This has initiated an active impetus for extensive research on polymers that can be derived from completely renewable natural resources like corn and sugar beet.<sup>7-10</sup> These polymers are not only biodegradable, but also bioassimilable as their hydrolysis in physiological media furnishes non-toxic side products.<sup>10</sup> At the same time, they are completely environmentally benign. Besides, they have tremendous impact on the biomedical and pharmaceutical industry in vital applications like drug delivery, fabrication of biodegradable sutures, medical implants, ligating clips, bone pins and scaffolds for tissue engineering.3,11-15 Synthesis of these biodegradable polymers by ROP of cyclic esters and LA is

# Imino phenoxide complexes of group 4 metals: synthesis, structural characterization and polymerization studies<sup>†</sup>

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A complete library of new alkoxides containing group 4 metals and the imino phenol ligand were synthesized in high yields and purity. These compounds showed catalytic activity towards the polymerization of L-lactide (L-LA), *rac*-lactide (*rac*-LA),  $\varepsilon$ -caprolactone (CL),  $\delta$ -valerolactone (VL), *rac*- $\beta$ -butyrolactone (*rac*-BL), ethylene and propylene. The zirconium catalysts were found to yield better polymerization results in comparison to the titanium and hafnium analogues. The number average molecular weight ( $M_n$ ) values of the polymers are very high for LA and CL with controlled molecular weight distributions (MWDs). Analyses of MALDI-TOF and <sup>1</sup>H NMR spectra of low  $M_n$  oligomers reveal that the ligand initiates the ring-opening polymerization (ROP). For ethylene and propylene polymerization, we have achieved moderate to good activity using MAO as a co-catalyst.

a hot area of current interest<sup>16-19</sup> since it is a very convenient and easy method to synthesize these polymers. Out of the numerous methods available, the coordination-insertion mechanism<sup>20-28</sup> is a popular choice for ROP as it has the ability to produce high molecular weight polymers  $(M_n)$  with narrow MWDs. In recent times, we have reported several group 4 metal catalysts containing a bis(imino)phenoxide ligand backbone for the ROP of cyclic esters and lactides (LA)<sup>29,30</sup> as group 4 metal catalysts<sup>31,32</sup> are very efficient and popular for performing such polymerization. We observed excellent activity of these complexes towards the ROP of cyclic esters and LA, but the major drawback was that the observed  $M_{\rm p}$  was far higher than the theoretical value. Inspired by these results, we wanted to explore the effect of the imino phenoxide ligand complexes of group 4 metals upon the polymerization of cyclic esters and LA. In 2008, Davidson's group reported group 4 metal catalysts comprising of a chiral imino phenoxide type ligand that has a benzyl spacer arm.<sup>32c</sup> Our goal was to see the electronic effect of the imino phenoxide ligand without any spacer.

The invention of high density polyethylene and methylaluminoxane (MAO) as a potent activator of sandwich type metallocene complexes showed a new path in the area of olefin polymerization.<sup>33</sup> An important reason for the synthesis of molecular catalysts stems from the provision of opportunities related to the issues concerning polymerization mechanism and stereospecificity. Although single site homogeneous catalysts have gained appreciable attention for olefin polymerization,

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Includes NMR spectra and experimental details. CCDC 891894–891896. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3nj40916c

scientists are interested in catalysts based on non-metallocene systems. The non-metallocene complexes discovered in recent times have enabled the synthesis of hyperbranched poly(ethylene)s, copolymers containing ethylene and polar monomers, mono-disperse poly(higher- $\alpha$ -olefin)s and higher  $\alpha$ -olefin based block copolymers that are otherwise not possible to produce using group 4 metallocene catalysts and constrained geometry catalyst systems.<sup>34</sup>

Among the several highly active catalytic systems for olefin polymerization, the chloro complexes of group 4 metals containing an imino phenoxide ligand developed by Fujita and later by Coates deserve considerable attention.<sup>35</sup> These compounds are popularly called "FI" catalysts. There has been active impetus in developing high performance group 4 metalcontaining FI catalysts by both academic and industrial research groups. Our compounds have a good deal of structural resemblance to these FI catalysts and this prompted us to investigate their catalytic activity towards the polymerization of ethylene and propylene. We have tested these compounds towards the polymerization of ethylene and propylene as they would contribute towards the synthesis of new "FI" nonmetallocene compounds.

### 2 Experimental

#### 2.1 General information and instrumentation

All the reactions were performed under a dry argon atmosphere using standard Schlenk techniques or glove box techniques with the rigorous exclusion of moisture and air. Toluene was dried by heating under refluxing conditions for 6 h over sodium and benzophenone and distilled fresh prior to use. CDCl<sub>3</sub> used for NMR spectral measurements was dried over calcium hydride for 48 h, distilled and stored in a glove box. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Bruker Avance 400 or Bruker Ascend 500 instrument. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced to residual solvent resonances and are reported as parts per million relative to SiMe<sub>4</sub>. ESI-MS spectra of the samples were recorded using Waters Q-Tof micro mass spectrometer. MALDI-TOF measurements were performed on a Bruker Daltonics or Bruker Ultraflextreme instrument in a dihydroxybenzoic acid matrix. Elemental analyses were performed with a Perkin Elmer Series 11 analyzer.

Molecular weights  $(M_n)$  and the polydispersity indices (MWDs) of the polymer samples produced by the ROP of various cyclic ester monomers and LA were determined by using a GPC instrument with Waters 510 pump and Waters 410 differential refractometer as the detector. Three columns, WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8 × 300 mm) were serially connected one after another. Measurements were done in THF at 27 °C for all the cases. Measurement of number average molecular weights ( $M_n$ ), weight average molecular weights ( $M_w$ ) and polydispersity ( $M_w/M_n$ ) (MWDs) of the polymers were performed relative to polystyrene standards. Molecular weights ( $M_n$  and  $M_w$ ) and the polydispersity indices ( $M_w/M_n$ ) of polyethylene and poly(propylene) samples were obtained by using a GPC instrument with Waters 510 pump and Waters 2414 differential refractometer as the detector. The column used, namely WATERS STRYGEL-HR4 of dimensions (4.6 × 300 mm), was connected during the experiment. Measurements were done in trichlorobenzene. Number average molecular weights ( $M_n$ ) and molecular weight distributions (MWDs) of the poly olefins were ascertained relative to polystyrene standards.

#### 2.2 Materials

Methylaluminoxane (MAO), Ti(O–iPr)<sub>4</sub>, Zr(O–iPr)<sub>4</sub>(HO–iPr) and Hf(O–tBu)<sub>4</sub> were purchased from Sigma-Aldrich and used without further purification. *rac*-LA, L-LA, CL, VL and *rac*-BL were purchased from Sigma-Aldrich. *rac*-LA and L-LA were sublimed under an argon atmosphere and stored in a glove box. Ligands L1, L2 and L3 were prepared according to literature reported procedures.<sup>36–38</sup> CL, VL and *rac*-BL were dried over calcium hydride overnight and distilled fresh prior to use. Highly pure ethylene and propylene gas were purchased from Indogas, Bangalore, India.

#### 2.3 Syntheses and characterization

Compound 1. In an argon filled glove box, a solution of Ti(O-iPr)<sub>4</sub> (0.050 g, 0.176 mmol) in 5 mL of dry toluene and ligand L1 (0.138 g, 0.351 mmol) in 10 mL of dry toluene were cooled for 6 h at -25 °C. After cooling, these solutions were mixed and stirred for 24 h at ambient temperature. Subsequently, the mixture was evaporated to dryness to afford a greenish-yellow residue. The residue was crystallized from dry toluene. Yield = 0.141 g (84%). Mp: 163  $^{\circ}$ C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ ):  $\delta = 1.20-1.28$  (m, O-CH(CH\_3)<sub>2</sub>, 12 H), 1.29-1.50  $(m, CH(CH_3)_2, 24 H), 1.53 (s, C(CH_3)_3, 18 H), 1.57 (s, C(CH_3)_3, 18 H))$ 18 H), 2.98-3.05 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 4 H), 4.49-4.54 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 7.18–7.54 (m, Ar–H, 10 H), 8.33 (s, CH=N, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 22.59$  (Ar-CH<sub>3</sub>), 23.77 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 25.94 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.25 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.70 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.83  $(CH(CH_3)_2)$ , 31.56  $(C(CH_3)_3)$ , 31.77  $(C(CH_3)_3)$ , 34.35  $(C(CH_3)_3)$ , 35.13 (C(CH<sub>3</sub>)<sub>3</sub>), 76.83 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 123.11 (Ar-CH<sub>3</sub>), 123.30 (Ar-C), 123.39 (Ar-C), 125.36 (Ar-C), 125.51 (Ar-C), 126.80 (Ar-C), 128.25 (Ar-C), 129.18 (Ar-CH<sub>3</sub>), 137.29 (Ar-C), 139.01 (Ar-CH<sub>3</sub>), 140.60 (Ar-C), 146.53 (Ar-C), 158.59 (Ar-O), 167.66 (CH=N). ESI<sup>†</sup> m/z calculated for  $[M + H]^+$ . C<sub>60</sub>H<sub>90</sub>N<sub>2</sub>O<sub>4</sub>Ti: 950.638 found 951.906. Anal. calc. for C<sub>60</sub>H<sub>90</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 75.76, H 9.54, N 2.94. Found: C 75.61, H 9.41, N 2.88.

**Compound 2.** In an argon filled glove box, a solution of Ti(O-*i*Pr)<sub>4</sub> (0.050 g, 0.176 mmol) in 5 mL of dry toluene and L2 ligand (0.101 g, 0.351 mmol) in 10 mL of dry toluene were mixed and heated at 100 °C for 24 h. After 24 h, the mixture was evaporated to dryness to afford a yellow residue. The residue was purified from dry toluene. Yield = 0.103 g (83%). Mp: 151 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.22–1.35 (m, O–CH(CH<sub>3</sub>)<sub>2</sub>, 12 H), 1.47 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H), 1.49 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H), 1.57 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H), 4.49–4.53 (m, O–CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 7.11 (s, Ar–H, 2 H), 7.37 (s, Ar–H, 2 H), 8.36 (s, CH=N, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 25.94 (O–CH(CH<sub>3</sub>)<sub>2</sub>), 29.62 (C(CH<sub>3</sub>)<sub>3</sub>), 29.87 (C(CH<sub>3</sub>)<sub>3</sub>), 31.69 (C(CH<sub>3</sub>)<sub>3</sub>), 34.28 (C(CH<sub>3</sub>)<sub>3</sub>), 35.18 (C(CH<sub>3</sub>)<sub>3</sub>), 56.89 (N–C(CH<sub>3</sub>)<sub>3</sub>), 76.35 (O–CH(CH<sub>3</sub>)<sub>2</sub>),

118.07 (Ar–*C*), 126.01 (Ar–*C*), 126.66 (Ar–*C*), 136.93 (Ar–*C*), 139.75 (Ar–*C*), 158.88 (*Ar*–O), 160.82 (*C*H=N). ESI<sup>†</sup> *m*/*z* calculated for  $[M]^+$ . C<sub>44</sub>H<sub>74</sub>N<sub>2</sub>O<sub>4</sub>Ti: 742.936 found 742.252. Anal. calc. for C<sub>44</sub>H<sub>74</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 71.13, H 10.04, N 3.77. Found: C 71.22, H 10.15, N 3.69.

Compound 3. In an argon filled glove box, a solution of Ti(O-iPr)<sub>4</sub> (0.050 g, 0.176 mmol) in 5 mL of dry toluene and ligand L3 (0.154 g, 0.351 mmol) in 10 mL of dry toluene were cooled for 6 h at -25 °C. After cooling, these solutions were mixed and stirred for 24 h at ambient temperature. Subsequently, the mixture was evaporated to dryness to afford a yellow residue. The residue was crystallized from dry toluene. Yield = 0.163 g (88%). Mp: 168 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$ = 0.98-1.14 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 12 H), 1.15-1.22 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 24 H), 3.26-3.40 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 4 H), 4.56-4.61 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 7.05-7.74 (m, Ar-H, 10 H), 8.03 (s, CH=N, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.60 (Ar-CH<sub>3</sub>), 24.66 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 25.13 (CH(CH<sub>3</sub>)<sub>2</sub>), 25.99 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.77 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.99 (CH(CH<sub>3</sub>)<sub>2</sub>), 78.62 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 123.28 (Ar-C), 123.75 (Ar-C), 125.43 (Ar-C), 126.05 (Ar-C), 126.38 (Ar-C), 128.36 (Ar-C), 129.16 (Ar-CH<sub>3</sub>), 134.43 (Ar-CH<sub>3</sub>), 139.56 (Ar-C), 140.41 (Ar-C), 150.51 (Ar-C), 161.83 (Ar-O), 165.97 (CH=N). ESI<sup>+</sup> m/z calculated for [M]<sup>+</sup>. C<sub>44</sub>H<sub>54</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>4</sub>Ti: 1042.394 found 1042.182. Anal. calc. for C<sub>44</sub>H<sub>54</sub>Br<sub>4</sub>N<sub>2</sub>O<sub>4</sub>Ti: C 50.70, H 5.22, N 2.69. Found: C 50.77, H 5.15, N 2.78.

Compound 4. In an argon filled glove box, a solution of Zr(O-*i*Pr)<sub>4</sub> (HO-*i*Pr) (0.050 g, 0.129 mmol) in 5 mL of dry toluene and L1 ligand (0.102 g, 0.257 mmol) in 10 mL of dry toluene were heated at 100 °C for 24 h. After 24 h, the mixture was evaporated to dryness to afford a yellow residue. The residue was purified from dry toluene. Yield = 0.102 g (80%). Mp: 165 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.20–1.29 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 12 H), 1.31-1.41 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 24 H), 1.52 (s,  $C(CH_3)_3$ , 18 H), 1.53 (s,  $C(CH_3)_3$ , 18 H), 2.99-3.06  $(m, CH(CH_3)_2, 4 H), 4.34-4.41 (m, O-CH(CH_3)_2, 2 H),$ 7.18-7.54 (m, Ar-H, 10 H), 8.32 (s, CH=N, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 22.59 (Ar-CH<sub>3</sub>), 23.77 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 26.07 (CH(CH<sub>3</sub>)<sub>2</sub>), 26.67 (CH(CH<sub>3</sub>)<sub>2</sub>), 27.00 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.17  $(CH(CH_3)_2)$ , 31.62  $(C(CH_3)_3)$ , 31.81  $(C(CH_3)_3)$ , 34.35  $(C(CH_3)_3)$ , 35.34 (C(CH<sub>3</sub>)<sub>3</sub>), 71.65 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 123.30 (Ar-C), 125.36 (Ar-C), 125.45 (Ar-C), 126.80 (Ar-C), 128.25 (Ar-C), 128.37 (Ar-C), 129.18 (Ar-CH<sub>3</sub>), 137.29 (Ar-C), 139.01 (Ar-CH<sub>3</sub>), 140.60 (Ar-C), 146.25 (Ar-C), 158.59 (Ar-O), 167.66 (CH=N). ESI<sup>+</sup> m/z calculated for  $[M + H]^+$ . C<sub>60</sub>H<sub>90</sub>N<sub>2</sub>O<sub>4</sub>Zr: 992.595 found 993.267. Anal. calc. for C60H90N2O4Zr: C 72.46, H 9.12, N 2.82. Found: C 72.34, H 9.23, N 2.89.

**Compound 5.** In an argon filled glove box, a solution of  $Zr(O-iPr)_4$  (HO-*i*Pr) (0.050 g, 0.129 mmol) in 5 mL of dry toluene and L2 ligand (0.075 g, 0.257 mmol) in 10 mL of dry toluene were mixed and heated at 100 °C for 24 h. After 24 h, the mixture was evaporated to dryness to afford a yellow residue. The residue was purified from dry toluene. Yield = 0.083 g (82%). Mp: 157 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.18–1.36 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 12 H), 1.40 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H), 1.45 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H), 1.48 (s, C(CH<sub>3</sub>)<sub>3</sub>, 18 H), 4.24-4.51 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 7.10 (s, Ar-H, 2 H), 7.36 (s, Ar-H, 10 H),

8.35 (s, CH=N, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 26.05 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 26.82 (C(CH<sub>3</sub>)<sub>3</sub>), 29.86 (C(CH<sub>3</sub>)<sub>3</sub>), 31.68 (C(CH<sub>3</sub>)<sub>3</sub>), 34.27 (C(CH<sub>3</sub>)<sub>3</sub>), 35.18 (C(CH<sub>3</sub>)<sub>3</sub>), 56.89 (N-C(CH<sub>3</sub>)<sub>3</sub>), 74.95 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 118.09 (Ar-C), 126.00 (Ar-C), 126.67 (Ar-C), 137.03 (Ar-C), 139.75 (Ar-C), 158.89 (Ar-O), 160.81 (CH=N). ESI<sup>†</sup> *m*/*z* calculated for [M]<sup>+</sup>. C<sub>44</sub>H<sub>74</sub>N<sub>2</sub>O<sub>4</sub>Zr: 742.936 found 742.252. Anal. calc. for C<sub>44</sub>H<sub>74</sub>N<sub>2</sub>O<sub>4</sub>Zr: C 67.21, H 9.49, N 3.56. Found: C 67.10, H 9.59, N 3.67.

Compound 6. In an argon filled glove box, a solution of Zr(O-*i*Pr)<sub>4</sub> (HO-*i*Pr) (0.050 g, 0.129 mmol) in 5 mL of dry toluene and ligand L3 (0.113 g, 0.257 mmol) in 10 mL of dry toluene were cooled for 6 h at -25 °C. After cooling, those solutions were mixed and stirred for 24 h at ambient temperature. Subsequently, the mixture was evaporated to dryness to afford a vellow residue. The residue was crystallized from dry toluene. Yield = 0.130 g (92%). Mp: 168 °C. <sup>1</sup>H NMR (400 MHz,  $CDCl_3$ :  $\delta = 0.99-1.27$  (m, O-CH(CH\_3)<sub>2</sub>, 12 H), 1.27-1.35 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 24 H), 2.95-3.01 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 4 H), 3.52-3.60 (m, O-CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 7.17-7.74 (m, Ar-H, 10 H), 8.03 (s, CH=N, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 21.60 (Ar-CH<sub>3</sub>), 23.42 (O-CH( $CH_3$ )<sub>2</sub>), 25.37 (CH( $CH_3$ )<sub>2</sub>), 26.60 (CH( $CH_3$ )<sub>2</sub>), 27.58 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.01 (CH(CH<sub>3</sub>)<sub>2</sub>), 70.69 (O-CH(CH<sub>3</sub>)<sub>2</sub>), 122.16 (Ar-CH<sub>3</sub>), 123.59 (Ar-C), 123.77 (Ar-C), 124.44 (Ar-C), 125.44 (Ar-C), 127.06 (Ar-C), 128.37 (Ar-C), 129.18 (Ar-CH<sub>3</sub>), 136.29 (Ar-C), 140.85(Ar-C), 141.60 (Ar-C), 161.16 (Ar-O), 171.72 (CH=N). ESI<sup>†</sup> m/z calculated for  $[M]^+$ .  $C_{44}H_{54}Br_4N_2O_4Zr$ : 1085.751 found 1085.374. Anal. calc. For C444H54Br4N2O4Zr: C 48.67, H 5.01, N 2.58. Found: C 48.59, H 5.10, N 2.51.

Compound 7. In an argon filled glove box, a solution of Hf(O-tBu)<sub>4</sub> (0.050 g, 0.106 mmol) in 5 mL of dry toluene and ligand L1 (0.041 g, 0.106 mmol) in 10 mL of dry toluene were cooled for 6 h at -25 °C. After cooling, these solutions were mixed and stirred for 24 h at ambient temperature. Subsequently, the mixture was evaporated to dryness to afford a greenish-yellow residue. The residue was crystallized from dry toluene. Yield = 0.074 g (88%). Mp: 168 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.14 (s, O-C(CH<sub>3</sub>)<sub>3</sub>, 27 H), 1.20-1.37 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 12 H), 1.52 (s, C(CH<sub>3</sub>)<sub>3</sub>, 9 H), 1.57 (s, C(CH<sub>3</sub>)<sub>3</sub>, 9 H), 2.37 (Ar-CH<sub>3</sub>), 3.03-3.09 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 6.94 (s, Ar-H, 1 H), 7.18-7.29 (m, Ar-H, 3 H), 7.55 (s, Ar-H, 1 H), 8.15 (s, CH=N, 1 H). <sup>13</sup>C NMR (100 MHz,  $CDCl_3$ :  $\delta = 22.60 (Ar-CH_3), 23.09 (O-C(CH_3)_3), 25.31(CH(CH_3)_2),$ 28.37 (CH(CH<sub>3</sub>)<sub>2</sub>), 31.63 (C(CH<sub>3</sub>)<sub>3</sub>), 31.75 (C(CH<sub>3</sub>)<sub>3</sub>), 34.15  $(C(CH_3)_3)$ , 35.60  $(C(CH_3)_3)$ , 75.47  $(O-C(CH_3)_3)$ , 123.76 (Ar-C), 125.46 (Ar-C), 125.92 (Ar-C), 128.38 (Ar-C), 128.59 (Ar-C), 129.19 (Ar-CH<sub>3</sub>), 131.23(Ar-C), 139.17 (Ar-CH<sub>3</sub>), 140.07(Ar-C), 140.60 (Ar-C), 143.55 (Ar-C), 154.89 (Ar-O), 164.46 (CH=N). ESI<sup>+</sup> m/z calculated for [M]<sup>+</sup>. C<sub>39</sub>H<sub>65</sub>NO<sub>4</sub>Hf: 790.428 found 790.300. Anal. calc. For C39H65NO4Hf: C 59.26, H 8.29, N 1.77. Found: C 59.37, H 8.23, N 1.85.

**Compound 8.** In an argon filled glove box, a solution of  $Hf(O-tBu)_4$  (0.050 g, 0.106 mmol) in 5 mL of dry toluene and L2 ligand (0.031 g, 0.106 mmol) in 10 mL of dry toluene were mixed and heated at 100 °C for 24 h. After 24 h, the mixture was evaporated to dryness to afford a yellow residue. The residue was purified from dry toluene. Yield = 0.057 g (79%). Mp: 160 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.39 (s, O-C(CH<sub>3</sub>)<sub>3</sub>, 27 H),

1.51 (s, C(CH<sub>3</sub>)<sub>3</sub>, 9 H), 1.59 (s, C(CH<sub>3</sub>)<sub>3</sub>, 9 H), 1.66 (s, C(CH<sub>3</sub>)<sub>3</sub>, 9 H), 7.15 (s, Ar–H, 1 H), 7.42 (s, Ar–H, 1 H), 8.48 (s, CH=N, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 29.85 (O–C(CH<sub>3</sub>)<sub>3</sub>), 31.18 (C(CH<sub>3</sub>)<sub>3</sub>), 31.67 (C(CH<sub>3</sub>)<sub>3</sub>), 33.56 (C(CH<sub>3</sub>)<sub>3</sub>), 34.28 (C(CH<sub>3</sub>)<sub>3</sub>), 35.16 (C(CH<sub>3</sub>)<sub>3</sub>), 60.85 (N–C(CH<sub>3</sub>)<sub>3</sub>), 75.30 (O–C(CH<sub>3</sub>)<sub>3</sub>), 122.59 (Ar–CH<sub>3</sub>), 125.99 (Ar–C), 126.65 (Ar–C), 129.03 (Ar–CH<sub>3</sub>), 129.13 (Ar–CH<sub>3</sub>), 139.06 (Ar–C), 139.71 (Ar–C), 158.91 (Ar–O), 160.79 (CH=N). ESI<sup>†</sup> m/z calculated for [M + Na]<sup>+</sup>. C<sub>31</sub>H<sub>57</sub>NO<sub>4</sub>Hf: 686.279 found 709.235. Anal. calc. for C<sub>31</sub>H<sub>57</sub>NO<sub>4</sub>Hf: C 54.25, H 8.37, N 2.04. Found: C 54.36, H 8.25, N 2.10.

Compound 9. In an argon filled glove box, a solution of Hf(O-tBu)<sub>4</sub> (0.050 g, 0.129 mmol) in 5 mL of dry toluene and ligand L3 (0.046 g, 0.106 mmol) in 10 mL of dry toluene were cooled for 6 h at -25 °C. After cooling, these solutions were mixed and stirred for 24 h at ambient temperature. Subsequently, the mixture was evaporated to dryness to afford a yellow residue. The residue was crystallized from dry toluene. Yield = 0.080 g (90%). Mp: 172 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 1.49-1.79$ (m, CH(CH<sub>3</sub>)<sub>2</sub>, 12 H), 1.80 (m, (O-C(CH<sub>3</sub>)<sub>3</sub>), 27 H), 3.63-3.69 (m, CH(CH<sub>3</sub>)<sub>2</sub>, 2 H), 7.72-7.88 (m, Ar-H, 10 H), 8.48 (s, CH=N, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = 23.00$  (O-C(CH<sub>3</sub>)<sub>3</sub>), 28.02 (CH(CH<sub>3</sub>)<sub>2</sub>), 28.40 (CH(CH<sub>3</sub>)<sub>2</sub>), 32.48 (CH(CH<sub>3</sub>)<sub>2</sub>), 75.68 (O-C(CH3)3), 122.67 (Ar-C), 123.65 (Ar-C), 123.84 (Ar-C), 126.52 (Ar-C), 129.19 (Ar-CH<sub>3</sub>), 135.23 (Ar-C), 137.45 (Ar-C), 140.14 (Ar-C), 140.56 (Ar-C), 151.52 (Ar-C), 159.48 (Ar-O), 170.63 (CH=N). ESI<sup>†</sup> m/z calculated for  $[M]^+$ . C<sub>31</sub>H<sub>47</sub>Br<sub>2</sub>NO<sub>4</sub>Hf: 836.007 found 836.389. Anal. Calc. For C31H47Br2NO4Hf: C 44.54, H 5.67, N 1.68. Found: C 44.48, H 5.73, N 1.63.

# 2.4 General procedure for the bulk polymerization of *rac*-LA, L-LA, CL, VL and *rac*-BL

These polymerizations were performed under bulk solvent-free condition. For L-LA and rac-LA polymerization, 173.4 µmol of catalyst and 5 g L-LA or rac-LA (34.7 mmol) (867.2 µmol of benzyl alcohol was added wherever benzyl alcohol was used during LA polymerization) and for CL polymerization, 236.6 µmol of catalyst and 5.4 g CL (5 mL, 47.3 mmol) (1183 µmol of benzyl alcohol was added wherever benzyl alcohol was used during CL polymerization) were used during the polymerization. The contents were taken into a 100 mL stainless steel autoclave reactor with mechanical stirring under an argon atmosphere. The steel autoclave was heated to 110 °C in the case of CL polymerization and 130 °C in the case of LA. The contents were rapidly stirred. The progress of polymerization was monitored by periodically recording the <sup>1</sup>H NMR spectra of the reaction mixture. The polymerization was quenched by gradually cooling the autoclave to ambient temperature in almost 30 min and pouring the contents into cold heptane in the case of CL and cold methanol in the case of L-LA and rac-LA. The polymer formed was collected by filtration. The filtered product was dried in a vacuum until a constant weight was achieved. For VL and rac-BL, the same procedure and workup were followed.

# 2.5 General procedure for solution polymerization of *rac*-LA, L-LA and CL

The solution polymerization was done in dry toluene. These polymerizations were done by taking 173.4  $\mu$ mol of catalyst and

5 g L-LA or *rac*-LA (34.7 mmol) (867.2  $\mu$ mol of benzyl alcohol was added wherever benzyl alcohol was used during LA polymerization) and for CL polymerization, 236.6  $\mu$ mol of catalyst and 5.4 g CL (5 mL, 47.3 mmol) (1183  $\mu$ mol of benzyl alcohol was added wherever benzyl alcohol was used during CL polymerization) in 20 mL of toluene. The reaction mixture was charged into a 100 mL stainless steel autoclave reactor with mechanical stirring under an inert atmosphere. The autoclave was heated up to 80 °C and stirred for 12 h. The contents were quenched by pouring the material into cold heptane in the case of CL and cold methanol in the case of L-LA and *rac*-LA after cooling it to ambient temperature. The polymer was collected by filtration. The filtered material was dried in vacuum continuously to attain a constant weight.

# 2.5 General procedure for ethylene and propylene polymerization

The polymerizations were performed in a 100 mL stainless steel autoclave reactor with mechanical stirring under an argon atmosphere. The container was charged with an argon atmosphere with 50 mg of catalyst, 45 mL of toluene along with the required amount of MAO. Consequently, the autoclave was heated up to 80  $^{\circ}$ C and gas was continuously bubbled through the proper channel. The gas feed was passed for 30 min at a pressure of 8 atm and subsequently the polymerization was quenched with acidic methanol. The polymer produced was collected by filtration and dried until a constant weight was achieved.

### 2.6 X-ray structure determination of compounds 3, 6 and 7

Amongst all the compounds synthesized in this study, suitable crystals for X-ray diffraction studies were obtained from 3, 6 and 7. Single crystals were grown in a glove box at -25 °C from diluted toluene and acetonitrile (few drops) solutions of the respective compounds over a period of 10 days. X-ray data was collected with a Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with a graphite monochromated Mo (K $\alpha$ ) ( $\lambda$  = 0.7107 Å) radiation source. The data were collected with 100% completeness for  $\theta$  up to 25°.  $\omega$ and  $\phi$  scans were employed to collect the data. The frame width for  $\omega$  was fixed to 0.5° for data collection. The frames were subjected to integration and data were reduced for Lorentz and polarization corrections using SAINT-NT. The multi-scan absorption correction was applied to the data set. All structures were solved using SIR-92 and the refinement was done using SHELXL-97.39 Location of all the hydrogen atoms could be found in the difference Fourier map. The hydrogen atoms attached to carbon atoms were fixed at chemically meaningful positions and were allowed to ride with the parent atom during refinement. Compound 7 has four molecules in the asymmetric unit, which gave rise to the doubt that this might be due to the doubling of any axis due to pseudo-translations. PLATON was used to confirm it's non-existence.

# 3 Results and discussion

### 3.1 Synthesis and spectral characterization of compounds

All the complexes **1–9** were synthesized by reacting various imino phenol ligands, **L1–L3** with group 4 metal alkoxides in



Published on 09 January 2013 on http://pubs.rsc.org | doi:10.1039/C3NJ40916C Downloaded by Duke University on 05/04/2013 07:00:15.

toluene in 1:1 and 2:1 stoichiometric ratios (Scheme 1). The products formed were completely purified by crystallization from toluene at -25 °C and isolated in high yield and purity after removing the solvent under reduced pressure. For L1 and L3 the reactions went to completion at room temperature. However, in the case of L2, the reaction was not complete at room temperature as understood from spectroscopic analysis of the crude reaction mixture. The reaction mixture was heated up to 100 °C for completion. We have tried the reactions in a 1:1 stoichiometric ratio for all the cases, but we observed that the unreacted metal alkoxides remained along with the expected product involving Ti and Zr, as per the conclusion drawn from <sup>1</sup>H NMR of the crude. Whereas we have not observed any unreacted metal alcoholate signal in the <sup>1</sup>H NMR spectrum for Hf. However, an unreacted phenolic -OH signal was found in all reactions with Hf in 1:2 stoichiometric ratios even after heating at 100 °C. On the other hand, the unreacted phenolic -OH signal is completely absent in case of Ti or Zr. All these derivatives were completely characterized using various spectroscopic techniques and their purity was assured by the proper elemental analysis results. Electrospray ionization mass spectrometry (ESI-MS) spectra reveal that these compounds have a mononuclear structure.

### 3.2 Single crystal X-ray diffraction studies

From single crystal X-ray diffraction studies, it is clear that compounds 3, 6 and 7 (Fig. 1-3) are monomeric in the solid

state and the corresponding metal atom is present in a distorted octahedral geometry. The crystal data is shown in Table 1 for 3, 6 and 7. Compound 3 has a crystallographically imposed twofold symmetry with the Ti1 atom on the twofold axis. Moreover, the two coordinated N centers are trans to each other and the alkoxide groups are *cis* to each other. All bond distances are identical in the case of Ti and the difference is marginal for Zr. On the other hand, for 7, an acetonitrile molecule has coordinated to the metal center in order to make it octahedral. The Hf-O (alkoxide) bond lengths are almost the same and shorter than the bond distance of the Hf-O (phenolic) moiety. Both Hf-N bond distances are also almost identical.

From Fig. 1 and 2 it is clear that the trans-N, cis-O and cis-OiPr isomer is predominant in the solid state. This isomer is predominant because the steric repulsion between the isopropyl groups contained as part of the ligand is minimum. This is different to the observations gathered from analogous halide containing derivatives. Contributions from the research group of Fujita clearly indicate the possibility of the presence of six different octahedral isomers. This was ascertained on the basis of the appearance of different signals for the imine moieties in the <sup>1</sup>H NMR at different temperatures.<sup>35</sup> In order to understand, we performed variable temperature <sup>1</sup>H NMR and <sup>13</sup>C NMR studies employing compounds 1 and 4, respectively (see ESI,† Fig. S28-S31). To our surprise we did not find any significant changes in the NMR results at different temperatures, implying that this isomer is predominant in solution.



**Fig. 1** Molecular structure of **3**; thermal ellipsoids were drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Ti(1)–O(1), 2.000(3); Ti(1)–O(3), 1.790(3); Ti(1)–N(1), 2.242(3); Ti(1)–O(1)\_1, 2.000(3); Ti(1)–O(3)\_1, 1.790(3); Ti(1)–N(1)\_1, 2.242(3); O(3)–Ti(1)–O(1), 168.32(12); O(3)–Ti(1)–O(3)\_1, 99.66(18); O(3)\_1–Ti(1)–O(1), 90.18(12); O(3)–Ti(1)–O(1)\_1, 90.18(12); N(1)\_1–Ti(1)–O(1)\_1, 83.33(11); N(1)–Ti(1)–N(1)\_1, 169.28(18). The superscript i in the atom labels indicates that these atoms are at an equivalent position (2 – x, y, 1/2 – z).



**Fig. 2** Molecular structure of **6**; thermal ellipsoids were drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Zr(01)–O(1), 2.107(3); Zr(01)–O(2), 2.099(3); Zr(01)–O(3), 1.925(3); Zr(01)–O(4), 1.918(3); Zr(01)–N(1), 2.378(4); Zr(01)–N(2), 2.378(4); O(4)–Zr(01)–O(3), 99.41(13); O(4)–Zr(01)–O(2), 92.65(13); O(2)–Zr(01)–O(3), 161.56(12); O(2)–Zr(01)–N(1), 89.65(12); O(1)–Zr(01)–N(1), 77.17(12); N(2)–Zr(01)–N(1), 165.95(12).

#### 3.3 Polymerization characteristics and activities

We wanted to test the potential of **1–9** as catalysts towards the ROP of L-LA, *rac*-LA,  $\varepsilon$ -CL,  $\delta$ -VL and *rac*-BL. Our prime intention was to see the effect of one imine group in the ligand upon the polymerization. Here, complexes **1–9** have shown high catalytic activity towards the polymerization of these monomers. All the polymerizations were done under solvent free conditions first. In this regard, we have performed all the polymerization in a 200:1 monomer to catalyst ratio. Polymerization at ambient



**Fig. 3** Molecular structure of **7**; thermal ellipsoids were drawn at 30% probability level. Selected bond lengths (Å) and angles (°): Hf(04)–O(4c), 1.923(3); Hf(04)–O(2c), 1.948(3); Hf(04)–O(3c), 1.952(4); Hf(04)–O(1c), 2.068(3); Hf(04)–N(1c), 2.450(4); Hf(04)–N(2c), 2.430(4); O(4c)–Hf(4)–O(2c), 99.75(16); O(4c)–Hf(4)–O(3c), 102.25(16); O(3c)–Hf(4)–O(2c), 100.95(17); O(4c)–Hf(4)–O(1c), 95.23(14); O(4c)–Hf(4)–N(2c), 81.90(16); N(2c)–Hf(4)–N(1c), 81.11(13). One of the four independent molecules in the asymmetric unit is depicted.

temperature resulted in the formation of low molecular weight oligomers. For cyclic ester polymerizations, the temperature was set at 80  $^{\circ}$ C and for LA, the polymerizations were done at 130  $^{\circ}$ C. The polymerization results are summarized in Table 2.

From Table 2, it can be easily inferred that the  $M_n$  value is highest for zirconium catalysts followed by the titanium catalyst and finally the hafnium catalyst. In addition, all  $M_n$ values are much higher than the theoretical value, indicating slow initiation during the polymerization with MWDs between 1.11–1.39. We observed very high  $M_n$  in the cases of CL and LA. The earlier report of imino phenoxide complexes of Ti and Zr had shown good reactivity with greater degree of stereoselectivity.<sup>32c</sup> In these cases, solution polymerization of *rac*-LA produced moderate  $M_n$  with well controlled MWDs (1.02–1.08). However, MWDs were much broader in bulk polymerization of *rac*-LA. Screening all these results we can say that our results are better than these reports and literature reports based on group 4 metals.<sup>31c,d,m,r,32h</sup>

Again, we have extended our study by doing solution polymerization for *rac*-LA, L-LA and CL in toluene using these catalysts (see ESI<sup>†</sup>). It is clear that there is a close proximity between observed  $M_n$  and theoretical  $M_n$  value and MWDs are extremely narrow (1.02–1.09) for the polymers concerned. In these solution polymerizations, we were able to control  $M_n$  and MWDs in an efficient manner.

To see the effect of a co-initiator like benzyl alcohol, we have performed polymerizations of *rac*-LA, L-LA and CL using **1–9** as catalysts in the presence of benzyl alcohol (BnOH) (Table 3). Here, we have found that  $M_n$  values of the respective polymers are higher compared to the theoretical value expected. This actually reveals that we were not able to control the  $M_n$  when the polymerizations were done in the presence of benzyl alcohol. MWDs (1.10–1.17) are controlled in a much better

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Table 1Crystal data for the structures 3, 6 and 7
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Compound	3	6	7
Empirical formula	$C_{48}H_{60}Br_4N_4O_4Ti$	$C_{51}H_{62}Br_4N_2O_4Zr$	C <sub>41</sub> H <sub>68</sub> N <sub>2</sub> O <sub>4</sub> Hf
Formula weight	1124.54	1177.89	831.46
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	P2(1)/n	P1
Temp/K	173(2)	173(2)	173(2)
Wavelength (Å)	0.71073	0.71073	0.71073
a (Å)	24.4152(13)	21.9206(11)	16.4326(9)
b (Å)	13.1350(6)	10.1128(5)	21.7830(11)
c (Å)	18.3821(10)	23.1925(12)	25.0841(13)
α (°)	90	90	88.239(2)
β(°)	116.306(3)	96.119(2)	85.703(2)
γ(°)	90	90	79.019(2)
$V(Å^3)$	5284.5(5)	5112.0(4)	8788.5(8)
Z	4	4	8
$D_{\text{calc}} (\text{g cm}^{-3})$	1.413	1.530	1.257
Reflns collected	22480	28555	118536
No. of indep reflns	4878	9436	42436
GOF	1.052	1.007	1.074
Final R indices $(I > 2\sigma(I))^a$	$R_1 = 0.0458, wR_2 = 0.1233$	$R_1 = 0.0453, wR_2 = 0.1042$	$R_1 = 0.0474, wR_2 = 0.1171$
<i>R</i> indices (all data) <sup><i>a</i></sup>	$R_1 = 0.0804, wR_2 = 0.1408$	$R_1 = 0.0864, wR_2 = 0.1211$	$R_1 = 0.0741, wR_2 = 0.1360$
$^{a}R_{1} = \sum  F_{0}  -  F_{c}  / \sum  F_{0} , wR_{2} = [$	$\sum (F_0^2 - F_c^2)^2 / \sum w (F_0^2)^2 ]^{1/2}.$		

fashion than without co-initiator in these polymerizations. However, in the presence of toluene, the same polymerization results depict a close correlation between observed  $M_n$  and theoretical  $M_n$  with narrow MWDs (1.10–1.14) (see ESI<sup>†</sup>). It was independently verified that BnOH reacts with 4 at the respective temperatures of the various polymerizations to yield the benzyloxide compound, which is the true catalyst (see ESI,<sup>†</sup> Fig. S45 and S46).

We were very curious to study the variation of  $M_n$  and MWDs with increasing [*rac*-LA]/[C] ratio using **3**, **6** and **9**. In these cases, we have observed that with increase of [*rac*-LA]/[C] ratio,  $M_n$  increased continuously and appreciably. A plot of molecular weight ( $M_n$ ) vs. [M]<sub>o</sub>/[C]<sub>o</sub> ratio depicts that  $M_n$  is rising steeply with the variation of ratios. The MWDs ( $M_w/M_n$ ) remain almost invariant with increasing ratios (Fig. 4).

Again, a plot of  $M_n$  against % conversion of monomer (see ESI<sup>†</sup>) shows a sharp increment of  $M_n$  with increasing conversion of monomer.

Another interesting observation is that the PHB sample from entry 30 (Table 2) showed a very strong contribution from the *r*-centered diad ( $\delta$  = 169.32 ppm) indicating syndiotacticity. The methylene region showed one prominent signal ( $\delta$  = 40.80 ppm) corresponding to the *rr* triad. On the other hand, the polymerization of *rac*-LA leads to the high  $M_n$  polymer with predominantly heterotactic enchainment and not much difference in heterotacticity was observed when the polymerizations were done in the absence or presence of benzyl alcohol.

It must be noted that the structures of the Hf compounds (7–9) is different from the others. Hence, it is not reasonable to compare the polymerization activity of these with the others.

#### 3.4 Kinetics of polymerization

In the next part of our study, we have performed the kinetics of *rac*-LA polymerization using **3**, **6** and **9**. The kinetic studies for the polymerization of *rac*-LA in ratio  $[rac-LA]_o/[C]_o = 200$  were

done at 130 °C. A plot of % conversion of *rac*-LA against time (see ESI,<sup>†</sup> Fig. S42) produces a sigmoidal curve. This disclosed that the polymer formation was at a very high rate initially and after some time conversion rate was almost constant. From the kinetic experiment results, it was ascertained that there is a first-order dependence of the rate of polymerization on *rac*-LA concentration without any induction period. The plot of  $\ln([rac-LA]_o/[rac-LA]_t)$  vs. time was found to be linear (Fig. 5). The values of the apparent rate constant ( $k_{app}$ ) for *rac*-LA polymerization catalyzed by **3**, **6** and **9** were evaluated from the slope of these straight lines and were found to be  $33.82 \times 10^{-2} \text{ min}^{-1}$ , 24.14 ×  $10^{-2} \text{ min}^{-1}$  and  $18.28 \times 10^{-2} \text{ min}^{-1}$ , respectively. From the rate contants of polymerization, it can be concluded that the rate is fastest for Ti followed by Zr and then Hf. This is justified by the time taken for the polymerization.

#### 3.5 Polymerization mechanism

Low molecular weight oligomers of rac-LA were synthesized by stirring rac-LA with 6 in 10:1 molar ratio under solvent free conditions at 130 °C. The product was extracted with heptane. After removal of heptane, the residue was examined thoroughly using MALDI-TOF and <sup>1</sup>H NMR techniques. The predominant product comprised of the ligand fragment as one of the end terminal groups in the oligomer chain, as determined through the analysis of MALDI-TOF and <sup>1</sup>H NMR spectra. The oligomer did not contain any proportions of the corresponding product initiated by the isopropoxide fragment. The same observations were seen using the Hf catalyst 7. In addition to the above, peaks corresponding to intramolecular transesterification products were seen (see ESI,<sup>†</sup> Fig. S35-S38). When the same reaction was done in the presence of benzyl alcohol in 10:1:2 using 4, the resultant polymer had the OBn moiety as one of the end groups. This was ascertained using MALDI-TOF and <sup>1</sup>H NMR spectra. Besides there were peaks corresponding to the ligand initiated oligomer along with products of

**Table 2** Polymerization data for L-LA, rac-LA, CL, VL and rac-BL using 1–9 in200:1 ratio

Entry	Initiator	Monomer	T/ °C	Yield (%)	Time <sup>a</sup> / min	$\frac{M_{\mathrm{n}}{}^{b}}{\mathrm{kg}}\mathrm{mol}^{-1}$	$M_{ m w}/M_{ m n}$	$P_{\rm r}^{\ c}$
1	1	rac-LA	130	98	12	38.55	1.13	0.70
2	2	rac-LA	130	99	17	40.55	1.16	0.69
3	3	rac-LA	130	99	14	41.62	1.11	0.71
4	4	rac-LA	130	98	13	88.22	1.12	0.72
5	5	rac-LA	130	98	18.5	77.54	1.14	0.68
6	6	rac-LA	130	97	18	82.52	1.12	0.73
7	7	rac-LA	130	99	15	42.22	1.18	0.68
8	8	rac-LA	130	99	21	40.96	1.22	0.70
9	9	rac-LA	130	99	29	41.44	1.18	0.69
10	1	L-LA	130	99	11	42.81	1.12	
11	2	L-LA	130	98	15	38.33	1.14	
12	3	L-LA	130	98	12.5	40.22	1.11	
13	4	L-LA	130	96	15	92.61	1.11	
14	5	L-LA	130	96	17	76.42	1.15	
15	6	L-LA	130	97	15	81.62	1.13	
16	7	L-LA	130	98	22	40.26	1.20	
17	8	L-LA	130	97	28	38.55	1.21	
18	9	L-LA	130	97	28	38.55	1.21	
19	1	CL	80	97	8	68.27	1.33	
20	2	CL	80	99	13	64.11	1.29	
21	3	CL	80	99	10	67.77	1.31	
22	4	CL	80	98	10	76.82	1.36	
23	5	CL	80	99	16.5	70.81	1.34	
24	6	CL	80	98	12.5	74.98	1.34	
25	7	CL	80	99	16	47.62	1.39	
26	8	CL	80	94	19	44.29	1.37	
27	9	CL	80	99	17.5	45.26	1.35	
28	1	VL	80	96	6	56.72	1.35	
29	2	VL	80	98	11	53.99	1.28	
30	3	VL	80	97	9.5	55.34	1.26	
31	4	VL	80	97	8.5	60.44	1.31	
32	5	VL	80	98	12	55.81	1.30	
33	6	VL	80	95	11	57.22	1.23	
34	7	VL	80	98	10	43.32	1.37	
35	8	VL	80	98	14	39.67	1.32	
36	9	VL	80	96	12.5	42.52	1.31	
37	1	rac-BL	80	95	14	33.01	1.29	
38	2	rac-BL	80	97	20.5	29.01	1.32	
39	3	rac-BL	80	96	18	31.02	1.36	
40	4	rac-BL	80	96	17	35.92	1.24	
41	5	rac-BL	80	97	24	31.39	1.27	
42	6	rac-BL	80	96	21	33.12	1.36	
43	7	rac-BL	80	98	22	30.21	1.29	
44	8	rac-BL	80	97	27	27.71	1.21	
45	9	rac-BL	80	98	24	29.65	1.24	

<sup>*a*</sup> Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. <sup>*b*</sup> Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark–Houwink corrections for  $M_n$  for LA polymerization. <sup>*c*</sup> Calculated from homonuclear decoupled <sup>1</sup>H NMR spectrum.

intramolecular transesterification. This was understood from the MALDI-TOF spectrum. In an independent study, it was seen that compound **4** reacts with BnOH to produce the corresponding OBn product. This initiates the polymerization (see ESI,<sup>†</sup> Fig. S39 and S40).

#### 3.6 Ethylene polymerization

After achieving good results with cyclic esters and LA, we investigated the polymerization of ethylene. Interestingly, here we found that compounds **1–9**, in the presence of MAO, are potent catalysts towards the polymerization of ethylene. These polymerizations were performed at 80 °C in toluene. From

Table 3 Polymerization data for *rac*-LA, L-LA and CL using 1-9 in the presence of benzyl alcohol in 200:1:5 ratio at 80 °C for CL and 130 °C for LA

Entry	Initiator <sup>a</sup>	Monomer	Time (min)	$M_{\rm n}^{{\rm obs}b}/{ m kg}~{ m mol}^{-1}$	$M_{\rm w}/M_{\rm n}$	$P_{\rm r}^{\ c}$
1	1	rac-LA	10	14.56	1.13	0.69
2	2	rac-LA	15	13.20	1.14	0.70
3	3	rac-LA	9	16.34	1.12	0.71
4	4	rac-LA	8	17.45	1.16	0.73
5	5	rac-LA	9.5	18.98	1.11	0.72
6	6	rac-LA	7	19.56	1.15	0.70
7	7	rac-LA	8.5	17.88	1.13	0.68
8	8	rac-LA	11	15.31	1.14	0.69
9	9	rac-LA	12	17.22	1.11	0.70
10	1	L-LA	5	15.55	1.10	
11	2	L-LA	7.5	14.85	1.12	
12	3	L-LA	6.5	12.11	1.11	
13	4	L-LA	8	17.76	1.14	
14	5	L-LA	8.5	15.97	1.12	
15	6	L-LA	5.5	15.35	1.13	
16	7	L-LA	12	14.20	1.14	
17	8	L-LA	13	12.19	1.13	
18	9	L-LA	11.5	15.49	1.14	
19	1	CL	4	10.32	1.11	
20	2	CL	8	12.78	1.13	
21	3	CL	6	12.36	1.14	
22	4	CL	5	14.54	1.12	
23	5	CL	9	13.25	1.14	
24	6	$\mathbf{CL}$	4.5	15.21	1.15	
25	7	CL	10	13.65	1.17	
26	8	CL	12	12.40	1.15	
27	9	CL	11	11.51	1.16	

<sup>*a*</sup> Time of polymerization measured by quenching the polymerization reaction when all monomer was found consumed. <sup>*b*</sup> Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark–Houwink corrections for  $M_n$  for LA polymerization;  $M_n$  (theoretical) at 100% conversion =  $[M]_o/[C]_o \times \text{mol wt (monomer)} + 108.14$ ;  $M_n$  (theoretical)<sub>LA</sub> = 5.87 kg mol<sup>-1</sup> and  $M_n$  (theoretical)<sub>CL</sub> = 4.67 kg mol<sup>-1</sup>. <sup>*c*</sup> Calculated from homonuclear decoupled <sup>1</sup>H NMR spectrum.



**Fig. 4** Plot of  $M_n$  and  $M_w/M_n$  vs.  $[M]_o/[C]_o$  for *rac*-LA polymerization at 130 °C using **3**, **6** and **9**.

Table 4, it is clear that molecular weight is highest for Zr catalysts and lowest for Hf catalysts. Ti catalysts show intermediate activity. The activity followed the order Zr > Ti > Hf. In all the cases, we have achieved good polymer yield. In most cases our activities are lower than Fujita's catalysts.<sup>35a</sup>

These polymerizations were carried out in different solvents to investigate the effect on activity of these catalysts.



**Fig. 5** Semi-logarithmic plots of *rac*-LA conversion in time initiated by **3**, **6** and **9**:  $[rac-LA]_o/[C]_o = 200$  at 130 °C.

Table 4 Polymerization data for ethylene using 1-9 along with MAO

Entry	Catalyst <sup>a</sup>	$\mathbf{A}^{b}$	$Yield^{c}(g)$	$M_{\rm w}  ({\rm kg \ mol^{-1}})$	$M_{\rm n}  ({\rm kg \ mol^{-1}})$	$M_{\rm w}/M_{\rm n}$
1	1	5.65	1.54	109.72	61.30	1.79
2	2	5.31	1.79	100.13	55.02	1.82
3	3	5.42	1.30	110.67	59.50	1.86
4	4	5.85	1.55	117.88	64.42	1.83
5	5	5.43	1.83	110.59	59.14	1.87
6	6	6.07	1.40	111.81	60.44	1.85
7	7	3.80	1.20	109.66	56.82	1.93
8	8	4.09	1.49	94.82	48.38	1.96
9	9	3.71	1.11	98.36	51.50	1.91
a						

<sup>*a*</sup> All experiments were performed in toluene at MAO: catalyst ratio = 1000, ethylene pressure = 8 atm, 80 °C for 30 min, catalyst = 50 mg, solvent = 45 mL. <sup>*b*</sup> A = Activity in (g PE per mol cat  $\times$  h)  $\times$  10<sup>4</sup>. <sup>*c*</sup> g of PE obtained after 30 min.

From Fig. 6, we can conclude with ease that toluene is the best solvent for doing these polymerizations since the activity of **4** is highest in toluene.

Again, when we varied the [MAO]/[C] ratio from 500 to 4000 for **1**, **4** and **7**, we observed that a [MAO]/[C] ratio of 1000 is optimum for performing these polymerizations, as other ratios led to reduction of the activity value of these catalysts (Fig. 7).

#### 3.7 Propylene polymerization

Our next goal was to investigate the effectiveness of these compounds as catalysts towards the polymerization of



Fig. 6 Activity of 4 in different solvent in ethylene polymerization.



Fig. 7 Plot of activity vs [MAO]/[C] ratio for 1, 4 and 7 for ethylene polymerization.

Table 5 Polymerization data for propylene using 1-9 along with MAO

Entry	Catalyst <sup>a</sup>	Activity <sup>b</sup>	Yield <sup>c</sup> (g)	${M_{ m w}} \ ({ m kg\ mol}^{-1})$	$M_{ m n}$ (kg mol <sup>-1</sup> )	$\frac{M_{ m w}}{M_{ m n}}$	% mmmm
1	1	4.66	1.23	66.78	40.23	1.65	14.2
2	2	3.41	1.15	62.43	38.78	1.61	13.1
3	3	4.58	1.10	61.56	39.21	1.57	16.9
4	4	4.96	1.25	71.38	42.24	1.69	20.1
5	5	4.24	1.43	61.57	37.54	1.64	18.4
6	6	4.95	1.14	61.21	39.49	1.55	20.3
7	7	3.98	1.26	56.72	34.80	1.63	12.9
8	8	3.21	1.17	54.79	35.12	1.56	11.7
9	9	3.74	1.12	52.56	34.35	1.53	13.6

<sup>*a*</sup> All experiments were performed in toluene at MAO: catalyst ratio = 1000, propylene pressure = 8 atm, 80 °C for 30 min, catalyst = 50 mg, solvent = 45 mL. <sup>*b*</sup> Activity in (g PP per mol cat  $\times$  h)  $\times$  10<sup>4</sup>. <sup>*c*</sup> g of PP obtained after 30 min.

propylene. Noticeably, here we have seen that compounds **1–9** are quite active catalysts towards the polymerization of propylene using MAO as a co-catalyst. These polymerizations were done at 80 °C in toluene. Table 5 depicts that  $M_n$  value is highest for Zr cases and lowest for Hf systems. Here, polymer yield was found to be moderate.

Table 6 denotes the pentad distribution for selected samples of polymer obtained using 4 along with different ratios of MAO. Here, we have noticed that the percentage of *mmmm* pentad distributions is reduced with increasing ratio of MAO. The polymerization is not stereoselective and the polymer produced is atactic.

Further, these polymerizations were performed in different solvents to find out the effect on activity of these compounds. We have inferred that toluene is the preferred solvent for carrying out these polymerizations as the activity of **4** is much greater in toluene in comparison with other solvents (see ESI,<sup>†</sup> Fig. S32).

We wanted to see the effect on activity upon the variation of [MAO]/[C] ratio from 500 to 4000 for **1**, **4** and **7**. A plot of activity vs [MAO]/[C] ratio clearly reveals that the 1000 ratio is the best option in order to perform propylene polymerization. (see ESI,† Fig. S33). Once again it may be noted that the activity of **7–9** 

[MAO] /[4] ratio	[mmmm]	[mmmr]	[rmmr]	[mmrr]	[mmrm] + [rrmr]	[mrmr]	[rrrr]	[rrrm]	[mrrm]
500	21.2	14.2	6.9	11.9	12.3	9.1	7.7	9.3	5.6
1000	20.1	15.3	7.4	14.6	13.7	6.7	9.5	8.2	4.9
2000	18.7	13.1	8.2	15.8	9.8	9.3	8.3	5.9	10.1

Table 6 Pentad distributions (in %) for selected polymers obtained in propylene polymerization catalyzed by complex 4

may not be compared with the rest or Fujita's work since their structures are different.

The polymerization proceeds through the activation of the catalyst using MAO as a result of abstraction of an alkoxide moiety and proceeds through a cationic intermediate, which is the true active species. Such abstraction of an alkoxide group by MAO is well documented in the literature.<sup>40</sup>

## 4 Conclusion

We have synthesized a complete library of new alkoxide complexes containing group 4 metals and the imino phenol ligand. These compounds have catalytic activity towards the polymerization of different cyclic esters, LA, ethylene and propylene. The zirconium catalysts were found to yield better polymerization results in comparison to the titanium and hafnium analogues. The presence of different substituents either on the aryl ring or on different anilines present in the various ligands does not affect the polymerizations in a significant manner. Good control over MWDs and  $M_n$  were achieved when these polymerizations were performed in toluene. Using MAO as a cocatalyst, we achieved good results in the ethylene and propylene polymerizations.

The ligand moiety is responsible for initiating the ROP instead of the isopropoxide groups, as understood from the MALDI-TOF and <sup>1</sup>H NMR spectra analysis. In the presence of BnOH, the polymers contain the OBn moiety as one of the end groups. The formed poly(3-hydroxy butyrate) is a syndiotactic polymer as it clearly gave the corresponding <sup>13</sup>C NMR signals. Homonuclear decoupled spectra of the poly(lactic acid) formed showed that the polymer was heterotactically enriched. Tacticity is not influenced in an appreciable manner with increasing steric bulk of the complexes.

# Acknowledgements

TKS thanks The Council of Scientific and Industrial Research Delhi for a fellowship. This work was supported by the Department of Science and Technology, New Delhi.

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