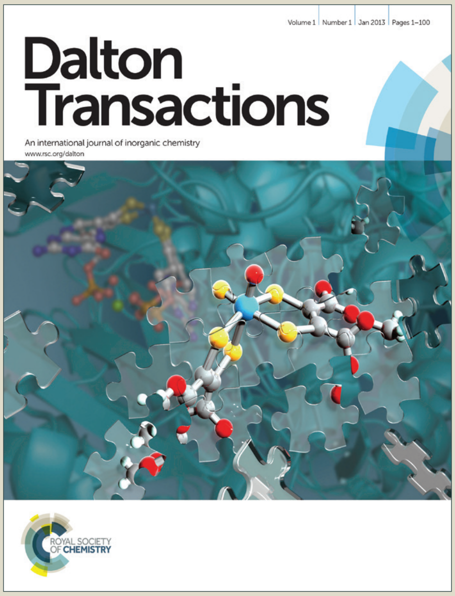
Dalton Transactions

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/dalton

Journal Name

Dalton Transactions

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis and characterization of group 4 metal alkoxide complexes containing imine based bis-bidentate ligands: Effective catalysts for the ring opening polymerization of lactides, epoxides and polymerization of ethylene

Sagnik K. Roymuhury,[a] Debashis Chakraborty,*[a] and Venkatachalam Ramkumar[b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A series of Ti(IV), Zr(IV) and Hf(IV) complexes containing imine based bis-bidentate ligands were synthesized and characterized by various spectroscopic techniques, elemental analysis and X-ray crystallography. The ligands *m*-xysal-(^{t}Bu)$_4$ (L^1(^{t}Bu)$_4$), *m*-xysal-(Me)$_2$(^{t}Bu)$_2$ (L^{2}Me$_2$(^{t}Bu)$_2$) and *m*-xysal-(Cl)$_4$ (L^{3}Cl$_4$) were reacted with Ti(O^{i}Pr)$_4$, Zr(O^{i}Pr)$_4$·^{i}PrOH and Hf(O^{t}Bu)$_4$ in a 1:1 stoichiometric ratio to form complexes **1-3** (L$_2$M$_2$(OR)$_4$, where L = *m*-xysal-(^{t}Bu)$_4$, *m*-xysal-(Me)$_2$(^{t}Bu)$_2$ and *m*-xysal-(Cl)$_4$, M = Ti and R = ^{i}Pr), **4-6** (L$_2$M$_2$(OR)$_4$, L = *m*-xysal-(^{t}Bu)$_4$, *m*-xysal-(Me)$_2$(^{t}Bu)$_2$ and *m*-xysal-(Cl)$_4$, M = Zr and R = ^{i}Pr) and **7-9** (L$_3$M$_3$(OR)$_6$, L = *m*-xysal-(^{t}Bu)$_4$, *m*-xysal-(Me)$_2$(^{t}Bu)$_2$ and *m*-xysal-(Cl)$_4$, M = Hf and R = ^{t}Bu) respectively. Complex **5** was crystallized from 1:1:1 mixture of chloroform, ethanol and toluene to yield the ethoxy substituted complex **5a (**L$_2$M$_2$(OR)$_4$, L = *m*-xysal-(Me)$_2$(^{t}Bu)$_2$, M = Zr and R = Et). The X-ray structrures of **1**, **5a** and **7** explain that **1** and **5a** are binuclear helical complexes whereas **7** is trinuclear. These complexes were found to be active for the ring opening polymerization (ROP) of lactides (*rac*-LA, *L*-LA) and epoxides. All the complexes produced atactic poly(lactic acid) (PLA) with good number average molecular weight (M_n) and narrow molecular weight distributions (MWDs). The magnetic isotropic shielding constants were calculated by GIAO/B3LYP/LANL2DZ approach and correlated with the experimental values. The HOMO-LUMO energy band gaps and Mulliken charges were calculated using DFT method to explain the reactivity of these complexes according to the relation between chemical hardness and reactivity established by Pearson. In addition, complexes **1-9**, activated by methylaluminoxane (MAO), were used and found to be moderately active for ethylene polymerization.

Introduction

Besides tremendous industrial applications, synthetic petrochemical based polymers have some major drawbacks such as the use of non-renewable petroleum resources in its production, its harmful effect on the wildlife and sea life and the pollution hazards associated with the ultimate fate of these polymers. As an alternative, a wide range of research over the past two decades has been focused on the synthesis, manufacture and processing of environmentally friendly biodegradable polymers.[1] Of the variety of biodegradable polymers, linear aliphatic polyesters especially poly(lactic acid) (PLA), which is composed of lactide repeat units, has attracted widespread attention as it undergoes hydrolytic degradation to form lactic acid which can be metabolised *in vivo* and also in the environment. Lactic acid, used to synthesize its cyclic dimer lactide, is fermented from glucose, which is in turn derived from starch harvested from annually renewable feed stocks such as corn and sugar beet.[2] Due to its unique properties, a broad range of biomedical as well as pharmaceutical applications of biodegradable polymers[3] have also been considered such as controlled drug delivery, production of biomedical sutures, long term medical implants, bone repairing, scaffolds for tissue engineering etc.[4] The ROP is the method used commercially for the polymerization of lactides and epoxides to form PLA and polyethers respectively.[5] The ROP is initiated by metal complexes since they can give rise to controlled polymerization product with well defined M_n and narrow MWDs. Various catalytic systems have been designed and synthesized to initiate the ROP of lactides to produce well characterized PLA. Bis(phenolate) complexes (salen, salan, salalen) of group 4 metals have had and continue to play an important role in the synthesis of PLA in a controlled and stereoselective manner.[6] Several complexes of tin,[7] lanthanides,[8] aluminium,[9] lithium,[10] magnesium,[11] calcium,[12] iron,[13] zinc[14], bismuth[15], group 4 metals[6a,16,17,18] as well as small organic molecules like ammonium betaines[19] and *N*-heterocyclic carbenes (NHCs)[20] have been reported as initiators for ROP of lactides and cyclic esters.[21] The ROP of epoxides have also attracted considerable interest due to its large commercial value. Poly(propene oxide) (PPO) is a key component for the synthesis of polyurethanes which is used as a bulk commodity material.[22] The ROP of cyclohexene oxide (CHO), propylene oxide (PO), and styrene oxide (SO) has been previously reported with zinc[23], aluminum[24], cobalt[25] catalysts but there are very few reports with group 4 alkoxide complexes towards the homopolymerization of epoxides. In addition to the ROP of lactides and epoxides, extensive research has been devoted to the preparation and activity of group 4 alkoxide complexes in ethylene polymerization as an alternative to metallocene catalysts due to high demand for polyolefin resins and α-olefin feedstocks.[26] Since the discovery of homogenous Ziegler-Natta catalysts by group 4 metallocenes, a wide range of metallocenes have been used and explored thoroughly in order to gain a better control over the polymer properties such as stereoregularity, microstructures and co-monomer incorporation.[27] Single-site group 4 metallocene and half metallocene catalysts were proved to stabilze the homogenous olefin polymerization whereas non metallocene group 4 metal complexes considered for olefin polymerization were mainly dihalide or dialkyl complexes.[28] The recent development of group 4 alkoxide complexes having resemblance to the "FI" catalysts and their good catalytic activity towards olefin polymerization have shown a good scope for the imino-phenoxide complexes of group 4 metals.[29] Herein, we introduce a series of group (IV) metal alkoxide complexes based on the imine based bis-bidentate ligand backbone and demonstrate the catalytic activity towards the ROP of lactides and epoxides and the polymerization of ethylene.

Results and Discussion

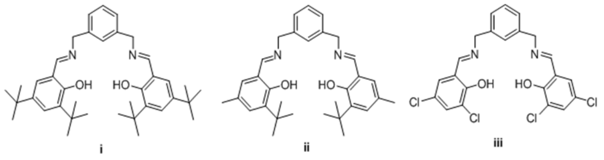


Figure 1. Ligand precursors used in this study: (i) $L^1(^tBu)_4$; (ii) $L^2Me_2(^tBu)_2$; (iii) L^3Cl_4

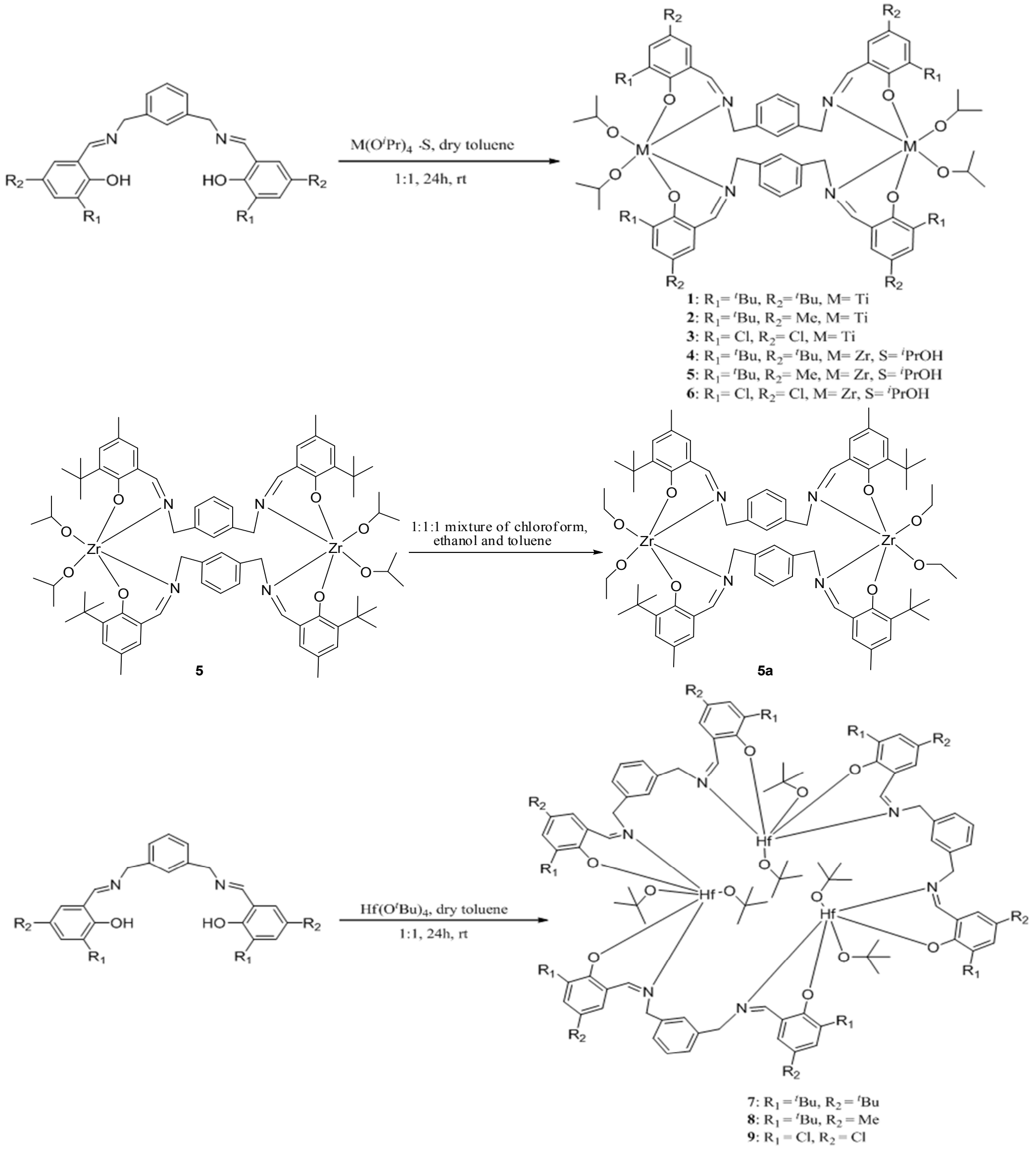
Synthesis and characterization

The Schiff base ligands employed in the study are depicted in Figure 1. Each of these ligands consists of *m*-xylylenediamine and they differ only in the backbone of the ligands which are employed in the condensation reaction for their synthesis, namely 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, 3-*tert*-butyl-2-hydroxy-5-methylbenzaldehyde and 3,5-dichloro-2-hydroxybenzaldehyde. The ligands are abbreviated as *m*-xysal-$(^tBu)_4$ ($L^1(^tBu)_4$), *m*-xysal-$(Me)_2(^tBu)_2$ ($L^2Me_2(^tBu)_2$) and *m*-xysal-$(Cl)_4$ (L^3Cl_4). The synthetic routes to the group 4 metal alkoxides bonded to the ligands are illustrated in Scheme 1. These ligand precursors were complexed to titanium by the reaction with $Ti(O^iPr)_4$ in 1:1 stoichiometric ratio in an argon filled glove box resulting in the formation of **1**, **2** and **3** respectively. Complex **1** was crystallized from toluene solution over a period of 2 weeks. Following the same procedure, treatment of all the ligands with $Zr(O^iPr)_4\cdot{}^iPrOH$ and $Hf(O^tBu)_4$ in 1:1 stoichiometric ratio resulted in the formation of **4-9**. Complex **9** was crystallized from saturated toluene solution. In case of complex **5**, crystals suitable for X-ray diffraction studies were grown after several attempts only from a solution in 1:1:1 mixture of chloroform, ethanol and toluene. Due to the presence of ethanol, the isopropoxide groups bonded to the Zr center were replaced by the ethoxide groups resulting in the formation of **5a**. All the complexes were fully characterized by ^1H, ^{13}C NMR, X-ray crystallography, mass spectroscopy and elemental analysis. Schubert *et al*. reported the synthesis of **1** and **5** but were unable to crystallize those complexes.[30] The formation of these complexes **1-9** were clearly explained by the disappearance of the O-H signals of the ligands $L^1(^tBu)_4$, $L^2Me_2(^tBu)_2$ and L^3Cl_4 (~ 13.7, 13.4 and 14.4 respectively) in the ^1H NMR spectra of the crude products. Complex **1-6** were found to be binuclear whereas **7-9** were found to be trinuclear in the solid state. In case of ^1H NMR spectra of the Hf complexes **7** and **8**, the N-CH_2 protons show two sets of singlet peaks whereas in case of complexes **1-6** and **9**, the N-CH_2 protons show singlet signals. This can be explained by the different spatial arrangement of the N-CH_2 protons in the trinuclear complexes **7** and **8** due to the steric hindrance caused by the bulky substituents in the salicylaldehyde backbone of the ligands. In case of **7** and **8**, the ^1H and ^{13}C NMR spectra exhibited two different sets of the azomethine protons and azomethine carbons appearing upfield shifted as compared to the azomethine ^1H and ^{13}C signals of the ligands $L^1(^tBu)_4$, $L^2Me_2(^tBu)_2$ respectively. This observation can also be attributed to the fact that the sterical crowding of the bulky substituents of the ligands and the O^tBu groups in the trinuclear Hf complexes forces the azomethine protons and carbons of the complexes to adopt different spatial arrangements. The ^{13}C NMR studies are in good agreement with the conclusions drawn from the ^1H NMR studies. Due to the high molecular weights of the metal complexes, MALDI-TOF analysis was preferred over ESI-MS analysis. The MALDI-TOF mass spectra of **1-9** clearly explain that complex **1-6** are binuclear whereas complex **7-9** are trinuclear. We further performed the diffusion-ordered NMR experiment on complex **5a** to estimate the size of the molecule. The Diffusion coefficient came out to be 3.84×10^{-6} $cm^2\ s^{-1}$ (Figure S47, see ESI). The Stokes-Einstein equation is used to derive the hydrodynamic radius (R_H) of a solute from its diffusion coefficient value $D = k_BT/(6\pi\eta R_H)$, where k_B is the Boltzman constant, T is absolute temperature and η is the fluid viscosity (η for $CDCl_3$ at 298K is 0.55×10^{-3} kg s^{-1} m^{-1}).[31] The hydrodynamic radius as measured from ^1H DOSY NMR spectrum of **5a** is 10.28 Å which is very close to the calculated hydrodynamic radius of 10.07 Å from the single crystal X-ray structure. The general procedure for the calculation of R_H from the single crystal X-ray structure is given in ESI. Hence, we can say that the complexes are polynuclear even in the solution.The purity of these compounds was assured through the correct elemental analysis results.

X-ray diffraction studies of 1, 5a and 7

In order to understand the structural details, single crystal X-ray diffraction studies were carried out on **1**, **5a** and **7** respectively. The molecular structures of **1** (with four toluene molecules as solvent of crystallization), **5a** and **7** are illustrated in Figure 2, 3 and 4 and the crystal data are summarized in Table 1.

Complexes **1** and **5a** crystallized from centrosymmetric triclinic space group *P*1 whereas complex **7** crystallized from centrosymmetric monoclinic space group *P*2(1)/*n*. The structures show that **1** and **5a** are binuclear whereas **7** is trinuclear. As depicted in Figures 2, 3 and 4, each metal center of **1** and **5a** and **7** adopts a distorted octahedral geometry coordinating with the oxygen atoms of the two alkoxide groups and N_2O_2 donor atoms of the deprotonated phenolate oxygens and the nitrogens of the azomethine groups from two different Schiff base ligands in a symmetry related bidentate fashion. In case of complex **5a**, the isopropoxide groups were replaced by the ethoxide groups during crystallization from a 1:1:1 mixture of toluene, chloroform and ethanol. The axial Ti-O, Zr-O and Hf-O bond distances, ranging between 1.88-1.89 Å, 2.03-2.04 Å, 2.02-2.04 Å respectively, are slightly greater than the equatorial Ti-O, Zr-O and Hf-O bond distances (1.75-1.77 Å, 1.92-1.93 Å and 1.91-1.92 Å respectively). The larger bond distances between the metal centers and the nitrogens of the azomethine groups (2.24-2.27 Å, 2.40-2.41 Å and 2.36-2.41 Å for **1**, **5a** and **7** respectively) resulting from the donation of unshaired pair of electrons on the N atoms to the empty metal *d* orbitals are in good agreement with the literature values for the coordinate covalent bonds.[16a,16b,28a,32]



Scheme 1. Synthesis of 1−**9**

The phenolic oxygen atoms in each octahedron are slightly bent toward the nitrogen atoms in the equatorial plane, thus making the *trans*-angle deviated from the ideal octahedral geometry (165.2°, 161.3°, 158.4° for O1-Ti1-O2, O1-Zr1-O4 and O1-Hf1-O2 respectively).[33] The distortion in the equatorial plane of each octahedron was resulted due to the widening of the *cis*-angle subtended by the alkoxide oxygen atoms with the metal center (104.4°, 106.1°, 102.7° for O3-Ti1-O4, O2-Zr1-O3 and O3-Hf1-O4 respectively) which further decreases the *cis*-angle formed by the azomethine nitrogens with the metal center (78.1°, 76.2°, 81.1° for N1-Ti1-N2, N1-Zr1-N2 and N1-Hf1-N2 respectively). Selected bond lengths and bond angles are listed in Table S1 (ESI).

Ring opening polymerization of *rac*-LA and *L*-LA

The performance of complexes **1-9** towards the ROP of lactide under solvent free condition was explored. Analysis of the data depicted in the Tables 2, 3 and 4 shows that there is a reasonable degree of control in these polymerizations. High conversions of monomer to polymer was seen within 10 minutes and PLAs with good number average molecular weight (M_n) and narrow MWDs (M_w/M_n = 1.07-1.24) were obtained. Variation of M_n and MWDs with $[M]_0/[Cat]_0$ ratio using **1, 4** and **7** for the polymerizations of *rac*-LA and *L*-LA monomer were studied. The linear plot in Figure 5 indicates that there is a continual rise in M_n with an increase in the $[M]_0/[Cat]_0$ ratio. Variations of the MWD with different $[M]_0/[Cat]_0$ ratios for a given monomer are almost invariable, suggesting that the polymerizations proceed in a controlled manner (Table 2, 3 and 4). The polymerizations of *rac*-LA and *L*-LA in the presence of benzyl alcohol were also performed using these complexes. The catalytic activity of the complexes towards the ROP of lactides increased with the addition of BnOH. The complexes withstand the addition of excess alcohol and the ligands do not fall apart. Rather there is a substitution of the alkoxide group by benzyloxy group during the addition of BnOH and the OBn group further initiates the polymerization (Figure S48, see ESI). In all cases, the observed M_n is in close proximity to the expected M_n and the narrow MWDs suggest a good control in these polymerizations.

Table 1. Crystal data for the structures **1**, **5a** and **7**

Compounds	**1·4C$_7$H$_8$**	**5a**	**7**
Molecular formula	$C_{116}H_{160}N_4O_8Ti_2$	$C_{72}H_{96}N_4O_8Zr_2$	$C_{138}H_{204}Hf_3N_6O_{12}$
Formula weight	1834.27	1327.96	2674.53
T/K	296(2) K	298(2) K	296(2) K
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system,	Triclinic,	Triclinic,	Monoclinic,
Space group	*P*1	*P*1	*P*2(1)/*n*
a/Å	11.524(8)	11.0938(12)	19.1043(7)
b/Å	15.116(11)	14.2299(19)	29.5065(11)
c/Å	16.715(12)	14.4174(19)	30.3372(10)
α (°)	74.45(3)	68.240(6)	90
β (°)	83.73(4)	88.659(6)	97.805(2)
γ (°)	73.38(4)	82.273(6)	90
V/Å^3	2686(3)	2093.8(5)	16942.7(11)
Z, Calculated density(Mg/ m^3)	1, 1.134	1, 1.053	4, 1.049
Absorption coefficient (mm^{-1})	0.204	0.303	1.880
Reflections collected/Independent reflections	24529 / 7331	24214/7194	116293 / 35986
Data/restraints/parameters	7331 / 0 / 581	7194 / 0 / 398	35986 / 357 / 1544
Goodness of fit on F^2	1.018	1.002	0.882
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0958$, $wR_2 = 0.2234$	$R_1 = 0.0490$, $wR_2 = 0.1297$	$R_1 = 0.0489$, $wR_2 = 0.1087$
R indices (all data)	$R_1 = 0.2500$, $wR_2 = 0.3125$	$R_1 = 0.0791$, $wR_2 = 0.1415$	$R_1 = 0.1113$, $wR_2 = 0.1219$

$R_1 = \sum|F_0| - |F_c|/\sum|F_0|$, $wR_2 = [\sum (F_0^2 - F_c^2)^2/\sum w(F_0^2)^2]^{1/2}$

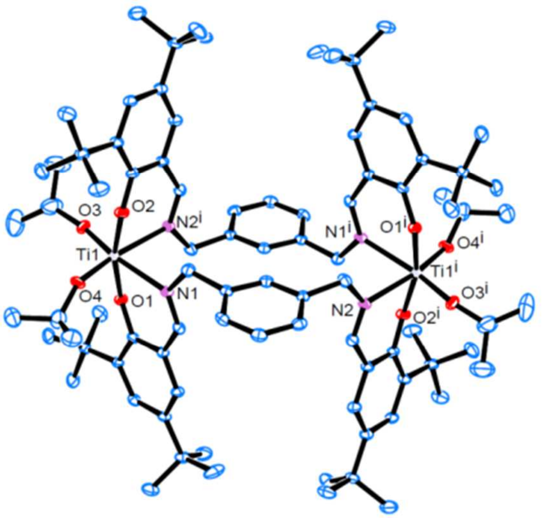


Figure 2. Molecular structure of **1**; thermal ellipsoids were drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in °) are: O1-Ti1 1.89(7), O3-Ti1 1.75(5), O2-Ti1 1.89(7), N2-Ti1 2.24(7), N1-Ti1 2.27(7), O1-Ti1-O3 94.4(3), O1-Ti1-O2 165.2(3), O3-Ti1-O4 104.4(3), O1-Ti1-N2 87.6(3), N2-Ti1-N1 78.1(3).

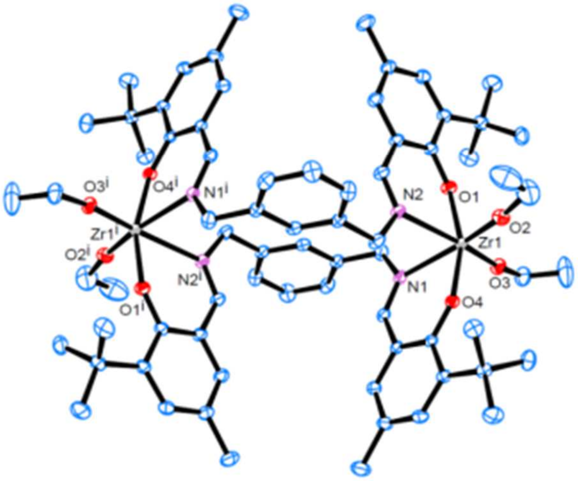


Figure 3. Molecular structure of **5a**; thermal ellipsoids were drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in °) are: O1-Zr1 2.03(3), O2-Zr1 1.93(5), O4-Zr1 2.03(3), N2-Zr1 2.41(3), N1-Zr1 2.41(4), O2-C36 1.39(1), O3-C34 1.41(9), O1-Zr1-O2 96.8(2), O1-Zr1-N2 76.4(1), O1-Zr1-O3 106.2(2), N2-Zr1-N1 76.2(1), O1-Zr1-O4 161.4(1), O2-C36-C37 115(1), O3-C34-C35 112.2(8).

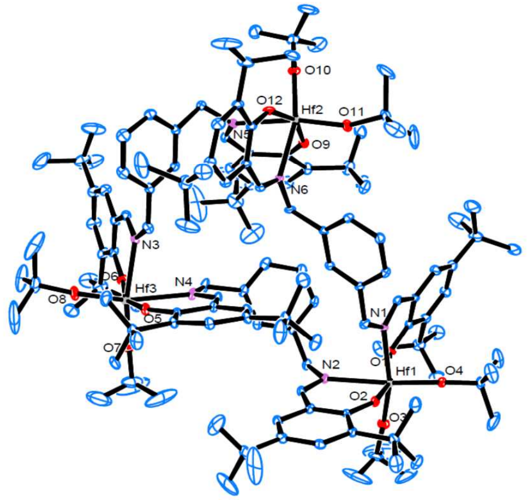


Figure 4. Molecular structure of **7**; thermal ellipsoids were drawn at 30% probability level, hydrogen atoms have been omitted for clarity. Selected bond lengths (in Å) and bond angles (in °) are: O1-Hf1 2.04(7), O4-Hf1 1.91(6), O3-Hf1 1.91(8), N1-Hf1 2.36(8), O12-Hf2 2.02(8), O10-Hf2 1.92(8), N5-Hf2 2.41(9), N6-Hf2 2.39(8), O1-Hf1-O4 96.8(3), O1-Hf1-O2 156.8(3), O3-Hf1-O4 102.7(3), N1-Hf1-N2 81.1(3), O9-Hf2-O12 156.8(3), O9-Hf2-O11 95.9(3), N5-Hf2-N6 80.5(3), O10-Hf2-O11 102.7(3)

In general, all these complexes were proved to be highly active initiators for the ROP of lactide. Variation in activity was marginal with Hafnium complexes being slightly more active than Titanium and Zirconium complexes. In case of Hf complexes (**7**-**9**), the TOFs in the polymerizations were found to be higher than the TOFs observed in case of Ti (**1**-**3**) and Zr complexes (**4**-**6**). The ineffective shielding of the Hf metal in the trinuclear complexes **7**-**9** tends to expose more open coordination sphere for the lactide monomers. This may be the reason behind the higher polymerization rate of Hf complexes.[6a] To understand the influence of the substituents in the bis(iminophenoxide) ligands on the activity towards ROP and the microstructure of the produced PLAs, the lactide polymerization abilities of complexes **1**-**9** were examined in detail. The ROPs are anticipated to proceed via coordination-insertion mechanism in which the Lewis acidity of the metal centre is important. If we compare the electron-releasing effect of the three substituents in the phenolic moiety of the ligand, the order will be ^{t}Bu > Me > Cl. As the electron donating tendency of the substituent on the phenyl ring increases, the Lewis acidic character of the metal centre decreases leading to the loss of reactivity towards ROP. Hence, the order of the reactivity towards ROP of a given monomer is Cl > Me > ^{t}Bu. This hypothesis is in good agreement with our experimental observation. Analysis of the polymer microstructure by homonuclear decoupled ^{1}H NMR reveals that all the complexes yielded atactic PLAs (Figure S29 and S30, see ESI). The plot of M_n *vs* % conversion for *rac*-LA and *L*-LA polymerization using complex **3**, **4** and **7** is shown in Figure 6. The linear relationship of the plot suggests that a good degree of control in these polymerizations were achieved.

Table 2. Polymerization data for *rac*-LA and *L*-LA catalyzed by complexes **1**-**9** in 200:1 ratio at 140 °C

Entry	Cat.	LA	[LA]$_0$/[Cat]$_0$	time^a (min)	Yield (%)	M_n(GPC)^b (kg/mol)	$M_n$$^{(theoretical)c}$ (kg/mol)	TOF^d (min^{-1})	M_w/M_n
1	**1**	*rac*-LA	200/1	7	99	41.23	28.89	28.29	1.08
2	**2**	*rac*-LA	200/1	6	98	38.14	28.89	32.67	1.16
3	**3**	*rac*-LA	200/1	5	98	35.37	28.89	39.20	1.18
4	**4**	*rac*-LA	200/1	8	99	44.24	28.89	24.75	1.13
5	**5**	*rac*-LA	200/1	8	97	36.05	28.89	24.25	1.14
6	**5a**	*rac*-LA	200/1	5	97	35.37	29.31	38.80	1.11
7	**6**	*rac*-LA	200/1	6	99	38.91	28.89	33.00	1.08
8	**7**	*rac*-LA	200/1	5	98	42.39	28.90	39.20	1.09
9	**8**	*rac*-LA	200/1	4	99	38.71	28.90	49.50	1.14
10	**9**	*rac*-LA	200/1	4	99	35.78	28.90	49.50	1.17
11	**1**	*L*-LA	200/1	6	99	35.21	28.89	33.00	1.07
12	**2**	*L*-LA	200/1	4	99	36.07	28.89	49.50	1.11
13	**3**	*L*-LA	200/1	4	98	35.59	28.89	49.00	1.17
14	**4**	*L*-LA	200/1	7	98	38.49	28.89	28.00	1.13
15	**5**	*L*-LA	200/1	7	98	35.40	28.89	28.00	1.16
16	**5a**	*L*-LA	200/1	6	97	37.16	29.31	32.33	1.17
17	**6**	*L*-LA	200/1	5	99	35.91	28.89	39.60	1.15
18	**7**	*L*-LA	200/1	4	99	43.28	28.90	49.50	1.16
19	**8**	*L*-LA	200/1	4	97	40.37	28.90	48.50	1.15
20	**9**	*L*-LA	200/1	3	98	37.09	28.90	65.33	1.17

^{a}Time of polymerization measured by quenching the polymerization reaction when all monomer were found consumed. ^{b}Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. ^{c}$M_n$$^{(theoretical)}$ at 100% = [M]$_0$/[C]$_0$ × mol weight of monomer + molecular weight of end group. ^{d}TOFs calculated as (mol of LA consumed) / (mol of catalyst × time of polymerization).

Table 3. Polymerization data for *rac*-LA catalyzed by complexes **1**, **4** and **7** in different [*rac*-LA]$_0$/[Cat]$_0$ ratio at 140 °C

Entry	Cat.	[*rac*-LA]$_0$/ [Cat]$_0$	time^a (min)	Yield (%)	M_n(GPC)^b (kg/mol)	$M_n^{\text{(theoretical)}c}$ (kg/mol)	TOF^d (min^{-1})	M_w/M_n
1	**1**	200/1	7	99	41.23	28.89	28.29	1.08
2	**1**	400/1	9	98	75.69	57.71	43.56	1.09
3	**1**	800/1	12	98	138.37	115.36	65.33	1.14
4	**4**	200/1	8	99	44.24	28.89	24.75	1.13
5	**4**	400/1	10	99	78.61	57.71	39.60	1.18
6	**4**	800/1	12	98	141.32	115.36	65.33	1.18
7	**7**	200/1	5	98	42.39	28.90	49.50	1.09
8	**7**	400/1	6	98	76.25	57.73	65.33	1.12
9	**7**	800/1	10	98	144.54	115.39	78.40	1.18

^{a}Time of polymerization measured by quenching the polymerization reaction when all monomer were found consumed. ^{b}Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. $^c M_n^{\text{(theoretical)}}$ at 100% = [M]$_0$/[C]$_0$ × molecular weight of monomer + molecular weight of end group. ^{d}TOFs calculated as (mol of LA consumed) / (mol of catalyst × time of polymerization).

Table 4. Polymerization data of *rac*-LA in presence of BnOH catalyzed by complexes **1**, **4** and **7** in 100:1:5 ratio at 140 °C

Entry	Cat.	LA	[LA]$_0$/ [Cat]$_0$/[BnOH]$_0$	time^a (min)	Yield (%)	M_n(GPC)^b (kg/mol)	$M_n^{\text{(theoretical)}c}$ (kg/mol)	TOF^d (min^{-1})	M_w/M_n
1	**1**	*rac*-LA	100/1/5	4	99	3.34	2.99	4.95	1.08
2	**2**	*rac*-LA	100/1/5	3	99	3.26	2.99	6.60	1.07
3	**3**	*rac*-LA	100/1/5	3	98	3.24	2.99	6.53	1.11
4	**4**	*rac*-LA	100/1/5	4	99	3.46	2.99	4.95	1.14
5	**7**	*rac*-LA	100/1/5	3	97	3.53	2.99	6.47	1.08
6	**1**	*L*-LA	100/1/5	4	98	3.38	2.99	4.90	1.09
7	**4**	*L*-LA	100/1/5	5	99	3.27	2.99	3.96	1.09
8	**5**	*L*-LA	100/1/5	5	98	3.32	2.99	3.92	1.12
9	**5a**	*L*-LA	100/1/5	3	98	3.34	2.99	6.53	1.14

^{a}Time of polymerization measured by quenching the polymerization reaction when all monomer were found consumed. ^{b}Measured by GPC at 27 °C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. $^c M_n^{\text{(theoretical)}}$ at 100% = [M]$_0$/[C]$_0$ × molecular weight of monomer + molecular weight of end group. ^{d}TOFs calculated as (mol of LA consumed) / (mol of catalyst × mol of BnOH × time of polymerization).

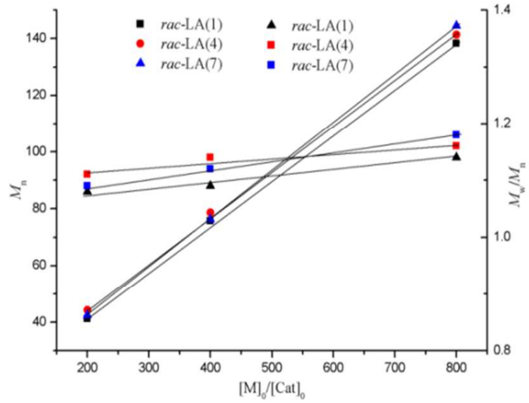


Figure 5. Plot of M_n and MWD *vs*. [M]$_0$/[Cat]$_0$ for *rac*-LA polymerization at 140 °C using **1, 4** and **7**

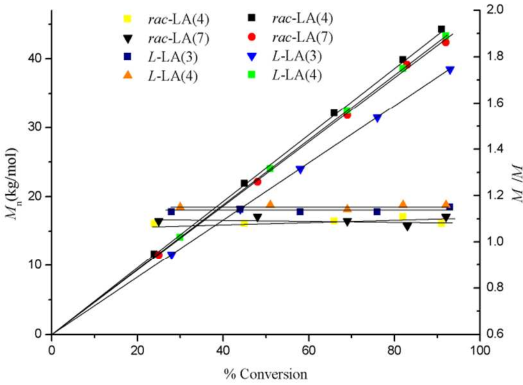


Figure 6. Plot of M_n and M_w/M_n *vs*. % conversion for *L*-LA and *rac*-LA polymerization at 140 °C using **3, 4** and **7**

In order to understand the polymerization mechanism, low molecular weight oligomers of *rac*-LA were synthesized by reacting *rac*-LA with complex **1** and **5a** in 10:1 and 20:1 ratio respectively at 140 °C under solvent free condition. The resultant residue in each case was dissolved in minimum amount of CH_2Cl_2 and then poured into cold methanol. The oligomers (PLA-1 and PLA-5) were isolated and subjected to MALDI-TOF and ^{1}H NMR analysis. The ^{1}H NMR of purified PLA-1 (Figure S31, see ESI) clearly shows that the oligomer is end capped with one isopropyl ester group and one hydroxyl group whereas in case of PLA-5, the oligomer is end capped with one bis(imino)phenoxide and one hydroxyl group (Figure S32, Supporting Information). The MALDI-TOF mass spectrum of PLA-1 and PLA-5 contains all the peaks as CH_3CN adduct (Figure 7) and as Na adduct respectively (Figure S33, see ESI). The peaks are equally spaced by 72 a.u. and having masses consistent with a linear PLA bearing the initiating group at the chain end. It is noted that the peaks (m) corresponding to the molecular masses of the intermolecular transesterification products were also observed but no peak corresponding to intramolecular transesterification product was present. The results indicate that the polymerization proceeds through the coordination-insertion mechanism.[1a] The kinetic studies for the polymerization of *rac*-LA using **4** and **7** were studied next. The linear plots without induction period of ln[*rac*-LA]$_0$/[*rac*-LA]$_t$ *vs*. time suggest that there is a first-order dependence of the rate of polymerization on the monomer concentration. The values of k_{obs} for *rac*-LA polymerization catalyzed by **4** and **7** were evaluated from the slope of these lines and were found to be 0.297 min^{-1} and 0.492 min^{-1} respectively according to the literature.[34]

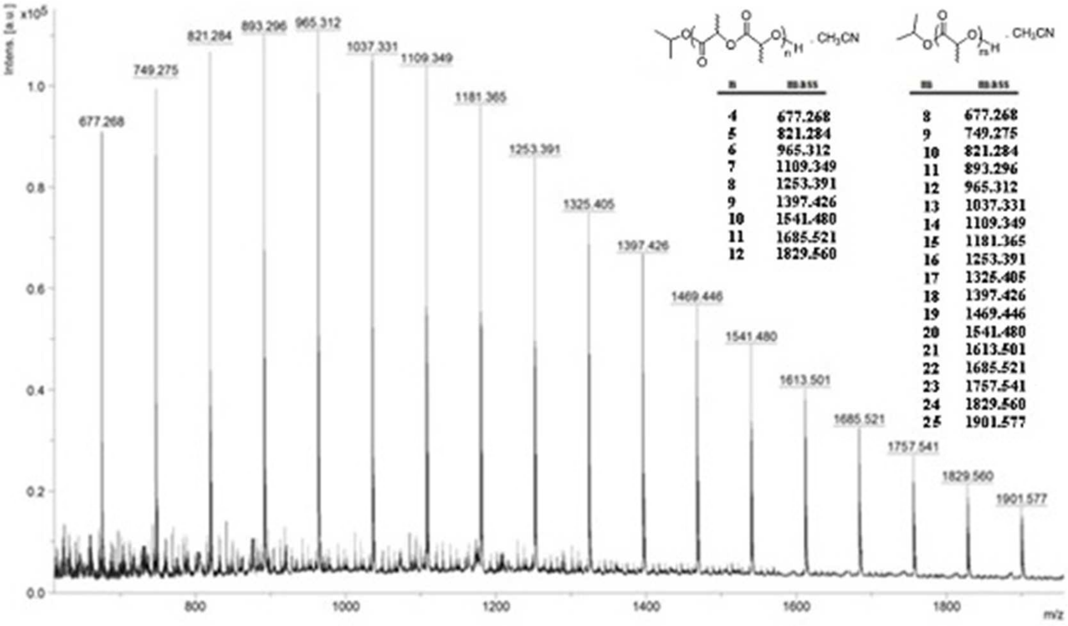


Figure 7. MALDI-TOF spectrum of the crude product obtained from a reaction between *rac*-LA and **1** in 10:1 ratio at 140˚C

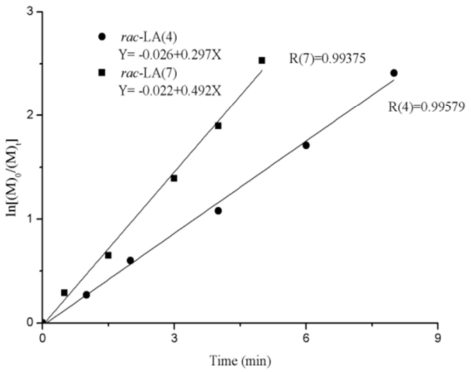


Figure 8. Semi-logarithmic plots of *rac*-LA, conversion in time initiated by complex **4** and **7**

Ring opening homopolymerization of epoxides

The reactivity of **1-9** towards the ring opening homo polymerization of cyclohexene oxide (CHO), styrene oxide (SO) and propylene oxide (PO) was explored under solvent free condition. The results of the initial screening of **1-9** for the homopolymerization of epoxides are depicted in Table 5. Complexes **1-9** were found to be active in the solvent free ROP of epoxides. Yield and molecular weight of polymer increase with extension of the reaction time (Figure 9). From Figure 10, it is found that for **1**, **4** and **7**, with the extension of the reaction time, % conversion of CHO to the respective polymers increases and the MWDs of polycyclohexenoxides (PCHOs) produced remains controlled (1.10-1.29). All the polymerization reactions of PO, CHO and SO were performed in high pressure autoclave under argon atmosphere at 60 °C, 100 °C and 130 °C respectively and two different monomer to catalyst ratios (1000:1 and 10000:1) were considered. Good conversion was achieved in each case. Polymerization of PO yielded oily polypropylene oxide (PPO) polymer, the ^{13}C NMR spectrum of which shows numerous resonances in the regions of 75.3 and 73.4 ppm assignable to methine and methylene carbons, respectively (Figure S34, ESI). The ^{13}C NMR spectrum of the oily polymer revealed that the PPO component was atactic. The ^{1}H NMR and the MALDI-TOF spectra analysis of the obtained polymer of CHO and SO catalyzed by **1** and **7** in 1000:1 ratio respectively indicates that polymerization is initiated by the alkoxide fragment (Figures S35-S38, see ESI)

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Table 5: Selected polymerization data for epoxides catalyzed by **1-9**

Entry	Cat.	Monomer	$[M]_0$:$[Cat]_0$	time^a (h)	Yield (%)	TOF^b (h^{-1})	M_n $^{(GPC)c}$ (kg/mol)	M_w/M_n
1	**1**	CHO	1000:1	12	93	77.5	95.46	1.19
2	**1**	CHO	10000:1	45	81	180	677.23	1.21
3	**2**	CHO	1000:1	12	91	75.8	88.03	1.21
4	**4**	CHO	1000:1	12	87	72.5	94.31	1.14
5	**5a**	CHO	1000:1	12	86	71.7	92.60	1.14
6	**5a**	CHO	10000:1	45	78	173.3	758.07	1.24
7	**7**	CHO	1000:1	12	91	75.8	85.38	1.25
8	**1**	PO	1000:1	12	92	76.7	48.14	1.19
9	**5a**	PO	1000:1	12	84	70	43.87	1.15
10	**7**	PO	1000:1	12	85	70.8	48.09	1.21
11	**1**	SO	1000:1	12	89	74.2	104.33	1.27
12	**5a**	SO	1000:1	12	83	69.2	96.38	1.24
13	**7**	SO	1000:1	12	88	73.3	97.62	1.19

Polymerization was run with 2 ml of epoxide (cyclohexene oxide, styrene oxide, propene oxide) for 12 h. [a]Based on crude polymer weight and ^1H NMR analysis. [b]TOFs calculated as (mol of epoxide consumed) / (mol of catalyst × time of polymerization). [c]M_n Measured by GPC at 27°C in THF relative to polystyrene standards with Mark-Houwink corrections for M_n. Theoretical molecular weights of PCHO for entry 1-7, PPO for entry 8-10, PSO for entry 11-13 are 98.20 kg/mol, 58.14 kg/mol and 120.20 kg/mol respectively.

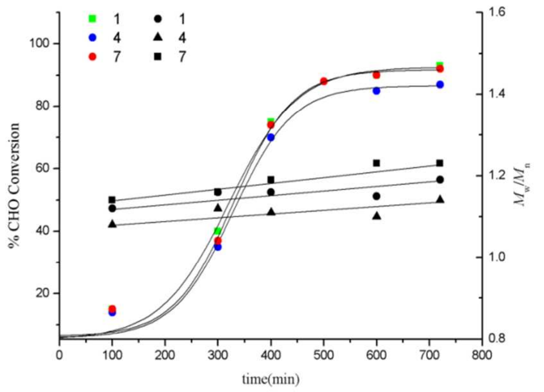


Figure 9. Plot of % Conversion and M_w/M_n *vs.* time (min) for CHO polymerization at 100 °C using **1**, **4** and **7**

Ethylene polymerization

The catalytic activity of the complexes **1-9** activated by MAO towards the polymerization of ethylene were evaluated. With MAO as co-catalyst, all the complexes exhibited moderate to good catalytic activity (Table 6). The plot of the activity *vs* [MAO]/[C] ratio is depicted in Figure S39 (see ESI). Different solvents were used to explore the effect on activity and highest activity in toluene proved it to be the correct solvent for the polymerizations (Figure S40, see ESI).

Table 6. Data for the Polymerization of ethylene catalyzed by complexes **1–9** with MAO

Entry	**Catalyst**	**Activity**^{a}	**Yield**^{b} **(g)**	M_n^{c} **(Kg/mol)**	M_w/M_n
1	**1**	5.88	1.0	57.42	1.96
2	**2**	6.15	1.2	59.77	2.01
3	**3**	6.22	1.2	56.39	1.98
4	**4**	5.62	0.9	61.78	2.07
5	**5a**	5.79	1.1	58.34	1.95
6	**6**	6.67	1.2	57.46	2.11
7	**7**	8.42	0.8	60.08	1.89
8	**8**	8.57	0.8	61.36	1.95
9	**9**	9.52	1.0	64.59	2.03

All experiments were done in toluene at MAO:catalyst ratio = 1000, unless otherwise indicated. Ethylene pressure = 8 atm, 80 °C for 30 min, catalyst = 50 mg, solvent = 45 ml. [a]A = Activity in (g PE/mol cat ×h) ×104. [b]g of PE obtained after 30min. [c]Determined by GPC in 1,2,4-$C_6Cl_3H_3$ vs. narrow polystyrene standards.

Computational studies

In order to get a better insight into the structures and reactivity of the molecules, geometries of all the molecules were first optimized at B3LYP/LANL2DZ level. The actual and optimized bond lengths and bond angles obtained from X-ray crystallographic studies as well as theoretical calculations of the structures **1, 5a, 7** are reported in Table S1 (see ESI). The bond lengths and bond angles prove that the ligands are oriented in distorted octahedral geometries around the metal centres in all the complexes. The structural similarity between experimental and theoretical values is depicted in Table S1 (see ESI). The slight variations in bond parameters are observed because single crystal

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

X-ray structures were recorded in the solid state and DFT calculations belong to gaseous phase.

The ^{1}H and ^{13}C NMR spectra were analysed by gauge including atomic orbital (GIAO) method using the same LANL2DZ basis set, solvation in chloroform being expressed by the integral equation formalism phase continuum model (IEFPCM) (Figures S45-S46, see ESI).[35] The calculated isotropic shielding constants were converted into chemical shifts in ppm relative to TMS (optimized at B3LYP/6-31G**).[36] The experimental and calculated chemical shifts for compound **5a** and **8** correlate well and are reported in Table S2 (ESI). The Pearson Correlation coefficient between calculated and experimental ^{1}H and ^{13}C chemical shifts in case of compound **5a** are 0.9937 and 0.9997 and in case of compound **8** are 0.9995 and 0.9974 (Figures 11-12). The optimized geometry of **5a** with atom numbering scheme is shown in Figure 10. In order to understand the activity towards ROP, HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) energy gaps were calculated for all the complexes at B3LYP/LANL2DZ level.

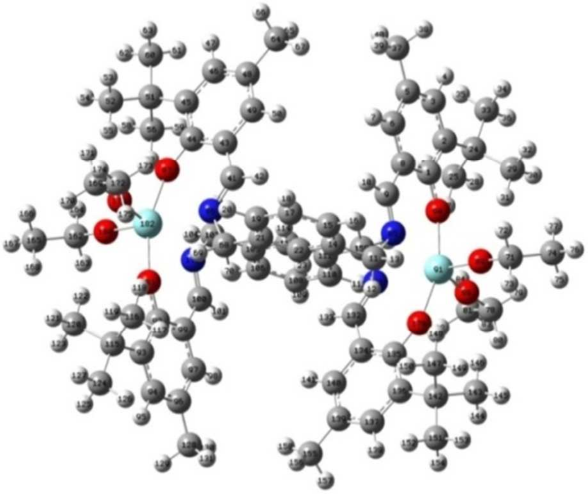


Figure **10.** Optimized geometry of compounds **5a**

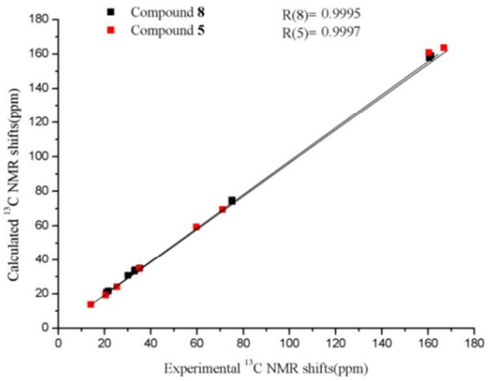


Figure 11. Plot of the calculated vs. the experimental ^{13}C NMR chemical shifts (ppm) of **5a** and **8**

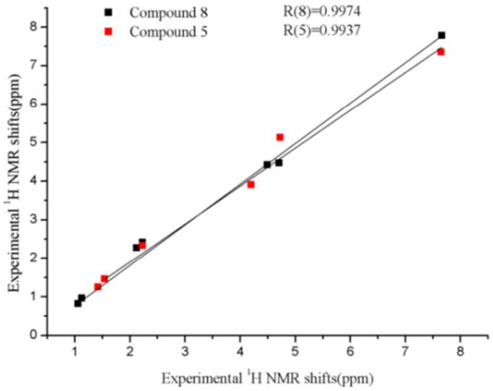


Figure 12. Plot of the calculated vs. the experimental ^{1}H NMR chemical shifts (ppm) of **5a** and **8**

Applying Koopman's theorem that frontier orbital energies HOMO and LUMO are given by ionization potential (I) and electron affinity (A) respectively, Pearson established a relation between chemical hardness (η) of a complex with the HOMO-LUMO energy gap by the equation $\eta = (I - A)/2$. The equation showed that small HOMO-LUMO energy gap resulted in higher polarizability and softness of the complex. The harder the complex is, the more stable it is towards a reaction.[37] We adopted this concept in explaining the reactivity of complexes **1**-**9** towards ROP. The low energy differences between HOMO and LUMO for all the complexes result in high reactivity towards ROP. As shown in Figure S41 (ESI), all the complexes exhibit very low band gap between HOMO and LUMO with slight variations from each other. A diagram showing the electron dispersion of HOMO and LUMO for compound **3**, **6** and **9** is depicted in Figure 13. It is noted that complex **9** has the lowest energy difference (3.75 eV) between HOMO (-6.34 eV) and LUMO (-2.58 eV) followed by **3** and **6** respectively in an increasing order of energy difference. This calculation correlates well with the experimental values as the highest activity towards ROP was observed for **9** among these three complexes. The frontier molecular orbital diagrams of **1**, **2**, **4**, **5a** and **8** are depicted in S41 (see ESI).

In case of **1**, Mulliken net charges for the O atoms of the O^{i}Pr groups are -0.577 and -0.568, which are more electron rich than the O atoms (-0.558 and -0.554 respectively) of the phenolic ligand resulting in more nucleophilic character of the O^{i}Pr group (Figure S43, ESI). Hence, the O^{i}Pr group has more tendency to initiate the ROP. Similarly, in case of **7**, more electron rich O atoms (Mulliken net charges are -0.641 and -0.643) of the O^{t}Bu result in more nucleophilic character of the O^{t}Bu group (S43-S45, Supporting Information). In case of complex **5a**, the phenolic O atoms (Mulliken net charges are -0.605 and -0.599) are more electron rich than the O atoms of the OEt groups (Mulliken net charges are -0.592 and -0.589). Hence, the OPh group initiates the ROP in case of **5a**. Computed mulliken charges (Q/e) on various atoms of **1**, **5a** and **7** are reported in Table 7. It is noted that complex **4** and **6,** having O^{i}Pr groups, do not exhibit similar characteristics shown by **5a**. So, Zr(IV) metal alkoxide complexes (**4**, **5a** and **6**) have different initiating groups towards ROP depending on the nature of the alkoxide groups present in the complexes.

Table 7. Computed Mulliken Net charges (Q/e) on various atoms of metal complexes **1**, **5a** and **7**

COMPLEX 1		COMPLEX 5a		COMPLEX 7	
Position	Mulliken Charge (Q/e)	Position	Mulliken Charge (Q/e)	Position	Mulliken Charge (Q/e)
Ti181	1.111	Zr91	1.550	Hf1	1.561
O79	-0.558	O90	-0.599	O8	-0.605
O164	-0.554	O178	-0.605	O31	-0.600
N78	-0.190	N85	-0.248	N5	-0.232
N159	-0.198	N177	-0.233	N42	-0.234
O162	-0.577	O88	-0.592	O4	-0.641
O163	-0.568	O89	-0.589	O6	-0.643

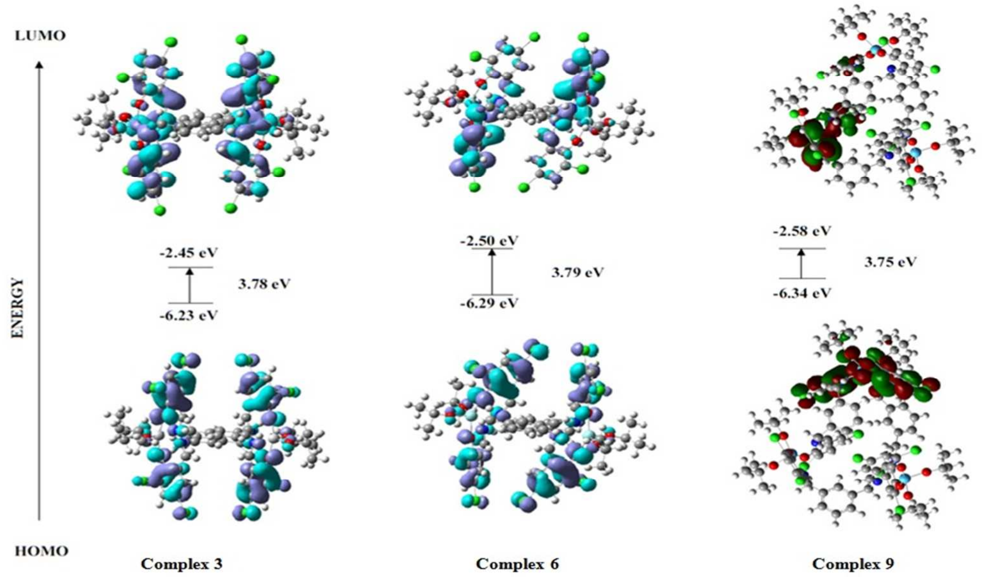


Figure 13. Frontier molecular orbital diagrams of complexes **3**, **6** and **9**

Conclusion

This work describes the synthesis of a series of group 4 metal complexes containing imine based bis-bidentate ligands and their reactivity towards the ROP of *rac*-LA, *L*-LA and epoxides. All the complexes have shown very good reactivity towards the polymerization in a controlled manner with slight variations from each other. The most noteworthy observation of the polymerization studies was the significant TOFs in the polymerizations which are comparatively better than those found for the recently reported group 4 metal complexes.[2d,5,6a,16a,16d,17a,17b,17h,17o,38] All the catalysts were proved to be highly active towards ROP even at higher monomer to catalyst ratios. Experimental results show that the modifications of the alkoxide groups present in the catalysts do affect the initiation of ROP. The catalysts were also found to be active towards the polymerization of ethylene using MAO as cocatalyst.

General Experimental Methods

Materials and general details

For the preparation and characterization of metal complexes, all reactions and manipulations were carried out under an inert atmosphere of argon using either standard schlenk or glove box techniques. All solvents were freshly distilled from suitable drying agent (toluene over sodium/benzophenone and chloroform over calcium hydride) and degassed prior to use. *rac*-LA, *L*-LA, cyclohexene oxide, propylene oxide, styrene oxide, $CDCl_3$ for NMR studies were purchased from Aldrich and Acros. *rac*-LA and *L*-LA were purified by sublimation twice whereas CHO, PO and SO and $CDCl_3$ were dried over calcium hydride followed by distillation before use. All chemicals needed for the preparation of ligands, $Ti(O^iPr)_4$, $Zr(O^iPr)_4{\cdot}{}^iPrOH$, $Hf(O^tBu)_4$ were purchased from Aldrich and used as such without any further purification. The ligands *m*-xysal-(^{t}Bu)$_4$ (L^1(^{t}Bu)$_4$), *m*-xysal-(Me)$_2$(^{t}Bu)$_2$ (L^{2}Me$_2$(^{t}Bu)$_2$) and *m*-xysal-(Cl)$_4$ (L^{3}Cl$_4$) were prepared according to the standard literature procedures[39] and purified by azeotropic distillation prior to use. All ^{1}H and ^{13}C NMR spectra were recorded on 400 MHz Bruker Avance with chemical shifts given in parts per million (ppm). The diffusion-ordered NMR spectrum was recorded on 500 MHz Bruker Avance NMR spectrometer. MALDI-TOF mass spectra for metal complexes and oligomers were recorded on a Bruker Daltonics instrument using dihydroxybenzoic acid matrix. Data concerning molecular weights and the polydispersity indices of the polymer samples obtained by the ring opening polymerization of lactide monomers and homopolymerization of epoxide monomers were determined by using a GPC instrument with Waters 510 pump and Waters 410 differential refractometer as the detector. Three columns namely WATERS STRYGEL-HR5, STRYGEL-HR4 and STRYGEL-HR3 each of dimensions (7.8×300 mm) were connected in series. Measurements were done in THF at 27 ºC. In case of ethylene samples, number average molecular weights (M_n) and MWDs were determined by GPC instrument with Waters 510 pump and Waters 2414 differential refractometer as the detector. The column namely WATERS STRYGEL-HR4 of dimensions (4.6×300 mm) was connected during the experiment. Measurements were done in tri-chloro benzene. Number average molecular weights (M_n) and molecular weight distributions (M_w/M_n) (MWDs) of polymers were measured relative to polystyrene standards.

Preparation of Complex 1

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2,4-di-*tert*-butylphenol) or L^1(^{t}Bu)$_4$ (0.1 g, 0.18 mmol) in 10 mL of dry toluene was added a solution of $Ti(O^iPr)_4$ (0.05 g, 0.18 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box. The colour of the reaction mixture changed to yellow. The solution was allowed to come to room temperature and stirred for an additional 24h. The solvent was removed under reduced pressure to give reddish yellow solid (Yield 0.11 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.18 (d, J = 6.8 Hz, 24H, -CH(C*H*$_3$)$_2$), 1.27 (s, 36H, -C(C*H*$_3$)$_3$), 1.35 (s, 36H, -C(C*H*$_3$)$_3$), 4.79 (s, 8H, -C*H*$_2$-N=), 4.64-4.74 (sept, J = 6.4 Hz, 8H, -C*H*(CH$_3$)$_2$), 6.36 (s, 2H, Ar-*H* xylyl), 6.61 (m, 4H, Ar-*H* xylyl), 6.88 (m, 2H, Ar-*H* xylyl), 7.06 (m, 4H, Ar-*H*), 7.49 (m, 4H, Ar-*H*), 7.66 (s, 4H, N=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 21.8 (-CH(*C*H$_3$)$_2$), 26.0 (Ar-C(*C*H$_3$)$_3$), 30.0 (Ar-C(*C*H$_3$)$_3$), 35.2 (-*C*(CH$_3$)$_3$), 43.7(-*C*(CH$_3$)$_3$), 61.9 (N-*C*H$_2$), 68.2 (-*C*H(CH$_3$)$_2$), 124.8 (Ar-*C*), 125.5 (Ar-*C*), 128.46 (Ar-*C*), 128.5 (Ar-*C*), 129.2 (Ar-*C*), 129.27 (Ar-*C*), 129.3 (Ar-*C*), 132.1 (Ar-*C*), 132.5 (Ar-*C*), 152.1 (Ar-*C*), 164.9 (-*C*=N). MALDI-TOF *m/z* calculated for [M+H]$^+$. $C_{88}H_{133}N_4O_8Ti_2$: 1466.72, found 1466.50. Anal. Calc. for $C_{88}H_{128}N_4O_8Ti_2$: C, 72.11; H, 8.80; N, 3.82; found C, 72.38; H, 8.33; N, 4.04.

Preparation of Complex 2

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-*tert*-butyl-4-methylphenol) or L^1(Me)$_4$ (0.1 g, 0.21 mmol) in 10 mL of dry toluene was added a solution of $Ti(O^iPr)_4$ (0.059 g, 0.21 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1** (Yield 0.11 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.50 (d, J = 6 Hz, 24H, -CH(C*H*$_3$)$_2$), 1.53 (s, 36H, -C(C*H*$_3$)$_3$), 2.17 (s, 12H, Ar-C*H*$_3$), 4.82 (s, 8H, -C*H*$_2$-N=), 4.65-4.74 (sept, J = 6.8 Hz, 8H, -C*H*(CH$_3$)$_2$), 6.30 (s, 2H, Ar-*H* xylyl), 6.63 (m, 4H, Ar-*H* xylyl), 6.83 (m, 4H, Ar-*H*), 7.08 (m, 2H, Ar-*H* xylyl), 7.47 (m, 4H, Ar-H), 7.66 (s, 4H, N=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 21.4 (-CH(*C*H$_3$)$_2$), 25.7 (Ar-*C*H$_3$), 30.7 (-C(*C*H$_3$)$_3$), 43.4 (-*C*(CH$_3$)$_3$), 61.9 (N-*C*H$_2$), 70.2 (-*C*H(CH$_3$)$_2$), 124.5 (Ar-*C*), 125.7 (Ar-*C*), 128.6 (Ar-*C*), 128.1 (Ar-*C*), 129.5 (Ar-*C*), 129.2 (Ar-*C*), 129.3 (Ar-*C*), 132.5 (Ar-*C*), 132.6 (Ar-*C*), 151.5 (Ar-*C*), 164.6 (-*C*=N). MALDI-TOF *m/z* calculated for [M+Na]$^+$. $C_{76}H_{104}N_4O_8Ti_2Na$: 1298.39, found 1299.51. Anal. Calc. for $C_{76}H_{104}N_4O_8Ti_2$: C, 70.36; H, 8.08; N, 4.32; found C, 70.83; H, 8.12; N, 4.27.

Preparation of Complex 3

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2,4-dichlorophenol) or L^{1}Cl$_4$ (0.1 g, 0.21 mmol) in 10 mL of dry toluene was added a solution of $Ti(O^iPr)_4$ (0.059 g, 0.21 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1** (Yield 0.12 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.10-1.15 (d, J = 6 Hz, 24H, -CH(C*H*$_3$)$_2$), 4.79 (s, 8H, -C*H*$_2$-N=), 4.68-4.85 (sept, J = 8 Hz, 8H, -C*H*(CH$_3$)$_2$), 6.33 (s, 2H, Ar-*H* xylyl), 6.90 (m, 4H, Ar-*H* xylyl), 6.96 (m, 2H, Ar-*H* xylyl), 7.19 (m, 4H, Ar-*H*), 7.46 (m, 4H, Ar-*H*), 7.58 (s, 4H, N=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 25.5 (-CH(*C*H$_3$)$_2$), 63.9 (N-*C*H$_2$), 80.1(-*C*H(CH$_3$)$_2$), 120.8 (Ar-*C*), 122.7 (Ar-*C*), 125.0 (Ar-*C*), 125.6 (Ar-*C*), 128.5 (Ar-*C*), 129.3 (Ar-*C*), 131.0 (Ar-*C*), 133.7 (Ar-*C*), 136.1 (Ar-*C*), 158.9 (Ar-*C*), 163.5 (-*C*=N). MALDI-TOF *m/z* calculated for [M+Na]$^+$. $C_{56}H_{56}Cl_8N_4O_8Ti_2Na$: 1315.42, found 1316.73. Anal. Calc. for $C_{56}H_{56}Cl_8N_4O_8Ti_2$: C, 52.04; H, 4.37; N, 4.34; found C, 52.72; H, 4.78; N, 4.81.

Preparation of Complex 4

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2,4-di-*tert*-butylphenol) or L1(tBu)4 (0.1 g, 0.18 mmol) in 10 mL of dry toluene was added a solution of $Zr(O^iPr)_4{\cdot}{}^iPrOH$ (0.07 g, 0.18 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box. The colour of the reaction mixture changed to yellow. The solution was allowed to come to room temperature and stirred for an additional 24h. The solvent was removed under reduced pressure to give yellow solid

(Yield 0.11 g, 85%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.43 (d, J = 5.6 Hz, 24H, -CH(C*H*$_3$)$_2$), 1.46 (s, 36H, -C(C*H*$_3$)$_3$), 1.53 (s, 36H, -C(C*H*$_3$)$_3$),4.82 (s, 8H, -C*H*$_2$-N=), 4.29-4.38 (sept, J = 5.6 Hz, 8H, -C*H*(CH$_3$)$_2$), 6.33 (s, 2H, Ar-*H* xylyl), 6.50 (m, 4H, Ar-*H* xylyl), 6.61 (m, 2H, Ar-*H* xylyl), 6.88 (m, 4H, Ar-*H*), 7.49 (m, 4H, Ar-*H*), 7.65 (s, 4H, N=C*H*). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 19.5 (-CH(*C*H$_3$)$_2$), 26.2 (Ar-C(*C*H$_3$)$_3$), 30.2 (Ar-C(*C*H$_3$)$_3$), 36.9 (-*C*(CH$_3$)$_3$), 45.0 (-*C*(CH$_3$)$_3$), 61.9 (N-*C*H$_2$), 70.0 (-*C*H(CH$_3$)$_2$), 125.2 (Ar-*C*), 126.5 (Ar-*C*), 127.7 (Ar-*C*), 128.4 (Ar-*C*), 129.0 (Ar-*C*), 129.6 (Ar-*C*), 130.3 (Ar-*C*), 132.1 (Ar-*C*), 134.5 (Ar-*C*), 150.1 (Ar-*C*), 162.9 (-*C*=N). MALDI-TOF *m/z* calculated for [M]$^+$. $C_{88}H_{128}N_4O_8Zr_2$: 1552.43, found 1553.10. Anal. Calc. for $C_{88}H_{128}N_4O_8Zr_2$: C, 68.08; H, 8.31; N, 3.61; found C, 68.37; H, 8.30; N, 3.80.

Preparation of complex 5a

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-*tert*-butyl-4-methylphenol) or L^1(Me)$_4$ (0.1 g, 0.21 mmol) in 10 mL of dry toluene was added a solution of Zr(O^{i}Pr)$_4$·^{i}PrOH (0.08 g, 0.21 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1**. The resulting solid (complex **5**) was crystallized from toluene: chloroform: ethanol solvent mixture to yield yellow crystals of **5a** (Yield 0.11 g, 82%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.42(t, 12H, -CH$_2$C*H*$_3$), 1.54(s, 36H, -C(C*H*$_3$)$_3$), 2.18 (s, 12H, Ar-C*H*$_3$), 4.73 (s, 8H, -C*H*$_2$-N=), 4.19-4.21 (sept, J = 8 Hz, 8H, -C*H*(CH$_3$)$_2$), 6.35 (s, 2H, Ar-*H* xylyl), 6.48 (m, 4H, Ar-*H* xylyl), 6.64 (m, 4H, Ar-*H*), 6.77 (m, 2H, Ar-*H* xylyl), 7.48 (m, 4H, Ar-*H*), 7.65 (s, 4H, N=C*H*). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 20.6 (-CH$_2$*C*H$_3$), 25.4 (Ar-*C*H$_3$), 29.7 (-C(*C*H$_3$)$_3$), 43.4 (-*C*(CH$_3$)$_3$), 59.9 (N-*C*H$_2$), 71.1 (-*C*H(CH$_3$)$_2$), 122.0 (Ar-*C*), 125.3 (Ar-*C*), 128.2 (Ar-*C*), 129.0 (Ar-*C*), 131.8 (Ar-*C*), 132.3 (Ar-*C*), 133.3 (Ar-*C*), 137.9 (Ar-*C*), 139.5 (Ar-*C*), 160.3 (Ar-*C*), 166.8 (-*C*=N). MALDI-TOF *m/z* calculated for [M+CH$_3$CN]$^+$. $C_{74}H_{99}N_5O_8Zr_2$: 1369.0, found 1369.54. Anal. Calc. for $C_{72}H_{96}N_4O_8Zr_2$: C, 65.12; H, 7.29; N, 4.22; found C, 65.86; H, 6.95; N, 4.24. Diffusion coefficient (D) as recorded from ^{1}H DOSY NMR spectrum is 3.84×10^{-6} cm^2 s^{-1}.

Preparation of Complex 6

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2,4-dichlorophenol) or L^{1}Cl$_4$ (0.1 g, 0.21 mmol) in 10 mL of dry toluene was added a solution of Zr(O^{i}Pr)$_4$·^{i}PrOH (0.08 g, 0.21 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1** (Yield 0.12 g, 83%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.11-1.16 (d, J = 6 Hz, 24H, -CH(C*H*$_3$)$_2$), 4.75 (s, 8H, -C*H*$_2$-N=), 4.24-4.33 (sept, J = 5.6 Hz, 8H, -C*H*(CH$_3$)$_2$), 6.26 (s, 2H, Ar-*H* xylyl), 6.82 (m, 2H, Ar-*H* xylyl), 6.97 (m, 4H, Ar-*H* xylyl), 7.19 (m, 4H, Ar-*H*), 7.50 (m, 4H, Ar-*H*), 7.59 (s, 4H, N=C*H*). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 23.4 (-CH(*C*H$_3$)$_2$), 63.1 (N-*C*H$_2$), 73.9(-*C*H(CH$_3$)$_2$), 120.1 (Ar-*C*), 122.6 (Ar-*C*), 124.0 (Ar-*C*), 125.4 (Ar-*C*), 128.5 (Ar-*C*), 129.3 (Ar-*C*), 132.0 (Ar-*C*), 134.4 (Ar-*C*), 136.1 (Ar-*C*), 155.9 (Ar-*C*), 161.9 (-*C*=N). MALDI-TOF *m/z* calculated for [M+Na]$^+$. $C_{56}H_{56}Cl_8N_4O_8Zr_2Na$: 1402.14, found 1402.73. Anal. Calc. for $C_{56}H_{56}Cl_8N_4O_8Zr_2$: C, 48.77; H, 4.09; N, 4.06; found C, 48.17; H, 4.51; N, 4.32.

Preparation of complex 7

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2,4-di-*tert*-butylphenol) or L1(tBu)$_4$ (0.1 g, 0.18 mmol) in 10 mL of dry toluene was added a solution of Hf(O^{t}Bu)$_4$ (0.051 g, 0.18 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1**. The resulting solid was crystallized from concentrated solution of toluene to yield yellow crystals (Yield 0.14 g, 85%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.01 (s, 27H, O-C(C*H*$_3$)$_3$), 1.03 (s, 27H, O-C(C*H*$_3$)$_3$), 1.16 (s, 27H, -C(C*H*$_3$)$_3$), 1.23 (s, 27H, -C(C*H*$_3$)$_3$), 1.51(s, 27H, -C(C*H*$_3$)$_3$), 1.54 (s, 27H, -C(C*H*$_3$)$_3$), 4.73 (s, 6H, -C*H*$_2$-N=), 4.79 (s, 6H, -C*H*$_2$-N=), 6.48 (s, 3H, Ar-*H* xylyl), 6.64 (m, 3H, Ar-*H* xylyl), 6.70 (m, 3H, Ar-*H* xylyl), 6.83 (m, 3H, Ar-*H* xylyl), 6.99 (m, 3H, Ar-*H*), 7.00 (m, 3H, Ar-*H*), 7.39 (m, 3H, Ar-*H*), 7.46 (m, 3H, Ar-*H*), 7.63 (s, 3H, N=C*H*), 7.84 (s, 3H, N=C*H*). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 21.7 (-C(*C*H$_3$)$_3$), 25.9 (-C(*C*H$_3$)$_3$), 30.1 (Ar-C(*C*H$_3$)$_3$), 30.2 (Ar-C(*C*H$_3$)$_3$), 31.7 (Ar-C(*C*H$_3$)$_3$), 31.8 (Ar-C(*C*H$_3$)$_3$), 32.8 (Ar-*C*(CH$_3$)$_3$), 32.9 (Ar-*C*(CH$_3$)$_3$), 35.6 (Ar-*C*(CH$_3$)$_3$), 43.7 (Ar-*C*(CH$_3$)$_3$), 61.3 (N-*C*H$_2$), 62.4 (N-*C*H$_2$), 68.3 (O-*C*(CH$_3$)$_3$), 75.1 (O-*C*(CH$_3$)$_3$), 125.6 (Ar-*C*), 127.9 (Ar-*C*), 128.4 (Ar-*C*), 128.5 (Ar-*C*), 128.6 (Ar-*C*), 129.1 (Ar-*C*), 129.2 (Ar-*C*), 129.3 (Ar-*C*), 129.4 (Ar-*C*), 129.7 (Ar-*C*), 130.0 (Ar-*C*), 137.3 (Ar-*C*), 137.4 (Ar-*C*), 138.1 (Ar-*C*), 138.3 (Ar-*C*), 138.9 (Ar-*C*), 160.0 (Ar-*C*), 161.9 (Ar-*C*), 168.6 (-*C*=N), 169.3 (-*C*=N). MALDI-TOF *m/z* calculated for [M+Na]$^+$. $C_{138}H_{204}Hf_3N_6O_{12}Na$: 2697.60, found 2698.65. Anal. Calc. for $C_{138}H_{204}Hf_3N_6O_{12}$: C, 61.97; H, 7.69; N, 3.14; found C, 62.43; H, 7.66; N, 3.91.

Preparation of Complex 8

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2-*tert*-butyl-4-methylphenol) or L^1(Me)$_4$ (0.1 g, 0.21 mmol)) in 10 mL of dry toluene was added a solution of Hf(O^{t}Bu)$_4$ (0.099 g, 0.21 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1** (Yield 0.14 g, 81%). ^{1}H NMR (400 MHz, CDCl$_3$, ppm): δ = 1.06 (s, 27H, O-C(C*H*$_3$)$_3$), 1.14 (s, 27H, O-C(C*H*$_3$)$_3$), 1.50 (s, 27H, -C(C*H*$_3$)$_3$), 1.55 (s, 27H, -C(C*H*$_3$)$_3$), 1.51(s, 9H, Ar-C*H*$_3$), 1.54 (s, 9H, Ar-C*H*$_3$), 4.68(s, 6H, -C(H)*H*-N=), 4.72 (s, 6H, -C(*H*)H-N=), 6.31 (s, 3H, Ar-*H* xylyl), 6.48 (m, 3H, Ar-*H* xylyl), 6.56 (m, 3H, Ar-*H* xylyl), 6.63 (m, 3H, Ar-*H* xylyl), 6.82 (m, 3H, Ar-*H*), 6.97 (m, 3H, Ar-*H*), 6.99 (m, 3H, Ar-*H*), 7.26 (m, 3H, Ar-*H*), 7.59 (s, 3H, N=C*H*), 7.66 (s, 3H, N=C*H*). ^{13}C NMR (100 MHz, CDCl$_3$, ppm): δ = 20.9 (Ar-*C*H$_3$), 21.7 (Ar-*C*H$_3$), 29.9 (Ar-C(*C*H$_3$)$_3$), 30.2 (Ar-C(*C*H$_3$)$_3$), 33.1 (-C(*C*H$_3$)$_3$), 33.2 (-C(*C*H$_3$)$_3$), 35.3 (Ar-*C*(CH$_3$)$_3$), 35.4 (Ar-*C*(CH$_3$)$_3$), 60.1 (N-*C*H$_2$), 62.4 (N-*C*H$_2$), 75.2 (O-*C*(CH$_3$)$_3$), 75.3 (O-*C*(CH$_3$)$_3$), 122.6 (Ar-*C*), 124.7 (Ar-*C*), 125.1 (Ar-*C*), 125.6 (Ar-*C*), 128.5 (Ar-*C*), 129.3 (Ar-*C*), 130.8 (Ar-*C*), 132.2 (Ar-*C*), 132.6 (Ar-*C*), 133.3 (Ar-*C*), 133.8 (Ar-*C*), 137.0 (Ar-*C*), 137.7 (Ar-*C*), 138.2 (Ar-*C*), 139.7 (Ar-*C*), 140.0 (Ar-*C*), 160.6 (Ar-*C*), 161.3 (Ar-*C*), 167.3 (-*C*=N), 168.3 (-*C*=N). MALDI-TOF *m/z* calculated for [M]$^+$. $C_{120}H_{168}Hf_3N_6O_{12}$:

2422.11, found 2422.25. Anal. Calc. for $C_{120}H_{168}Hf_3N_6O_{12}$: C, 59.51; H, 6.99; N, 3.47; found C, 60.21; H, 7.30; N, 3.58.

Preparation of Complex 9

To a stirred solution of 6,6'-(1E,1'E)-(1,3-phenylenebis(methylene))bis(azan-1-yl-1-ylidene)bis(methan-1-yl-1-ylidene)bis(2,4-dichlorophenol) or L^1Cl_4 (0.1 g, 0.21 mmol) in 10 mL of dry toluene was added a solution of $Hf(O^tBu)_4$ (0.05 g, 0.21 mmol) in 5 mL of dry toluene in 1:1 ratio at -24 °C in an argon filled glove box and was carried out in the same manner as it was employed for the synthesis of complex **1** (Yield 0.14 g, 82%). ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.15 (s, 54H, -C(C*H*$_3$)$_2$), 4.80 (s, 12H, -C*H*$_2$-N=), 6.72 (s, 3H, Ar-*H* xylyl), 6.79-6.81 (d, J = 4Hz, 6H, Ar-*H* xylyl), 6.92 (m, 3H, Ar-*H* xylyl), 6.97 (d, J = 2.7Hz , 6H, Ar-*H*), 7.53 (d, J = 2.6Hz , 6H, Ar-*H*), 7.59 (s, 6H, N=C*H*). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 32.6 (-C(*C*H$_3$)$_2$), 63.6 (N-*C*H$_2$), 75.9 (-*C*(CH$_3$)$_2$), 120.9 (Ar-*C*), 122.8 (Ar-*C*), 125.5 (Ar-*C*), 126.7 (Ar-*C*), 128.5 (Ar-*C*), 129.3 (Ar-*C*), 134.1 (Ar-*C*), 135.4 (Ar-*C*), 138.1 (Ar-*C*), 158.2 (Ar-*C*), 165.7 (-*C*=N). MALDI-TOF *m/z* calculated for $[M]^+$. $C_{90}H_{96}Cl_{12}N_6O_{12}Hf_3$: 2414.67, found 2414.27. Anal. Calc. for $C_{90}H_{96}Cl_{12}N_6O_{12}Hf_3$: C, 44.77; H, 4.01; N, 3.48; found C, 45.12; H, 4.57; N, 3.39.

X-ray crystallography

Single crystals of the metal complexes were obtained by crystallization from a saturated solution of toluene (in case of **1** and **7**) and a 1:1:1 mixture of chloroform, toluene and ethanol (in case of **5a**) for X-ray structural determination. In each case, a crystal of suitable size was selected from mother liquor and mounted on Bruker AXS (Kappa Apex 2) CCD diffractometer equipped with graphite monochromated Mo (Kα) (λ = 0.7107 Å) radiation source. A full sphere of data was collected with 100% completeness for θ up to 25°. ω and φ scans were employed to collect the data. The frame width for ω was set to 0.5 for data collection. The frames were integrated 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 refined using SHELXL-97.[40] All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. In case of **5a**, the disordered toluene molecule was deleted and the PLATON SQUEEZE was used to refine the data. The R factor reduced from 6.06 % to 4.89 %. The solvent accessible cavity associated with a toluene molecule (estimated volume 389 Å^3 for **5a** and 2068 Å^3 for **7**) contains disordered toulene molecule, for which no reasonable model could be developed. Therefore, the observed structure was modified by PLATON SQUEEZE (Spek, 2009) to eliminate the diffused electron density (100 electrons for **5a** and 272 electrons for **7**) found in the cavity. These data were deposited with CCDC with the following CCDC numbers: 1018937 (**1**), 1018938 (**5a**) and 1018939 (**7**).

General procedure for the polymerization of *rac*-LA and *L*-LA

The polymerizations were carried out in a solvent free environment by heating the monomer and the catalyst in a closed glass vessel to 140 °C for a period of time by which the melt had become viscous. Here, 8.67 µmol of the desired catalyst and 0.25 g of *rac*-LA or *L*-LA were introduced in 200:1 ratio into a dry reaction vessel equipped with a magnetic stirrer bar (0.25 g of *rac*-LA or *L*-LA, 17.34 µmol of the catalyst and 86.72 µmol of benzyl alcohol were used for the polymerizations in presence of benzyl alcohol at 100:1:5 ratio). After the reaction time (judged by ^1H NMR), the reaction mixture was dissolved in dichloromethane. The polymers were then precipitated in cold methanol and dried to a constant weight. The conversion yield of *rac*-LA and *L*-LA were analyzed by ^1H NMR spectroscopic studies. Molecular weight determination and M_w/M_n (MWDs) analysis were done by GPC measurements. In presence of excess alcohol (1:10 catalyst to alcohol ratio), the ligands did not fall apart and the alkoxide groups were substituted by benzyloxy groups.

General procedure for the homopolymerization of epoxides

A 100 mL high pressure autoclave equipped with a mechanical stirrer was dried under vacuum at 100 °C for 4 h and then transferred to a drybox to cool to 23 °C. Here, 20 mg of the desired catalyst was put into a metal vessel in the autoclave. Epoxide monomers (1000 mol or 10,000 mol) were added under nitrogen atmosphere via an injection port. The autoclave was then heated to desired temperature for desired time. The autoclave was cooled to yield a large polymer mass. The crude was dissolved in dichloromethane and poured into acidic methanol with stirring to precipitate polymer. The polymer was collected by filtration and then dried in vacuum to a constant mass. This polymer was used for ^1H NMR analysis.

General procedure for ethylene polymerization

A 100 mL flask, equipped with an ethylene inlet, a magnetic stirrer, and a vacuum line, was charged in an argon filled glove box with 45 mL of freshly distilled toluene and 50 mg of **1-9** along with the required amount of MAO to activate the catalyst and placed in a bath at 80 °C. The toluene solution of the desired catalyst precursor was added with a syringe to initiate the polymerization. Then the solvent toluene was added to bring the total volume of the solution to 50 mL. The ethylene gas was bubbled for 30 min and then quenched subsequently with acidic methanol. The resultant polymer was filtered and dried until constant weight was achieved.

General procedure for kinetic studies of lactides

The polymerizations of *rac*-LA using **4** and **7** were carried out in 200:1 ratio at 140 °C in a sealed tube. In a sealed tube under argon atmosphere, 0.035 mmol of **4** or **7** was added to 1 g of monomer. The contents were stirred and immersed in a bath at 140 °C. 0.2 mL aliquots were removed at appropriate interval of time from the reaction mixture and analyzed by ^1H NMR. The $[rac\text{-LA}]_0/[rac\text{-LA}]_t$ ratio was calculated by integration of the peak corresponding to the methine proton for the monomer and polymer. Observed rate constants (k_{obs}) were obtained from the slopes of the best-fit lines.

Computational details

The molecular geometry optimization and ^1H and ^{13}C NMR spectra calculations were performed by using GAUSSIAN 09

(Rev C.01) package of quantum chemical programs. The calculations employed B3LYP method, a version of the DFT method that uses Becke's three parameter functional (B3) and includes a mixture of HF with DFT exchange terms associated with the gradient corrected correlation functional of Lee, Yang and Parr (LYP) and LANL2DZ basis set.[41]

Acknowledgement

This work was supported by the Department of Science and Technology, New Delhi. SKR thanks the University Grants Commission, New Delhi for research fellowship.

Notes and references

[a] *Department of Chemistry, Indian Institute of Technology Patna, Patna-800 013, Bihar, India. Fax: +91 612 2277383; Tel: +91 612 2552171; E-mail: dc@iitp.ac.in, debashis.iitp@gmail.com*
[b] *Department of Chemistry, Indian Institute of Technology Madras, Chennai- 600 036, Tamil Nadu, India.*

† Electronic Supplementary Information (ESI) available: Crystallographic data for the structural analysis of complexes **1**, **5a** and **7** have been deposited at the Cambridge Crystallographic Data Center (CCDC). CCDC 1018937-1018939. See DOI: 10.1039/b000000x/

1) (*a*) O. Dechy-Cabaret, B. Martin-Vaca and D. Bourissou, *Chem. Rev.*, 2004, **104**, 6147-6176; (*b*) F. E. Kohn, J. G. V. Ommen and J. Feijen, *Eur. Polym. J.*, 1983, **19**, 1081-1088; (*c*) F. D. Monica, E. Luciano, G. Roviello, A. Grassi, S. Milione and C.Capacchione, *Macromolecules*, 2014, **47,** 2830-2841.
2) *(a)* A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Jr. Fredrick, J. P. Hallett, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer and T. Tschaplinski, *Science*, 2006, **311**, 484–489; *(b)* R. H. Platel, L.M. Hodgson and C.K. Williams, *Polymer Reviews*, 2008, **48,** 11-63; *(c)* R. Langer, *Acc. Chem. Res.*, 2000, **33,** 94-101; *(d)* C. J. Chuck, M. G. Davidson, G. G. du Sart, P. K. Ivanova-Mitseva, G. I. Kociok-Köhn and L. B. Manton, *Inorg. Chem.*, 2013, **52**, 10804-10811.
3) Z. Zhong, P. J. Dijkstra and J. Feijen, *Angew. Chem. Int. Ed.*, 2002, **41**, 4510-4513.
4) *(a)* R. G. Sinclair, *Pure Appl. Chem.*, 1996, **A33**, 585-597; *(b)* E. Chiellini and R.Solaro, *Adv. Mater.*, 1996, **8**, 305-313; *(c)* W. Amass, A. Amass and B. Tighe, *Polym. Int.*, 1998, **47**, 89-144; *(d)* Y. Ikada and H. Tsuji, *Macromol. Rapid Commun.*, 2000, **21**, 117-132; *(e)* J. C. Middleton and A. J. Tipton, *Biomaterials*, 2000, **21**, 2335-2346; *(f)* C. T. Altaf, H. Wang, M. Keram, Y. Yang and H. Ma, *Polyhedron*, 2014, **81**, 11-20; *(g)* Y. Sun, L. Wang, D. Yu, N. Tang and J. Wu, *Journal of Molecular Catalysis A: Chemical*, 2014, **393**, 175-181.
5) A. Amgoune, C. M. Thomas, T. Roisnel and J.-F. Carpentier, *Chem. Eur. J.*, 2006, **12,** 169-179.
6) *(a)* A. Sauer, A. Kapelski, C. Fliedel, S. Dagorne, M. Kol and J. Okuda, *Dalton Trans.*, 2013, **42**, 9007-9023; *(b)* H.-L. Chen, S. Dutta, P.-Y. Huang and C.-C. Lin, *Organometallics*, 2012, **31**, 2016-2025.
7) *(a)* J. Zhang, C. Jian, Y. Gao, L. Wang, N. Tang and J. Wu, *Inorg. Chem.*, 2012, **51**, 13380-13389; *(b)* H. R. Kricheldorf, S. R. Lee and S. Bush, *Macromolecules*, 1996, **29**, 1375-1381; *(c)* A. Kowalski, J. Libiszowski, A. Duda and S. Penczek, *Macromolecules*, 2000, **33**, 1964-1971; *(d)* M. H. Chisholm and E. E. Delbridge, *Chem. Commun.*, 2001, **14**, 1308-1309; *(e)* K. B. Aubrecht, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 2002, **35**, 644-650; *(f)* M. H. Chisholm and E. E. Delbridge, *New J. Chem.*, 2003, **27**, 1177-1183; *(g)* A. Kowalski, J. Libiszowski, T. Biela, M. Cypryk, A. Duda and S. Penczek, *Macromolecules*, 2005, **38**, 8170-8176; *(h)* A. P. Dove, V. C. Gibson, E. L. Marshall, H. S. Rzepa, A. J. P. White and D. J. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 9834-9843; *(i)* N. Nimitsiriwat, V. C. Gibson, E. L. Marshall and M. R. J. Elsegood, *Inorg. Chem.*, 2008, **47**, 5417-5424; *(j)* V. Poirier, T. Roisnel, S. Sinbandhit, M. Bochmann, J. F. Carpentier and Y. Sarazin, *Chem. Eur. J.*, 2012, **18**, 2998-3013; *(k)* H.-Y. Chen, H.-J. Fang, Y.-J. Chen, S. C. N. Hsu, Y.-C. Lai, H.-W. Ou, W.-T. Peng, Y.-J. Chang, Y.-C. Tsou, T.-Y. Wu, H. Chung, Y. Chen, T. C. Huang and B. S. J. Wu, *Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 3286-3294.
8) *(a)* B. M. Chamberlain, Y. Sun, J. R. Hagadorn, E. W. Hemmesch, V. G. Jr. Young, M. Pink, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 1999, **32**, 2400; *(b)* B. M. Chamberlain, B. A. Jazdzewski, M. Pink, M. A. Hillmyer and W. B. Tolman, *Macromolecules*, 2000, **33**, 3970-3977; *(c)* K. B. Aubrecht, K. Chang, M. A. Hillmyer and W. B. J. Tolman, *Polym. Sci., Part A: Polym.Chem.*, 2001, **39**, 284-293; *(d)* H. Y. Ma and J. Okuda, *Macromolecules*, 2005, **38**, 2665-2673; *(e)* H. Y. Ma, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2008, **47**, 3328-3339; *(f)* Z. J. Zhang, X. P. Xu, W. Y. Li, Y. M. Yao, Y. Zhang, Q. Shen and Y. J. Luo, *Inorg. Chem.*, 2009, **48**, 5715-5724; *(g)* I. Peckermann, A. Kapelski, T. P. Spaniol and J. Okuda, *Inorg. Chem.*, 2009, **48**, 5526-5534; *(h)* A. Pietrangelo, M. A. Hillmyer and W. B. Tolman, *Chem. Commun.*, 2009, **19**, 2736-2737; *(i)* Y. Luo, W. Li, D. Lin, Y. Yao, Y. Zhang and Q. Shen, *Organometallics*, 2010, **29**, 3507-3514; *(j)* J.-C. Buffet and J. Okuda, *Dalton Trans.*, 2011, **40**, 7748-7754; *(k)* M. Sinenkov, E. Kirillov, T. Roisnel, G. Fukin, A. Trifonov and J. F. Carpentier, *Organometallics*, 2011, **30**, 5509-5523; *(l)* W. Li, Z. Zhang, Y. Yao, Y. Zhang and Q. Shen, *Organometallics*, 2012, **31**, 3499-3511.
9) *(a)* Z. Zhong, P. J. Dijkstra and J. Feijen, *J. Am. Chem. Soc.*, 2003, **125**, 11291-11298; *(b)* D. Chakraborty and E. Y. X. Chen, *Organometallics*, 2002, **21**, 1438-1442; *(c)* M.-L. Hsueh, B.-H. Huang and C.-C. Lin, *Macromolecules*, 2002, **35**, 5763-5768; *(d)* Z.-Y. Chai, C. Zhang and Z.-X. Wang, *Organometallics*, 2008, **27**, 1626-1633; *(e)* C. P. Radano, G. L. Baker and M. R. Smith, *J. Am.Chem. Soc.*, 2000, **122**, 1552-1553; *(f)* N. Nomura, R. Ishii, M. Akakura and K. Aoi, *J. Am. Chem. Soc.*, 2002, **124**, 5938-5939; *(g)* K. Majerska and A. Duda, *J. Am. Chem. Soc.*, 2004, **126**, 1026-1027; *(h)* Y.-C. Liu, B.-T. Ko and C.-C. Lin, *Macromolecules*, 2001, **34**, 6196-6201; *(i)* H. Li, C. Wang, F. Bai, J. Yue and H. G. Woo, *Organometallics*, 2004, **23**, 1411-1415; *(j)* T. M. Ovitt and G. W. Coates, *J. Am. Chem. Soc.*, 2002, **124**, 1316-1326; *(k)* D. J. Darensbourg and O. Karroonnirun, *Organometallics*, 2010, **29**, 5627-5634; *(l)* C.-Y. Li, D.-C. Liu and B.-T. Ko, *Dalton Trans.*, 2013, **42**, 11488-11496; *(m)* X.-F. Yu and Z.-X. Wang, *Dalton Trans.*, 2013, **42**, 3860-3868.
10) *(a)* H. R. Kricheldorf, *Makromol. Chem.*, 1993, **194**, 1665-1669; *(b)* B.-T. Ko and C.-C. Lin, *J. Am. Chem. Soc.*, 2001, **123**, 7973-7977; *(c)* C.-A. Huang and C.-T. Chen, *Dalton. Trans.*, 2007, **47**, 5561-5566; *(d)* A. K. Sutar, T. Maharana, S. Dutta, C. T. Chen and C. C. Lin, *Chem. Soc. Rev.*, 2010, **39**, 1724-1746; *(e)* Y. Huang, Y.-H. Tsai, W.-C. Hung, C.-S. Lin, W. Wang, J.-H. Huang, S. Dutta and C.-C. Lin, *Inorg. Chem.*, 2010, **49**, 9416-9425.
11) *(a)* H. R. Kricheldorf, M. Berl and N. Scharnagl, *Macromolecules*, 1988, **21**, 286-293; *(b)* M. H. Chisholm, N. W. Eilerts, J. C. Huffman, S. S. Iyer, M. Pacold and K. Phomphrai, *J. Am. Chem. Soc.*, 2000, **122**, 11845-11854; *(c)* M. H. Chisholm, J. Gallucci and K. Phomphrai, *Inorg. Chem.*, 2002, **41**, 2785-2794; *(d)* M.-L. Shueh, Y.-S. Wang, B.-H. Huang, C.-Y. Kuo and C.-C. Lin, *Macromolecules*, 2004, **37**, 5155-5162; *(e)* J. Ejfler, M. Kobyłka, L. B. Jerzykiewicz and P. Sobota, *Dalton Trans.*, 2005, **11**, 2047-2050; *(f)* T.-L. Yu, C.-C. Wu, C.-C. Chen, B.-H. Huang, J. Wu and C.-C. Lin, *Polymer*, 2005, **46**, 5909-5917; *(g)* H.-Y. Tang, H.-Y. Chen, J.-H. Huang and C.-C. Lin, *Macromolecules*, 2007, **40**, 8855-8860; *(h)* C. A. Wheaton, P. G. Hayes and B. J. Ireland, *Dalton Trans.*, 2009, **25**, 4832-4846; *(i)* L. Wang and H. Ma, *Macromolecules*, 2010, **43**, 6535-6537.
12) J. P. Davin, J. C. Buffet, T. P. Spaniol and J. Okuda, *Dalton Trans.*, 2012, **41**, 12612-12618.

13) *(a)* B. J. O'Keefe, L. E. Breyfogle, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2002, **124**, 4384-4393; *(b)* B. J. O'Keefe, S. M. Monnier, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2001, **123**, 339-340; *(c)* M. Stolt, K. Krasowska, M. Rutkowska, H. Janik, A. Rosling and A. Södergård, *Polym. Int.*, 2005, **54**, 362-368; *(d)* M.-Z. Chen, H.-M. Sun, W.-F. Li, Z.-G. Wang, Q. Shen and Y. Zhang, *J. Organomet. Chem.*, 2006, **691**, 2489-2494; *(e)* J. Chen, J. L. Gorczynski and C. L. Fraser, *Macromol. Chem. Phys.*, 2010, **211**, 1272-1279.

14) *(a)* G. Schwach, J. Coudane, R. Engel and M. Vert, *Polym. Int.*, 1998, **46**, 177-182; *(b)* M. Bero, J. Kasperczyk and G. Adamus, *Makromol. Chem.*, 1993, **194**, 907-912; *(c)* M. H. Chisholm, J. C. Gallucci and H. Zhen, *Inorg. Chem.*, 2001, **40**, 5051-5054; *(d)* C. K. Williams, L. E. Breyfogle, S. K. Choi, W. Nam, V. G. Young, M. A. Hillmyer and W. B. Tolman, *J. Am. Chem. Soc.*, 2003, **125**, 11350-11359; *(e)* H.-Y. Chen, H.-Y. Tang and C.-C. Lin, *Macromolecules*, 2006, **39**, 3745-3752; *(f)* B.-H. Huang, C.-N. Lin, M.-L. Hsueh, T. Athar and C.-C. Lin, *Polymer*, 2006, **47**, 6622-6629; *(g)* C.M. Silvernail, L. J. Yao, L. M. R. Hill, M. A. Hillmyer and W. B. Tolman, *Inorg. Chem.*, 2007, **46**, 6565-6574; *(h)* W.-C. Hung, Y. Huang and C.-C. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, 2008, **46**, 6466-6476; *(i)* D. J. Darensbourg and O. Karroonnirun, *Inorg. Chem.*, 2010, **49**, 2360-2371; *(j)* S. Abbina and G. Du, *ACS Macro Lett.*, 2014, **3**, 689-692.

15) V. Balasanthiran, M. H. Chisholm, C. B. Durr and J. C. Gallucci, *Dalton Trans.*, 2013, **42**, 11234-11241.

16) *(a)* T. K. Saha, B. Rajashekhar and D. Chakraborty, *RSC Adv.*, 2012, **2**, 307-318; *(b)* R. R. Gowda, D. Chakraborty and V. Ramkumar, *Polymer*, 2010, **51**, 4750-4759; *(c)* H.-W. Ou, H.-Y. Chen, H.-C. Tseng, M.-W. Hsiao, Y.-L. Chang, N.-Y. Jheng, Y.-C. Lai, T.-Y. Shih and Y.-T. Lin, Chen, H.-Y. *Journal of Molecular Catalysis A: Chemical*, 2014, **394**, 97-104; *(d)* T. R. Forder, M. F. Mahon, M. G. Davidson, T. Woodman and M. D. Jones, *Dalton Trans.*, 2014, **43**, 12095-12099.

17) *(a)* A. Stopper, K. Press, J. Okuda, I. Goldberg and M. Kol, *Inorg. Chem.*, 2014, **53**, 9140-9150; *(b)* A. Sauer, J.-C. Buffet, T. P. Spaniol, H. Nagae, K. Mashima and J. Okuda, *Inorg. Chem.* 2012, **51**, 5764-5770; *(c)* A. Stopper, J. Okuda and M. Kol, *Macromolecules*, 2012, **45**, 698-704; *(d)* J.-C. Buffet, A. N. Martin, M. Kol and J. Okuda, *Polym. chem.*, 2011, **2**, 2378-2384; *(e)* J.-C. Buffet and J. Okuda, *Chem. Commun.* 2011, **47**, 4796-4798; *(f)* Y. Takashima, Y. Nakayama, K. Watanabe, T. Itono, N. Ueyama, A. Nakamura, H. Yasuda, A. Harada and J. Okuda, *Macromolecules*, 2002, **35**, 7538-7544; *(g)* E. Sergeeva, J. Kopilov, I. Goldberg and M. Kol, *Inorg. Chem.*, 2010, **49**, 3977-3979; *(h)* M. D. Jones, S. L. Hancock, P. McKeown, P. M. Schäfer, A. Buchard, L. H. Thomas, M. F. Mahon and J. P. Lowe, *Chem. Commun.* 2014, **50**, 15967-15970; *(i)* S. L. Hancock, M. F. Mahon and M. D. Jones, *New J. Chem.*, 2003, **37**, 1996-2001; *(j)* B. J. Jeffery, E. L. Whitelaw, D. Garcia-Vivo, J. A. Stewart, M. F. Mahon, M. G. Davidson and M. D. Jones, *Chem. Commun.* 2011, **47**, 12328-12330; *(k)* S. L. Hancock, M. F. Mahon and M. D. Jones, *Chem. Cent. J.*, 2013, **7**, 135; *(l)* S. L. Hancock, M. F. Mahon, G. Kociok-Köhn and M. D. Jones, *Eur. J. Inorg. Chem.*, 2011, **29**, 4596-4602; *(m)* E. L. Whitelaw, M. G. Davidson and M. D. Jones, *Chem. Commun.* 2011, **47**, 10004-10006; *(n)* S. L. Hancock, M. F. Mahon and M. D. Jones, *Dalton Trans.*, 2011, **40**, 2033-2037; *(o)* E. L. Whitelaw, M. D. Jones and M. F. Mahon, *Inorg. Chem.*, 2010, **49**, 7176-7181; *(p)* M. D. Jones, M. G. Davidson and G. Kociok-Köhn, *Polyhedron*, 2010, **29**, 697-700; *(q)* E. L. Whitelaw, M. D. Jones, M. F. Mahon and G. Kociok-Köhn, *Dalton Trans.*, 2009, **41**, 9020-9025; *(r)* A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones and M. D. Lunn, *Chem. Commun.* 2008, **48**, 6611; *(s)* A. J. Chmura, M. G. Davidson, C. J. Frankis, M. D. Jones and M. D. Lunn, *Chem. Commun.* 2008, **11**, 1293-1295; *(t)* A. J. Chmura, D. M. Cousins, M. G. Davidson, M. D. Jones, M. D. Lunn and M. F. Mahon, *Dalton Trans.*, 2008, **11**, 1437-1443; *(u)* A. J. Chmura, M. G. Davidson, M. D. Jones, M. D. Lunn, M. F. Mahon, A. F. Johnson, P. Khunkamchoo, S. L. Roberts and S. S. F. Wong, *Macromolecules*, 2006, **39**, 7250-7257; *(v)* C. J. Chuck, M. G. Davidson, M. D. Jones, G. Kociok-Köhn, M. D. Lunn and S. Wu, *Inorg. Chem.*, 2006, **45**, 6595-6597.

18) *(a)* C. Romain, L. Brelot, S. B. Laponnaz and S. Dagorne, *Organometallics*, 2010, **29**, 1191-1198; *(b)* C. Romain, B. Heinrich, S. B. Laponnaz and S. Dagorne, *Chem. Commun.*, 2012, **48**, 2213-2215; *(c)* L. Azor, C. Bailly, L. Brelot, M. Henry, P. Mobian and S. Dagorne, *Inorg. Chem.*, 2012, **51**, 10876-10883.

19) B. Guillerm, V. Lemaur, J. Cornil, R. Lazzaroni, P. Dubois and O. Coulembier, *Chem. Commun.*, 2014, **50**, 10098-10101.

20) *(a)* R. Stephen, R. B. Sunoj and P. Ghosh, *Dalton Trans.*, 2011, **40**, 10156-10161; *(b)* M. Fèvre, J. Vignolle and D. Taton, *Polym. Chem.*, 2013, **4**, 1995-2003; *(c)* E. Brulé, V. Guérineau, P. Vermaut, F. Prima, J. Balogh, L. Maron, A. M. Z. Slawin, S. P. Nolan and C. P. Thomas, *Polym. Chem.*, 2013, **4**, 2414-2423; *(d)* J. Raynaud, C. Absalon, Y. Gnanou and D. Taton, *J. Am. Chem. Soc.*, 2009, **131**, 3201-3209; *(e)* H. A. Brown, S. Xiong, G. A. Medvedev, Y. A. Chang, M. M. Abu-Omar, J. M. Caruthers and R. M. Waymouth, *Macromolecules*, 2014, **47**, 2955-2963; *(f)* A. K. Acharya, Y. A. Chang, G. O. Jones, J. E. Rice, J. L. Hedrick, H. W. Horn and R. M. Waymouth, *J. Phys. Chem. B*, 2014, **118**, 6553-6560.

21) H.-J. Chuang, S.-F. Weng, C.-C. Chang, C.-C. Lin and H.-Y. Chen, *Dalton Trans.*, 2011, **40**, 9601-9607.

22) Y. Sarazin, M. Schormann and M. Bochmann, *Organometallics*, 2004, **23**, 3296-3302.

23) W. Kuran, A. Rokicki and J. Pienkowski, *J. Polym. Sci., Part A: Polym. chem.* 1979, **17**, 1235−1238.

24) B. Antelmann, M. H. Chisholm, S. S. Iyer, J. C. Huffman, D. Navarro-Llobet and M. Pagel, *Macromolecules*, 2001, **34**, 3159−3175.

25) K. L. Peretti, H. Ajiro, C. T. Cohen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc*., 2005, **127**, 11566 –11567.

26) *(a)* J. Zhang, Y.-J. Lin and G.-X. Jin, *Organometallics*, 2007, **26**, 4042-4047; *(b)* H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger and R. M. Waymouth, *Angew. Chem.*, *Int. Ed. Engl*., 1995, **34**, 1143-1170; *(c)* A. Mehta, G. Tembe, P. Umare, M. Bialek, P. Parikh and G. Mehta, *J. Polym. Res.*, 2012, **19**, 1-12.

27) H. Sinn, W. Kaminsky, H.-J. Vollmer and R. Woldt, *Angew. Chem.*,*Int. Ed. Engl.*, 1980, **19**, 390-392.

28) *(a)* S. Pappuru, E. R. Chokkapu, D. Chakraborty and V. Ramkumar, *Dalton Trans.*, 2013, **42**, 10304-10314; *(b)* S. V. Kulangara, A. Jabri, Y. Yang, I. Korobkov, S. Gambarotta and R. Duchateau, *Organometallics*, 2012, **31**, 6085-6094.

29) *(a)* T. K. Saha, M. Mandal, D. Chakraborty and V. Ramkumar, *New J. Chem.*, 2013, **37**, 949-960; *(b)* K. Kawai and T. Fujita, *Top. Organomet. Chem.*, 2009, **26**, 3–46; *(c)* M. Mitani, J.-I. Mohri, Y. Yoshida, J. Saito, S. Ishii, K. Tsuru, S. Matsui, R. Furuyama, T. Nakano, H. Tanaka, S. Kojoh, T. Matsugi, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2002, **124**, 3327–3336; *(d)* H. Makio, N. Kashiwa and T. Fujita, *Adv. Synth. Catal.*, 2002, **344**, 477–493; *(e)* S. Matsui, M. Mitani, J. Saito, Y. Tohi, H. Makio, N. Matsukawa, Y. Takagi, K. Tsuru, M. Nitabaru, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *J. Am. Chem. Soc.*, 2001, **123**, 6847–6856; *(f)* M. Fujita and G. W. Coates, *Macromolecules* 2002, **35**, 9640–9647.

30) C. Maurer, E. Pittenauer, M. Puchberger, G. Allmaier and U. Schubert, *ChemPlusChem*, 2013, **78**, 343-351.

31) E. Durand, M. Clemancey, A.-A. Quoineaud, J. Verstraete, D. Espinat and J.-M. Lancelin, *Energy Fuels*, 2008, **22**, 2604-2610.

32) *(a)* T. K. Saha, D. Chakraborty and V. Ramkumar, *Inorg. Chem.*, 2011, **50**, 2720-2722; *(b)* Y. Kim, G. K. Jnaneshwara and J. G. Verkade, *Inorg. Chem.*, 2003, **42**, 1437-1447; *(c)* S. Gendler, S. Segal, I. Goldberg, Z. Goldschmidt and M. Kol, *Inorg. Chem.*, 2006, **45**, 4783-4790.

33) M. Grellier, L. Vendier, B. Chaudret, A. Albinati, S. Rizzato, S. Mason and S. Sabo-Etienne, *J. Am. Chem. Soc.*, 2005, **127**, 17592-17593.

34) *(a)* C. Jian, J. Zhang, Z. Dai, Y. Gao, N. Tang and J. Wu, *Eur. J. Inorg. Chem.*, 2013, 3533-3541; *(b)* H.-Y. Chen, B.-H. Huang and C.-C. Lin, *Macromolecules*, 2005, **38**, 5400-5405.

35) J. S. Lomas, *Magn. Reson. Chem.*, 2013, **51**, 469-481.

36) R. Gupta and R. P. Chaudhary, *J. Mol. Struct.*, 2013, **1049**, 189-197.

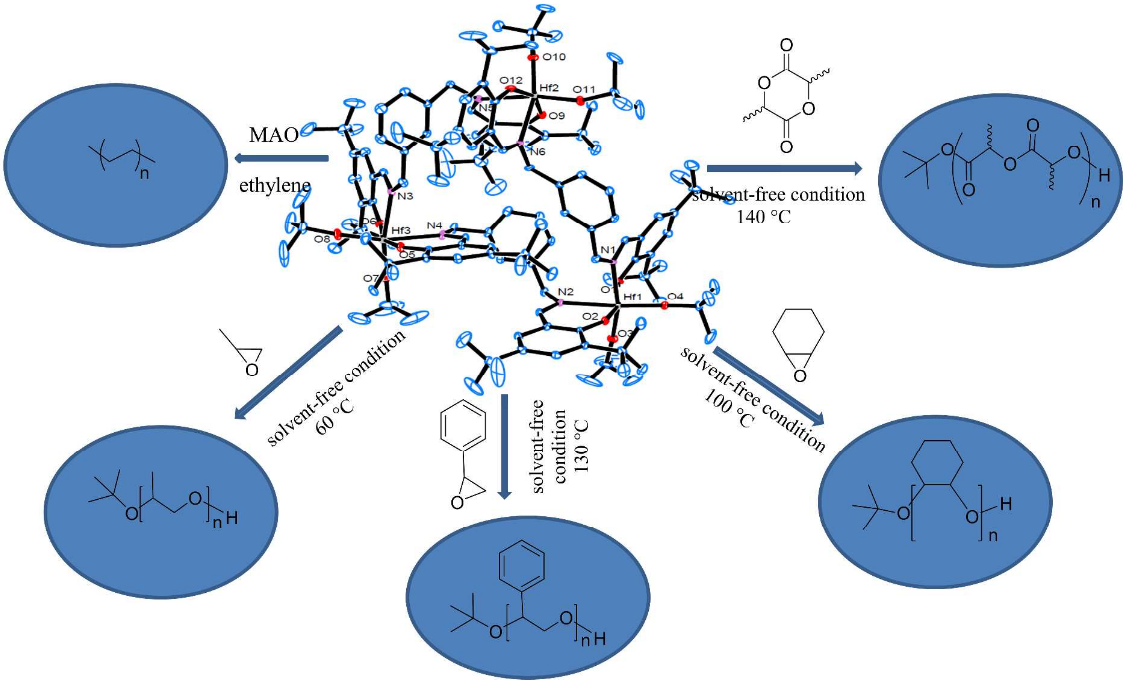
37) *(a)* N. de Sousa Sousa, R. B. de Lima, A. L. P. Silva, A. A. Tanaka, A. B. F. da Silva and J. de Jesus Gomes Varela Júnior, *Comput. Theor. Chem.*, 2015, **1054**, 93-99; *(b)* T. M. Pappenfus, B. J. Hermanson, T. J. Helland, G. G. W. Lee, S. M. Drew, K. R. Mann, K. A. McGee and S. C. Rasmussen, *Org. Lett.*, 2008, **10**, 1553-1556; *(c)* R. G. Pearson, Inorg. Chem., 1988, **27**, 734-740; *(d)* R. G. Parr and R. G. Pearson, J. Am. Chem. Soc., 1983, **105**, 7512-7516.

38) *(a)* M. J. Go, J. M. Lee, K. M. Lee, C. H. Oh, K. H. Park, S. H. Kim, M. Kim, H.-R. Park, M. H. Park, Y. Kim and J. Lee, *Polyhedron*, 2014, **67**, 286-294; *(b)* F. D. Monica, E. Luciano, G. Roviello, A. Grassi, S. Milione and C. Capacchione, *Macromolecules*, 2014, **47**, 2830-2841; *(c)* Z. R. Turner, J.-C. Buffet and D. O'Hare, *Organometallics*, 2014, **33**, 3891-3903.

39) P. M. Selvakumar, S. Nadella, K. J. Prathap, R. I. Kureshy, E. Suresh and P. S. Subramanian, *Inorg. Chim. Acta*, 2011, **375**, 106-113.

40) G. M. Sheldrick, **SHELXL97**. *Program for crystal structure refinement*, Göttingen, Germany.

41) *(a)* I. B. Obot and N. O. Obi-Egbedi, *Corros. Sci.* 2010, **52**, 657-660; *(b)* C. G. Zhan, J. A. Nicholes and D. A. Dixon, *J. Phys. Chem. A*, 2003, **107**, 4184-4195.



O10
O12
Hf2
O11
N5
O9
N6
N3
O6
Hf3
N4
O8
O5
O7
N1
N2
Hf1
O4
O2
O3
MAO
ethylene
n
solvent-free condition
140 °C
H
n
solvent-free condition
60 °C
O
n H
solvent-free
condition
130 °C
solvent-free condition
100 °C