Zirconium and hafnium complexes supported by linked bis(β -diketiminate) ligands: synthesis, characterization and catalytic application in ethylene polymerization[†]

Shaogang Gong, Haiyan Ma* and Jiling Huang*

Received 17th March 2009, Accepted 7th July 2009 First published as an Advance Article on the web 10th August 2009 DOI: 10.1039/b905392a

Zirconium and hafnium complexes bearing new 1,2-ethanediyl- or 1,3-propanediyl-linked bis(β -diketiminate) ligands, [{C_nH_{2n}-(BDI^{Ar})₂}MCl₂] (Ar = 2,6-Me₂-C₆H₃, 2,6-Cl₂-C₆H₃, 2,6-^{*i*}Pr₂-C₆H₃; M = Zr, n = 2 (4a–c), n = 3 (5a–c); M = Hf, n = 2 (6b)), were synthesized via the reaction of MCl₄.2THF and one equivalent of dilithium salt of the corresponding ligand. Distorted trigonal prismatic and octahedral coordination geometries as well as C₁-symmetric structures are found for zirconium complexes 4c and 5c in the solid state. Variable temperature ¹H NMR spectra indicated the fluxional nature of 4a and 5a in solution. Upon activation with methylaluminoxane (MAO), all these complexes except hafnium complex **6b** displayed moderate catalytic activities for ethylene polymerization. 1,2-Ethanediyl-linked complexes 4a and 4b are generally more active than their 1,3-propanediyl-linked analogues. The substituents at the ortho-positions of the phenyl rings have different effect on the catalytic activities of 1,2-ethanediyl-linked series or 1,3-propanediyl-linked series. It is noteworthy that even at a low Al/Zr molar ratio of 500, the catalytic activities of these zirconium complexes could be retained. Polyethylenes with broad molecular weight distributions (MWD = 15.3–20.3) were produced, which might result from the fluxional character of the zirconium complexes. The linear structure of obtained polyethylenes was further determined by ¹³C NMR spectroscopy and DSC analysis.

Introduction

Among a variety of polydentate ligands adopted for synthesizing non-metallocene complexes, β -diketiminate ligands attract considerable attention due to their isoelectronic relationship with the cyclopentadienyl anion, and convenient preparation in high yields from cheap and readily available materials, as well as versatile modulation of steric and electronic requirements by varying the amine moieties and the backbone.¹ For example, Collins' and Andres' groups^{2,3} reported group 4 metal complexes bearing β -diketiminate ligands with electronwithdrawing groups, which displayed high catalytic activities for ethylene polymerization $(1.1 \times 10^7 \text{ g PE/mol-Zr}\cdot\text{h})$ and afforded polyethylenes with narrow molecular weight distributions (MWD = ~2.7). Bis(β -diketiminate) titanium complexes,⁴ $[(BDI^{Ar})_2TiCl_2]$ (Ar = 2,6-*i*Pr₂-C₆H₃), showed moderate catalytic activities both in ethylene homo-polymerization and in ethylene/norbornene copolymerization. Xie's group⁵ prepared mono(β -diketiminate) titanium trichloride complexes, which displayed high catalytic activities for the copolymerization of ethylene

and 1-hexene (2.6×10^7 g copolymer/mol-Zr·h), and the molar percentage of 1-hexene incorporation increased while the feed of 1-hexene was enhanced. Recently, we found that zirconium complexes bearing symmetrically or unsymmetrically substituted β -diketiminate ligands could provide ultra-high molecular weight polyethylenes (UHMWPE) or polyethylenes with broad molecular weight distribution *via* the modulation of N-aryl moieties.⁶ All these facts show that the versatile β -diketiminate ligand sets afford great opportunity to produce polyolefins with variable properties when binding with group 4 metals.⁷

More recently, bridged-bis(phenolate)-type dianionic tetradentate ligands have been developed and thoroughly introduced to group 4 metals; versatile catalytic behavior and stereoselectivities for α -olefin⁸ or styrene⁹ polymerization have been gained through fine-tuning the phenoxide ortho-substituents or the bridging unit sterically and electronically. Grassi's group¹⁰ revealed that the bridged bis(phenoxy-iminate) zirconium complexes could produce polyethylene with narrow MWD (MWD = ~2.0) and regioregular 1,2-insertion of α -olefin took place during the copolymerization of ethylene with propylene or 1-hexene. Kol et al.^{8a,8b} and Busico et al.^{8c,8d} found that, with bulky ortho-substituents on the phenolate rings, the tetradentate diamino bis(phenolate) zirconium complexes catalyzed the isoselective polymerizations of propylene or 1-hexene. For titanium complexes with [OSSO]-type bis(phenolate) ligands, the elongation of the bridging unit from 1,2-ethanediyl to 1,3-propanediyl switched the selectivity for styrene polymerization from isotactic to syndiotactic.9 In most of the cases, such linear tetradentate

Laboratory of Organometallic Chemistry, East China University of Science and Technology, 130 Meilong Road, Shanghai, 200237, People's Republic of China. E-mail: haiyanma@ecust.edu.cn, qianling@online.sh.cn; Fax: +86 2164253519

[†] Electronic supplementary information (ESI) available: ¹H NMR spectra of **4a** and **4c**, variable temperature spectra of **4a** and **5a**, ¹³C NMR spectrum of typical polyethylene sample. CCDC reference numbers for **4c** and **5c** 724272 and 724273. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b905392a

ligands were capable of generating rigid chirality at a metal center and hence achieved stereoselective olefin enchainment. It is conceivable that a [NN^NNN]-type tetradentate dianionic ligand formed by linking two β -diketiminate moieties with a bridging unit may also provide a rigid ligand framework for group 4 metals to construct most likely a C2-symmetric configuration, thus affording the potential of stereoselective polymerization of α -olefin by elegantly modifying the ortho-substituents on the phenolate rings and/or the bridge between the two β -diketiminate moieties, in addition to the single-site character. Some examples of linked bis(β -diketimine)s have been synthesized¹¹ and adopted for rare earth metals to catalyze the copolymerization of epoxides and CO2.12 Here, we would like to expand the ligand categories and report a series of 1,2-ethanediyl and 1,3-propanediyl-linked bis(β diketiminate) zirconium and hafnium dichloride complexes and their catalytic behavior in ethylene polymerization.

Results and discussion

Synthesis of linked bis(β -diketiminate) zirconium and hafnium complexes

As depicted in Scheme 1, in order to investigate in detail the effect of ligand framework on the catalytic behavior of the corresponding metal complexes, a series of linked bis(β -diketimine)s **2a–d** and **3a–c** with different *ortho*-substituents and alkanediyl bridges were synthesized in reasonable yields of 62–76% by using a classic two-step condensation route.¹²



The synthesis of analogous linked bis(β -diketimine)s with *meta*-substituted *N*-phenyl groups was, however, unsuccessful.

Attempts at synthesizing 1,2-ethanediyl-linked bis(β -diketimine) with *meta*-trifluoromethyl substitution on the phenyl rings *via* the reaction of corresponding enaminoketone and diamine failed to give any target product. Only *meta*-trifluoromethylaniline, *N*-(*meta*-trifluoromethyphenyl) substituted β -diketimine (3-CF₃-C₆H₄N=C(Me)CH=C(Me)NHC₆H₄-CF₃-3), and some unknown compounds with high boiling points were detected in the reaction mixture. Previously, we found that successful synthesis of β diketimines with two different *N*-aryl moieties was limited to those having bulky *ortho*-substituents on at least one of the two phenyl rings, such as (2,6-¹Pr₂C₆H₃N=C(Me)CH=C(Me)NHC₆H₅).¹³ Therefore, it seems that a sufficient space hindrance arising from substituents at the *ortho*-positions of the *N*-phenyl moiety is crucial to prevent the undesired recomposition reaction.

The profound influence of a bridging unit on the polymerization performance of resultant metal complexes⁹ also encouraged us to use an aromatic group as bridge. Thus, enaminoketone **1b** pretreated with $[Et_3O]^+[BF_4]^-$, was reacted with 1,2-diaminobenzene in the presence of Et_3N . However, only compound **7** (2,6-Cl₂-C₆H₃N=C(Me)CH=C(Me)OC₂H₃), and unreacted 1,2-diaminobenzene were isolated from the reaction mixture (Scheme 2). Obviously, no reaction occurred between the generated borate intermediate and 1,2-diaminobenzene.



Zirconium and hafnium complexes **4a–c**, **5a–c** and **6b** bearing linked bis(β -diketiminate) ligands were synthesized *via* the reaction of ZrCl₄·2THF or HfCl₄·2THF and one equivalent of dilithium salt of the corresponding ligand in toluene under mild conditions (Scheme 1). Analytically pure complexes were obtained as yellow to orange yellow crystalline solids in moderate yields after recrystallization from hot toluene. Spectroscopic data and elemental analysis results are consistent with the stoichiometry of one linked bis(β -diketiminate) ligand per metal. The monomeric nature of this series of complexes was further confirmed by X-ray diffraction studies (*vide post*).

Great effort was made to prepare zirconium complex bearing *ortho*-trifluoromethyl substituted **2d**. The ¹H NMR spectrum of

the reddish solids isolated from the reaction mixture indicated an unknown structure containing β -diketiminate fragment but without the 1,2-ethanediyl bridge; a decomposition reaction was then deduced accordingly. The lithium salt of ligand **2d** prepared either in toluene or in diethyl ether was hydrolyzed, which gave an untraceable mixture rather than **2d**. Most likely, the existence of strong electron-withdrawing *ortho*-CF₃ groups led to the decomposition of **2d** when treated with *n*-BuLi.

Complexes **4a–6b** are quite sensitive to air and moisture. Partial decomposition occurred when isolated crystalline solids were redissolved in dry toluene. It is of note that a counterintuitive influence of *ortho*-substituents on the phenyl rings on the solubility of resultant complexes was observed: complexes **4c** and **5c** with *ortho*-isopropyl substitution were sparingly soluble in toluene, whereas the rest with either *ortho*-methyl or chlorine substituents were smoothly dissolvable. In general, 1,3-propanediyl-linked complexes **5a–c** show better solubility in aromatic solvents than **4a–c** containing 1,2-ethanediyl bridge. When compared with the non-linked β -diketiminate zirconium congeners,⁶ complexes **4a–6b** in this work exhibit superior solubility in toluene.

Structures of zirconium complexes in solution

For a linear tetradentate ligand, depending on the nature of donors, the size of metal ion, and the spatial requirements of the ligand framework, a number of structural isomers can form when wrapping around a group 4 metal (Scheme 3). From the ¹H NMR spectra (C_6D_6 , 25 °C) of complexes 4a ($R^1 = R^2 =$ CH_3) and 4b ($R^1 = R^2 = Cl$) with 1,2-ethanediyl-bridged ligands, only a single isomer is observed in each case, which is highly symmetric in solution, as is evident from the symmetry-related two β -diketiminate fragments. Complexes 4a and 4b appear to be $C_{2\nu}$ symmetric in solution according to the sharp singlet displayed by the four N-C H_2 protons in the ¹H NMR spectra. All of the above mentioned features observed at 25 °C are still present at -70 °C (C₇D₈) for 4a. Such symmetry could result either from a trans-Cl,Cl, cis-N₁,N₁, cis-N₂,N₂ isomer of C_{2y} symmetric octahedral configuration (trans in Scheme 3) or from fast-exchanging cis-Cl,Cl, trans-N₁,N₁, cis-N₂,N₂ C₂-symmetric octahedral enantiomers of Δ and Λ -configuration (*cis*- α). Based on the most reasonable coordination of tetradentate ligands and the X-ray crystal structure of 4c, we assume a C_2 -symmetric ground state for 4a and 4b.14



Scheme 3 The possible stereoisomers of metal complex with general formula of $[N_1N_2^{\,\circ}N_2N_1]ZrCl_2$ (only diastereomers are shown).

In contrast to them, complex $4c (R^1 = R^2 = {}^{i}Pr)$ displays two separate resonances in AA'BB' spin pattern for the four N-CH₂ protons in the ¹H NMR spectrum as well as four doublets for the methyl protons of isopropyl groups, two multi-peaks for the methine protons, apparently suggesting a rigid C₂-symmetric configuration in solution. It seems that the introduction of sterically demanding diisopropyl groups in **4c** effectively hinders the fluxional interconversion between Δ and Λ -isomers.¹⁴ Due to the partial overlapping of N-CH₂ and isopropyl methine resonances in the ¹H NMR spectrum, detailed investigation concerning the solution behavior of **4c** at higher temperature was cumbered.

The ¹H NMR spectra of complexes **5a** ($R^1 = R^2 = CH_3$), **5b** $(\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{C}\mathbf{I})$ and **5c** $(\mathbf{R}^1 = \mathbf{R}^2 = {}^i\mathbf{P}\mathbf{r})$ also indicate two symmetryrelated β -diketiminate fragments in each case at room temperature. The fluxionality of the 1,3-propanediyl-bridge in 5a and 5b is somewhat frozen out on the NMR time scale, showing two broad signals for the four protons of $N-CH_2$; whereas only one multiple signal is displayed for the two $N-CH_2$ units in 5c, which is in contrast to the rigidity observed for 4c. The restricted rotation of aromatic rings is further observed for **5a** and **5c**, with more than one set of resonances being displayed for the Ar-alkyl groups. Variable-temperature ¹H NMR spectra of **5a** (in toluene- d_8) give evidence of a gradual coalescence of two N-CH₂ signals to a broad singlet at $\delta = 3.8$ ppm at elevated temperatures up to 60 °C (Fig. 1).¹⁵ When cooled to -60 °C, in spite of slight sharpening of these two resonances, no identifiable fine-coupling patterns could be observed. From line broadening analysis, the activation energy for **5a** of this process is found to be $\Delta G^{\neq} = 59.2$ kJ mol⁻¹ (for N–CH₂ signals, $\Delta v = 599.5$ Hz, $T_c = 319$ K). Likewise, by using the Erying equation to plot $\ln(K/T)$ versus 1/T, $\Delta H^* = 5.1$ kcal mol^{-1} , $\Delta S^{\neq} = -28.5$ kcal mol^{-1} K⁻¹ can be obtained.



Fig. 1 Variable temperature ¹H NMR spectra of complex **5a** ($\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{M}e$) (toluene- d_8). Only the $-\mathbf{N}CH_2CH_2N-$ moiety is shown.

Fluxional behavior of octahedral complexes with linear tetradentate ligand was often observed for those having softdonor-containing ligands (such as S^{14,16,17} and P¹⁸). Depending on the ligand framework, different processes have been suggested. For instance, the solution behavior of titanium complexes with [OSSO]-type bisphenolate ligands might involve either a rapid enantiomerization between the Δ and Λ -isomers occurring likely *via* a tetrahedrally coordinated transition state or an interconversion between *cis*-Cl,Cl, *trans*-N₁,N₁, *cis*-N₂,N₂ *C*₂-symmetric (*cis*- α) and *cis*-Cl,Cl, *cis*-N₁,N₁, *cis*-N₂,N₂ *C*₁-symmetric (*cis*- β) configurations *via* a Bailar twist process.^{14,16a,17} As shown in Scheme 4, being different from the case of octahedral complexes with two bidentate or three bidentate ligands, a single Bailar twist process of an octahedral complex wrapped by a "linear"



Scheme 4 Possible interconversion among stereoisomers via Bailar twist process.

tetradentate ligand (for example, $[N_1N_2^{\circ}N_2N_1]$ -type) with *cis*- α configuration (Λ -isomer) will, however, lead to the other isomers, instead of direct enantiomerization between the Δ - and Λ -isomers. Thus, more than one set of resonances accounting for the N_1 - N_2 units might be observed in addition to the decoalescence of the bridging moiety in the ¹H NMR spectra at decreased temperature.

The variable temperature ¹H NMR spectra of **5a** show that, besides the gradual decoalescence of two broad N–CH₂ signals, the two β -diketiminate fragments keep symmetric and only one singlet is displayed for the two γ -protons within the temperature range of -60–60 °C, giving no convincing evidence for a Bailar twist process. According to the obtained dynamic and variable ¹H NMR spectroscopic data, the observed fluxionality of **5a** might be caused by the rapid enantiomerization between the Δ and Λ -isomers in solution likely *via* a tetrahedrally coordinated transition state (Scheme 5).¹⁴ This might also be the case for **4a** in solution.



Scheme 5 Possible interconversion of Λ - and Δ -isomers *via* tetrahedrally coordinated transition state assumed for **5a** (Ar = 2,6-Me₂-C₆H₃).

From VT-NMR experiments, it is unusual that the 1,2ethanediyl-linked complex **4a** seems configurationally more flexible than 1,3-propanediyl-linked **5a**.¹⁴ This behavior however may be rationalized if we take into account the considerable strain of the 6–5–6 chelating skeleton arising from the short 1,2-ethanediyl linkage in complex **4a** (evident from the X-ray crystal structures of **4c** and **5c**), which should facilitate the weakening or detachment of N (middle)-Zr bonds.

Crystal structures of zirconium complexes 4c and 5c

Single crystals of zirconium complexes 4c and 5c suitable for X-ray diffraction measurement were obtained by slowly cooling a saturated toluene solution to -20 °C. Crystallographic data, results of structure refinements, selected bond lengths and angles are summarized in Tables 1, 2 and 3.

The X-ray crystal structure of **4c** (Fig. 2) shows that the zirconium center is six coordinated with the tetradentate bis(diketiminate) ligand and two chloride atoms. Although consisting of *cis*-N(2), N(4), *trans*-N(1), N(3) and *cis*-Cl(1), Cl(2) orientation (*cis*- α), the geometry around Zr atom in **4c** is distorted significantly from octahedral coordination, which is more likely trigonal prismatic as evidenced by the considerably large angles of N(1)–Zr–N(4) = 119.91(10)° and N(2)– Zr–N(3) = 118.89(10)°. The slight differences between the

Table 1 Crystal data and structure refinement details for 4c and 5c

	4c	5c
Formula	$C_{36}H_{52}Cl_2N_4Zr \cdot 0.5C_7H_8$	$C_{37}H_{54}Cl_2N_4Zr \cdot 0.5C_7H_8$
Formula weight	749.00	763.03
Crystal size/mm ³	$0.498 \times 0.419 \times 0.347$	$0.293 \times 0.262 \times 0.204$
Crystal system	monoclinic	monoclinic
Space group	<i>P</i> 2(1)/c	<i>P</i> 2(1)/c
a/Å	11.4820(11)	11.6509(13)
b/Å	31.485(3)	31.598(4)
c/Å	11.7046(11)	11.6510(13)
$\alpha /^{\circ}$	90.00	90.00
$\beta/^{\circ}$	111.609(2)	110.906(2)
$\gamma/^{\circ}$	90.00	90.00
Volume/Å ³	3933.9(6)	4006.9(8)
Ζ	4	4
Calcd density/mg m ⁻³	1.265	1.264
Absorp coeff/mm ⁻¹	0.447	0.440
F(000)	1580	1610
θ range for data collection/°	1.91 to 27.00	1.87 to 25.50
Limiting indices	$-14 \le h \le 13, -35 \le$	$-14 \le h \le 12, -38 \le$
c	$k \le 40, -14 \le l \le 14$	$k \le \overline{36}, -14 \le l \le 14$
No. of reflns	22563/8553 R(int) =	21032/7437 [R(int) =
collected/unique	0.0853]	0.1133]
Data/restrains/	8553/4/446	7437/8/426
parameters		
Goodness-of-fit on F^2	1.011	0.799
Final R indices	$R_1 = 0.0552$	$R_1 = 0.0565$
$[I > 2\sigma(I)]$	$wR_2 = 0.1165$	$wR_2 = 0.1133$
R indices (all data)	$R_1 = 0.0796$	$R_1 = 0.1237$
	$wR_2 = 0.1255$	$wR_2 = 0.1296$
Largest diff. peak/hole/e Å ⁻³	0.738 and -0.680	0.824 and -0.596

Zr-N(1)	2.314(3)	Zr-N(2)	2.176(3)
Zr-N(3)	2.322(2)	Zr-N(4)	2.174(3)
Zr-Cl(1)	2.4241(9)	Zr-Cl(2)	2.4187(9)
N(1) - C(1)	1.337(4)	N(2) - C(3)	1.347(4)
C(1) - C(2)	1.398(5)	C(2) - C(3)	1.374(5)
N(1)-C(14)	1.453(4)		
N(1) - Zr - N(2)	78.15(10)	N(3) - Zr - N(4)	77.42(10)
N(2) - Zr - N(4)	72.68(11)	N(1)– Zr – $N(3)$	160.03(10)
N(1) - Zr - N(4)	119.91(10)	N(2) - Zr - N(3)	118.89(10)
Cl(1)– Zr – $Cl(2)$	117.40(4)	N(2)– Zr – $Cl(2)$	90.35(8)
N(4)– Zr – $Cl(1)$	92.13(8)		

Table 3 Selected bond distances (Å) and angles (°) for complex 5c

$\overline{Zr-N(1)}$	2,303(4)	Zr-N(2)	2 193(4)
Zr-N(3)	2.282(4)	Zr-N(4)	2.204(4)
Zr-Cl(1)	2.4238(14)	Zr-Cl(2)	2.4282(16)
N(1) - C(1)	1.328(6)	N(2) - C(3)	1.325(6)
C(1) - C(2)	1.406(7)	C(2) - C(3)	1.393(7)
N(1)-C(14)	1.488(6)		
N(1)– Zr – $N(2)$	81.89(15)	N(3)– Zr – $N(4)$	82.13(16)
N(2)– Zr – $N(4)$	76.71(16)	N(1)-Zr-N(3)	167.15(14)
N(1)– Zr – $N(4)$	107.41(15)	N(2)-Zr-N(3)	109.16(15)
Cl(1)– Zr – $Cl(2)$	112.89(5)	N(2)– Zr – $Cl(2)$	87.90(12)
N(4)– Zr – $Cl(1)$	87.50(12)		



Fig. 2 ORTEP diagram of the molecular structure of **4c** ($R^1 = R^2 = {}^{t}Pr$). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecule are omitted for clarity.

two β -diketiminate parts in bond lengths and angles suggest a C_1 -symmetric configuration of **4c** in the solid state. The angle of N(2)–Zr–N(4) = 72.68(11)° is rather small when compared to those in non-linked bis(β -diketiminate) zirconium complexes (83.19(6)–91.21(3)°).^{6,7e} On the other hand, the angle of Cl(1)–Zr–Cl(2) (117.40(4)°) is significantly enlarged (*ca.* 90° in six coordinate non-linked bis(β -diketiminate) zirconium complexes).^{2a,7e} All these features imply significant strains of the tetradentate ligand possibly arising from the short 1,2-ethanediyl linkage. The obviously longer Zr–N(1) and Zr–N(3) bonds in comparison with those of Zr–N(2) and Zr–N(4) are typical for six coordinate bis(β -diketiminate) zirconium complexes, probably due to the bulky steric hindrance of two *ortho*-isopropyls on the phenyl rings.

The modification of the linkage within the ligand leads to considerable change in the coordination geometry around the metal center. In the solid state, complex **5c** possesses C_1 -symmetric structure (*cis-* α , Fig. 3) and has a distorted octahedral coordination geometry with two *cis*-Cl atoms at an angle of 112.89(5)°, which is smaller than that of **4c** (117.40(4)°). The bigger angle of N(1)–Zr–N(3) = 167.15(14)° in **5c** than that of **4c** (160.03(9)°) further shows the more crowded space structure of the whole ligand framework. The angle of N(2)–Zr–N(4) = 76.71(16)° is bigger than that in **4c**, but still smaller than those in non-linked bis(β -diketiminate) zirconium complexes, indicative of the presence of strains to a certain degree. The other bond distances and angles in **5c** are, however, similar to those of **4c**.



Fig. 3 ORTEP diagram of the molecular structure of **5c** ($R^1 = R^2 = {}^tPr$). Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms and solvent molecule are omitted for clarity.

Polymerization of ethylene with complexes 4a-6b/MAO systems

Ethylene polymerization by these linked bis(β -diketiminate) zirconium complexes **4a–c**, **5a–c** and hafnium complex **6b** was investigated under different conditions using excess methylaluminoxane (MAO) as the cocatalyst. The results of zirconium complexes are collected in Tables 4 and 5. Hafnium complex **6b** ($\mathbb{R}^1 = \mathbb{R}^2 = \mathbb{C}$]) showed hardly any activity for the polymerization of ethylene. It is of note that, due to the extreme sensitivity, the toluene solution of zirconium pre-catalyst had to be prepared freshly and consumed within 1–2 hours, otherwise visible decomposition of the zirconium complexes would lead to significant uncertainty of the polymerization data.

Optimization of polymerization parameters showed that the polymerization temperature and adopted molar ratio of Al/Zr had a significant influence on the catalytic activities of these zirconium complexes. All complexes kept moderate activities when polymerization temperature was increased from 30 to 90 °C, but the range of 50–70 °C seemed to be superior conditions. For most of the complexes, the highest catalytic activity was reached at about 70 °C. It is notable that considerable activities could be retained for **4a** and **5a** with *ortho*-dimethyl substitution even at 90 °C (Entries

Table 4 The polymerization of ethylene with 4a-c/MAO catalytic syst

Entry	Catalyst	[Al]/[Zr]	Temp/°C	Yield/g	Activity/kg PE (mol-Zr) ⁻¹ $[C_2H_4]^{-1}$ h ⁻¹	$M_{\eta^{b}}/10^{5} { m g mol^{-1}}$
1	4 a	1000	30	0.2188	72	18.32
2		1000	50	0.3669	156	6.13
3°		1000	70	0.3152	336	n.d.ª
4		1000	90	0.3002	196	0.66
5		500	70	0.2990	160	2.82
6		2000	70	0.1066	57	6.14
7	4b	1000	30	0.3017	98	4.51
8		1000	70	0.3520	188	4.96 ^e
9		1000	90	0.1463	97	1.88
10		300	70	0.3381	180	5.65
11		500	70	0.4827	257	4.96
12		2000	70	0.2412	128	6.18
13	4c	1000	30	0.1900	62	26.85
14		1000	50	0.1833	78	12.05
15		1000	70	0.2122	113	8.67 ^f
16		1000	90	0.1563	103	0.36
17		500	70	0.2769	148	9.09
18		2000	70	0.1874	100	2.13

^{*a*} In toluene, V = 25 mL, [Zr] = 2×10^{-4} mol/L, $P_{\text{ethylene}} = 1.0$ MPa, $t_p = 0.5$ h. ^{*b*} Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and molecular weight was calculated using the relation: [η] = $6.77 \times 10^{-4} M_{\eta}^{0.67}$. ^{*c*} $t_p = 0.25$ h. ^{*a*} Not determined, polymer sample only partially dissolved in decahydronaphthalene at 135 °C. ^{*e*} M_w and M_w/M_n were determined by GPC. For Entry 8, $M_w = 4.17 \times 10^5$ g mol⁻¹, $M_w/M_n = 15.3$. ^{*f*} For Entry 15, $M_w = 7.83 \times 10^5$ g mol⁻¹, $M_w/M_n = 16.9$.

Table 5	The polymerization	of ethylene with 5a-	c/MAO catalytic systems ^a
---------	--------------------	----------------------	--------------------------------------

Entry	Catalyst	[Al]/[Zr]	Temp/°C	Yield/g	Activity/kg-PE (mol-Zr) ⁻¹ $[C_2H_4]^{-1}$ h ⁻¹	$M_{\eta}{}^{b}/10^{5} \mathrm{g \ mol^{-1}}$
19	5a	1000	30	0.1197	40	n.d. ^c
20		1000	50	0.2309	98	n.d. ^c
21		1000	70	0.3208	170	5.31
22		1000	90	0.2136	139	1.80
23		2000	70	0.2630	140	3.94
24	5b	1000	30	0.1401	46	8.76
25		1000	50	0.2590	110	6.58
26		1000	70	0.2188	117	8.60^{d}
27		1000	90	0.1357	89	2.17
28		500	70	0.3364	180	4.63
29		2000	70	0.1720	92	7.70
30	5c	1000	30	0.1492	49	9.64
31		1000	50	0.2931	125	7.88
32 ^e		1000	70	0.2296	245	n.d. ^c
33		500	70	0.3239	173	5.58
34		2000	70	0.0623	33	2.16

^{*a*} In toluene, V = 25 mL, $[Zr] = 2 \times 10^{-4}$ mol/L, $P_{ethylene} = 1.0$ MPa, $t_p = 0.5$ h. ^{*b*} Intrinsic viscosity was determined in decahydronaphthalene at 135 °C and molecular weight was calculated using the relation: $[\eta] = 6.77 \times 10^{-4} M_{\eta}^{0.67}$. ^{*c*} Not determined, polymer sample only partially dissolved in decahydronaphthalene at 135 °C. ^{*d*} M_w and M_w/M_n were determined by GPC, for Entry 26, $M_w = 5.04 \times 10^5$ g mol⁻¹, $M_w/M_n = 20.3$. ^{*e*} $t_p = 0.25$ h.

4 and 22). Comparably, zirconium complexes **4b** and **5b** with *ortho*-dichlorine substituents are somewhat thermally unstable; they displayed higher activities than **4a** and **5a** within the temperature range of 30–50 °C but lower activities at higher temperature. This is, however, consistent with the thermal instability of these complexes observed during their synthesis. Some β -diiminato titanium complexes were reported to exhibit optimized catalytic activities at about 25 °C.^{4,5,7k} In our previous work, zirconium complexes bearing non-linked β -diketiminate ligands exhibited a maximal value of catalytic activities at about 50 °C.⁶ This series of alkanediyl-linked bis(β -diketiminate) zirconium complexes seem to be able to abide higher polymerization temperature.

As shown in Tables 4 and 5, in general, good catalytic activities of these zirconium pre-catalysts could be obtained with the enhancement of [Al]/[Zr] molar ratio from 500 to 1000. However,

further increasing of the [Al]/[Zr] molar ratio to 2000 led to a decrease of catalytic activity. Probably, as suggested in the literature,^{10a,19} the surface of active species being overlaid with an excess of MAO and the increased amount of AlMe₃ embodied in MAO led to the deactivation of the active species. As is wellunderstood, when MAO is used as the cocatalyst, a large excess amount has to be adopted to ensure a good activation of the metal complex pre-catalyst; especially for non-metallocene group 4 metal complexes, the value of the Al/Zr molar ratio could be higher than 10 000 occasionally.²⁰ For example, group 4 metal complexes with [O,N]-type phenoxy-iminate ligands were reported to be activated with large amounts of MAO ([Al]/[M] > 2000–62500) to reach the optimum catalytic activities;²⁰ we found that the non-linked bis(β diketiminate) zirconium complexes⁶ displayed optimum catalytic activities for ethylene polymerization at [Al]/[Zr] = 2000. It

View Article Online

is noteworthy that, in this work, in spite of different *ortho*substituents or bridging units being introduced to the ancillary ligands, all of the formed zirconium complexes could display comparatively high catalytic activities for ethylene polymerization at a low [Al]/[Zr] molar ratio of 500.

Due to the difficulty encountered in the synthesis of linked bis(β -diketimine)s, the modification of the ligand framework was limited to introducing *ortho*-substitution on the phenyl rings. Nearly similar activities were observed for all the zirconium complexes, as listed in Tables 4 and 5; the steric and electronic nature of the *ortho*-substituents on the phenyl rings exhibited some influence on the polymerization of ethylene. When Al/Zr = 500–1000, in general, for complexes **4a**–**c**, the catalytic activities for ethylene polymerization within the temperature range of 30–70 °C increased in the order of **4c** (R¹ = R² = ⁱPr) < **4a** (R¹ = R² = Me) < **4b** (R¹ = R² = Cl) (see Entries 1, 7, 13 and Entries 5, 11, 17). The introduction of bulky *ortho*-isopropyl groups to the aryl rings in complex **4c** was not favored, which might have cumbered remarkably the coordination sphere of the metal center and restrained the coordination/insertion of ethylene monomer.

In the case of previously reported non-linked $bis(\beta$ diketiminate) zirconium complexes,6 the introduction of parachlorine substituents led to a decrease of catalytic activity, probably due to the dominant electron-donating behavior via the p- π conjugated effect from chlorine to phenyl ring. An improvement of catalytic activity for ethylene polymerization was observed for a mono-diiminato titanium complex with ortho-fluorine substituents on the aromatic rings, where the strong electronwithdrawing effect of fluorine atoms enhanced the electrophilicity of metal center and led to the increase of activity.5 Herein, we think that the higher activity of **4b** ($\mathbf{R}^1 = \mathbf{R}^2 = \mathbf{Cl}$) than **4a** ($\mathbf{R}^1 =$ $R^2 = Me$) at a lower temperature range could result from the electron-withdrawing effect of ortho-chlorine substituents, which might become dominant when a chlorine atom is situated at the *ortho*-positions of the phenyl ring *versus* the *para*-position. Owing to the thermal instability, complex 4b lost its advantage at higher polymerization temperatures, despite bearing electronwithdrawing ortho-chloro substituents.

A similar trend of the influence of *ortho*-substituents on ethylene polymerization was also found for complexes **5a** and **5b**, but not for **5c** (Table 5). Complex **5c** with *ortho*-isopropyl substituents displayed the highest catalytic activity among the three 1,3-propanediyl bridged bis(β -diketiminate) zirconium complexes, unexpectedly. At present we do not have a reasonable explanation for this counterintuitive phenomenon. Besides, the length of the bridging unit also had some effect on the catalytic properties of the corresponding complexes; complexes **5a–b** showed slightly lower catalytic activities than complexes **4a–b** with the 1,2-ethanediyl-bridge, which might result from the more hindered coordination sphere in **5a–b**.²¹

In our opinion, the introduction of an alkanediyl linkage may provide a rigid ligand framework and consequently afford zirconium complexes with a stereorigid C_2 -symmetric configuration capable of catalyzing a stereoselective α -olefin polymerization with single-site nature. However, selective GPC analysis results revealed the production of polyethylenes with very broad MWD (MWD = 15.3–20.3). In our previous work, polyethylenes with broad MWD (14.8) were obtained by zirconium complexes bearing non-linked asymmetrically substituted bis(β -diketiminate) ligands, where the introduction of two differient N-aryl moieties to the ligand backbone led to the existence of multiple active species under polymerization conditions.⁶ As mentioned above, the VT-NMR experiments of complexes **4a** and **5a** suggested that these zirconium complexes are highly fluxional in solution, possibly involving the weakening or partial detachment of the Zr–N bonds; it becomes conceivable that different active species might have formed under polymerization conditions, hence producing polyethylenes with broad MWD.²²

Indicated by the single peak at $\delta = 29.7$ ppm in the ¹³C{¹H} NMR spectrum (Fig. S6, ESI[†]) and small resonances of $\delta = 31.9$, 22.6 and 13.8 ppm assignable to the terminal *n*-propyl group, linear character without any branch is evident for the obtained PE samples, which is in agreement with previous reports of group 4 complexes with *N*,*N*-bidentate ligands.²³ Melting temperatures (sample of Entry 8, 134.6°; sample of entry 26, 137.1°) measured by DSC also prove the polymers are typical linear polyethylene. Moreover, complexes **4b** and **5b** were applied to study the polymerization of propylene or 1-hexene in the presence of MAO as the cocatalyst, but no polymer could be obtained.

Conclusions

Novel linked bis(β -diketiminate) zirconium and hafnium complexes 4a-6b were prepared via the reaction of $ZrCl_4$ ·2THF or HfCl₄·2THF and the dilithium salt of corresponding ligand at 1:1 molar ratio in toluene. Either a distorted trigonal prismatic geometry or a distorted octahedral geometry around the metal center was found for 4c and 5c, respectively, via X-ray crystal structure analysis. In the solid state, both 4c and 5c possess C_1 symmetry, which however could be regarded as quasi- C_2 symmetry when taking into account the very slight differences between the two β -diketiminate parts. In the presence of MAO, the zirconium complexes showed moderate catalytic activities for ethylene polymerization. The influence of substituents at the ortho-positions of the aromatic rings on the catalytic activities was significant. When a low Al/Zr molar ratio of 500 was adopted, these zirconium complexes could retain comparatively high catalytic activities. Although the mechanism is still ambiguous, we consider that the production of polyethylenes with broad MWD (MWD = 15.3-20.3) by these complexes was related with the fluxional property of these complexes, which was confirmed by variable temperature ¹H NMR measurements.

Experimental

General considerations and materials

All manipulations were carried out under a dry argon atmosphere using dry-box or standard Schlenk techniques unless otherwise stated. Toluene was refluxed over sodium benzophenone ketyl prior to use. Benzene- d_6 and toluene- d_8 were dried over sodium under argon. *n*-BuLi (Chemetall, 2.5 M in *n*-hexane) was used as received. Methylaluminoxane (MAO, 1.53 M in toluene) was purchased from Witco. ZrCl₄·2THF,²⁴ HfCl₄·2THF,²⁴ enaminoketones **1a** and **1c**,^{1b} and linked bis(β -diketimine) **2c**¹² were prepared according to the literature procedures. NMR spectra were recorded on Bruker AVANCE-300, 400 and 500 spectrometers

with CDCl₃, C_6D_6 or C_7D_8 as solvent. Chemical shifts for ¹H NMR spectra were referenced internally using the residual solvent resonances and reported relative to tetramethylsilane (TMS). Melting points were determined in sealed glass capillaries under argon and reported without correction. Elemental analyses were performed on an EA-1106 instrument. ESI-MS spectra were recorded on a Micromass LCT mass instrument. Polymeric grade ethylene was directly used for polymerization without further purification. ¹³C NMR spectra of polymers were recorded on a Bruker AVANCE-500 spectrometer with 1,2-dichlorobenzene- d_4 as solvent at 100 °C. The intrinsic viscosities [n] of polyethylenes (PE) were measured with an Ubbelohde viscometer in decahydronaphthalene at 135 °C. The viscosity average molecular weights of PE were calculated according to the equation:²⁵ [η] (dL g⁻¹) = $6.77 \times 10^{-4} M_n^{0.67}$. Differential scanning calorimetry (DSC) was performed on a Universal V2.3C TA instrument at a heating rate of 10 °C min⁻¹. Gel permeation chromatography (GPC) performed on a Waters 150 ALC/GPC system in a 1,2-dichlorobenzene solution at 135 °C was used to determine the weight-average molecular weights (M_w) and the molecular weight distributions $(M_{\rm w}/M_{\rm n})$ of the polymers.

Syntheses of zirconium and hafnium complexes

4-(2,6-Dichlorophenyl)amino-3-penten-2-one (1b). 2,6-Dichloroaniline (16.20 g, 100.0 mmol) was mixed with 2,4-pentanedione (20.02 g, 200.0 mmol) in 100 mL of toluene containing a catalytic amount of *p*-toluenesulfonic acid. The reaction solution was refluxed for 24 h with water removed using a Dean–Stark trap. All the volatiles were removed *in vacuo*, and the residue was distilled under 110–113 °C/(0.05 Torr). The obtained pale yellow solids were recrystallized with ethanol to give **1b** as pale yellow crystals (20.01 g, 82%); mp 77–79 °C; $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.74 (s, 3H, CH₃), 2.14 (s, 3H, CH₃), 5.32 (s, 1H, *γ*-CH), 7.20 (t, ³J = 8.0 Hz, 1H, *p*-Ar-H), 7.39 (d, ³J = 8.0 Hz, 2H, *m*-Ar-H), 12.06 (br s, 1H, NH); $\delta_{\rm C}$ (100 MHz, CDCl₃) 19.0 (NCM*e*), 29.3 (OCM*e*), 97.4 (CH), 127.8 (Ar-C), 128.4 (Ar-C), 128.8 (Ar-C), 135.0 (Ar-C), 161.3 (NCMe), 197.1 (OCMe).

4-(2-Trifluoromethylphenyl)amino-3-penten-2-one (1d). Enaminoketone **1d** was synthesized similarly as **1b**. 16.11 g (100.0 mmol) of 2-trifluoromethylaniline and 20.02 g of 2,4-pentanedione (200.0 mmol) were used to give **1d** as light yellow crystals (20.67 g, 85%); mp 57–58 °C; $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.88 (s, 3H, CH₃), 2.13 (s, 3H, CH₃), 5.28 (s, 1H, γ -CH), 7.23 (d, ${}^{3}J = 7.7$ Hz, 1H, *o*-Ar-H), 7.35 (t, ${}^{3}J = 7.7$ Hz, 1H, *p*-Ar-H), 7.54 (t, ${}^{3}J = 7.7$ Hz, 1H, *m*-Ar-H). 7.70 (d, ${}^{3}J = 7.7$ Hz, 1H, *m*-Ar-H), 12.45 (br s, 1H, NH); $\delta_{\rm C}$ (100 MHz, CDCl₃) 19.4 (NCM*e*), 29.1 (OCM*e*), 98.5 (CH), 123.4 (q, ${}^{1}J_{\rm CF} = 271.3$ Hz, CF₃), 126.2 (Ar-C), 126.6 (q, ${}^{2}J_{\rm CC-F} = 39.0$ Hz, Ar-C), 128.7 (Ar-C), 132.4 (Ar-C), 136.9 (Ar-C), 137.0 (Ar-C), 159.8 (NCMe), 196.8 (OCMe).

N,*N*'-(1,2-Ethanediyl)-bis[2-(2,6-dimethylphenyl)amino-4-imino-2-pentene] (2a). Following the procedure reported for 2c.¹² Under an argon atmosphere, a solution of $[Et_3O]^+[BF_4]^-$ (9.501 g, 50.00 mmol) in CH₂Cl₂ (40 mL) was slowly added to a solution of 4-(2,6-dimethylphenyl)amino-3-penten-2-one (1a) (10.19 g, 50.00 mmol) in CH₂Cl₂ (40 mL) at 0 °C, then the reaction solution was stirred overnight at ambient temperature. Et₃N (5.051 g, 50.00 mmol) was added at 0 °C and the mixture was stirred for another 0.5 h at room temperature. A solution of ethylene diamine (1.503 g, 25.00 mmol) in Et₃N (15.15 g, 150.0 mmol) was added to the reaction solution and the stirring was continued overnight. The volatiles were removed in vacuo and the obtained residue was treated with 50 mL of toluene for 2 h. [Et₃NH]⁺[BF₄]⁻ precipitated as an oily solid. After filtration, toluene was removed under reduced pressure to afford a yellow solid. After recrystallization from ethanol at -20 °C, colorless crystals were obtained (7.751 g, 72%) (Found: C, 78.11; H, 8.97; N, 13.1. Calc. for C₂₈H₃₈N₄: C, 78.10; H, 8.89; N, 13.01%); mp 140.5–141.5 °C; $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.57 (s, 6H, CH₃), 1.95 (s, 6H, CH₃), 2.00 (s, 12H, Ar-CH₃), 3.34 (s, 4H, N-CH₂), 4.59 (s, 2H, γ -CH), 6.84 (t, ${}^{3}J = 7.5$ Hz, 2H, *p*-Ar-*H*), 7.01 (d, ${}^{3}J = 7.5$ Hz, 4H, *m*-Ar-*H*), 10.77 (br s, 2H, NH); δ_{C} (100 MHz, CDCl₃) 18.6 (Ar-Me), 19.6 (CMe), 21.5 (CMe), 44.8 (N-CH2), 94.0 (CH), 122.2 (Ar-C), 127.8 (Ar-C), 128.2 (Ar-C), 149.8 (Ar-C), 155.5 (NCMe), 166.24 (NCMe).

N,*N*'-(1,2-Ethanediyl)-bis[2-(2,6-dichlorophenyl)amino-4-imino-2-pentene] (2b). Ligand 2b was synthesized similarly as 2a. 9.501 g (50.00 mmol) of [Et₃O]⁺[BF₄]⁻, 12.21 g (50.00 mmol) of 1b and 1.503 g (25.00 mmol) of ethylene diamine were used to give 2b as colorless crystals (9.733 g, 76%) (Found: C, 56.38; H, 5.11; N, 11.02. Calc. for C₂₄H₂₆Cl₄N₄: C, 56.27; H, 5.12; N, 10.94%); mp 179–180 °C; δ_H (500 MHz, CDCl₃) 1.69 (s, 6H, *CH*₃), 1.99 (s, 6H, *CH*₃), 3.41 (s, 4H, N-*CH*₂), 4.66 (s, 2H, γ-*CH*), 6.85 (t, ³J = 8.0 Hz, 2H, *p*-Ar-*H*), 7.27 (d, ³J = 8.0 Hz, 4H, *m*-Ar-*H*), 10.61 (br s, 2H, N*H*); δ_C (100 MHz, CDCl₃) 19.8 (*CMe*), 22.4 (*CMe*), 44.7 (N-*CH*₂), 94.1 (*CH*), 123.1 (Ar-*C*), 127.7 (Ar-*C*), 128.1 (Ar-*C*), 146.8 (Ar-*C*), 157.74 (N*C*Me), 169.1 (N*C*Me).

N,*N*'-(1,2-Ethanediyl)-bis[2-(2-trifluoromethylphenyl) amino-4imino-2-pentene] (2d). Ligand 2d was synthesized similarly as 2a. 9.501 g (50.00 mmol) of [Et₃O]⁺[BF₄]⁻, 12.16 g (50.00 mmol) of 1d and 1.503 g (25.00 mmol) of ethylene diamine were used to give 2d as yellow crystals (8.679 g, 68%) (Found: C, 60.77; H, 5.51; N, 10.98. Calc. for C₂₆H₂₈F₆N₄: C, 61.17; H, 5.53; N, 10.97%); mp 144.5–145.5 °C; $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.80 (s, 6H, *CH*₃), 1.96 (s, 6H, *CH*₃), 3.35 (s, 4H, N-*CH*₂), 4.64 (s, 2H, *γ*-*CH*), 6.77 (d, ³*J* = 7.6 Hz, 2H, *o*-Ar-*H*), 7.04 (t, ³*J* = 7.6 Hz, 2H, *p*-Ar-*H*), 7.40 (t, ³*J* = 7.6 Hz, 2H, *m*-Ar-*H*), 7.58 (d, ³*J* = 7.6 Hz, 2H, *m*-Ar-*H*), 10.68 (br s, 2H, N*H*); $\delta_{\rm C}$ (100 MHz, CDCl₃) 19.4 (*CMe*), 21.5 (*CMe*), 44.5 (N-*CH*₂), 95.1 (*CH*), 121.6 (Ar-*C*), 121.9 (Ar-*C*), 122.5 (q, ¹*J*_{C-F} = 275.1 Hz, *CF*₃), 123.2 (Ar-*C*), 126.4 (q, ²*J*_{C-C-F} = 52.0 Hz, Ar-*C*), 132.3 (Ar-*C*), 150.1 (Ar-*C*), 157.1 (N*C*Me), 167.1 (N*C*Me).

N,*N*'-(1,3-Propanediyl)-bis[2-(2,6-dimethylphenyl)amino-4-imino-2-pentene] (3a). Ligand 3a was synthesized similarly as 2a. 9.501 g (50.00 mmol) of [Et₃O]⁺[BF₄]⁻, 10.15 g (50.00 mmol) of 1a and 1.851 g (25.00 mmol) of propylene diamine were used to give 3a as light yellow crystals (6.892 g, 62%) (Found: C, 78.31; H, 8.88; N, 12.54. Calc. for C₂₉H₄₀N₄: C, 78.33; H, 9.07; N, 12.60%); mp 80.5–81.5 °C; δ_H (500 MHz, CDCl₃) 1.58 (s, 6H, *CH*₃), 1.73 (p, ³*J* = 6.7 Hz, 2H, -CH₂-*CH*₂-*C*H₂-), 1.87 (s, 6H, *CH*₃), 2.01 (s, 12H, Ar-*CH*₃), 3.29 (t, ³*J* = 6.7 Hz, 4H, -*CH*₂-*CH*₂-*C*H₂-), 4.60 (s, 2H, γ-*CH*), 6.84 (t, ³*J* = 7.5 Hz, 2H, *p*-Ar-*H*), 7.01 (d, ³*J* = 7.5 Hz, 4H, *m*-Ar-*H*), 10.72 (br s, 2H, N*H*); δ_C (100 MHz, CDCl₃) 18.7 (Ar-*Me*), 19.4 (*CMe*), 21.5 (*CMe*), 32.1 (*CH*₂), 40.5 (N-CH₂), 93.5 (CH), 122.1 (Ar-C), 127.9 (Ar-C), 128.3 (Ar-C), 149.9 (Ar-C), 155.9 (NCMe), 166.3 (NCMe).

N,*N*′-(1,3-Propanediyl)-bis[2-(2,6-dichlorophenyl)amino-4-imino-2-pentene] (3b). Ligand 3b was synthesized similarly as 2a. 9.501 g (50.00 mmol) of [Et₃O]⁺[BF₄][−], 12.21 g (50.00 mmol) of 1b and 1.851 g (25.00 mmol) of propylene diamine were used to give 3b as yellow crystals (8.947 g, 68%) (Found: C, 56.81; H, 5.45; N, 10.55. Calc. for C₂₅H₂₈Cl₄N₄: C, 57.05; H, 5.36; N, 10.64%); mp 109–110 °C; $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.70 (s, 6H, *CH*₃), 1.78 (p, ³*J* = 6.7 Hz, 2H, -CH₂-CH₂-CH₂-), 1.85 (s, 6H, *CH*₃), 3.35 (t, ³*J* = 6.7 Hz, 4H, -CH₂-CH₂-CH₂-), 4.66 (s, 2H, γ-CH), 6.84 (t, ³*J* = 8.0 Hz, 2H, *p*-Ar-*H*), 7.25 (d, ³*J* = 8.0 Hz, 4H, *m*-Ar-*H*), 10.55 (br s, 2H, N*H*); $\delta_{\rm C}$ (100 MHz, CDCl₃) 19.6 (*CMe*), 22.4 (*CMe*), 31.3 (*C*H₂), 40.4 (N-*C*H₂), 93.4 (*C*H), 123.1 (Ar-*C*), 127.8 (Ar-*C*), 128.1 (Ar-*C*), 146.9 (Ar-*C*), 158.1 (N*C*Me), 169.9 (N*C*Me).

N, N'-(1,3-Propanediyl)-bis[2-(2,6-diisopropylphenyl) amino-4imino-2-pentene] (3c). Ligand 3c was synthesized similarly as 2a. 9.501 g (50.00 mmol) of [Et₃O]⁺[BF₄]⁻, 12.97 g (50.00 mmol) of 1c and 1.851 g (25.00 mmol) of propylene diamine were used to give light yellow crystals (9.051 g, 65%) (Found: C, 79.98; H, 9.91; N, 10.00. Calc. for C₃₇H₅₆N₄: C, 79.80; H, 10.14; N, 10.06%); mp 114.5–115.5 °C; $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.07 (d, ³J = 6.9 Hz, 12H, $CH(CH_3)_2$), 1.14 (d, ${}^{3}J = 6.9$ Hz, 12H, $CH(CH_3)_2$), 1.60 (s, 6H, CH_3), 1.69 (p, ${}^{3}J = 6.7$ Hz, 2H, $-CH_2-CH_2-CH_2-$), 1.88 (s, 6H, CH_3), 2.84 (sep, ${}^{3}J = 6.9$ Hz, 4H, $CH(CH_3)_2$), 3.27 (t, ${}^{3}J = 6.7$ Hz, 4H, -CH₂-CH₂-CH₂-), 4.60 (s, 2H, γ -CH), 7.01 (t, ${}^{3}J = 7.5$ Hz, 2H, p-Ar-H), 7.08 (d, ${}^{3}J = 7.5$ Hz, 4H, m-Ar-H), 10.83 (br s, 2H, NH); $\delta_{\rm C}$ (100 MHz, CDCl₃) 19.5 (CMe), 21.9 (CMe), 23.1 (CHMe2), 24.1 (CHMe2), 28.3 (CHMe2), 31.9 (CH2), 40.5 (N-CH₂), 93.4 (CH), 122.8 (Ar-C), 123.0 (Ar-C), 138.3 (Ar-C), 147.1 (Ar-C), 156.0 (NCMe), 166.5 (NCMe).

Reaction of 1b with 1,2-diaminobenzene. Under an argon atmosphere, a solution of $[Et_3O]^+[BF_4]^-$ (9.501 g, 50.00 mmol) in CH₂Cl₂ (40 mL) was slowly added to a solution of 4-(2,6dichlorophenyl)amino-3-penten-2-one (1b) (12.15 g, 50.00 mmol) in CH₂Cl₂ (40 mL) at 0 °C, then the reaction solution was stirred overnight at room temperature. Et₃N (5.051 g, 50.00 mmol) was added at 0 °C and the mixture was stirred for another 0.5 h at ambient temperature. A solution of 1,2-diaminobenzene (2.703 g, 25.00 mmol) in Et₃N (15.15 g, 150.0 mmol) was added to the reaction solution and the stirring was continued for 48 h. All the volatiles were removed in vacuo and the obtained residue was treated with 50 mL of toluene for 2 h. [Et₃NH]⁺[BF₄]⁻ precipitated as an oily solid. After filtration, toluene was removed under reduced pressure to afford a brown solid. Colorless crystals of 7 (4.551 g) were obtained by column chromatography on silica gel with petroleum ether as eluent. $\delta_{\rm H}$ (500 MHz, CDCl₃) 1.30 (t, ³J = 7.0 Hz, 3H, OCH₂CH₃), 1.80 (s, 3H, CH₃), 2.38 (s, 3H, CH₃), 3.85 (q, ${}^{3}J = 7.0$ Hz, 2H, OCH₂CH₃), 5.26 (s, 1H, γ -CH), 6.87 (t, $^{3}J = 8.0$ Hz, 1H, *p*-Ar-*H*), 7.27 (t, $^{3}J = 8.0$ Hz, 2H, *m*-Ar-*H*); $\delta_{\rm C}$ (CDCl₃, 100 MHz) 14.8 (CH₂CH₃), 20.6 (CMe), 23.6 (CMe), 63.5 (CH₂CH₃), 100.1 (CH), 123.4 (Ar-C), 125.5 (Ar-C), 128.3 (Ar-C), 147.0 (Ar-C), 166.4 (NCMe), 169.0 (NCMe).

 $\{N, N'-(1, 2-Ethanediyl)-bis[pent-2-ene-4-imino-2-(2, 6-dimethyl-phenyl)aminate]\}$ zirconium dichloride (4a). To a solution of ligand 2a (0.861 g, 2.00 mmol) in 10 mL of toluene was added

This journal is © The Royal Society of Chemistry 2009

dropwise n-BuLi (2.5 M in hexane, 0.80 mL, 2.0 mmol) at -78 °C. The mixture was stirred and allowed to warm to ambient temperature slowly. After being stirred for an additional 12 h, the obtained yellow solution was added dropwise to a stirred suspension of ZrCl₄·2THF (0.755 g, 2.00 mmol) in 20 mL of toluene at -78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The mixture was evaporated to dryness under reduced pressure and the obtained yellow solid was extracted several times with hot toluene. All the filtrates were combined and concentrated to ca. 30 mL under vacuum. Yellow crystals were obtained after deposition at -20 °C overnight (0.662 g, 56%) (Found: C, 56.73; H, 6.17; N, 9.22. Calc. for C28H36Cl2N4Zr: C, 56.93; H, 6.14; N, 9.48%); mp 185-190 °C (Dec.); $\delta_{\rm H}$ (500 MHz, C₆D₆) 1.34 (s, 6H, CH₃), 1.65 (s, 6H, CH₃), 2.04 (s, 12H, Ar-CH₃), 3.31 (s, 4H, N-CH₂), 5.25 (s, 2H, γ-CH), 6.88 (d, ${}^{3}J = 7.5$ Hz, 4H, *m*-Ar-*H*), 6.97 (t, ${}^{3}J = 7.5$ Hz, 2H, p-Ar-H); δ_C (125 MHz, C₆D₆) 20.2 (Ar-Me), 24.6 (CMe), 24.7 (CMe), 54.0 (N-CH₂), 105.4 (γ-CH), 127.4 (Ar-C), 130.3 (Ar-C), 137.9 (Ar-C), 144.5 (Ar-C), 165.5 (NCMe), 166.7 (NCMe).

{*N,N'*-(1,2-Ethanediyl)-bis[pent-2-ene-4-imino-2-(2,6-dichlorophenyl)aminate]} zirconium dichloride (4b). Complex 4b was synthesized similarly as 4a. 1.024 g (2.000 mmol) of 2b, 0.80 mL of *n*-BuLi (2.5 M in hexane, 2.0 mmol), and 0.755 g (2.00 mmol) of ZrCl₄·2THF were used to give yellow crystals (0.739 g, 55%) (Found: C, 42.87; H, 3.60; N, 8.33. Calc. for $C_{24}H_{24}Cl_6N_4Zr$: C, 42.88; H, 3.71; N, 8.14%); mp 168–172 °C (Dec.); $\delta_{\rm H}$ (500 MHz, C_6D_6) 1.60 (s, 6H, CH_3), 1.63 (s, 6H, CH_3), 3.47 (s, 4H, N- CH_2), 5.44 (s, 2H, γ -CH), 6.42 (t, ³*J* = 8.0 Hz, 2H, *p*-Ar-H), 7.06 (d, ³*J* = 8.0 Hz, 4H, *m*-Ar-H); $\delta_{\rm C}$ (125 MHz, C_6D_6) 23.6 (*CMe*), 25.4 (*CMe*), 56.4 (N-*C*H₂), 108.2 (γ -CH), 126.9 (Ar-*C*), 129.7 (Ar-*C*), 133.1 (Ar-*C*), 152.3 (Ar-*C*), 167.9 (NCMe), 168.5 (NCMe).

{N,N'-(1,2-Ethanediyl)-bis[pent-2-ene-4-imino-2-(2,6-diisopropylphenyl)aminate]} zirconium dichloride (4c). Complex 4c was synthesized similarly as 4a. 1.085 g (2.000 mmol) of 2c, 0.80 mL of n-BuLi (2.5 M in hexane, 2.0 mmol), and 0.755 g (2.00 mmol) of ZrCl₄·2THF were used to give yellow crystals (0.829 g, 59%) (Found: C, 62.81; H, 7.78; N, 7.33. Calc. for C₃₆H₅₂Cl₂N₄Zr·0.4(C₇H₈): C, 62.99; H, 7.52; N, 7.57%); mp 204– 210 °C (Dec.); $\delta_{\rm H}$ NMR (500 MHz, C₆D₆) 1.04 (d, ³J = 6.5 Hz, 6H, CH(CH₃)₂), 1.26 (d, ${}^{3}J = 6.5$ Hz, 6H, CH(CH₃)₂), 1.31 (d, ${}^{3}J = 6.5$ Hz, 6H, CH(CH₃)₂), 1.61 (s, 6H, CH₃), 1.63 (d, ${}^{3}J =$ 6.5 Hz, 6H, CH(CH₃)₂), 1.72 (s, 6H, CH₃), 2.89 (sep, ${}^{3}J = 6.5$ Hz, 2H, $-CH(CH_3)_2$, 3.10 (d, $^2J = 6.7$ Hz, 2H, N-CH₂), 3.64 (sep, $^3J =$ 6.7 Hz, 2H, $-CH(CH_3)_2$), 3.86 (d, $^2J = 6.7$ Hz, 2H, N-CH₂), 5.40 (s, 2H, γ -CH), 7.01–7.22 (m, 6H, Ar-H); $\delta_{\rm C}$ (125 MHz, C₆D₆) 22.9 (CHMe₂), 24.9 (CMe), 25.3 (CHMe₂), 25.4 (CHMe₂), 26.2 (CHMe2), 26.7 (CMe), 29.4 (CHMe2), 29.6 (CHMe2), 56.3 (N-CH₂), 108.4 (γ-CH), 123.9 (Ar-C), 125.4 (Ar-C), 126.3 (Ar-C), 126.7 (Ar-C), 129.9 (Ar-C), 140.5 (Ar-C), 142.9 (Ar-C), 152.5 (Ar-C), 165.5 (NCMe), 168.6 (NCMe).

{*N,N'*-(1,3-Propanediyl)-bis[pent-2-ene-4-imino-2-(2,6-dimethylphenyl)aminate]} zirconium dichloride (5a). Complex 5a was synthesized similarly as 4a. 0.899 g (2.00 mmol) of 3a, 0.80 mL of *n*-BuLi (2.5 M in hexane, 2.0 mmol), and 0.755 g (2.00 mmol) of ZrCl₄·2THF were used to give yellow crystals (0.556 g, 46%) (Found: C, 57.88; H, 6.71; N, 8.45. Calc. for $C_{29}H_{38}Cl_2N_4Zr$: C, 57.59; H, 6.33; N, 9.26%); mp 175–179 °C (Dec.); $\delta_{\rm H}$ (500 MHz, C₇D₈, 60 °C) 1.37 (s, 6H, CH₃), 1.48 (p, ${}^{3}J$ = 6.5 Hz, 2H, -CH₂-), 1.79 (s, 6H, CH₃), 1.94 (br s, 12H, Ar-CH₃), 3.79 (br s, 4H, N-CH₂), 5.32 (s, 2H, γ-CH), 6.86 (d, 4H, ${}^{3}J$ = 7.5 Hz, Ar-H), 6.97 (t, 2H, ${}^{3}J$ = 7.5 Hz, Ar-H); $\delta_{\rm H}$ (500 MHz, C₇D₈, 20 °C) 0.92 (s, 6H, CH₃), 1.34 (s, 6H, CH₃), 1.58 (m, 2H, -CH₂-), 1.70 (s, 12H, Ar-CH₃), 3.25 (br s, 2H, N-CH₂), 4.35 (br s, 2H, N-CH₂), 5.36 (s, 2H, γ-CH), 6.90–7.02 (m, 6H, Ar-H); $\delta_{\rm C}$ (125 MHz, C₇D₈, 25 °C) 20.8 (-CH₂-), 23.3 (CMe), 23.7 (Ar-Me), 24.5 (CMe), 47.3 (N-CH₂), 106.5 (CH), 126.5 (Ar-C), 127.5 (Ar-C), 138.1 (Ar-C), 145.1 (Ar-C), 166.5 (NCMe), 168.9 (NCMe).

{*N*,*N*'-(1,3-Propanediyl)-bis[pent-2-ene-4-imino-2-(2,6-dichlorophenyl)aminate]} zirconium dichloride (5b). Complex 5b was synthesized similarly as 4a. 1.052 g (2.000 mmol) of 3b, 0.80 mL of *n*-BuLi (2.5 M in hexane, 2.0 mmol), and 0.755 g (2.00 mmol) of ZrCl₄·2THF were used to give yellow crystals (0.578 g, 43%) (Found: C, 43.30; H, 3.95; N, 7.87. Calc. for $C_{25}H_{26}Cl_6N_4Zr$: C, 43.74; H, 3.82; N, 8.16%); mp 211–220 °C (Dec.); $\delta_{\rm H}$ (500 MHz, C_6D_6) 1.00 (br s, 2H, -CH₂-), 1.57 (s, 6H, CH₃), 1.72 (s, 6H, CH₃), 3.60 (br s, 2H, N-CH₂), 4.04 (br s, 2H, N-CH₂), 5.36 (s, 2H, γ -CH), 6.40 (m, 2H, *p*-Ar-H), 7.03 (br s, 4H, *m*-Ar-H); $\delta_{\rm C}$ (125 MHz, C_6D_6) 19.7 (-CH₂-), 23.4 (CMe), 27.0 (CMe), 46.9 (N-CH₂), 107.7 (CH), 123.7 (Ar-C), 127.0 (Ar-C), 129.9 (Ar-C), 158.5 (Ar-C), 166.7 (NCMe).

{N,N'-(1,3-Propanediyl)-bis[pent-2-ene-4-imino-2-(2,6-diisopropylphenyl)aminatel} zirconium dichloride (5c). Complex 5c was synthesized similarly as 4a. 1.114 g (2.000 mmol) of 3c, 0.80 mL of n-BuLi (2.5 M in hexane, 2.0 mmol), and 0.755 g (2.00 mmol) of ZrCl₄·2THF were used to give yellow crystals (0.760 g, 53%) (Found: C, 63.75; H, 7.24; N, 7.78. Calc. for C₃₇H₅₄Cl₂N₄Zr·0.3C₇H₈: C, 63.44; H, 7.65; N, 7.42%); mp 211– 216 °C (Dec.); $\delta_{\rm H}$ (500 MHz, C₆D₆) 1.04 (br s, 2H, -CH₂-, partially overlapped), 1.06 (d, ${}^{3}J = 6.5$ Hz, 6H, CH(CH₃)₂), 1.22 (d, ${}^{3}J =$ 6.5 Hz, 6H, CH(CH₃)₂), 1.26 (d, ${}^{3}J = 6.5$ Hz, 6H, CH(CH₃)₂), 1.60 (d, ${}^{3}J = 6.5$ Hz, 6H, CH(CH₃)₂), 1.63 (s, 6H, CH₃), 1.71 (s, 6H, CH₃), 2.83 (sep, ${}^{3}J = 6.5$ Hz, 2H, CH(CH₃)₂), 3.67 (m, 4H, N- CH_2), 3.92 (sep, ${}^{3}J = 6.5$ Hz, 2H, $CH(CH_3)_2$), 5.30 (s, 2H, γ -CH), 7.01–7.19 (m, 6H, Ar-H); $\delta_{\rm C}$ (125 MHz, C₆D₆) 23.9 (-CH₂-), 25.4 (CHMe₂), 25.5 (CHMe₂), 26.9 (CMe), 27.7 (CMe), 28.9 (CHMe₂), 29.3 (CHMe₂), 46.9 (N-CH₂), 106.8 (γ-CH), 123.9 (Ar-C), 125.6 (Ar-C), 126.9 (Ar-C), 129.2 (Ar-C), 130.0 (Ar-C), 141.3 (Ar-C), 143.7 (Ar-C), 152.5 (Ar-C), 165.9 (NCMe), 169.2 (NCMe).

{*N,N'*-(1,2-Ethanediyl)-bis[pent-2-ene-4-imino-2-(2,6-dichlorophenyl)aminate]} hafnium dichloride (6b). Complex 6b was synthesized similarly as 4a. 1.024 g (2.000 mmol) of 2b, 0.80 mL of *n*-BuLi (2.5 M in hexane, 2.0 mmol), and 0.928 g (2.00 mmol) of HfCl₄·2THF were used to give yellow crystals (1.018 g, 67%) (Found: C, 40.89; H, 3.55; N, 6.91. Calc. for $C_{24}H_{24}Cl_6N_4Hf\cdot 0.5(C_7H_8)$: C, 40.98; H, 3.49; N, 6.96%); mp 180– 185 °C (Dec.); $\delta_{\rm H}$ (500 MHz, C_6D_6) 1.58 (s, 6H, *CH*₃), 1.62 (s, 6H, *CH*₃), 3.52 (s, 4H, N-*CH*₂), 5.40 (s, 2H, γ -*CH*), 6.42 (t, ³*J* = 8.0 Hz, 2H, *p*-Ar-*H*), 7.06 (d, ³*J* = 8.0 Hz, 4H, *m*-Ar-*H*).

X-Ray diffraction measurements of 4c and 5c

The crystallographic data for complexes 4c and 5c were collected on a Bruker AXSD8 diffractometer with graphitemonochromated Mo-K α radiation ($\lambda = 0.71073$ Å). All data were collected at 20 °C using omega-scan techniques. The structures of **4c** and **5c** were solved by direct methods and refined using Fourier techniques. An absorption correction based on SADABS was applied.²⁶ All non-hydrogen atoms were refined by full-matrix least-squares on *F*² using the SHELXTL program package.²⁷ Hydrogen atoms were located and refined by the geometry method. The cell refinement, data collection, and reduction were done by Bruker SAINT.²⁸ The structure solution and refinement were performed by SHELXS-97²⁹ and SHELXL-97,³⁰ respectively. Both in **4c** and **5c**, inclusion of solvent molecule was detected; the quality of the crystals was not good enough to allow a satisfactory location of the solvent molecules at ambient temperature. Hydrogen atoms of solvent molecules in **4c** and **5c** that could not be located were included directly. Molecular structures were generated using ORTEP-III.³¹

Typical procedure for ethylene polymerization

A 100 mL autoclave, equipped with a magnetic stirrer, was heated at 100 °C under vacuum for 30 min and then cooled to the desired temperature by immersing into a thermostatically heated bath, then filled with ethylene. The appropriate amount of MAO solution, toluene solution of zirconium complex, and toluene to bring the final volume to 25 mL were added to the autoclave in that sequence; the reactor was then pressurized with ethylene. The ethylene pressure was kept constant during the polymerization. The reaction mixture was stirred vigorously for a certain time and the ethylene pressure in the autoclave was slowly vented. Then the polymerization was quenched with 3% HCl in ethanol (50 mL). The contents of the reactor were transferred to a beaker and then separated from the solution by filtration. The collected polymer was washed to neutral with ethanol and then dried overnight in a vacuum oven at 60 °C to constant weight.

The concentration of ethylene in toluene was evaluated according to Herry's law:³²

$$C_{\rm ethylene} = P_{\rm ethylene} H_0 \exp(\Delta H_{\rm L}/(RT))$$

where $C_{\text{ethylene}} = \text{ethylene concentration (mol L⁻¹)}$, $P_{\text{ethylene}} = \text{ethylene}$ pressure (atm), $H_0 = \text{the Herry coefficient}$, 0.00175 mol L⁻¹ atm⁻¹, $\Delta H_L = \text{enthalpy of salvation of ethylene in toluene}$, 2569 cal mol⁻¹, R = universal gas constant, 1.989 cal mol⁻¹ K⁻¹) and T =polymerization temperature (K).

Acknowledgements

This work is subsidized by the National Basic Research Program of China (2005CB623801), National Natural Science Foundation of China (NNSFC, 20604009 and 20774027), the Program for New Century Excellent Talents in University (for H. Ma, NCET-06-0413), Shanghai Rising-Star Program (06QA14014). All the financial supports are gratefully acknowledged. Authors also thank the very kind donation of a Braun glove-box by AvH foundation.

Notes and references

 (a) L. Bourget-Merle, M. F. Lappert and J. R. Severn, *Chem. Rev.*, 2002, **102**, 3031–3065; (b) A. P. Dove, V. C. Gibson, E. L. Marshall, J. P. White and D. J. Williams, *Dalton Trans.*, 2004, 570–578; (c) J. E. Parks and R. H. Holm, *Inorg. Chem.*, 1968, **7**, 1408–1416; (d) S. G. McGeachin, *Can. J. Chem.*, 1968, **46**, 1903–1911; (e) Y. Yao, M. Xue, Y. Luo, Z. Zhang, R. Jiao, Y. Zhang, Q. Shen, W. Wong, K. Yu and J. Sun, J. Organomet. Chem., 2003, **678**, 108–116; (f) K. H. Park and W. J. Marshall, J. Org. Chem., 2005, **70**, 2075–2081; (g) H. Hamaki, N. Takeda, T. Yamasaki, T. Sasamori and N. Tokitoh, J. Organomet. Chem., 2007, **692**, 44–54; (h) S. Fustero, M. G. Torre, B. Pina and A. S. Fuentes, J. Org. Chem., 1999, **64**, 5551–5556.

- 2 (a) M. Rahim, N. J. Taylor, S. Xin and S. Collins, Organometallics, 1998, 17, 1315–1323; (b) R. Vollmerhaus, M. Rahim, R. Tomaszewski, S. Xin, N. J. Taylor and S. Collins, Organometallics, 2000, 19, 2161–2169.
- 3 R. Andrés, E. F. Jesús, J. Mata, J. C. Flores and R. Gómez, J. Organomet. Chem., 2005, 690, 939–940.
- 4 Y. Li, H. Gao and Q. Wu, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 93–101.
- 5 G. Xie and C. Qian, J. Polym. Sci., Part A: Polym. Chem., 2008, 46, 211-217.
- 6 S. Gong, H. Ma and J. Huang, J. Organomet. Chem., 2008, 693, 3509– 3518.
- 7 (a) B. Deelman, P. B. Hitchcock, M. F. Lappert, W. Leung, H. Lee and T. Mak, J. Organomet. Chem., 1996, 513, 281-285; (b) B. Deelman, P. B. Hitchcock, M. F. Lappert, W. Leung, H. Lee and T. Mak, Organometallics, 1999, 18, 1444-1452; (c) L. Kakaliou, W. J. Scanlon, B. Qian, S. W. Baek and M. R. Smith, Inorg. Chem., 1999, 38, 5964-5977; (d) X. Jin and B. M. Novak, Macromolecules, 2000, 33, 6205-6207; (e) M. Zhou, S. Huang, L. Weng, W. Sun and D. Liu, J. Organomet. Chem., 2003, 665, 237–245; (f) B. Qian, W. J. Scanlon and M. R. Smith, Organometallics, 1999, 18, 1693-1698; (g) F. Basuli, U. J. Kilgore, D. Brown, J. C. Huffman and D. J. Mindiola, Organometallics, 2004, 23, 6166-6175; (h) P. L. Franceschini, M. Morstein, H. Berke and H. W. Schmalle, Inorg. Chem., 2003, 42, 7273-7282; (i) P. H. Budzelaar, B. V. Oorta and A. G. Orpenb, Eur. J. Inorg. Chem., 1998, 1485-1494; (j) G. B. Nikiforov, H. W. Roesky, J. Magull, T. Labahn, D. Vidovic, M. Noltemeyer, H. Schmidt and N. S. Hosmane, Polyhedron, 2003, 22, 2669-2681; (k) L. Tang, Y. Duan, X. Li and Y. Li, J. Organomet. Chem., 2006, 691, 2023-2031.
- 8 (a) E. Y. Tshuva, I. Goldberg and M. Kol, J. Am. Chem. Soc., 2000, 122, 10706–10707; (b) S. Segal, I. Goldberg and M. Kol, Organometallics, 2005, 24, 200–202; (c) V. Busico, R. Cipullo, S. Ronca and P. H. M. Budzelaar, Macromol. Rapid Commun., 2001, 22, 1405–1410; (d) V. Busico, R. Cipullo, N. Friederichs, S. Ronca, G. Talarico, M. Togrou and B. Wang, Macromolecules, 2004, 37, 8201–8203.
- 9 (a) C. Capacchione, A. Proto, H. Ebeling, R. Mulhaupt, K. Moller, T. P. Spaniol and J. Okuda, *J. Am. Chem. Soc.*, 2003, **125**, 4964–4965; (b) B. Lian, K. Beckerle, T. P. Spaniol and J. Okuda, *Angew. Chem., Int. Ed.*, 2007, **46**, 8507–8510.
- 10 (a) C. Cuomo, M. Strianese, T. Cuenca, M. Sanz and A. Grassi, *Macromolecules*, 2004, **37**, 7469–7476; (b) P. D. Knight, A. J. Clarke, B. S. Kimberley, R. A. Jackson and P. Scott, *Chem. Commun.*, 2002, 352–353; (c) M. Sanz, M. Cuenca, M. Galakhow, A. Grassi, D. L. Hughes, R. K. Bott and M. Bochmann, *Organometallics*, 2004, **23**, 5324–5331.
- 11 (a) M. F. Pilz, C. Limberg and B. Ziemer, J. Org. Chem., 2006, 71, 4559– 4564; (b) T. J. Hebden, W. W. Brennessel, C. J. Flaschenriem and P. L. Holland, Dalton Trans., 2006, 3855–3857; (c) J. Vela, L. W. Zhu, C. J. Flaschenriem, W. W. Brennessel, R. J. Lachicotte and P. L. Holland, Organometallics, 2007, 26, 3416–3423.
- 12 (a) D. V. Vitanova, F. Hampel and K. C. Hultzsch, *Dalton Trans.*, 2005, 1565–1566; (b) D. V. Vitanova, F. Hampel and K. C. Hultzsch, *J. Organomet. Chem.*, 2005, **690**, 5182–5197.

- 13 S. Gong and H. Ma, Dalton Trans., 2008, 3345-3357.
- 14 C. Capacchione, R. Manivannan, M. Barone, K. Beckerle, R. Centore, L. Oliva, A. Proto, A. Tuzi, T. P. Spaniol and J. Okuda, *Organometallics*, 2005, 24, 2971–2982.
- 15 Due to the overlapping of resonances observed in the spectrum of 5c, only complex 5a was selected to carry on the variable-temperature ¹H NMR analysis.
- 16 (a) K. Beckerle, R. Manivannan, T. P. Spaniol and J. Okuda, Organometallics, 2006, 25, 3019–3026; (b) A. Yeori, I. Goldberg, M. Shuster and M. Kol, J. Am. Chem. Soc., 2006, 128, 13062–13063.
- 17 A. Cohen, A. Yeori, I. Goldberg and M. Kol, *Inorg. Chem.*, 2007, 46, 8114–8116.
- 18 R. J. Long, D. J. Jones, V. C. Gibson and A. J. P. White, Organometallics, 2008, 27, 5960–5967.
- 19 E.-Y. Chen and T. J. Marks, Chem. Rev., 2000, 100, 1391-1434.
- 20 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.
- 21 Herein an exception was again observed for **5c**. At present we have not reasonable explanation, but the counterintuitive phenomenon that complex **5c** exhibited the highest activity among the 1,3-propanediyl bridged series and higher activity than **4c** should have some correlation with the fluxionality of **5c** in solution.
- 22 The reaction of zirconium complex **4a** with excess MAO (30 quiv.) was monitored by ¹H NMR measurements in C_6D_6 , which excluded the possibility of complete detachment of the ligand from the metal center, no free ligand or aluminum complex bearing the linked bis(β -diketiminate) ligand was characterized in the ¹H NMR spectra. Further study concerning the active species is still on-going.
- (a) Y. Yoshida, S. Matsui, Y. Takagi, M. Mitani, T. Nakano, H. Tanaka, N. Kashiwa and T. Fujita, *Organometallics*, 2001, **20**, 4793–4799; (b) K. Mashima and H. Tsurugi, *J. Organomet. Chem.*, 2005, **690**, 4414– 4423; (c) N. Adams, N. Arts, P. Bolton, D. Cowell, S. Dubberley, N. Friederichs, C. Grant, M. Kranenbury, A. Sealey, B. Wang, P. Wilson, A. Cowley, P. Mountford and M. Schroder, *Chem. Commun.*, 2004, 434–435.
- 24 L. E. Manzer, Inorg. Synth., 1982, 21, 135-136.
- 25 P. Francis, R. Cooke and J. Elliott, J. Polym. Sci., 1958, 31, 453– 466.
- 26 SADABS, Bruker Nonius area detector scaling and absorption correction-V2.05, Bruker AXS Inc., Madison, WI, 1996.
- 27 G. M. Sheldrick, SHELXTL 5.10 for windows NT, Structure Determination Software Programs, Bruker Analytical X-ray Systems, Inc., Madison, WI, 1997.
- 28 SAINT, Version 6.02, Bruker AXS Inc., Madison, WI, 1999.
- 29 G. M. Sheldrick, SHELXS-97, Program for solution of crystal structures, University of Göttingen, Germany, 1997.
- 30 G. M. Sheldrick, SHELXL-97, Program for refinement of crystal structures, University of Göttingen, Germany, 1997.
- 31 L. J. Farrugia, ORTEP-III for Windows—Version 2.0, J. Appl. Crystallogr., 1997, 30, 565University of Glasgow (2008 Copyright).
- 32 (a) N. N. Bhriain, H.-H. Brintzinger, D. Ruchatz and G. Fink, *Macromolecules*, 2005, **38**, 2056–2063; (b) A. L. McKnight and R. M. Waymouth, *Macromolecules*, 1999, **32**, 2816–2825; (c) J. Wu, Q. Pan and G. L. J. Rempel, *J. Appl. Polym. Sci.*, 2005, **96**, 645– 649.