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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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1. Introduction

Group 4 transition metal single site catalysts [1–7] have been extensively studied in the past decades as high performance olefin polymerization catalysts, which have made the production of high performance polyolefin materials with tailored structures and properties becoming possible. Since the first non-metallocene single site olefin polymerization catalysts were developed in 1990s, group 4 transition metal complexes with chelating ligands have drawn considerable attention due to their high catalytic activity and unique ability to control the polymer's microstructure [2]. Fujita et al. developed a family of group 4 transition metal catalysts with a pair of phenoxy-imine chelating ligands (so-called FI-catalysts) that show exceptional catalytic performance for olefin polymerization [3,4]. Of these catalysts, the titanium ones were reported to catalyze the living polymerization of ethylene at high temperatures and the zirconium ones were found to produce polyethylene with ultra high molecular weight. These pioneering works have invoked much research interest on the group 4 non-metallocene catalysts with phenoxy-imine ligands or similar ligands [5]. Recently, some group 4 transition metal complexes bearing N.Nbidentate chelating ligands have also been studied as olefin poly-

ABSTRACT

A series of binuclear zirconium complexes of the type $[ortho-(Me_2N)C_6H_4CH_2NArZrCl_2(\mu-Cl)]_2$ [Ar = 2,6- $Me_2C_6H_3$ (1), 2,6- $Et_2C_6H_3$ (2), 2,6- $iPr_2C_6H_3$ (3)] were synthesized by reactions of ZrCl₄ with corresponding *ortho*-(Me_2N)C₆H₄CH_2NArLi. All new zirconium complexes were characterized by ¹H and ¹³C NMR spectroscopy and elemental analyses. The molecular structures of complexes 1 and 2 were determined by single crystal X-ray diffraction analysis. Upon activation with AliBu₃ and Ph₃CB(C₆F₅)₄, complexes 1–3 exhibit moderate catalytic activity for ethylene polymerization and copolymerization with 1-hexene, producing high or ultra high molecular weight polyethylene or relatively high molecular weight poly (ethylene-*co*-1-hexene) with reasonable 1-hexene incorporation.

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merization catalysts. Zirconium complexes with a 4-membered metallocyclic ring supported by a NSiN bidentate ligand [6] were reported to be efficient catalysts for ethylene polymerization and copolymerization with 1-hexene to produce polyethylenes with high to ultra high molecular weight. Titanium and zirconium complexes with a 5-membered metallocyclic ring chelated by a (anilidomethyl)pyridine ligand were found to catalyze the polymerization of ethylene, propylene and 1,3-butadiene [7].

To develop new group 4 transition metal catalysts with N,N-bidentate chelating ligands, we have synthesized several new zirconium complexes containing a more stable 6-membered metallocyclic ring with the general formula [*ortho*-(Me₂N)C₆H₄ CH₂NArZrCl₂(μ -Cl)]₂ [Ar = 2,6-Me₂C₆H₃ (**1**), 2,6-Et₂C₆H₃ (**2**), 2,6-^{*i*}Pr₂C₆H₃ (**3**)], and found that they show good catalytic performance for ethylene polymerization and copolymerization. In this paper, we report the synthesis and characterization of these new zirconium complexes as well as their catalytic properties for ethylene polymerization with 1-hexene.

2. Results and discussion

2.1. Synthesis and characterization of new complexes

The free ligands *ortho*- $(Me_2N)C_6H_4CH_2NHAr$ [Ar = 2,6-Me₂C₆H₃ (HLa), 2,6-Et₂C₆H₃ (HLb), 2,6-*i*Pr₂C₆H₃ (HLc)] were synthesized



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^{0277-5387/\$ -} see front matter @ 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.poly.2012.09.044

according to the method published previously [8]. Reactions of ZrCl₄ with one equiv of corresponding ortho-(Me₂N)C₆H₄CH₂NArLi $[Ar = 2,6-Me_2C_6H_3 (LiLa), 2,6-Et_2C_6H_3 (LiLb), 2,6-iPr_2C_6H_3 (LiLc)]$ in diethyl ether afforded the zirconium complexes 1-3 in high yields (70-80%) as shown in Scheme 1. Analytically pure complexes 1-3 were obtained as pale yellow crystals from a concentrated *n*-hexane/CH₂Cl₂ solution at -30 °C. Complexes **1**-**3** are soluble in CH₂Cl₂, CHCl₃ and toluene, but less soluble in diethyl ether and hexane. These new zirconium complexes were all characterized by ¹H and ¹³C NMR spectroscopy together with elemental analyses. The ¹H NMR spectra of complexes **1**, **2**, **3** show no broad signal for the NH proton in their free ligands, and the resonances of the N- CH_2 protons appear at 4.62, 4.52, and 4.64 ppm, respectively, which are obviously shifted downfield in comparison to the corresponding signals in their free ligands (4.17, 4.15, and 4.07 ppm, respectively). These observations demonstrate that the ligands are attached to the zirconium centers of these complexes. The ¹H NMR spectrum of complex 2 shows two quartets for the two methylene protons of the CH₂CH₃ group in the ligand, and the ¹H NMR spectrum of complex 3 shows two doublets for the methyl protons of the CHMe₂ group in its ligand. Furthermore, the ¹³C NMR spectrum of complex **3** gives two signals for the two methyl carbons of the CHMe₂ group. These results indicate that the rotation of the 2,6-R₂C₆H₃ group about the N-C bond is restricted in complexes 2 and 3 [9].

Molecular structures of complexes 1 and 2 were determined by single crystal X-ray diffraction analysis. The ORTEP drawings of the two molecular structures and selected bond lengths and angles are shown in Figs. 1 and 2, respectively. In the solid state structures, complexes 1 and 2 both exist in a binuclear form in which each zirconium atom is six coordinated and possesses a pseudo-octahedral coordination environment with two chloride atoms bridging the two zirconium atoms. The average terminal Zr-Cl bond lengths (2.415 Å in 1 and 2.408 Å in 2) are in line with the values previously observed in related complexes [4,6]. The bridging zirconium-chloride bond lengths Zr(1)-Cl(1) [2.5620(19) Å in 1 and 2.5672(6)Å in **2**] and Zr(1)-Cl(1A) [2.725(2)Å in **1** and 2.7133(6) Å in **2**] are obviously longer than the terminal Zr-Cl bond lengths. The Zr(1)-N(2) covalent bond lengths [2.013(6) Å in 1 and 2.0207(19) Å in 2] are similar to, while the Zr(1)-N(1) coordination bond lengths [2.460(6) Å in 1 and 2.4609(19) Å in 2] are obviously longer than the corresponding values reported for the related complex $[ZrN(Me_2)SiMe_2N(2,6-iPrC_6H_3)Cl_2(\mu-Cl)]_2$ [6a].

2.2. Olefin polymerization reactions

Ethylene polymerization reactions with complexes 1-3 as procatalysts under different conditions were studied in detail and the results are summarized in Table 1. It was found that these complexes exhibit moderate catalytic activity for ethylene polymerization upon activation with AliBu₃ and Ph₃CB(C₆F₅)₄. Under similar conditions, the catalytic activity decreases in the order of



Fig. 1. Perspective view of **1** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr(1)-N(1) 2.460(6); Zr(1)-N(2) 2.013(6); Zr(1)-Cl(1) 2.5620(19); Zr(1)-Cl(1A) 2.725(2); Zr(1)-Cl(2) 2.397(2); Zr(1)-Cl(3) 2.432(2); N(1)-Zr(1)-N(2) 80.9(2); Cl(1)-Zr(1)-Cl(1A) 72.85(7); Cl(2)-Zr(1)-Cl(3) 92.06(8); Zr(1)-N(1)-C(1) 106.9(4); Zr(1)-N(2)-C(7) 131.1(5); Zr(1)-N(2)-C(10) 118.3(4).



Fig. 2. Perspective view of **2** with thermal ellipsoids drawn at the 30% probability level. Hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Zr(1)–N(1) 2.4609(19); Zr(1)–N(2) 2.0207(19); Zr(1)–Cl(1) 2.5672(6); Zr(1)–Cl(1A) 2.7133(6); Zr(1)–Cl(2) 2.3945(7); Zr(1)–Cl(3) 2.4212(7); N(1)–Zr(1)–N(2) 80.16(7); Cl(1)–Zr(1)–Cl(1A) 73.32(2); Cl(2)–Zr(1)–Cl(3) 93.32(2); Zr(1)–N(1)–C(1) 106.55(13); Zr(1)–N(2)–C(7) 130.97(15); Zr(1)–N(2)–C(10) 118.03(14).

3 > 2 > 1, indicating that the catalytic activity of these zirconium complexes is remarkably influenced by the nature of the anilide



Scheme 1. Synthetic procedure of complexes 1-3.

Table 1
Summary of ethylene polymerization catalyzed by 1-3/AliBu ₃ /Ph ₃ CB(C ₆ F ₅) ₄ systems.

Run No.	Catal.	Al/Zr mol. ratio	Temp. (°C)	Yield (mg)	Activity ^b	${M_{\eta}}^{c}_{(imes 10^{-4})}$	T _m ^d (°C)
1	1	150	60	30	24	56.5	135.5
2	2	100	60	85	68	132.4	138.0
3	2	150	60	131	108	101.4	138.6
4	2	200	60	103	82	96.8	137.7
7	3	100	40	61	49	242.6	137.5
8	3	100	60	72	58	224.2	138.0
9	3	100	80	52	42	196.6	137.4
10	3	150	60	142	114	202.4	136.8
11	3	200	60	106	85	197.8	137.5

 $^a\,$ Polymerization condition: toluene 60 ml; catalyst 5 μ mol; B/Zr molar ratio 1.5; polymerization time 15 min; ethylene pressure 5 bar.

 b^{-} kg PE (mol Zr)⁻¹h⁻¹.

^c Measured in decahydronaphthalene at 135 °C.

 $^{\rm d}$ Determined by DSC at a heating rate of 10 $^{\circ}{\rm C}\ {\rm min}^{-1}$ and the data from the second scan are used.

moiety in their ligands. Complexes 2 and 3 with a sterically bulky 2,6-Et₂C₆H₃N- or 2,6-*i*Pr₂C₆H₃N-anilide group exhibit obviously higher catalytic activity than complex **1** that has a relatively less bulky 2,6-Me₂C₆H₃N-anilide group. It is well known that electron-donating substituents on the ligands of a catalyst would stabilize the catalytically active cationic species and improve the catalytic activity [10]. On the other hand, moderately bulky ligands would weaken the interaction between the cationic catalyst and the anionic cocatalyst species, and allow more space for ethylene to coordinate to the central metal and thus enhance the catalytic activity too [4a,11]. As observed in other zirconium catalyst systems, the catalytic activity of these zirconium catalyst systems is dependent on the Al/Zr molar ratio. The maximal values of their catalytic activity were obtained at Al/Zr molar ratios about 150. The catalytic activity of these catalyst systems was also examined at different polymerization temperatures and the maximal values were observed around 60 °C. The viscosity-average molecular weight (M_{η}) of the obtained polyethylenes with these catalyst systems was determined in decahydronaphthalene at 135 °C. and the data are given in Table 1. The polyethylenes produced by these catalysts possess high or ultra high molecular weight (56–243 \times 10⁴ g mol⁻¹), depending on the structure of the catalyst. As can be seen from the results, a catalyst with a bulkier ligand produces polyethylene with higher molecular weight, which can be attributed to that a catalyst with bulkier coordination environment would slow down the rate of both the β -hydride elimination [4a] and the chain transfer reactions [12]. The influence of the Al/Zr molar ratio and the polymerization temperature on the polymer molecular weight was also investigated. As expected, the molecular weight of the obtained polyethylene decreases with the increase in Al/Zr molar ratio and the elevation in polymerization temperature due to the acceleration of both the chain transfer reaction to alkylaluminum and the β -hydride elimination reaction. In addition, the melting temperature of the obtained polyethylenes ranges from 135 to 139 °C, being typical for linear polyethylene.

The copolymerization of ethylene with 1-hexene using 1-3/AliBu₃/Ph₃CB(C₆F₅)₄ catalyst systems was also studied, and the results are summarized in Table 2. The catalytic activity of these catalyst systems for the ethylene/1-hexene copolymerization under similar conditions changes in the same order of 3 > 2 > 1 as observed in the ethylene homopolymerization reaction. The obtained poly(ethylene-*co*-1-hexene)s were analyzed by ¹³C NMR spectroscopy. Based on the ¹³C NMR analysis [13], the comonomer content of the poly(ethylene-*co*-1-hexene)s was calculated and the data are listed in Table 2. The viscosity-average molecular weight (M_{η}) of the obtained copolymers by these catalyst systems was determined in xylene at 105 °C, and the results are also given in Table 2.

Table 2

Summary of copolymerization of ethylene with 1-hexene catalyzed by $1\!-\!3/AliBu_3/Ph_3CB(C_6F_{5)4}$ systems.^a

Run No.	Catal.	1- Hexene (mol/L)	Yield (mg)	Activity ^b	$M_{\eta}^{c}(imes 10^{-4})$	1-Hexene content (mol.%) ^d	T ^e (°C)
1	1	0.7	15	12	43.2	1.04	123.5
2	1	1.4	22	18	39.6	2.02	121.9
3	2	0.7	54	43	74.2	0.52	125.4
4	2	1.4	140	112	66.8	0.94	123.8
5	3	0.7	57	46	97.6	_f	128.4
6	3	1.4	148	118	90.1	_f	126.7

 $^{\rm a}$ Polymerization conditions: toluene + 1-hexene total 60 mL; catalyst 5 μ mol; Al/ Zr ratio 150; B/Zr molar ratio 1.5; polymerization time 15 min; ethylene pressure 5 bar.

^b kg polymer (mol Zr)⁻¹h⁻¹.

^c Measured in xylene at 105 °C.

^d Calculated on the basis of ¹³C NMR spectra.

 $^{\rm e}\,$ Determined by DSC at a heating rate of 10 $^{\circ}{\rm C}\,{\rm min^{-1}}$ and the data from second scan are used.

^f Copolymer is not soluble enough to run ¹³C NMR.

Table 3

Crystallographic parameters, data collections, and structure refinements for complexes 1 and 2.

$\begin{array}{llllllllllllllllllllllllllllllllllll$	Complex	1	2
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Formula	$C_{34}H_{42}C_{16}N_4Zr_2$	$C_{38}H_{50}Cl_6N_4Zr_2$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Formula weight	901.86	957.96
$\begin{array}{llllllllllllllllllllllllllllllllllll$	Wavelength (Å)	0.71073	0.71073
Space group $P\bar{1}$ $P\bar{1}$ $P\bar{1}$ Unit cell dimensions	Crystal system	triclinic	triclinic
Unit cell dimensions a (Å)9.4080(19)9.4371(11) b (Å)10.047(2)10.1034(12) c (Å)12.054(2)12.7111(15) α (°)91.08(3)94.105(2) β (°)107.75(3)109.410(2) γ (°)116.15(3)111.789(2) V (Å3)958.3(3)1034.8(2) Z 11 $F(000)$ 456488 D_{calc} (g cm ⁻³)1.5631.537Absorption coefficient (mm ⁻¹)0.9920.923 θ (°)3.16-25.001.74-26.03Number of reflections75205979Number of independent reflections33103992 R_{int} 0.07760.0144Data/restraints/parameters3310/0/2133992/0/230Goodness-of-fit1.0531.060 R_1, R_w (all data)0.0906, 0.20950.0341, 0.0712Max(min) difference in peak (e Å ⁻³)0.956, -0.7230.438, -0.261	Space group	$P\bar{1}$	ΡĪ
a (Å)9.4080(19)9.4371(11)b (Å)10.047(2)10.1034(12)c (Å)12.054(2)12.7111(15) α (°)91.08(3)94.105(2) β (°)107.75(3)109.410(2) γ (°)116.15(3)111.789(2)V (Å ³)958.3(3)1034.8(2)Z11F(000)456488D _{calc} (g cm ⁻³)1.5631.577Absorption coefficient (mm ⁻¹)0.9920.923 θ (°)3.16-25.001.74-26.03Number of reflections75205979Number of independent reflections33103992 R_{int} 0.07760.0144Data/restraints/parameters3310/0/2133992/0/230Goodness-of-fit1.0531.060 R_1, R_w (all data)0.0906, 0.20950.0341, 0.0712Max(min) difference in peak (e Å ⁻³)0.956, -0.7230.438, -0.261	Unit cell dimensions		
$\begin{array}{lll} b(\dot{A}) & 10.047(2) & 10.1034(12) \\ c(\dot{A}) & 12.054(2) & 12.7111(15) \\ \alpha(^{\circ}) & 91.08(3) & 94.105(2) \\ \beta(^{\circ}) & 107.75(3) & 109.410(2) \\ \gamma(^{\circ}) & 107.75(3) & 109.410(2) \\ \gamma(^{\circ}) & 116.15(3) & 111.789(2) \\ V(\dot{A}^3) & 958.3(3) & 1034.8(2) \\ Z & 1 & 1 \\ F(000) & 456 & 488 \\ D_{calc} (g cm^{-3}) & 1.563 & 1.537 \\ Absorption coefficient (mm^{-1}) & 0.992 & 0.923 \\ \theta(^{\circ}) & 3.16-25.00 & 1.74-26.03 \\ Number of reflections & 7520 & 5979 \\ Number of independent reflections & 3310 & 3992 \\ R_{int} & 0.0776 & 0.0144 \\ Data/restraints/parameters & 3310/0/213 & 3992/0/230 \\ Goodness-of-fit & 1.053 & 1.060 \\ R_1, R_w (all data) & 0.0966, 0.0295 & 0.0341, 0.0712 \\ Max(min) difference in peak (e \dot{A}^{-3}) & 0.956, -0.723 & 0.438, -0.261 \\ \end{array}$	a (Å)	9.4080(19)	9.4371(11)
$\begin{array}{lll} c \left(\dot{A} \right) & 12.054(2) & 12.7111(15) \\ \alpha \left(^{\circ} \right) & 91.08(3) & 94.105(2) \\ \beta \left(^{\circ} \right) & 107.75(3) & 109.410(2) \\ \gamma \left(^{\circ} \right) & 107.75(3) & 109.410(2) \\ \gamma \left(^{\circ} \right) & 116.15(3) & 111.789(2) \\ V \left(\dot{A}^3 \right) & 958.3(3) & 1034.8(2) \\ Z & 1 & 1 \\ F(000) & 456 & 488 \\ D_{calc} \left(g cm^{-3} \right) & 1.563 & 1.537 \\ Absorption coefficient (mm^{-1}) & 0.992 & 0.923 \\ \theta \left(^{\circ} \right) & 3.16-25.00 & 1.74-26.03 \\ Number of reflections & 7520 & 5979 \\ Number of independent reflections & 3310 & 3992 \\ R_{int} & 0.0776 & 0.0144 \\ Data/restraints/parameters & 3310/213 & 3992/0/230 \\ Goodness-of-fit & 1.053 & 1.060 \\ R_1, R_w \left(I > 2\sigma(I) \right) & 0.0669, 0.1824 & 0.0287, 0.0685 \\ R_1, R_w (all data) & 0.0906, 0.2095 & 0.0341, 0.0712 \\ Max(min) difference in peak (e \dot{A}^{-3}) & 0.956, -0.723 & 0.438, -0.261 \\ \end{array}$	b (Å)	10.047(2)	10.1034(12)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	<i>c</i> (Å)	12.054(2)	12.7111(15)
$\begin{array}{lll} \beta \left(^{\circ} \right) & 107.75(3) & 109.410(2) \\ \gamma \left(^{\circ} \right) & 116.15(3) & 111.789(2) \\ V \left(^{\lambda ^{3}} \right) & 958.3(3) & 1034.8(2) \\ Z & 1 & 1 \\ F(000) & 456 & 488 \\ D_{calc} \left(g cm^{-3} \right) & 1.563 & 1.537 \\ Absorption coefficient (mm^{-1}) & 0.992 & 0.923 \\ \theta \left(^{\circ} \right) & 3.16-25.00 & 1.74-26.03 \\ Number of reflections & 7520 & 5979 \\ Number of independent reflections & 3310 & 3992 \\ R_{int} & 0.0776 & 0.0144 \\ Data/restraints/parameters & 3310/0/213 & 3992/0/230 \\ Goodness-of-fit & 1.053 & 1.060 \\ R_{1}, R_{w} \left[l > 2\sigma(l) \right] & 0.0669, 0.1824 & 0.0287, 0.0685 \\ R_{1}, R_{w} \left(all data \right) & 0.996, -0.723 & 0.438, -0.261 \\ \end{array}$	α (°)	91.08(3)	94.105(2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	β(°)	107.75(3)	109.410(2)
$V(Å^3)$ 958.3(3) 1034.8(2) Z 1 1 $F(000)$ 456 488 $D_{calc}(g cm^{-3})$ 1.563 1.537 Absorption coefficient (mm ⁻¹) 0.992 0.923 $\theta(°)$ 3.16-25.00 1.74-26.03 Number of reflections 7520 5979 Number of independent reflections 3310 3992 R_{int} 0.0776 0.0144 Data/restraints/parameters 3310/0/213 3992/0/230 Goodness-of-fit 1.053 1.060 R_1, R_w (all data) 0.0906, 0.2095 0.0341, 0.0712 Max(min) difference in peak (e Å ⁻³) 0.956, -0.723 0.438, -0.261	γ(°)	116.15(3)	111.789(2)
$\begin{array}{cccc} Z & 1 & 1 \\ F(000) & 456 & 488 \\ D_{calc} \left(g cm^{-3} \right) & 1.563 & 1.537 \\ Absorption coefficient (mm^{-1}) & 0.992 & 0.923 \\ \theta \left(^{\circ} \right) & 3.16-25.00 & 1.74-26.03 \\ Number of reflections & 7520 & 5979 \\ Number of independent reflections & 3310 & 3992 \\ R_{int} & 0.0776 & 0.0144 \\ Data/restraints/parameters & 3310/0/213 & 3992/0/230 \\ Goodness-of-fit & 1.053 & 1.060 \\ R_1, R_w \left[I > 2\sigma(I) \right] & 0.0669, 0.1824 & 0.0287, 0.0685 \\ R_1, R_w (all data) & 0.0906, 0.2095 & 0.0341, 0.0712 \\ Max(min) difference in peak (e Å^{-3}) & 0.956, -0.723 & 0.438, -0.261 \\ \end{array}$	V (Å ³)	958.3(3)	1034.8(2)
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$\begin{array}{llllllllllllllllllllllllllllllllllll$	F(000)	456	488
Absorption coefficient (mm ⁻¹) 0.992 0.923 θ (°) 3.16–25.00 1.74–26.03 Number of reflections 7520 5979 Number of independent reflections 3310 3992 R_{int} 0.0776 0.0144 Data/restraints/parameters 3310/0/213 3992/0/230 Goodness-of-fit 1.053 1.060 R_1, R_w [$I > 2\sigma(I)$] 0.0669, 0.1824 0.0287, 0.0685 R_1, R_w (all data) 0.0906, 0.2095 0.0341, 0.0712 Max(min) difference in peak (e Å ⁻³) 0.956, -0.723 0.438, -0.261	D_{calc} (g cm ⁻³)	1.563	1.537
θ (°)3.16-25.001.74-26.03Number of reflections75205979Number of independent reflections33103992 R_{int} 0.07760.0144Data/restraints/parameters3310/0/2133992/0/230Goodness-of-fit1.0531.060 R_1, R_w [$l > 2\sigma(l)$]0.0669, 0.18240.0287, 0.0685 R_1, R_w (all data)0.0906, 0.20950.0341, 0.0712Max(min) difference in peak (e Å ⁻³)0.956, -0.7230.438, -0.261	Absorption coefficient (mm ⁻¹)	0.992	0.923
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R_{int} 0.0776 0.0144 Data/restraints/parameters 3310/0/213 3992/0/230 Goodness-of-fit 1.053 1.060 R_1, R_w [$I > 2\sigma(I)$] 0.0669, 0.1824 0.0287, 0.0685 R_1, R_w (all data) 0.0906, 0.2095 0.0341, 0.0712 Max(min) difference in peak (e Å ⁻³) 0.956, -0.723 0.438, -0.261	Number of independent reflections	3310	3992
Data/restraints/parameters $3310/0/213$ $3992/0/230$ Goodness-of-fit 1.053 1.060 R_1, R_w [$I > 2\sigma(I)$] $0.0669, 0.1824$ $0.0287, 0.0685$ R_1, R_w (all data) $0.0906, 0.2095$ $0.0341, 0.0712$ Max(min) difference in peak (e Å ⁻³) $0.956, -0.723$ $0.438, -0.261$	R _{int}	0.0776	0.0144
Goodness-of-fit1.0531.060 R_1, R_w [$l > 2\sigma(l)$]0.0669, 0.18240.0287, 0.0685 R_1, R_w (all data)0.0906, 0.20950.0341, 0.0712Max(min) difference in peak (e Å ⁻³)0.956, -0.7230.438, -0.261	Data/restraints/parameters	3310/0/213	3992/0/230
R_1 , R_w [$l > 2\sigma(l)$] 0.0669, 0.1824 0.0287, 0.0685 R_1 , R_w (all data) 0.0906, 0.2095 0.0341, 0.0712 Max(min) difference in peak (e Å ⁻³) 0.956, -0.723 0.438, -0.261	Goodness-of-fit	1.053	1.060
$\begin{array}{ll} R_1, R_w \mbox{ (all data)} & 0.0906, 0.2095 & 0.0341, 0.0712 \\ \mbox{Max(min) difference in peak (e Å^{-3})} & 0.956, -0.723 & 0.438, -0.261 \end{array}$	$R_1, R_w \left[I > 2\sigma(I) \right]$	0.0669, 0.1824	0.0287, 0.0685
Max(min) difference in peak (e Å ⁻³) 0.956, -0.723 0.438, -0.261	R_1, R_w (all data)	0.0906, 0.2095	0.0341, 0.0712
	Max(min) difference in peak (e Å ⁻³)	0.956, -0.723	0.438, -0.261

The copolymers produced by these catalyst systems possess relatively high molecular weight ($M_{\eta} = 39-98 \times 10^4 \text{ g mol}^{-1}$). As mentioned above for the ethylene homopolymerization reaction, the molecular weight values of the obtained copolymers are also dependent on the structure of the catalyst. The catalyst with a bulkier ligand produces copolymers with higher molecular weight. In addition, the comonomer content and the melting temperature of the poly(ethylene-*co*-1-hexene)s were also found to be influenced by the structure of the catalyst.

3. Conclusions

A series of binuclear zirconium complexes [ortho-(Me₂N) $C_6H_4CH_2NArZrCl_2(\mu-Cl)]_2$, with a bidentate N-(ortho-dimethylaminobenzyl)anilide ligand have been synthesized in high yields, and characterized by ¹H and ¹³C NMR spectroscopy, as well as elemental analyses. Single crystal X-ray diffraction analysis on complexes **1** and **2** reveals that both complexes exist in a binuclear form in which each zirconium atom is six coordinated and possesses a pseudo-octahedral coordination environment with two chloride atoms bridging the two zirconium atoms. Upon activation with AliBu₃ and Ph₃CB(C₆F₅)₄, complexes **1–3** exhibit moderate catalytic activity for ethylene polymerization and copolymerization with 1-hexene, producing polyethylene with high or ultra high molecular weight and poly(ethylene-*co*-1-hexene) with reasonable 1-hexene incorporation. The catalytic activity of complexes **1–3** for both ethylene polymerization and ethylene/1-hexene copolymerization, and the molecular weight of the polymers obtained with complexes **1–3**, vary in the order of **3** > **2** > **1** because of the effect of the substituents in their anilide ligands.

4. Experimental

4.1. General details

All manipulations involving air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere (ultra-high purity) using either standard Schlenk techniques or glove box techniques. Toluene, diethyl ether, and *n*-hexane were distilled under nitrogen in the presence of sodium and benzophenone. CH₂Cl₂ and 1-hexene were purified by distilling over calcium hydride before use. Ph₃CB(C₆F₅)₄ [14] and ortho-(Me₂N)C₆H₄CH₂NArLi [8] were prepared according to literature procedures. Polymerization grade ethylene was further purified by passage through columns of 5A molecular sieves and MnO. AliBu₃, n-BuLi, and ZrCl₄ were purchased from Aldrich. ¹H and ¹³C NMR spectra were measured using a Varian Mercury-300 NMR spectrometer. ¹³C NMR spectra of the copolymers were recorded on a Varian Unity-400 MHz spectrometer at 125 °C with $o-C_6D_4Cl_2$ as the solvent. The melting points of the polymers were measured by differential scanning calorimetry (DSC) on a NETZSCH DSC 204 with the heating/cooling rate at 10 °C/min from 35 to 180 °C, and the data from the second heating scans were used.

4.2. Synthesis of complex 1

To a stirred suspension of ZrCl₄ (0.501 g, 2.15 mmol) in 40 mL diethyl ether was added slowly Li**La** (0.560 g, 2.15 mmol) at 0 °C, and the reaction mixture was allowed to slowly warm to room temperature and stirred over night. After removal of the solvent, the product was extracted with hexane/CH₂Cl₂ (2:1, 30 mL) and filtrated to remove LiCl. The solution was concentrated to about 20 mL and stored at –30 °C to give pure **1** as pale yellow crystals (0.684 g, 0.76 mmol, 71%). *Anal.* Calc. for C₃₄H₄₂N₄Cl₆Zr₂ (901.86): C, 45.3; H, 4.69; N, 6.21. Found: C, 45.5; H, 4.73; N, 6.17%. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 7.06 (t, 2H, ArH), 6.96 (d, 1H, ArH), 6.70–6.90 (m, 4H, ArH), 4.62 (s, 2H, N–CH₂–), 2.05 (s, 6H, N(CH₃)₂), 1.96 (s, 6H, CH₃Ar) ppm. ¹³C NMR (CDCl₃, 75 MHz, 298 K): δ 154.1 (Ar), 145.2 (Ar), 135.5 (Ar), 134.4 (Ar), 132.7 (Ar), 128.0 (Ar), 127.9 (Ar), 124.7 (Ar), 123.9 (Ar), 120.1 (Ar), 46.7 (N–CH₂), 45.4 (N(CH₃)₂), 18.8 (CH₃Ar) ppm.

4.3. Synthesis of complex 2

Complex **2** was synthesized using a procedure identical to that for complex **1** with Li**Lb** (0.865 g, 3.00 mmol) and ZrCl₄ (0.699 g, 3.00 mmol) as starting materials. 1.12 g of pure **2** was obtained as pale yellow crystals (1.17 mmol, 78%). *Anal.* Calc. for $C_{38}H_{50}N_4$ - $C_{16}Zr_2$ (957.96): C, 47.6; H, 5.26; N, 5.85. Found: C, 47.8; H, 5.32; N, 5.80%. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 7.22–7.54 (m, 7H, ArH), 4.52 (s, 2H, N–CH₂–), 3.28 (s, 6H, N(CH₃)₂), 2.93 (q, 2H,

4.4. Synthesis of complex 3

24.0 (CH₂CH₃), 15.1 (CH₂CH₃) ppm.

Complex **3** was synthesized using a procedure identical to that for complex **1** with LiLc (0.949 g, 3.00 mmol) and ZrCl₄ (0.700 g, 3.00 mmol) as starting materials. 1.11 g of pure **3** was obtained as pale yellow crystals (1.09 mmol, 73%). *Anal.* Calc. for C₄₂H₅₈N₄Cl₆Zr₂ (1014.06): C, 49.7; H, 5.76; N, 5.52. Found: C, 49.6; H, 5.80; N, 5.45%. ¹H NMR (CDCl₃, 300 MHz, 298 K): δ 6.90–7.24 (m, 7H, Ar*H*), 4.64 (s, 2H, N–CH₂–), 3.49 (sept, 2H, CH(CH₃)₂, ³J_{H–H} = 6.6 Hz), 2.51 (s, 6H, N(CH₃)₂), 1.24 (d, 6H, CH(CH₃)₂, ³J_{H–H} = 6.6 Hz), 0.93 (d, 6H, CH(CH₃)₂, ³J_{H–H} = 6.6 Hz) ppm. ¹³C NMR (CDCl₃, 75 MHz, 298 K): δ 144.8 (Ar), 132.1 (Ar), 128.8 (Ar), 127.9 (Ar), 126.0 (Ar), 125.3 (Ar), 125.1 (Ar), 124.1 (Ar), 123.4 (Ar), 120.5 (Ar), 48.0 (N–CH₂), 46.7 (N(CH₃)₂), 27.7 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 25.3 (CH(CH₃)₂) ppm.

4.5. X-ray structural analysis of complexes 1 and 2

Single crystals of **1** and **2** suitable for X-ray structural analysis were obtained from their solution in CH₂Cl₂/hexane mixture. Diffraction data of **1** were collected at 293 K on a Rigaku R-AXIS RAPID IP diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Diffraction data of **2** were collected at 185 K with a Bruker SMART-CCD diffractometer equipped with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). Both structures were solved by direct methods and refined by fullmatrix least-squares on F^2 . All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL [15] crystallographic software packages. Details of the crystallographic parameters, data collections, and structure refinements are summarized in Table 3. CCDC reference numbers 874740 and 874741.

4.6. Polymerization reactions

The ethylene polymerization experiments were carried out as follows: a dry 250 mL steel autoclave with a magnetic stirrer was charged with 60 mL of toluene, thermostated at the desired temperature and saturated with ethylene (1.0 bar). The polymerization reaction was started by addition of a mixture of a catalyst and AliBu₃ in toluene (5 mL) and a solution of Ph₃CB(C₆F₅)₄ in toluene (5 mL) at the same time. The vessel was pressurized to 5 bar with ethylene immediately and the pressure was kept by continuously feeding of ethylene. The reaction mixture was stirred at the desired temperature for 15 min. The polymerization was then quenched by injecting acidified ethanol containing HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum. For the ethylene/1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

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Appendix A. Supplementary data

Single crystal X-ray diffraction data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 874740 (1) and 874741 (2). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retriev-ing.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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