

Trichlorozirconium η^2 -Hydrazonides: Synthesis, Characterization and Their Catalytic Behavior toward Ethylene Polymerization*

Xin-e Duan^{a,b,c}, Qi-feng Xing^c, Zhen-ming Dong^a, Jian-bin Chao^b, Sheng-di Bai^b,
Dian-sheng Liu^{b**} and Wen-hua Sun^{c**}

^a Institute of Applied Chemistry, Shanxi University, Taiyuan 030006, China

^b School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, China

^c Key Laboratory of Engineering Plastics and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

Abstract The trichlorozirconium η^2 -hydrazonides ($R=H$, **A**; $R=CH_3$, **B**) were synthesized through the finely controlled stoichiometrical reactions of anhydrous zirconium tetrachloride with the lithium salt of either 1-(furan-2-ylmethylene)-2-phenylhydrazonide or 1-(furan-2-ylethylidene)-2-phenyl hydrazonide in the solvent tetrahydrofuran (THF), respectively. These complexes were highly sensitive to air and moisture due to solely using less bulky ligand of hydrazonides. The molecular structures of the title complexes, determined by means of single crystal X-ray diffraction, were found to be the distorted pentagonal bipyramid geometry around zirconium atom, with three chlorides and the hydrazonato ligand acting as the η^2 -coordination mode as well as two incorporated THF molecules. Upon activation with either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), both complexes **A** and **B** exhibited catalytic activities toward ethylene polymerization, producing polyethylenes with ultra-high molecular weights.

Keywords: Titanium complexes; Phenylhydrazonide; Ethylene polymerization; Ultra-high molecular weight polyethylene.

INTRODUCTION

The rapid development of complex precatalysts toward ethylene polymerization has been witnessed in the past two decades, including IVB metal complexes^[1] and late transition metal complexes^[2, 3]. The coordination modes of amidinate^[4–12], β -diketiminato^[13–16], guanidinate^[17, 18] and η^3 -azaallyl ligands^[19, 20] have been extensively explored along with the catalytic influences of their metal complexes. Some of them showed high activities toward ethylene polymerization, more importantly, in which the polyethylenes obtained indicated either narrow polydispersity or ultra-high molecular weights^[4–8, 13–15, 17–20]. In addition, hydrazone derivatives and their metal complexes were investigated for their wide applications in biological, pharmaceutical, analytical, optoelectronic and catalytic fields^[21–24]; however, the η^2 -coordination was only observed within half-metallocene^[24] and metallocenes^[25, 26] as well as their multi-ligated metal complexes^[21–23]. Targeting the metal complexes bearing mono- η^2 -hydrazonides, the reaction of zirconium tetrachloride with lithium 2-furyl-phenylhydrazonides was finely controlled, and trichlorozirconium η^2 -hydrazonides ($R=H$, **A**; $R=CH_3$, **B**) were isolated and characterized. These zirconium complexes showed good activity toward ethylene polymerization, moreover,

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** Corresponding authors: Dian-sheng Liu (刘滇生), E-mail: dslu@sxu.edu.cn

Wen-hua Sun (孙文华), E-mail: whsun@iccas.ac.cn

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producing polyethylenes with ultra-high molecular weights. Herein we report the synthesis, characterization and ethylene polymerization of the title complexes.

EXPERIMENTAL

Reagents and Instrumentation

All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were pre-dried over sodium, refluxed and distilled from sodium-potassium alloy (toluene), sodium-benzophenone (diethyl ether and tetrahydrofuran) and stored over molecular sieves (4 Å). Methylaluminoxane (MAO, 1.46 mol·L⁻¹ solution in toluene) and *iso*-butyl-modified methylaluminoxane (MMAO, 1.93 mol·L⁻¹ in heptane, 3A) were purchased from Akzo Nobel Corp. High-purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. The deuterated solvent CDCl₃ was dried over activated molecular sieves (4 Å). Starting materials (2-furaldehyde, 2-furyl-methylketone and phenylhydrazine) for ligands synthesis were purchased from local suppliers and purified before use. The substances of 2-furaldehyde phenylhydrazone (**a**) and 2-furyl-methylketone phenylhydrazone (**b**) were synthesized according to the procedures reported in the literature^[27]. The ¹H- and ¹³C-NMR spectra were recorded on a Bruker DRX-300 spectrometer, using TMS as internal standard. Elemental analyses were carried out using a Vario EL-III analyzer. Molecular weights and molecular weight distributions (MWDs) of polyethylene were determined by a PL-GPC220 instrument at 150 °C, with 1,2,4-trichlorobenzene as the solvent. Melting points of polyethylenes were measured from the second scanning run on a PerkinElmer DSC-7 differential scanning calorimetry (DSC) analyzer under a nitrogen atmosphere; in the procedure, a sample of about 3.8–4.5 mg was heated to 180 °C at a rate of 20 K/min, kept for 5 min at 180 °C to remove the thermal history, and then cooled at a rate of 20 K/min to room temperature before the second scanning run.

Preparation and Characterization

Preparation of Zr[(C₄H₃O)CH=NNPh]Cl₃(THF)₂ (**A**)

To a stirred solution of 2-furaldehyde phenylhydrazone (0.47 g, 2.52 mmol) in diethyl ether (about 25 mL) at 0 °C, LDA (0.27 g, 2.52 mmol) was added in small portions to form yellow slurry. The slurry was slowly warmed to room temperature and kept stirring for about 10 h, then filtrated to collect yellow solid. The obtained yellow solid was dissolved with 25 mL tetrahydrofuran; to the solution, anhydrous ZrCl₄ (0.58 g, 2.52 mmol) was added in small portions at -78 °C. The resulting orange-yellow mixture was slowly warmed to room temperature and stirred overnight. Volatile compounds were removed *in vacuo*, and the resulting orange-yellow residue was extracted with toluene and filtered. The filtrate was concentrated *in vacuo* to about 10 mL and stored for 2 days. The solution was filtered and the residue was recrystallized from tetrahydrofuran to give light brown crystals of complex **A**. Yield: 0.69 g (52%). ¹H-NMR (300 MHz, CDCl₃, TMS, δ): 7.95 (s, 1H, CH=N), 7.51–7.12 (m, 7H, furanyl-H and Ph-H), 6.50 (s, 1H, furanyl-H), 4.38 (br s, 8H, OCH₂CH₂, THF), 1.99 (s, 8H, OCH₂CH₂, THF). ¹³C-NMR (75 MHz, CDCl₃, TMS, δ): 150.6, 143.8, 113.4, 112.1 (furanyl-C), 145.4, 130.3, 127.4, 124.5 (Ph-C), 121.5 (CH=N), 75.2 (OCH₂CH₂, THF), 26.5 (OCH₂CH₂, THF). Anal. Calcd for C₁₉H₂₅Cl₃N₂O₃Zr: C, 43.30; H, 4.78; N, 5.32. Found: C, 43.66; H, 4.65; N, 5.02.

Preparation of Zr[(C₄H₃O)C(CH₃)=NNPh]Cl₃(THF)₂ (**B**)

To a stirred solution of 2-furyl-methylketone phenylhydrazone (0.55 g, 2.75 mmol) in tetrahydrofuran (about 25 mL) at 0 °C, LDA (0.29 g, 2.75 mmol) was added in small portions to form an orange solution. The solution was warmed to room temperature and kept stirring for about 10 h. To the obtained solution, anhydrous ZrCl₄ (0.64 g, 2.75 mmol) was added in small portions at -78 °C. Similar to synthetic procedure of complex **A**, the yellow crystals of complex **B** was obtained in 0.85 g (58%). ¹H-NMR (300 MHz, CDCl₃, TMS, δ): 7.51–6.88 (m, 7H, furanyl-H and Ph-H), 6.64–6.46 (m, 1H, furanyl-H), 4.28 (br d, 8H, OCH₂CH₂, THF), 2.20–1.94 (t, 11H, CH₃ and OCH₂CH₂ of THF). ¹³C-NMR (75 MHz, CDCl₃, TMS, δ): 150.2, 144.3, 143.4, 130.1, 129.2, 124.7, 121.8, 121.2, 114.2, 113.3, 112.4 (C=N, furanyl-C and Ph-C), 74.5 (OCH₂CH₂, THF), 26.4

(OCH₂CH₂, THF), 19.4 (CH₃). Anal. Calcd for C₂₀H₂₇Cl₃N₂O₃Zr: C, 44.40; H, 5.03; N, 5.18. Found: C, 44.76; H, 4.58; N, 5.13.

X-ray crystallographic determinations

Single crystals of the zirconium complexes **A** and **B** were obtained through re-crystallization from their tetrahydrofuran solutions, respectively. X-ray diffraction data were collected with graphite monochromated Mo-K α radiation ($\lambda = 0.071073$ nm) on a Bruker Smart Apex CCD diffractometer, equipped with an Oxford Cryosystems CRYOSTREAM device. The collected frames were processed with the proprietary software SAINT and absorption corrections were applied (SADABS) to the collected reflections. The structures of the molecules were solved by direct methods and expanded by standard difference Fourier syntheses using the software SHELXTL^[28]. Structure refinements were made on F^2 using the full-matrix least-squares technique. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and allowed to ride on the respective parent atoms. Crystal data and refinement parameters for all complexes are given in Table 1.

Table 1. Crystal data and structure refinement for complexes **A** and **B**

Compounds	A	B
Empirical formula	C ₁₉ H ₂₅ Cl ₃ N ₂ O ₃ Zr	C ₂₀ H ₂₇ Cl ₃ N ₂ O ₃ Zr
Formula weight	526.98	541.01
Temperature (K)	243(2)	243(2)
Wavelength (nm)	0.071073	0.071073
Crystal system	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/n$
a (nm)	1.3794(5)	1.5195(7)
b (nm)	0.8056(3)	1.7876(7)
c (nm)	2.0446(8)	1.8023(8)
α (°)	90	90
β (°)	98.533(7)	97.916(10)
γ (°)	90	90
V (nm ³)	2.2468(14)	4.849(4)
Z	4	8
D_{calc} (g·cm ⁻³)	1.558	1.482
μ (mm ⁻¹)	0.868	0.806
$F(000)$	1072	2208
θ range (°)	1.49–25.05	1.61–25.05
Limiting indices	$-14 \leq h \leq 16$,	$-18 \leq h \leq 17$,
	$-9 \leq k \leq 9$,	$-19 \leq k \leq 21$,
	$-24 \leq l \leq 20$	$-21 \leq l \leq 15$
No. rflns collected	12 081	26 864
No. unique rflns [$R(\text{int})$]	3971 (0.0473)	8578 (0.1013)
Completeness to θ (%)	99.8%	100.0%
Goodness-of-fit on F^2	1.355	0.988
R_1, wR_2 [$I > 2\sigma(I)$]	0.0463, 0.1198	0.0544, 0.0927
R_1, wR_2 (all data)	0.0546, 0.1249	0.1408, 0.1227
Largest diff. peak and hole (e·nm ⁻³)	1222 and –1059	505 and –576

General procedure for ethylene polymerization

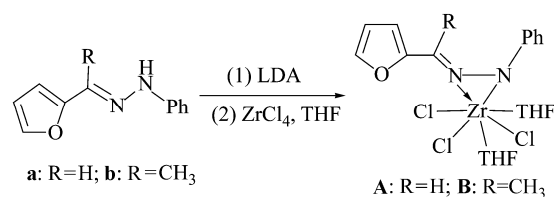
Ethylene polymerization at atmospheric pressure of ethylene was carried out as follows: the precatalyst was dissolved in toluene using standard Schlenk techniques. The mixture was stirred with a magnetic stir bar at a controlled temperature under one atmospheric ethylene (0.101 MPa), and then the desired amount of cocatalyst (MAO or MMAO) was added by a syringe. After the set period of time, a small amount of the reaction solution was collected and terminated by the addition of 10% aqueous hydrogen chloride immediately. The precipitated polymer was collected by filtration, washed with ethanol and finally dried.

Ethylene polymerization at elevated pressure (0.505 or 1.01 MPa) was carried out as follows: a 300 mL stainless steel autoclave, equipped with a mechanical stirrer and a temperature controller, was charged with ethylene atmosphere. 50 mL of toluene (freshly distilled) was first injected into the autoclave. Another 30 mL toluene containing the dissolved precatalyst and the required amount of co-catalyst (MAO or MMAO), plus the residual toluene were successively added using a syringe when the desired temperature was reached. The total volume was 100 mL. The reaction mixture was stirred intensely for the desired time under a corresponding pressure of ethylene throughout the entire experiment. The reaction mixture was immediately terminated by the addition of 10% aqueous hydrogen chloride. The precipitated polymer was collected by filtration, washed with ethanol and finally dried.

RESULTS AND DISCUSSION

Synthesis and Characterization

The stoichiometric reactions of 1-(furan-2-ylmethylene)-2-phenylhydrazone (**a**) and 1-(1-(furan-2-yl)ethylidene)-2-phenylhydrazone (**b**) with lithium diisopropylamide (LDA) were individually conducted; without any purification, the resultant solution *in situ* further reacted with zirconium tetrachloride in tetrahydrofuran. The obtained products were individually extracted with toluene, and crystallized to form the corresponding trichlorozirconium η^2 -hydrazonide complexes ($R = H$, **A**; $R = CH_3$, **B**) as black crystals in good yields (Scheme 1).



Scheme 1 Synthesis of the complexes **A** and **B**

Both complexes **A** and **B** are highly sensitive to air and moisture, therefore critical condition was required in handling these complexes using the standard Schlenk techniques under nitrogen atmosphere. However, it was recognizable that complex **B** was more stable than complex **A**, which is considered the stabilization ability is related to its methyl substituent to the cationic imino-carbon. These complexes were characterized by NMR measurements and elemental analysis; moreover, their crystals were individually obtained through recrystallization in their tetrahydrofuran solutions and studied by the single crystal X-ray diffraction.

Crystal Structures

X-ray diffraction analysis indicated complex **A** as a distorted tetragonal bipyramid geometry (see Fig. 1) around the seven-coordinated zirconium atom with three chlorides and oxygen of incorporated tetrahydrofuran forming an equatorial plane along with occupying the axial coordination sites by other oxygen of incorporated tetrahydrofuran as well as the η^2 -coordinating 1-(furan-2-ylmethylene)-2-phenylhydrazonide. Complex **B** demonstrates the similar structural geometry as its analogue **A**. In the unit cell of complex **B**, however, two independent molecules are found with slight differences of bond lengths and angles; one molecule is shown in Fig. 2. The selected bond lengths and angles of complexes **A** and **B** are listed in Table 2.

The monoanionic ligands of furyl-phenylhydrazonides act as η^2 - N,N' -coordination mode through using the imino nitrogen (N_i) and phenylamido nitrogen atom (N_a), forming the zirconadiaziridine. Such coordination mode of η^2 - N,N' -hydrazonide ligands has been observed within zirconocene compounds^[27, 28]. The anionic cyclopentadienyl ligands donate electrons to the electrophilic zirconium for stabilizing the complexes. To the best of our knowledge, the title complexes are first obtained as the halozirconium η^2 - N,N' -hydrazonides.

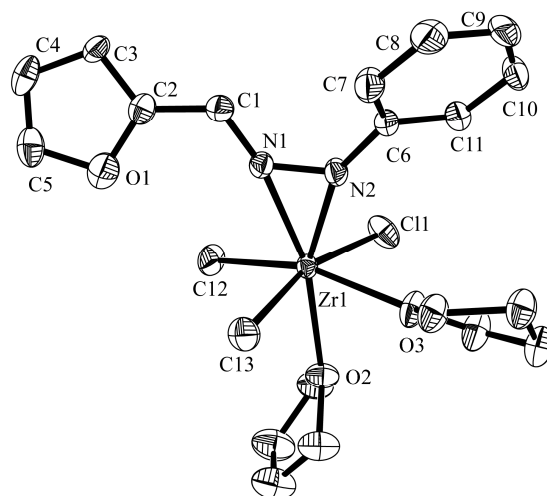


Fig. 1 Molecular structure of complex **A** with thermal ellipsoids drawn at 30% probability level (Hydrogen atoms are omitted for clarity.)

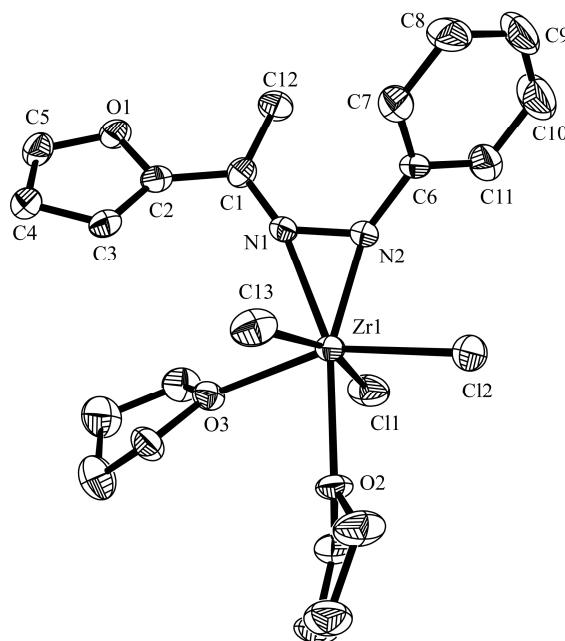


Fig. 2 Molecular structure of complex **B** with thermal ellipsoids drawn at 30% probability level (Hydrogen atoms are omitted for clarity.)

Concerning the N(1)—Zr(1)—N(2) angles, the newly observed data [$36.79(14)^\circ$ for **A**; $36.49(16)^\circ$ for **B**] are somewhat larger than those (35.7° – 33.9°) in the literature^[25, 26], indicating stronger interactions between the zirconium and the N—N bond. There are two types of the Zr—N bonds such as Zr—N_a [Zr(1)—N(2)] and Zr—N_i [Zr(1)—N(1)]. The Zr—N_i bond distances [0.2220(4) nm in complex **A**; 0.2236(5) nm in complex **B**] show well comparable data between the current work with the literature [from 0.2193(3) nm to 0.2283(3) nm]^[25, 26], however, the Zr—N_a bond lengths [0.2054(4) nm in complex **A**; 0.2065(5) nm in complex **B**] are shorter than previously observed data [from 0.2103(3) nm to 0.219(2) nm]^[25, 26], confirming the stronger bonds achieved within the title complexes and being consistent to the above observation that the stronger interaction is currently observed between the zirconium and the N—N bond. The Zr—N_a lengths in complexes **A** and **B** are shorter than

the corresponding Zr—N_i lengths, because of anionic amido-nitrogen (N_a) and neutral imino-nitrogen (N_i). The structural differences between complexes **A** and **B** include the individually dihedral angles of the furyl ring to the N—N—Zr and phenyl planes, 18.2° and 54.4° in complex **A** versus 27.6° and 80.3° in complex **B**, being caused by the steric repulsion from introducing the methyl group within complex **B**.

Table 2. Selected bond lengths (nm) and angles (°) for **A** and **B**

Compounds	A	B
Bond lengths (nm)		
Zr1-N2	0.2054(4)	0.2065(5)
Zr1-N1	0.2220(4)	0.2236(5)
Zr1-O2	0.2304(3)	0.2323(4)
Zr1-O3	0.2256(3)	0.2299(4)
Zr1-Cl1	0.24739(15)	0.2450(2)
Zr1-Cl2	0.24265(15)	0.2453(2)
Zr1-Cl3	0.24375(15)	0.2459(2)
N1-C1	0.1283(6)	0.1297(7)
N1-N2	0.1358(5)	0.1356(6)
N2-C6	0.1409(6)	0.1417(7)
C1-C2	0.1409(7)	0.1446(8)
Bond angles (°)		
N2-Zr1-N1	36.79(14)	36.49(16)
N1-Zr1-O3	114.77(14)	85.97(15)
O3-Zr1-O2	75.85(14)	75.81(14)
O2-Zr1-Cl2	83.65(10)	80.90(11)
N2-Zr1-Cl2	117.85(12)	83.00(15)
Cl3-Zr1-Cl1	165.17(6)	164.62(7)
O3-Zr1-Cl2	159.04(10)	156.61(11)
C1-N1-Zr1	165.7(3)	165.4(4)
N2-N1-Zr1	64.9(2)	64.9(3)
N1-N2-Zr1	78.3(2)	78.7(3)
C6-N2-Zr1	154.8(3)	147.1(4)
N1-N2-C6	126.0(4)	123.7(5)
C1-N1-N2	128.5(4)	128.9(5)
N1-C1-C2	122.6(5)	116.6(6)
N1-C1-C12		124.2(6)
C2-C1-C12		119.2(5)

Catalytic Behavior for Ethylene Polymerization

To explore their efficiencies in ethylene polymerization, both complexes **A** and **B** were investigated upon activation with either methylaluminoxane (MAO) or modified methylaluminoxane (MMAO), respectively. Activated with MAO, the conditions for ethylene polymerization were routinely optimized for the complex **A**, and the results are tabulated in Table 3.

The Al/Zr molar ratios were changed from 500 to 1250 at 20 °C (entries 1–4, Table 3), and the highest activity with 3.3×10^4 gPE·mol⁻¹(Zr)·h⁻¹ was achieved at the Al/Zr molar ratio of 1000 (entry 3 in Table 3). The resultant polyethylenes possessed gradient lower molecular weights, being consistent with that more chain migration and termination happened with higher ratios of MAO. Fixing the Al/Zr molar ratio as 1000 and changing reaction temperature between 20 and 50 °C (entries 3, 5–7 in Table 3), the optimum temperature was 40 °C with observing the activity as 7.6×10^4 gPE·mol⁻¹(Zr)·h⁻¹ (entry 6). Regarding a correlation between the

reaction period and catalytic performance, the ethylene polymerization was conducted over different reaction time lengths such as 15, 30, 45 and 60 min (entries 6, 8–10, Table 3), the highest activity was observed with 30 min (entry 6); both shorter and longer reaction time lengths gave the lower activities than the optimum period (30 min herein), indicating that the catalytic system has an initial period for the ethylene polymerization as well as the deactivation of the active species. Moreover, the ethylene polymerization was also carried out at lower ethylene pressures at 0.101 and 0.505 MPa (entries 11 and 12, Table 3), indicating that the higher pressure ethylene used, the better activity achieved. The polydispersity of obtained polyethylene (entry 12, Table 3) was relatively bigger because the ethylene concentration at 0.101 MPa was too low to maintain the continuous coordination and insertion of ethylene with random chain termination happened. Using the optimum condition of an Al/Zr molar ratio of 1000 at 40 °C under 1.01 MPa ethylene pressure, complex **B** was investigated to observe the activity as 4.0×10^4 gPE·mol⁻¹(Zr)·h⁻¹ (entry 13, Table 3).

Table 3. Ethylene polymerization results by complexes **A**/MAO and **B**/MAO systems ^a

Entry	Pre-cat.	Al/Zr	<i>T</i> (°C)	Time (min)	Activity ^b	<i>M_w</i> ^{c, d}	<i>M_w</i> / <i>M_n</i> ^d	<i>T_m</i> ^e (°C)
1	A	500	20	30	1.5	16.3	1.90	134.6
2	A	750	20	30	2.7	15.4	2.16	133.5
3	A	1000	20	30	3.3	13.1	2.65	133.9
4	A	1250	20	30	0.8	12.1	2.73	133.9
5	A	1000	30	30	4.1	10.4	2.99	140.5
6	A	1000	40	30	7.6	13.2	4.27	134.4
7	A	1000	50	30	4.5	14.8	2.23	134.9
8	A	1000	40	15	5.4	13.5	2.68	134.5
9	A	1000	40	45	6.1	16.3	2.40	134.2
10	A	1000	40	60	4.2	14.6	2.06	134.4
11 ^f	A	1000	40	30	2.4	12.8	3.94	134.6
12 ^g	A	1000	40	30	1.0	12.6	5.03	134.1
13	B	1000	40	30	4.0	15.3	4.82	133.5

^a General conditions: 2.0 μmol of Zr complexes, 1.01 MPa of ethylene, 100 mL of toluene; ^b Activity: 10⁴ gPE·mol⁻¹(Zr)·h⁻¹; ^c 10⁵ g·mol⁻¹; ^d Determined by GPC; ^e Determined by DSC; ^f 0.505 MPa of ethylene; ^g 0.101 MPa of ethylene

In general, the title complexes only showed the recognizable activities toward ethylene polymerization, which are consistent to literature observations of the complex precatalysts bearing η²-*N,N'*-fashion ligands^[17, 18, 29, 30] performing ethylene polymerization with moderate activities. However, targeting advanced polyolefin of ultrahigh molecular weight polyethylene, the catalytic systems are worthily investigated. GPC analysis revealed that the obtained polyethylenes generally possessed ultra-high molecular weights (*M_w*) over 1.0 × 10⁶ g·mol⁻¹; moreover, the resultant polyethylenes possess melting temperatures in the range of 133.5–140.5 °C, typical for high-density polyethylene (HDPE)^[31]. The properties and application of these polyethylenes should be explored with efforts of polymer physics.

Using MMAO as co-catalyst, parallel investigations were also conducted, and their results are collected in Table 4. On the basis of catalytic system with MAO, the polymerization was conducted at 40 °C (entries 1–4, Table 4) to find the optimum Al/Zr molar ratio of 1000 (entry 2, Table 4). However, the higher ratios of MMAO used, the higher molecular weights of polyethylenes obtained; it was believed that the active species were enhanced for the chain propagation with the bulkier *iso*-butyl from the cocatalyst of MMAO. Further finely tuning temperature (entries 2, and 5–7, Table 4) showed the highest activity of 3.6 × 10⁴ gPE·mol⁻¹(Zr)·h⁻¹ at 30 °C. The obtained polyethylenes were approved by GPC to be products of ultra-high molecular weight with narrow polydispersity in most cases.

Upon the activation with either MAO or MMAO (Tables 3 and 4), precatalyst **B** generally showed similar results as its analog **A**. All the resultant polyethylenes possessed high molecular weight in the range of million. According to the molecular structures of both complex precatalysts, there are more spaces around the titanium active species; which would favor ethylene coordination and insertion in order to produce polyethylenes with

high molecular weights^[7, 32, 33]. In addition, the narrow polydispersity of all polyethylenes (Table 3 and 4) suggested the single-site active species formed in the polymerization process^[31].

Table 4. Ethylene polymerization results by complexes **A**/MMAO and **B**/MMAO systems^a

Entry	Pre-cat.	Al/Zr	<i>T</i> (°C)	Activity ^b	<i>M_w</i> ^{c,d}	<i>M_w</i> / <i>M_n</i> ^d	<i>T_m</i> ^e (°C)
1	A	500	40	1.8	3.5	7.03	134.2
2	A	1000	40	3.2	11.5	2.16	134.2
3	A	1500	40	2.9	12.4	2.91	134.3
4	A	2000	40	2.5	12.6	2.09	134.4
5	A	1000	20	2.3	15.5	1.89	134.3
6	A	1000	30	3.6	20.5	1.49	134.5
7	A	1000	50	2.0	12.2	6.92	134.2
8	B	1000	30	3.1	20.4	1.64	133.9

^a General conditions: 2.0 μmol of Zr complexes, 30 min, 1.01 MPa of ethylene, 100 mL of toluene; ^b Activity: $10^4 \text{ gPE} \cdot \text{mol}^{-1}(\text{Zr}) \text{ h}^{-1}$; ^c $10^5 \text{ g} \cdot \text{mol}^{-1}$; ^d Determined by GPC; ^e Determined by DSC

CONCLUSIONS

The trichlorozirconium η^2 -hydrazonides, $\text{Zr}[(\text{C}_4\text{H}_3\text{O})\text{C}(\text{R})=\text{N}-\text{NPh}]\text{Cl}_3(\text{THF})_2$ ($\text{R}=\text{H}$, **A**; $\text{R}=\text{CH}_3$, **B**), were successfully prepared. On the basis of X-ray crystallographic analyses, both title complexes displayed as the distorted tetragonal bipyramid geometry containing the η^2 -*N,N'*-fashion hydrazonides as the first observation for mono-metallic complex beyond (half-)metallocene complexes. Upon activation with either MAO or MMAO, both complexes **A** and **B** exhibited moderate catalytic activities toward ethylene polymerization, indicating that metal complexes ligated by η^2 -hydrazonides would be hard to challenge highly active catalysts. The obtained polyethylenes showed ultra-high molecular weight along with narrow polydispersity.

SUPPLEMENTARY DATA

CCDC Nos. 1407816 (for **A**) and 1407817 (for **B**) contain the supplementary crystallographic data for this publication. These data can be obtained free of charge *via* <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

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