

New sterically hindered unbridged zirconocene complexes with 1,2-diphenylcyclopentadienyl ligands: synthesis, structure and properties as olefin polymerization catalysts

Fan Zhang ^a, Ying Mu ^{a,*}, Ligang Zhao ^a, Yuetao Zhang ^a, Weiming Bu ^b,
Congxi Chen ^a, Huimin Zhai ^a, Han Hong ^c

^a Department of Chemistry, Jilin University, 119 Jiefang Road, Changchun 130023, PR China

^b Key Laboratory of Supramolecular Structure and Spectroscopy, Jilin University, Changchun 130023, PR China

^c Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, PR China

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Abstract

New unbridged zirconocene complexes, bis(1,2-diphenylcyclopentadienyl)zirconium dichloride (**3**) and bis(4-methyl-1,2-diphenylcyclopentadienyl)zirconium dichloride (**4**) have been synthesized in high yield by reaction of ZrCl₄ with the lithium salt of 1,2-diphenylcyclopentadiene (**1**) or 4-methyl-1,2-diphenylcyclopentadiene (**2**), respectively. X-ray crystallographic analysis reveals both complexes are in racemic-like conformation with near C₂ symmetry in solid state. When activated with methylaluminoxane (MAO), **3** and **4** exhibit moderate catalytic activities for ethylene polymerization at relatively low Al:Zr ratios, producing high molecular weight (> 10⁶) polyethylenes with high melting transition temperatures. Atactic propylene oligomers with average molecular weight of ~ 10³ g mol⁻¹ were produced by both **3** and **4** at relatively high catalytic activities upon activation with MAO. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Zirconocene; Ligand; Modification; Catalyst; Olefin; Polymerization

1. Introduction

Since Kaminsky et al. discovered the highly active zirconocene dichloride–methylaluminoxane (MAO) catalytic system for olefin polymerization [1], intensive research work has been focused on developing new Group 4 metallocene catalysts for improving catalytic activities and polymer properties [2,3]. In the development of new metallocene catalyst systems, ligand design and modification have played a crucial role. In some cases, even minor modification of a given ligand framework could result in significant changes in catalyst activities and polymer properties [4]. So far, the steric and electronic effect of many types of substituents on the catalytic properties of metallocene

complexes has been studied [5]. As an example, it has been indicated by recent studies that modification of the cyclopentadienyl or indenyl ligand in Group 4 metallocene complexes with phenyl substituent could result in unusual catalytic properties for olefin polymerization due to the special steric and electronic effect of the phenyl group [4c,6–9]. In these respects, we have recently focused our research interest on the synthesis and catalysis of Group 4 metallocene complexes with phenyl-substituted cyclopentadienyl ligands. Herein we report the synthesis and crystal structures of two new unbridged zirconocene complexes, bis(1,2-diphenylcyclopentadienyl)zirconium dichloride (**3**) and bis(4-methyl-1,2-diphenylcyclopentadienyl)zirconium dichloride (**4**), as well as their properties as ethylene and propylene polymerization catalysts. To our knowledge, these are the first examples of metallocene complexes with 1,2-diphenylcyclopentadienyl or 4-alkyl-1,2-diphenylcyclopentadienyl ligand.

* Corresponding author. Tel.: +86-431-8922331/3120; fax: +86-431-8949334.

E-mail address: ymu@mail.jlu.edu.cn (Y. Mu).

2. Results and discussion

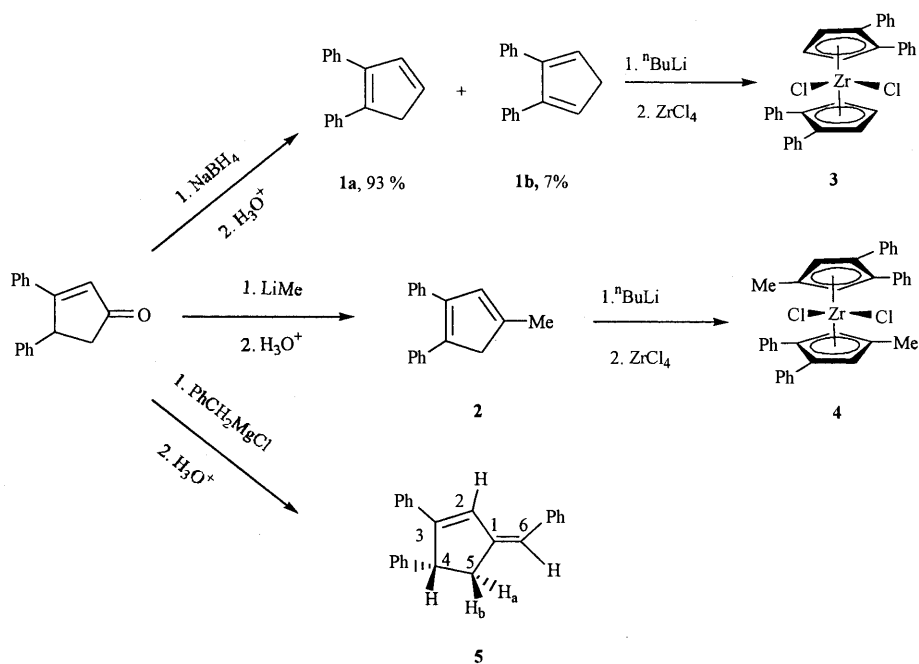
2.1. Ligand synthesis

The ligand precursor 1,2-diphenylcyclopentadiene (**1**) has been reported previously [10,11]. However, the published synthetic procedure is inefficient and gives low yields (10–20%). To improve the yield, **1** was prepared in our studies by a new synthetic route from different starting material as shown in Scheme 1, in which 3,4-diphenyl-2-cyclopentenone was treated with sodium borohydride (NaBH_4) in a mixed solvent system of THF–MeOH (4:1) to convert the cyclopentenone into 1-hydroxy-3,4-diphenyl-2-cyclopentene. The mixed solvent system was chosen to increase the solubility of 3,4-diphenyl-2-cyclopentenone and the reactivity of NaBH_4 . After the dehydration of 1-hydroxy-3,4-diphenyl-2-cyclopentene with concentrated HCl, pure **1** was obtained by column chromatography in 31% yield. $^1\text{H-NMR}$ analysis indicates that **1** was obtained mainly in 1,2-diphenyl-1,3-cyclopentadiene form (**1a**, ~93%) with small amount of 2,3-diphenyl-1,3-cyclopentadiene (**1b**, ~7%). KBH_4 was also tested as reductant and was found unsuitable for this reaction due to its low solubility. Attempts to prepare **1** by treating 3,4-diphenyl-2-cyclopentenone with LiAlH_4 in THF or diethyl ether were unsuccessful. In these cases, a complicated mixture was obtained and **1** could not be isolated, presumably due to poor selectivity of LiAlH_4 to reduce the keto group in 3,4-diphenyl-2-cyclopentenone. Ligand precursor 4-methyl-1,2-diphenyl-1,3-cyclopentadiene (**2**) was also synthesized by a modified

literature procedure [11]. Compound **2** was prepared in the literature by the reaction of 3,4-diphenyl-2-cyclopentenone with methyl Grignard reagent. In our studies, we found that the reaction of 3,4-diphenyl-2-cyclopentenone with methyllithium, followed by dehydration of the formed 1-hydroxy-1-methyl-3,4-diphenyl-2-cyclopentene with concentrated HCl, gives **2** in higher yield (68%). It is well known that organolithium reagents prefer 1,2-addition to the keto group of α - β unsaturated ketones. We have also attempted to synthesize 1-benzyl-3,4-diphenyl-1,3-cyclopentadiene as a ligand precursor by the reaction of 3,4-diphenyl-2-cyclopentenone with benzylmagnesium chloride. However, after dehydration of the product 1-hydroxy-1-benzyl-3,4-diphenyl-2-cyclopentene with concentrated HCl, 1-benzylidene-3,4-diphenyl-2-cyclopentene (**5**) was obtained as the only isolable product (yield: 54%).

2.2. Metallocene synthesis

Ligand precursor **1** was deprotonated with butyllithium in hexane since the solubility of **1** in hexane is pretty good and the produced lithio salt can be isolated easily in high yield (approximately 95%). Compound **2** is less soluble in hexane, and thus was deprotonated with butyllithium in toluene (92% yield). The deprotonation of **1** and **2** was also tried in diethyl ether or THF and it was found that these solvent systems led to lower yields. Zirconocene complexes **3** and **4** were prepared in good yields from the reaction of two equivalents of lithio salt of corresponding ligand with ZrCl_4



Scheme 1.

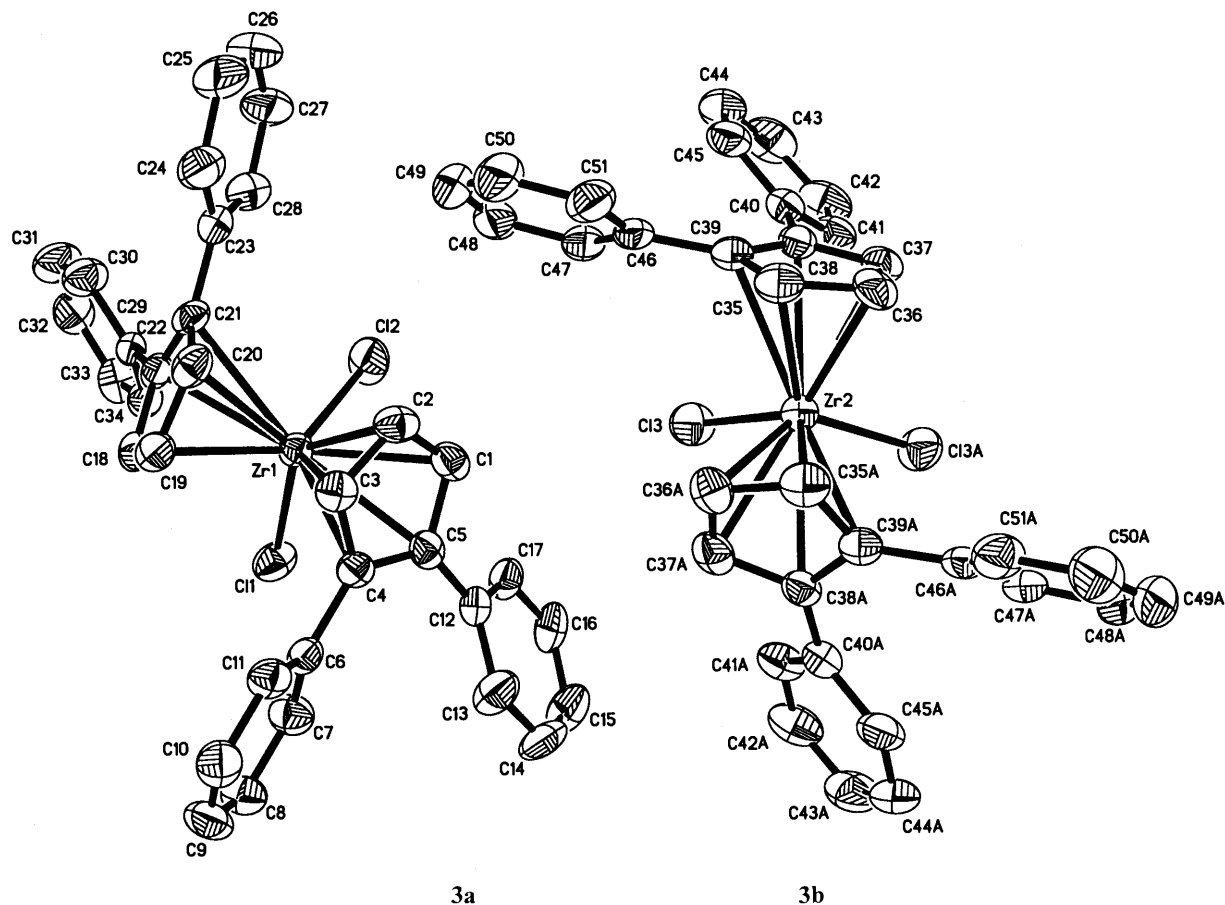


Fig. 1. ORTEP diagram of complex 3.

in toluene. Probably due to weak nucleophilicity and large steric hindrance of the ligand anions, it was found necessary to heat reaction mixtures to 60°C for 10–20 h to form **3** and **4**. Based on our experience, the formation of a heavy white precipitate and a bright yellow solution from an off-white suspension indicates the completion of the reaction. Pure **3** and **4** were obtained by recrystallization from hexane–CH₂Cl₂ in 78 and 77% yield, respectively. Complexes **3** and **4** were found to be considerably stable to air and moisture and could be exposed to air for several days without obvious decomposition.

¹H- and ¹³C-NMR spectra of **3** and **4** reveal their time-averaged *C*_{2v} symmetry in solution due to rapid rotation of the cyclopentadienyl rings about the Cent–Zr axis (Cent is the centroid of Cp ring). The NMR analysis also indicates the free rotating fashion of all phenyl groups in both complexes at room temperature in the NMR time scale. The down-field shifts of the signals for the Cp ring protons near phenyl groups (6.54 ppm in **3**, 6.35 ppm in **4**) in ¹H-NMR spectra and the signals for the Cp ring carbons connected to phenyl groups (127.8 ppm in **3**, 127.5 ppm in **4**) in ¹³C-NMR spectra reflect the electron-withdrawing effect of the phenyl groups in both complexes.

2.3. X-ray crystal structure analysis

The molecular structures of **3** and **4** are shown in Figs. 1 and 2. Selected bond lengths and angles are given in Table 1. Compound **3** exists as two independent molecules in a same unit cell with minor structural differences, which are labeled **3a** and **3b** (Fig. 1). There have been several examples for unbridged zirconocene complexes to crystallize as two independent molecules in solid state [7a,8,12]. The differences of the independent molecules in this type of zirconocenes are usually caused by the rotation of the Cp-type ligands about Cent–metal axis, or by different orientations of the substituents at the Cp-type ligands. In the present case, the two independent molecules of **3** differ mainly in the orientation of the phenyl rings. The geometry about zirconium in **3a** and **3b** can be described as distorted tetrahedral. Both **3a** and **3b** are in racemic-like conformation, with *C*₂ symmetry or near *C*₂ symmetry. In each of two independent molecules, one of the two phenyl groups at each Cp ring is nearly above one of the two Cl atoms while the other one is in the direction away from the corresponding phenyl group at another Cp ring.

The Cl–Zr–Cl angle is 94.25° for **3a** and 94.14° for **3b**. The values are similar to the angles of approxi-

mately 94° in analogous complexes [13–15]. The Cent–Zr–Cent angles (126.6° for **3a** and 126.9° **3b**) are close to the value of 126° found in $\text{Zr}(\text{C}_5\text{H}_4\text{CH}_2\text{Ph})_2\text{Cl}_2$ [13], but smaller than the one of 129.7° for $[\eta^5\text{-C}_5\text{H}_3\text{-1,3-(CMe}_3)_2\text{]ZrCl}_2$ [16]. The angles (φ) between two Cp planes (61.6° for **3a** and 62.3° for **3b**) are much larger than the typical 51.4° observed for $(\text{Bu}'\text{Cp})_2\text{ZrCl}_2$ and related compounds, even larger than that (60.5°) found in the staggered $[\text{C}_5\text{H}_4\text{C}(o\text{-MePh)=CH}_2]_2\text{ZrCl}_2$ [17] owing to the steric demanding of the phenyl groups. The angles between the phenyl and Cp planes (31.2, 39.6, 32.9 and 50.1°) for **3a** are quite different from those for **3b** (32.3 and 37.8°), which are all larger than those (13.6 and 18.8°) observed for $(1,2\text{-Me}_2\text{-4-PhC}_5\text{H}_2)_2\text{ZrCl}_2$ [9]. The Zr–Cl bond lengths (2.430(2)–2.435(2) Å) are in the typical range for zirconocene dichlorides [17]. The distances of Zr–Cent (2.234, 2.237 Å for **3a** and 2.248 Å for **3b**) are longer than those (2.215–2.223 Å) observed in similar bulky zirconocene compounds [15,18].

As in the case of **3**, the whole molecule of **4** is in pseudotetrahedral geometry and C_2 symmetry. The methyl group at each Cp ring is oriented backwards from the open front side of the molecule. The two phenyl groups at each Cp ring are arranged in the same way as in **3**, one is nearly above one of the two Cl atoms and the other is directed away from the corresponding phenyl group at another Cp ring (Fig. 2). The Zr–Cl bond length (2.4283 (11) Å) is also in the typical range for zirconocene dichlorides [17]. The distance (2.237 Å) of Zr–Cent is very similar to the value in **3a**, and longer than the one (2.22 Å) for $(1,2\text{-Me}_2\text{-4-}p\text{-}$

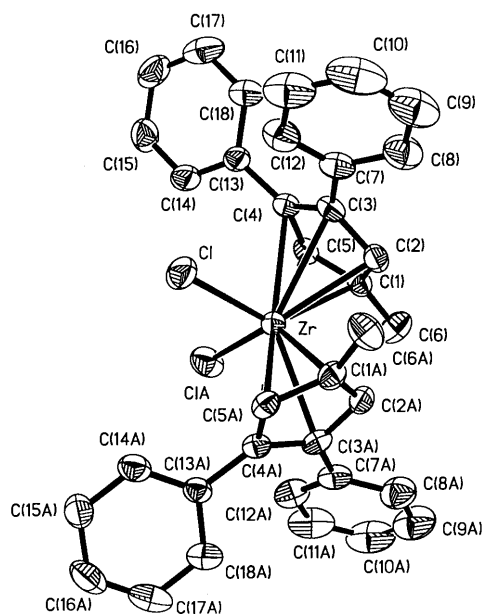


Fig. 2. ORTEP diagram of complex **4**.

Table 1
Selected bond lengths (Å) and angles (°) for complexes **3** and **4**

Complex 3a			
Zr1–Cl1	2.435(2)	C3–C4	1.416(7)
Zr1–Cl2	2.430(2)	C4–C5	1.433(7)
Zr1–C1	2.533(5)	C1–C5	1.412(7)
Zr1–C2	2.446(5)	C18–C19	1.399(7)
Zr1–C3	2.485(5)	C19–C20	1.420(7)
Zr1–C4	2.585(5)	C20–C21	1.404(7)
Zr1–C5	2.630(5)	C21–C22	1.426(7)
Zr1–C18	2.519(5)	C18–C22	1.423(7)
Zr1–C19	2.427(5)	C4–C6	1.499(7)
Zr1–C20	2.484(5)	C5–C12	1.465(8)
Zr1–C21	2.627(5)	C21–C23	1.493(7)
Zr1–C22	2.633(5)	C22–C29	1.473(7)
C1–C2	1.398(8)	Zr1–Cent1	2.234
C2–C3	1.405(7)	Zr1–Cent2	2.237
Cl1–Zr–Cl2	94.25(6)	C18–C19–C20	107.4(5)
C1–C2–C3	108.4(5)	C19–C20–C21	108.5(5)
C2–C3–C4	108.0(5)	C20–C21–C22	108.2(5)
C3–C4–C5	107.8(5)	C21–C22–C18	106.7(5)
C2–C1–C5	109.0(5)	Cent1–Zr1–Cent2	126.6
Complex 3b			
Zr2–Cl3	2.434(2)	C36–C37	1.388(8)
Zr2–C35	2.481(6)	C37–C38	1.409(7)
Zr2–C36	2.449(5)	C38–C39	1.446(7)
Zr2–C37	2.534(5)	C39–C35	1.401(7)
Zr2–C38	2.657(5)	C38–C40	1.459(8)
Zr2–C39	2.621(5)	C39–C46	1.493(7)
C35–C36	1.421(7)	Zr2–Cent3	2.248
Cl3–Zr2–Cl3A	94.14(8)	C37–C38–C39	106.7(5)
C35–C36–C37	107.2(5)	C38–C39–C35	107.1(5)
C36–C37–C38	110.0(5)	Cent3–Zr2–Cent3A	126.9
Complex 4			
Zr–Cl	2.4283(11)	C2–C3	1.407(5)
Zr–C1	2.484(3)	C3–C4	1.435(5)
Zr–C2	2.480(4)	C4–C5	1.416(4)
Zr–C3	2.585(3)	C3–C7	1.494(5)
Zr–C4	2.615(3)	C4–C13	1.477(5)
Zr–C5	2.533(3)	C1–C6	1.501(5)
C1–C2	1.416(5)	Zr–Cent	2.237
Cl–Zr–Cl # 1	94.41(6)	C3–C4–C5	106.3(3)
C1–C2–C3	110.2(4)	C4–C5–C1	110.8(3)
C2–C3–C4	106.9(3)	Cent–Zr–Cent #	129.5

toly C_5H_2) $_2\text{ZrCl}_2$ [8], but shorter than that (2.256 Å) for $[\text{bis}(\eta^5\text{-7,9-diphenylcyclopenta[a]acenaphthadienyl})\text{-zirconium dichloride}$ [6]. The Cent–Zr–Cent angle of 129.5° for **4** is larger than those for **3a** and **3b** due to the introduction of methyl group, while smaller than the values (132.6 and 131.5°) for analogous complexes $(1,2,4\text{-Me}_3\text{-C}_5\text{H}_2)_2\text{ZrCl}_2$ and $(1,2\text{-Me}_2\text{-4-Ph-C}_5\text{H}_2)_2\text{-ZrCl}_2$ [9]. The smaller Cent–Zr–Cent angles for **3** and **4** could be attributed to the steric demanding of the two adjacent phenyl groups at each Cp ring. As expected, the angle (56.8°) between two Cp planes in **4** is smaller than those in **3a** and **3b**. The smaller angle between Cp

planes, together with the larger Cent–Zr–Cent angle, would definitely generate a more crowded ligand environment in front of zirconium atom for **4**. The angles between the phenyl and Cp planes (29.9 and 43.9°) for **4** are also larger than those for complex (1,2-Me₂-4-Ph-C₅H₂)₂ZrCl₂ (13.6 and 18.8°) and (1,2-Me₂-4-*p*-tolyl-C₅H₂)₂ZrCl₂ (22.5°) [8,9]. The large angles between the phenyl and Cp planes for **3** and **4** reflect the large steric hindrance of the adjacent phenyl groups. As can be seen from the structures of **3** and **4**, the four phenyl groups indeed construct a bulky environment in the front side of Zr atom, which makes **3** and **4** having some interesting features as olefin polymerization catalysts.

2.4. Ethylene polymerization

Upon activation with MAO, both **3** and **4** show moderate catalytic activity for ethylene polymerization. The polymerization results are summarized in Table 2. For comparison purpose, some polymerization experiments were carried out with Cp₂ZrCl₂ as catalyst. As can be seen from the polymerization results, **3** and **4** show several interesting features as catalysts for ethylene polymerization. Firstly, the catalytic activity of **3** and **4** does not decrease very much when Al:Zr ratio changes from 1500 to 500. In contrast, the catalytic activity of Cp₂ZrCl₂ increases rapidly with the increase in Al:Zr ratio and the order of catalytic activity becomes Cp₂ZrCl₂ > **3** > **4** at higher Al:Zr ratios. It seems that the concentration of active catalyst species for Cp₂ZrCl₂ is low at low Al:Zr ratios and increases rapidly with the increase in Al:Zr ratio. Secondly, **3** and **4** produce high molecular weight polyethylenes ($M_n > 1.0 \times 10^6$ g mol⁻¹) with high melting transition temperatures at low Al:Zr ratios. To our knowledge, the melting transition temperatures for some polyethylene samples obtained with **3** and **4** are in the highest range (the highest one in our results is 144.8°C) observed so far for metallocene-

produced-polyethylene [19,20]. The results in Table 2 also show that the catalytic activity of the less bulky complex **3** for ethylene polymerization is higher than that of **4**. It is obvious that these observed features could be explained on the basis of the steric nature of the complexes. As mentioned above, the adjacent phenyl groups at the Cp rings of complex **3** and **4** construct a bulky environment in the front side of Zr atom, which could efficiently prevent the active catalyst from deactivation by bimolecular interaction and lower the rate of chain termination by β-H elimination. Therefore, less MAO is required to keep the catalyst in active state and relatively long polyethylene chain can be formed. The high molecular weight of the polyethylene produced by **3** and **4** also indicates that the rotatable flat phenyl groups in front of the central Zr atom in **3** and **4** probably have less effect on lowering the ethylene coordination and insertion rate than lowering the chain termination rate. In comparison with **3**, the lower catalytic activity of **4** due to its bulkier ligand environment apparently demonstrates that the steric effect of the Cp rings on the catalytic activity of **3** and **4** plays more important role than their electronic effect does. Otherwise, the electron-donating methyl groups at the Cp rings of **4** should increase its catalytic activity. It should be pointed out that steric effect has been believed to have less influence on the catalytic activity of mono-substituted zirconocene complexes for ethylene polymerization compared with electronic effect [21,22].

2.5. Propylene polymerization

Compounds **3** and **4** were also tested for propylene polymerization. It was found that, under ambient conditions, both complexes produce atactic oligomers of propylene with vinylidene and *n*-propyl end groups based on ¹H- and ¹³C-NMR spectroscopic analysis. The less sterically hindered complex **3** shows higher catalytic

Table 2
Ethylene polymerization results obtained with complexes **3**, **4** and Cp₂ZrCl₂ activated by MAO^a

No.	Catalyst	Al:Zr	Activity ^b × 10 ⁻³	M _n ^c × 10 ⁻⁶	T _m (°C) ^d
1	3	300	0.27	1.32	143.3
2		500	1.64	1.21	141.6
3		1000	1.93	1.34	144.8
4		1500	1.96	1.09	141.0
5	4	500	1.27	1.25	143.1
6		1000	1.42	0.91	140.0
7		1500	1.46	0.78	137.8
8	Cp ₂ ZrCl ₂	500	1.19	0.46	132.2
9		1000	2.26	0.43	131.9
10		1500	3.69	0.42	131.5

^a Polymerization conditions: solvent 50 ml of toluene, catalyst 1.7 μmol, time 1 h, temp. 18°C, ethylene pressure 6 bar.

^b kg PE (mol Zr)⁻¹ h⁻¹.

^c Measured in decahydronaphthalene at 135°C.

^d Determined with DSC at a heating rate of 10°C min⁻¹.

activity for propylene polymerization compared to the bulkier **4**, which is consistent with the ethylene polymerization result. In a typical experiment, 7.1 g of polypropylene [$M_n = 1150 \text{ g mol}^{-1}$, catalytic activity = $4.2 \times 10^6 \text{ g (mol Zr)}^{-1} \text{ h}^{-1}$] was obtained with 1.7 μmol of **3** and 1500 equivalents of MAO. Under similar conditions, 3.0 g of polypropylene [$M_n = 1016 \text{ g mol}^{-1}$, catalytic activity = $1.8 \times 10^6 \text{ g (mol Zr)}^{-1} \text{ h}^{-1}$] was obtained with **4** as catalyst. The number average molecular weight is calculated based on $^1\text{H-NMR}$ spectrum. The low molecular weight of the polypropylenes produced by **3** and **4** results from their large steric hindrance. The fact that vinylidene ($^1\text{H-NMR}$: 4.65 and 4.72 ppm) end group is the only olefinic group in the propylene oligomers produced by **3** and **4** reveals that $\beta\text{-H}$ elimination is the only chain termination pathway. $\beta\text{-Methyl}$ elimination was not observed in these systems although **3** and **4** are quite bulky. It has been reported that some zirconocenes and hafnocenes with bulky ligands favor $\beta\text{-methyl}$ elimination as main pathway of chain termination [6,23].

The lack of stereospecificity for the propylene polymerization catalyzed by **3** and **4** may arise from rapid rotation of the Cp rings. It was reported recently that polypropylene with relatively high isotacticity (49.8%) has been produced by *rac*-(1-Me-3-*t*-BuC₅H₃)₂ZrCl₂ due to restricted rotation of the Cp rings [9]. It is obvious that the flat phenyl groups at the Cp rings in **3** and **4** are less sterically hindered than *t*-Bu group and probably not bulky enough to slow down the rotation of the Cp rings to such an extent that blocks of isotactic polypropylene can be formed.

3. Experimental

3.1. General procedures

All reactions with moisture- and air-sensitive compounds were carried out under an argon atmosphere (ultra-high purity) using standard Schlenk techniques. Toluene and THF were refluxed over sodium benzophenone ketyl and distilled before use under nitrogen. Hexane and CH₂Cl₂ were refluxed and distilled from CaH₂ under nitrogen. Polymerization grade ethylene and propylene were further purified by passage through columns of 10-Å molecular sieves and MnO. 3,4-Diphenyl-2-cyclopenten-1-one was prepared according to literature procedure [24]. Methylaluminoxane (MAO, 10 wt.% solution in toluene, $M_n = 800 \text{ g mol}^{-1}$, Al = 5.3 wt.%) was purchased from Witco. MeLi (1.4 M in Et₂O), *n*-BuLi (1.6 M in hexanes), ZrCl₄, Cp₂ZrCl₂ and NaBH₄ were purchased from Aldrich. NMR spectra were recorded on Varian Unity-400 (FT 400 MHz, ^1H ; 100 MHz, ^{13}C) spectrometer. Elemental analyses were performed on PE-240 C elemental ana-

lyzer at the Center of Analysis and Test of Jilin University. Viscosity-average molecular weights of the polyethylenes were determined in decahydronaphthalene at 135°C using Schott Gerate model AVS/T2 Ubbelohde viscosimeter. Melting transition temperatures (T_m) of the polyethylenes were determined by DSC (Du Pont 910 differential scanning calorimeter) at a heating rate of 10°C min⁻¹.

3.2. 1,2-Diphenylcyclopentadiene (**1**)

Compound **1** was prepared by a route different from the literature procedure [10,11]. NaBH₄ (1.45 g, 38 mmol) was added to a solution of 3,4-diphenyl-2-cyclopentenone (5.95 g, 25.0 mmol) in THF–methanol (4/1, 100 ml) at 0°C. The mixture was stirred below 10°C for 24 h and quenched with 100 ml of saturated aqueous NH₄Cl solution. After extraction with 2 × 100 ml of ether, the organic layers were combined, concentrated and treated with concentrated HCl (30 ml) for 30 min. The mixture was then washed with 2 × 50 ml of water, dried over MgSO₄, filtered and concentrated by distillation under reduced pressure. Compound **1** (1.67 g, 31%) was obtained by column chromatography over silica gel (CH₂Cl₂–hexane, 1:10) as a mixture of **1a** (93%) and **1b** (7%). δ_{H} (400 MHz; solvent CDCl₃; standard SiMe₄) **1a**: 3.55 [2H, pseudo t, $J(\text{HH})$ 1.4 Hz, C₅H₄], 6.52 [1H, dt, $^3J(\text{HH})$ 5.6, $^3J(\text{HH})$ 1.4 Hz, C₅H₄], 6.71 [1H, dt, $^3J(\text{HH})$ 5.6, $^4J(\text{HH})$ 1.4 Hz, C₅H₄], 7.15–7.35 [10 H, m, C₆H₅]; **1b**: 3.21 [2H, t, $^3J(\text{HH})$ 1.4 Hz, C₅H₄], 6.53 [2H, t, $^3J(\text{HH})$ 1.4 Hz, C₅H₄], 7.13–7.34 [10H, m, C₆H₅]. Anal. Calc. for [C₁₇H₁₄]: C, 93.54; H, 6.46. Found: C, 93.45; H, 6.50%.

3.3. 4-Methyl-1,2-diphenylcyclopentadiene (**2**)

A modified literature procedure was used [11]. To a solution of MeLi (23ml, 1.4 M in Et₂O, 32.2mmol) in 50 ml of Et₂O was added dropwise a solution of 3,4-diphenyl-2-cyclopentenone (7.37 g, 31.5 mmol) in THF (30 ml) at –10°C in 1 h. The solution was slowly allowed to warm to room temperature (r.t.) and stirred overnight. After quenched with 20 ml of aqueous NH₄Cl, the organic layer was separated. The aqueous layer was extracted twice with Et₂O. The combined organic phases were treated with concentrated HCl (3 × 10 ml). After washed with saturated aqueous NH₄Cl, the combined organic layers were dried over MgSO₄, filtered and evaporated. Pure **2** (4.97 g, 68%) was obtained by chromatography through silica gel (hexane–CH₂Cl₂, 5:1) as small yellow needles. δ_{H} (400 MHz; solvent CDCl₃; standard SiMe₄) 2.14 [3H, s, CH₃], 3.44 [2H, s, C₅H₃], 6.31 [1H, s, C₅H₃], 7.10–7.34 [10H, m, C₆H₅].

Table 3
Crystallographic data for complexes **3** and **4**

	3	4
Empirical formula	C ₃₄ H ₂₆ Cl ₂ Zr	C ₃₆ H ₃₀ Cl ₂ Zr
Formula weight	596.67	624.72
Temperature (K)	293 (2)	293 (2)
Crystal color	Yellow	Yellow
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	16.226(3)	25.738(3)
<i>b</i> (Å)	6.9620(14)	7.2119(7)
<i>c</i> (Å)	36.006(7)	16.0244(14)
β (°)	90.75(3)	92.47(2)
<i>V</i> (Å ³)	4067.1(14)	2971.7(5)
<i>Z</i>	6	4
Absorption coefficient (mm ⁻¹)	0.625	0.573
<i>F</i> (000)	1824	1280
<i>D</i> _{calc} (mg m ⁻³)	1.462	1.396
Crystal size (mm ³)	0.52 × 0.26 × 0.18	0.25 × 0.16 × 0.12
Wavelength (Å)	0.71073	0.71073
Diffractometer	Siemens P4	Siemens P4
Collection region	–17 < <i>h</i> < 17 –1 < <i>k</i> < 7 –38 < <i>l</i> < 38	–32 < <i>h</i> < 32 –6 < <i>k</i> < 1 –20 < <i>l</i> < 20
θ range (°)	1.70 < θ < 22.48	1.58 < θ < 26.51
Scan type	ω –2 θ	ω –2 θ
Absorption correction	Empirical	Semi-empirical
Max/min transmission	0.27/0.26	0.84/0.36
Reflections collected	13076	6211
Independent reflections	5304 (<i>R</i> _{int} = 0.0525)	2722 (<i>R</i> _{int} = 0.0525)
Reflections collected (<i>F</i> _o ² > 3 σ (<i>F</i> _o ²))	3440	1943
Variables	501	237
Goodness-of-fit on <i>F</i> ²	0.876	1.026
<i>R</i> ₁ (<i>wR</i> ₂) ^a	0.0440 (0.0965)	0.0427 (0.0763)
Largest difference peak and hole (e Å ⁻³)	0.966 and –0.331	0.253 and –0.424

^a $R_1 = \sum |F_o - F_c| / \sum |F_o|$, $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum wF_o^4\}^{0.5}$, $w = 1 / [\sigma^2(F_o^2) + (bP)^2 + 0.0000P]$, $P = (F_o^2 + 2F_c^2) / 3$, (**3**, $b = 0.0537$; **4**, $b = 0.0321$).

3.4. 1-Benzylidene-3,4-diphenyl-2-cyclopentene (**5**)

Compound **5** was prepared in the same manner as **2** with 3,4-diphenyl-2-cyclopenten-1-one (8.0 g, 34.1 mmol) and benzylmagnesium chloride (40 ml, 0.89 M, 35.6 mmol). Pure **5** (4.3 g, 53.9%) was obtained as pale brown micro-crystals by recrystallization from CH₂Cl₂–hexane (1:3). δ_H (400 MHz; solvent CDCl₃; standard SiMe₄) 2.91 [1H, d, ²*J*(5-H_a–5-H_b) 17.2 Hz, 5-H_a], 3.60 [1H, dd, ³*J*(5-H_b–4-H) 8.0 Hz, ²*J*(5-H_b–5-H_a) 17.2 Hz, 5-H_b], 4.59 [1H, d, ³*J*(4-H–5-H_b) 8.0 Hz, 4-H], 6.55 [1H, s, 2-H], 7.00 [1H, s, 6-H], 7.20–7.60 [15H, m, C₆H₅]. Anal. Calc. for [C₂₄H₂₀]: C, 93.46; H, 6.54. Found: C, 93.38; H, 6.50%.

3.5. Bis(1,2-diphenylcyclopentadienyl)zirconium dichloride (**3**)

To a solution of **1** (0.62 g, 2.82 mmol) in 30 ml of hexane was added 1.84 ml of *n*-BuLi (1.6 M in hexane, 2.94 mmol) at –78°C. The mixture was allowed to warm to r.t. and stirred overnight. The solvent was removed by filtration, and the solid was suspended in 30 ml toluene and cooled to –15°C. ZrCl₄ (0.326 g, 1.40 mmol) was added. The reaction mixture was stirred for 8 h at r.t. and 18 h at 70°C. The precipitate was filtered off and the solvent was removed to leave a pale yellow solid. Recrystallization from CH₂Cl₂–hexane gave pure **3** (0.65 g, 78%). δ_H (400 MHz; solvent CDCl₃; standard SiMe₄) 6.02 [1H, t, ³*J*(HH) 3.2 Hz, C₅H₃], 6.54 [2H, d, ³*J*(HH) 3.2 Hz, C₅H₃], 7.24–7.34 [20H, m, C₆H₅]. δ_C (100 MHz; solvent CDCl₃; standard SiMe₄) 110.2, 117.9, 127.8 (C₅H₄), 128.1, 129.4, 130.0, 133.3 (C₆H₅). Anal. Calc. for [C₃₄H₂₆Cl₂Zr]: C, 68.46; H, 4.39. Found: C, 68.17; H, 4.31%.

3.6. Bis(1,2-diphenyl-4-methylcyclopentadienyl)-zirconium dichloride (**4**)

To a solution of compound **2** (0.78 g, 3.36 mmol) in toluene (30 ml), *n*-BuLi (2.3 ml, 1.6 M, 3.6 mmol) was added dropwise at –78°C and the mixture was stirred at r.t. for 8 h. ZrCl₄ (0.37 g, 1.6 mmol) was then added slowly at –15°C and the reaction mixture was stirred at r.t. over night, then was heated to 60°C and stirred for further 18 h. The precipitate was filtered off and the filtrate was concentrated to give crude **4**. Pure **4** (0.77 g, 77%) was obtained by recrystallization from CH₂Cl₂–hexane (1:4). δ_H (400 MHz; solvent CDCl₃; standard SiMe₄) 1.71 [6H, s, CH₃], 6.35 [4H, s, CpH], 7.20–7.35 [20H, m, C₆H₅]. δ_C (100 MHz; solvent CDCl₃; standard SiMe₄) 15.23 (CH₃), 118.98, 125.07, 127.45 (C₅H₂), 128.01, 128.88, 129.47, 133.30 (C₆H₅). Anal. Calc. For [C₃₆H₃₀Cl₂Zr]: C, 69.21; H, 4.84. Found: C, 69.55; H, 4.75%.

3.7. X-ray structural determination of **3**

Crystallographic data are collected in Table 3. Crystals of **3** suitable for X-ray analysis were grown from a solution of hexane–CH₂Cl₂ at r.t. A crystal of dimensions 0.52 × 0.26 × 0.18 mm sealed in a glass capillary was used. Data were collected on a Siemens P₄ four-circle diffractometer with a graphite monochromator using Mo–K α radiation. A total of 13 076 reflections were measured in ω –2 θ scan mode. The structure was solved by direct methods and refined by full-matrix least-squares methods on *F*². The hydrogen atoms were positioned geometrically and not refined. A total of 3440 independent data [*I* > 2 σ (*I*)] with 501 variable

parameters were refined to $R_1 = 0.0440$, $wR_2 = 0.0965$. Goodness-of-fit indicator was 0.876. All calculations were performed using SHELX86 and SHELX93 [25].

3.8. X-ray structural determination of 4

Crystallographic data are collected in Table 3. Single crystals of complex 4 suitable for X-ray diffraction were grown from a saturated solution in CH_2Cl_2 –hexane (1:3, v/v) in fridge (0–4°C). A yellow crystal of dimensions $0.25 \times 0.16 \times 0.12$ mm sealed in a glass capillary was used. Data were collected on a Siemens P₄ four-circle diffractometer with a graphite monochromator using Mo–K_α radiation. A total of 6211 reflections were measured in $\omega - 2\theta$ scan mode. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 . Hydrogen atoms were located by combination of difference Fourier map and HYDROGEN program. A total of 1943 independent data [$I > 2\sigma(I)$] with 237 variable parameters were refined to $R_1 = 0.0427$, $wR_2 = 0.0763$. Goodness-of-fit indicator was 1.026. All calculations were performed using SHELX86 and SHELX93 [25].

3.9. Polymerizations

A dry 250 ml thermostatable steel autoclave equipped a magnetic stirrer was evacuated and filled with ethylene to 1.0 bar. Toluene and appropriate MAO were added to the reactor through a septum port via syringe. After the solution was saturated with ethylene for 30 min, a solution of catalyst (1.7 μmol) in toluene was injected (total volume of the polymerization solution is 50 ml after the addition of catalyst). The vessel was repressurized to needed pressure with ethylene as soon as the catalyst was injected and the pressure was kept by a continuously feeding monomer. After the mixture was stirred for the desired reaction time, the reactor was vented and the polymerization was terminated by injecting acidified methanol [HCl (3 M)–methanol = 1:1]. The polymer was stirred in acidified methanol overnight, washed with water and methanol, dried in vacuo at 60°C. Polymerization of propylene was performed under ambient conditions (1 bar monomer pressure, room temperature). The procedure was similar to that for ethylene polymerization. After the reaction mixture was treated with acidified methanol and stirred overnight, the organic layer was separated and the aqueous phase was extracted with toluene. The organic layers were combined and dried over MgSO_4 . Removal of the solvent by distillation gave the propylene oligomer as colorless oil.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 141918/CCDC 141919. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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