Zirconocene complexes with a biphenyl substituted cyclopentadienyl ligand: synthesis, characterization, and olefin polymerization behavior

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Abstract

Novel zirconocene complexes (1-Biph-3,4-Me$_2$Cp)$_2$ZrCl$_2$ (**3**), (C$_5$Me$_5$)(1-Biph-3,4-Me$_2$Cp)ZrCl$_2$ (**4**), and (C$_5$H$_5$)(1-Biph-3,4-Me$_2$Cp)ZrCl$_2$ (**5**) containing a 1-biphenyl-3,4-dimethylcyclopentadienyl ligand (**2**) have been prepared and their solid state structures were characterized by X-ray diffraction method. The crystal structure of **3** revealed a *racemic*, C_2-symmetric nature in the solid state. In ethylene polymerization, they all afforded high-density polyethylene with very high activity. Especially, the catalytic properties of **3** were most marked in terms of both polymerization activity and molecular weight of polyethylene among them. They also showed good activity on the polymerization of propylene, but afforded nearly atactic, amorphous polypropylenes with a little higher [mmmm] methyl pentad values by **3** and **4** than that by the most active **5** under the given reaction conditions.
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1. Introduction

Homogeneous group 4 metallocene catalysts have provided various opportunities to tailor the microstructure and physical properties of polyolefins by manipulations of the catalyst ligand structure [1]. For propylene polymerization, especially, C_2- and C_s-symmetric *ansa*-metallocene catalysts can now afford high-melting stereoregular isotactic [2,4] and syndiotactic [3,4] polypropylenes, respectively, while stereorandom, amorphous atactic polypropylene [4] can be prepared using C_{2v}-symmetric metallocene catalysts.

Polypropylene consisting of isotactic and atactic blocks is a thermoplastic elastomer. Natta first discovered an elastomeric polypropylene and concluded that the polymer had a stereoblock microstructure in which amorphous and crystalline segments were parts of the same polypropylene chain [5]. After this finding, Collette et al. [6] reported that elastomeric polypropylene could be also produced by supported tetraalkyl group 4 catalysts. The first homogeneous catalyst for the production of elastomeric polypropylene was introduced by Chien et al. [7] using a chiral *ansa*-titanocene, [MeHC(C$_5$-Me$_4$)(Ind)]TiCl$_2$, in which the monomer insertion occurred sequentially at aspecific and isospecific coordination sites. The recent discovery by Waymouth et al. that the nonbridged metallocene, (2-PhInd)$_2$ZrCl$_2$ (**1**) can also produce elastomeric polypropylene when activated by methylaluminoxane (MAO) provided a new concept on the control of microstructure of polypropylene [8]. This zirconocene catalyst was designed to switch between chiral *rac*-like symmetric and achiral *meso*-like symmetric geometries generated alternately

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by hindered rotation of the indenyl ligands in order to give isotactic and atactic stereoblocks in the same polymer chain (Fig. 1). Followed by this important finding, they extensively investigated the effects of the 2-aryl groups on the indenyl ligand [9] and the nature of the metal [10] and cyclopentadienyl ring fragment [11], including mixed-ring complex systems [12] on the production of elastomeric polypropylene.

In this regard, it is of value to examine the catalytic properties of the Waymouth-type catalyst that contains a sterically demanding substituent, especially, on the 4-position of phenyl group attached to the cyclopentadienyl ligand in order to control the rate of mutual rotation of the ligands, by which the stereoblock length in the polymer chain can be varied. We present here the synthesis, characterization of nonbridged zirconocene complexes containing a biphenyl group on the cyclopentadienyl ring fragment and their catalytic behavior in olefin polymerization.

2. Experimental

2.1. General procedures

All operations were performed under an inert dinitrogen atmosphere using standard Schlenk and glove box techniques. THF, toluene, and n-hexane were distilled from Na–K alloy, Et$_2$O from Na-benzophenone ketyl, and CH$_2$Cl$_2$ from CaH$_2$. Chemicals were used without any further purification after purchasing from Aldrich (4-Bromobiphenyl, n-butyllithium (2.5 M solution in n-hexane), para-toluenesulfonic acid monohydrate (p-TsOH · H$_2$O)), and Strem (CpZrCl$_3$ and Cp*ZrCl$_3$

where Cp = C$_5$H$_5$, Cp* = C$_5$Me$_5$). ZrCl$_4$(thf)$_2$ [13] and 3,4-dimethylcyclopent-2-enone [14] were prepared according to the literature procedures. CDCl$_3$ was dried over activated molecular sieves (4A), and used after vacuum transfer to a Schlenk tube equipped with a J. Young valve. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 400 spectrometer at ambient temperature. All chemical shifts are reported in δ units with reference to the residual peaks of CDCl$_3$ for proton (7.24 ppm) and carbon (77.0 ppm) chemical shifts. Elemental analyses were carried out on an EA 1110-FI-SONS (CE Instruments) at KAIST.

2.2. X-ray structural determination

2.2.1. Crystal structures of 3 and 4

An air stable, single crystal suitable for X-ray structure determination was mounted on glass capillary. The measurements of diffraction intensity were carried out on an Enraf-Nonius CAD4TSB diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 293 K. Accurate unit cell parameters and orientation matrices were determined from the least-square fit of 25 accurately centered reflections in the range of $19.36° < 2\theta < 31.79°$ for 3 and $19.19° < 2\theta < 26.72°$ for 4. Intensity data were collected by using ω and $\omega - 2\theta$ scan mode with a range of $1.32° < \theta < 24.97°$ for 3 and $1.34° < \theta < 24.99°$ for 4, respectively. All the intensity data were corrected for Lorentz and polarization effects. The structures were solved by semi-invariant direct method (SIR 92 in MoleN) [15] and refined by full matrix least-squares refinement (SHELXL 93) [16] with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed at their geometrically
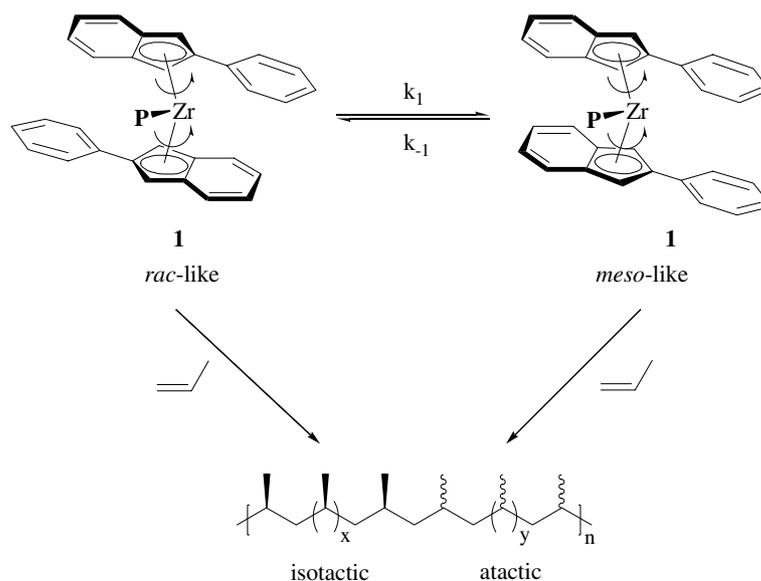
Fig. 1. Elastomeric polypropylene from (2-PhInd)$_2$ZrCl$_2$ (1).

calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Final refinement based on the reflections ($I > 2.0\sigma(I)$) converged at $R_1 = 0.0768$, $wR_2 = 0.1411$ and GOF = 1.112 for **3** and at $R_1 = 0.0451$, $wR_2 = 0.1018$ and GOF = 1.050 for **4**. All calculations were performed on a Silicon Graphics Indigo2XZ workstation. The detailed data for **3** and **4** are listed in Table 1.

2.2.2. Crystal structure of 5

X-ray diffraction measurements were performed on a Bruker AXS diffractometer with a CCD area detector, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Cell parameters and orientation matrices were obtained from a set of 20 data frames, followed by a least-squares refinement. A hemisphere of data was collected using ω scans. The frame data sets were processed using the SAINT and XPREP processing package. An empirical absorption correction was applied to each data set with the program SADABS. All the intensity data were corrected for Lorentz and polarization effects. The structure was solved by direct methods and refined by full matrix least-squares methods using the SHELXTL program package with anisotropic thermal parameters for all non-hydrogen atoms.

Hydrogen atoms were placed at their geometrically calculated positions and refined riding on the corresponding carbon atoms with isotropic thermal parameters. Final refinement based on the reflections ($I > 2.0\sigma(I)$) converged at $R_1 = 0.0298$, $wR_2 = 0.0771$ and GOF = 1.076 for **5**. All calculations were performed on a Pentium computer. The detailed data for **5** are listed in Table 1.

2.3. Ethylene polymerization

Into a well-degassed 250-mL glass reactor was charged with freshly distilled toluene (49 mL) and MMAO (0.5 mL, Al/Zr = 1000, Akzo), and the temperature was adjusted to a constant (25 and 50 °C) using an external bath. Ethylene monomer was then saturated at 1 bar with vigorous stirring after degassing with it several times. Polymerization was started by the injection of a toluene solution of catalyst (1.0 mL, 1.0 μmol). A formation of a white slurry and a rapid consumption of ethylene were observed. All the reactions were quenched by pouring the reaction mixture into the 50 mL of 10% HCl solution of MeOH, and the resulting polyethylene was further precipitated by the addition of 200 mL of MeOH after the given reaction time in Table 3. After stirring for 1 h, polyethylene was filtered off

Table 1
Crystallographic data and parameters for **3**, **4**, and **5**

Compound	3	4	5
Formula	$C_{38}H_{34}Cl_2Zr$	$C_{29}H_{32}Cl_2Zr$	$C_{24}H_{22}Cl_2Zr$
Fw	652.81	542.69	472.56
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/c$	$P\bar{1}$
Unit cell dimensions			
a (Å)	13.172(3)	16.454(3)	12.539(1)
b (Å)	15.586(5)	8.773(1)	16.030(1)
c (Å)	15.644(5)	18.989(4)	17.750(1)
α (°)	90.10(3)	90	71.02(0)
β (°)	99.65(3)	112.98(1)	86.91(0)
γ (°)	100.29(2)	90	69.19(0)
V (Å^3)	3113.7(2)	2523.6(8)	3145.9(3)
Z	4	4	6
D_{calc} (g/cm^3)	1.393	1.428	1.497
$F(0\,0\,0)$	1344	1120	1440
T (K)	293	293	293
μ(Mo Kα) (mm^{-1})	0.550	0.662	0.785
Scan mode	ω	$\omega/2\theta$	ω
θ Range (°)	1.32; 24.97	1.34; 24.99	1.55; 28.06
Number of unique reflections	8452	3957	14,137
Number of observed reflections ($I > 2\sigma(I)$)	4765	3222	11,133
Number of parameters refined	747	296	736
R_1[a]	0.0768	0.0451	0.0298
wR_2[b]	0.1411	0.1018	0.0771
GOF	1.112	1.050	1.076
Minimum and maximum deflections (e Å^{-3})	−0.647; 0.637	−0.451; 0.796	−0.623; 0.458

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

and washed with MeOH several times, and then dried under vacuum overnight at 60 °C.

2.4. Propylene polymerization

Into a well-degassed 250-mL glass reactor, freshly distilled toluene (45 mL) was transferred via cannula. Subsequently, 2.5 mL of a toluene solution of MMAO (Al/Zr = 1000, Akzo) was syringed into the reactor. The temperature was then adjusted to a constant (0 and 20 °C) using an external bath, and propylene was saturated at 1 bar with vigorous stirring after degassing with it several times. After pre-saturation of propylene for 30 min at 0 °C and 15 min at 20 °C, respectively, polymerization was started by the injection of a toluene solution of catalyst (2.5 mL, 5.0 μmol). Initial color change of the reaction mixture was observed. For the entry 1 in Table 4, the reaction was quenched by the addition of 5 mL of 10% HCl solution of MeOH after 1 h. The resulting solution was then washed with 50 mL of aqueous solution of 6 N HCl. The organic layer was separated, and the toluene was evaporated. The viscous polymer residue was finally dried under vacuum overnight at 60 °C. For the entries 2, 3, and 4 in Table 4, the reactions were stopped by the addition of 10 mL of MeOH after 30 min. The polymer products were precipitated by adding 10% HCl solution of MeOH (50 mL) followed by 200 mL of MeOH. After stirring for 1 h, polypropylene was filtered off and washed with MeOH several times, and then dried under vacuum overnight at 60 °C.

2.5. Polymer analysis

^{13}C NMR spectra of polypropylenes were recorded on a Bruker Avance 400 spectrometer in $C_2D_2Cl_4$ with reference to the residual peak of $C_2D_2Cl_4$ (δ 74.14 ppm) at 80 °C. Molecular weight and molecular weight distribution of polypropylenes and polyethylenes were determined by GPC (Waters 150C, 135 °C) in 1,2,4-trichlorobenzene using polystyrene columns as a standard. Melting temperatures (T_m) of polyethylenes were measured by differential scanning calorimetry (DSC, TA Instrument).

2.6. Synthesis

2.6.1. Synthesis of 1-Biphenyl-3,4-dimethylcyclopentadiene (2)

A solution of 4.66 g (20 mmol) of 4-bromobiphenyl in 30 mL of diethyl ether was treated with one equiv of *n*-BuLi (8 mL) at −30 °C. The reaction mixture was slowly allowed to warm to room temperature and stirred for an additional 2 h. To the resulting lithium solution was added 2.20 g (20 mmol) of 3,4-dimethylcyclopent-2-en-one in 30 mL of THF via cannula at −78 °C. The reac-

tion mixture was allowed to warm to room temperature and stirred overnight. The reaction was stopped by the addition of 30 mL of saturated aqueous solution of NH_4Cl, and the organic portion was separated. The aqueous layer was further extracted with diethyl ether (30 mL), and the combined organic portions were dried over $MgSO_4$, filtered and evaporated to dryness, affording a colorless oily product. The crude product was redissolved in CH_2Cl_2 (30 mL), and then a catalytic amount of *p*-TsOH (ca. 0.1 g) was added into the solution at room temperature. Immediate white precipitation was observed, and the stirring was further continued for about 30 min. A volume of the resulting reaction mixture was reduced to 10 mL, and 30 mL of *n*-hexane was poured in to the flask in order to precipitate the product. A large amount of a white shimmering solid formed was filtered on a glass frit and successively washed with ethanol (20 mL), diethyl ether (20 mL) and *n*-pentane (30 mL). Drying in vacuo gave 3.27 g of a white solid of **2** in 66% yield. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.60 (d, 2H), 7.52 (dd, 4H), 7.42 (t, 2H), 7.33 (t, 1H), 6.71 (s, 1H), 3.30 (s, 2H), 2.00 (s, 3H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$): δ 142.0, 140.9, 138.6, 136.1, 135.6, 135.4, 131.9, 128.7, 127.1, 127.0, 126.7, 124.9, 45.2, 13.5, 12.6. Anal. Calc. for $C_{19}H_{18}$: C, 92.64; H, 7.36. Found: C, 92.25; H, 7.28%.

2.6.2. Synthesis of Bis(1-biphenyl-3,4-dimethylcyclopentadienyl)zirconium dichloride (3)

The slurry of 0.739 g (3.0 mmol) of **2** in 20 mL of diethyl ether was treated with one equiv of *n*-BuLi (1.2 mL) at 0 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 6 h. The resulting reaction mixture was evaporated to dryness, and the gray lithium salt of **2** was combined with 0.5 equiv of $ZrCl_4(thf)_2$ (1.5 mmol, 0.566 g). Toluene (30 mL) was then introduced into the solid mixture at −78 °C. After allowing to room temperature, the reaction mixture was heated to 50 °C and stirred at this temperature overnight. The yellow suspension formed was filtered through a Celite pad, and the bright yellow filtrate was evaporated to dryness to give a yellow solid. The crude product was washed twice with 10 mL of a mixed solvent of *n*-hexane/diethyl ether (v/v = 9:1). Drying in vacuo afforded 0.711 g of a bright yellow solid of **3** in 73% yield. Single crystals suitable for X-ray diffraction study were grown up from the concentrated CH_2Cl_2 solution of **3** layered by *n*-hexane at room temperature. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.69 (d, 4H), 7.64 (d, 4H), 7.55 (d, 4H), 7.46 (t, 4H), 7.37 (t, 2H), 6.32 (s, 4H), 1.81 (s, 12H). ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$): δ 140.2, 139.9, 132.2, 128.9, 128.4, 127.7, 127.6, 126.8, 125.6, 121.9, 116.0, 13.2. Anal. Calc. for $C_{38}H_{34}Cl_2Zr$: C, 69.91; H, 5.25. Found: C, 70.46; H, 6.00%.

2.6.3. Synthesis of (Cp)(1-biphenyl-3,4-dimethylcyclopentadienyl)zirconium dichloride (4)*

0.505 g (2 mmol) of a lithium salt of **2** prepared by the same method described above was combined with the same equiv of Cp*ZrCl$_3$ (0.666 g), and the mixture was then treated with 30 mL of toluene at −78 °C. The resulting reaction mixture was allowed to warm to room temperature and further heated at 50 °C for 24 h. After work-up similar to that for **3** except for washing with *n*-hexane only, 0.875 g of a shimmering light yellow solid of **4** was obtained in 81% yield. Recrystallization of **4** in the concentrated CH$_2$Cl$_2$ solution layered by *n*-hexane at room temperature afforded single crystals suitable for X-ray diffraction study. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.63 (dd, 4H), 7.53 (d, 2H), 7.44 (t, 2H), 7.34 (t, 1H), 6.39 (s, 2H), 2.10 (s, 6H), 1.80 (s, 15H). ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$): δ 140.3, 139.7, 132.1, 128.8, 127.9, 127.7, 127.4, 126.9, 126.8, 124.4, 121.7, 116.6, 13.6, 12.1. Anal. Calc. for C$_{29}$H$_{32}$Cl$_2$Zr: C, 64.18; H, 5.94. Found: C, 64.64; H, 5.86%.

2.6.4. Synthesis of (Cp)(1-biphenyl-3,4-dimethylcyclopentadienyl)zirconium dichloride (5)

The mixture of 0.505 g (2 mmol) of a lithium salt of **2** and the same equiv of CpZrCl$_3$ (0.525 g) was treated with 30 mL of toluene at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred for an additional 36 h at this temperature. Filtration and evaporation of the resulting yellow solution gave a yellow solid, which was further washed with *n*-hexane/diethyl ether (v/v = 1:1). Drying in vacuo afforded 0.562 g of **5** in 59% yield. Single crystals were obtained by the similar method for **3** and **4**. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ 7.69 (d, 2H), 7.67 (d, 2H), 7.60 (d, 2H), 7.48 (t, 2H), 7.39 (t, 1H), 6.64 (s, 2H), 6.20 (s, 5H), 2.21 (s, 6H). ^{13}C{^{1}H} NMR (100.62 MHz, CDCl$_3$): δ 140.2, 140.0, 132.5, 128.9 (2C), 127.7, 127.6, 126.8, 125.6, 122.0, 116.5, 114.3, 13.8. Anal. Calc. for C$_{24}$H$_{22}$Cl$_2$Zr: C, 61.00; H, 4.69. Found: C, 60.86; H, 5.21%.

3. Results and discussion

3.1. Synthesis

The 3,4-dimethylcyclopentadienyl (Cp′) fragment in the ligand **2** was chosen as a steric equivalent to the indenyl ring in **1**. This moiety has often been used before in the studies for the preparation of the Waymouth-type catalysts [11a,17], while our main effort was focused on modification of 1-position of the Cp′ ring by introducing a biphenyl group.

All synthetic routes to the ligand **2** and the zirconium complexes **3**, **4**, and **5** are depicted in Scheme 1. The ligand **2** was prepared by the reaction of biphenyllithium
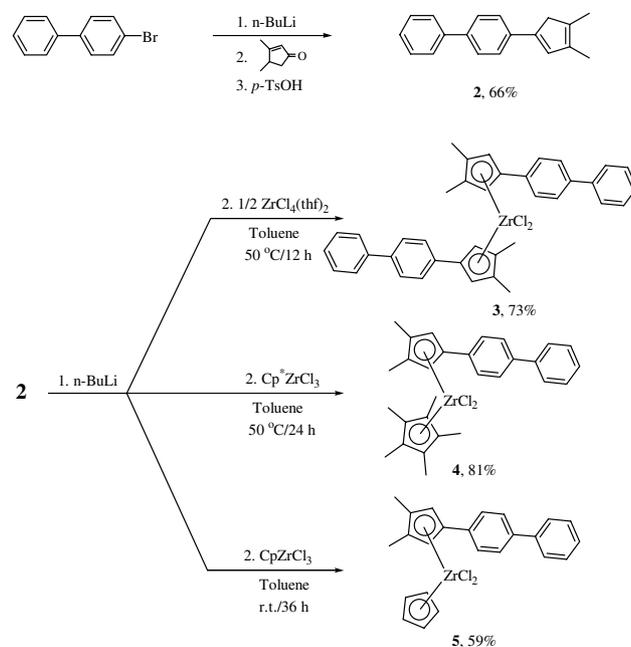
Scheme 1.

obtained from 4-bromobiphenyl and *n*-BuLi with 3,4-dimethylcyclopent-2-enone and subsequent dehydration by *p*-TsOH. The resulting white solid **2** is insoluble in hydrocarbon solvents, poorly soluble in diethyl ether, and moderately in chlorinated solvents such as CH$_2$Cl$_2$ and CHCl$_3$. The synthesis of bis-Cp′ zirconium complex **3** was achieved by the direct metallation of lithium salt of **2** with ZrCl$_4$(thf)$_2$ in toluene. Mixed-ring complexes **4** and **5** were also prepared by the similar method for **3** using appropriate starting zirconium compounds in order to investigate the ligand effects on olefin polymerization.

In contrast to the poor solubility of the ligand **2**, all of the complexes are well dissolved in organic solvents such as toluene, CH$_2$Cl$_2$, and CHCl$_3$, indicating that conjugation between the cyclopentadienyl ring and the biphenyl group in **2** is partially broken after complexation. The complexes were fully characterized by ^{1}H, ^{13}C NMR spectroscopy, elemental analysis, and finally X-ray diffraction method.

3.2. X-ray structures

The molecular structures of **3**, **4**, and **5** are shown in Figs. 2, 3 and 4, respectively and the listed in Tables 1 and 2 are the summaries of the detailed crystallographic data and the selected interatomic distances and angles. The complex **3** crystallizes, in space group P$\bar{1}$, as two independent molecules in the asymmetric unit, and both are *rac*-like isomers different from the catalyst **1** that contains both a *rac*-like and a *meso*-like isomer in the unit cell [8]. Fig. 2 shows only one of two molecules. The huge biphenyl groups are equally oriented away
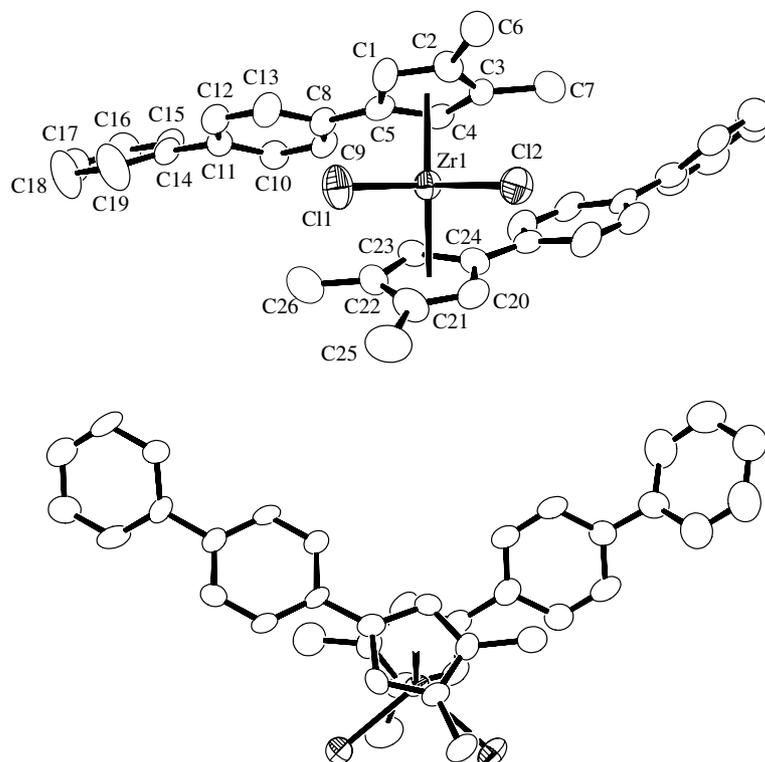
Fig. 2. Molecular structure of (1-Biph-3,4-Me$_2$C$_5$H$_2$)$_2$ZrCl$_2$ (**3**) (front and top views). Thermal ellipsoids are drawn at the 50% probability level.
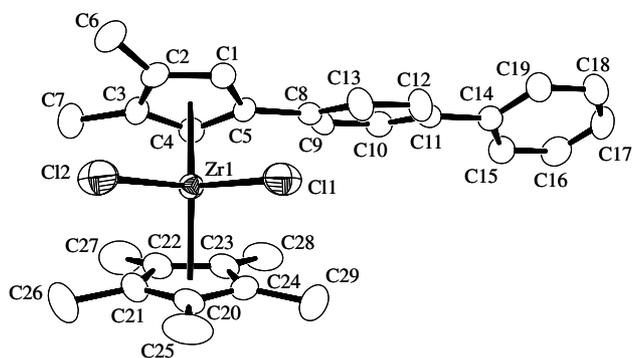
Fig. 3. Molecular structure of (Cp*)(1-Biph-3,4-Me$_2$C$_5$H$_2$)ZrCl$_2$ (**4**). Thermal ellipsoids are drawn at the 50% probability level.
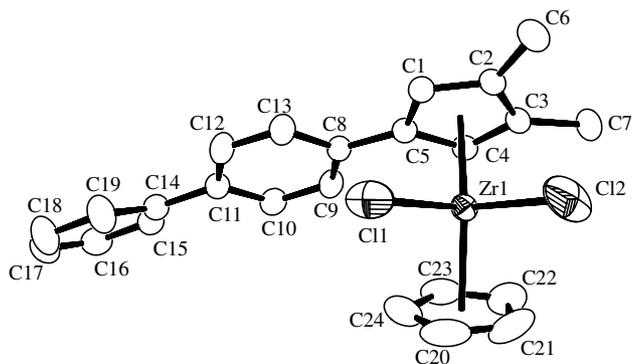
Fig. 4. Molecular structure of (Cp)(1-Biph-3,4-Me$_2$C$_5$H$_2$)ZrCl$_2$ (**5**). Thermal ellipsoids are drawn at the 35% probability level.

Table 2
Selected interatomic distances (Å) and angles (°) for **3**, **4**, and **5**

Compound	**3**	**4**	**5**
Angles			
Cl(1)–Zr(1)–Cl(2)	98.5(1)	95.1(1)	98.1(0)
Cn(1)–Zr(1)–Cn(2)[a]	131.5	132.6	131.0
Cp′(1)–Ph(1)[b]	6.4(5)	24.3(2)	3.0(1)
Ph(1)–Ph(2)[b]	33.2(5)	29.1(2)	25.1(1)
Distances			
Zr(1)–Cl(1)	2.420(3)	2.454(1)	2.437(1)
Zr(1)–Cl(2)	2.430(3)	2.436(1)	2.420(1)
Zr(1)–Cn(1)	2.216(4)	2.240(2)	2.216(1)
Zr(1)–Cn(2)	2.224(5)	2.229(2)	2.207(2)

[a] Cn(1) and Cn(2) are the centroids of the Cp rings of C(1–5) and C(20–24), respectively.

[b] Cp′(1); the plane of C(1–5), Ph(1); the plane of C(8–13), Ph(2); the plane of C(14–19).

from the chlorine atoms, by which the molecule ideally adopts C_2-symmetry in the solid state. Interestingly, the methyl groups of the Cp′ ring are eclipsed over the chlorine atoms contrary to that observed in the similar *para*-tolyl substituted zirconocene complex [11a].

Unlike the catalyst **3**, the mixed-ring complexes **4** and **5** shown in Figs. 3 and 4, respectively, have no symmetry group, exhibiting overall C_1-symmetry. Especially, the complex **5** which also crystallizes in space group $P\bar{1}$ abnormally contains three independent molecules in the asymmetric unit, and two of them are the same

conformers but the other one is inverted through an inversion center in the unit. Both complexes also show a similar orientation of the biphenyl group and the eclipsed conformation between one methyl group of the Cp′ ring and the chlorine atom as observed in **3**. The detailed relevant structural analysis indicates that some important bond distances and angles for **3**, **4**, and **5** (Table 2) are nearly identical or similar to those reported for **1** and related nonbridged zirconocenes [8–12,17,18]. When comparing the structural parameters between three complexes, the complexes **3** and **5** show a close resemblance in the values such as angles of Cl(1)–Zr(1)–Cl(2) and Cn(1)–Zr(1)–Cn(2) and distances of Zr(1)–Cl and Zr(1)–Cn(1) except for the slightly longer distance of Zr(1)–Cn(2) in **3** (2.224(5) Å) than that in **5** (2.207(2) Å). Therefore, it can be seen that the introduction of the ligand **2** instead of Cp ring does not influence significantly on the geometrical parameters around the metal center. However, the values for **4** are somewhat different from those for **3** and **5**; the reduced angle of Cl(1)–Zr(1)–Cl(2), the increased angle of Cn(1)–Zr(1)–Cn(2), and the slightly increased distances of Zr(1)–Cl and Zr(1)–Cn. These observations are well consistent with the consequence of an increased steric hindrance around the metal center exerted by the bulky Cp* group.

The small dihedral angles between the plane defined by the biphenyl substituted Cp′ ring and the phenyl ring adjacent to the Cp′ ring in both **3** (6.4(5)°) and **5** (3.0(1)°) are in a similar range of those found in **1** and its derivatives [8–12,18], while the angle exceptionally increased to 24.3(2)° in **4** similar to those for monophenyl and *para*-tolyl substituted analogues of **3** [11a,17]. However, the dihedral angles between two phenyl rings in the biphenyl group are not following the trend observed above, showing relatively large values in all complexes (Table 2). This different trend in dihedral angles can be explained by the different steric requirements around the metal center;

The nonbonded interaction between the methyl group, especially C(28) (Fig. 3), of the Cp* ring and the hydrogen atoms on the *ortho*-carbon atoms of the phenyl ring (Ph(1)) in **4** appears to push the phenyl ring out of the plane defined by the Cp′ ring, resulting in a large dihedral angle. In contrast, it can be expected that such interactions are little or weak in the sterically less demanding **3** and **5**, showing a small discrepancy of the angle and thus being capable of the retention of an electronic interaction between two ring planes. Because the dihedral angle between two phenyl rings is not directly related to the steric crowding around the metal center, the second phenyl rings (Ph(2)) in all the complexes can be distorted to the extent enough to minimize possible nonbonded interactions between the hydrogen atoms on the *ortho*-carbon atoms adjacent to the single bond (C11–C14) linking two phenyl rings.

3.3. Olefin polymerization

Ethylene and propylene polymerizations of the zirconium complexes **3**, **4**, and **5** were carried out in the presence of MMAO cocatalyst in toluene solution. According to the results of ethylene polymerization data given in Table 3, it can be known that all the complexes act as highly active catalysts for ethylene polymerization at both 25 and 50 °C, and furthermore these activities are several times higher than that of the known catalyst Cp_2ZrCl_2 under the same conditions. Polyethylenes produced show high melting temperature (T_m), indicating that they are high-density polyethylene generally observed in usual metallocene catalyst systems. Narrow molecular weight distribution (M_w/M_n) also indicates that these complexes consist of single active site catalysts.

Among three catalysts, **4** is most active and followed by **3** and **5** at both temperatures. However, molecular weight of polyethylene is decreasing in the order of **3**, **5**, and **4**. In particular, molecular weight of polyethylene from **4** at 50 °C is considerably low about 80,900 similar to that from Cp_2ZrCl_2. These observations suggest that catalytic activity correlates with the increase of an electron density at the metal center, while molecular weight of polyethylene depends more on the steric crowding around the metal center rather than the electronic effect of the ligands. In this regards, the catalyst **3** meets properly for the requirement of both steric and electronic effects, affording high molecular weight polyethylenes with high activity.

Propylene polymerization data in Table 4 show another polymerization behavior of the complexes **3**, **4**, and **5**. The activity of **3** at 20 °C is high enough to be comparable with those of similar nonbridged zirconocenes [11a,17], while the methyl pentad value [mmmm] of the polypropylene is low, indicating that atactic polypropylene was produced.

In order to partly enhance the stereospecificity of the resulting polypropylene, polymerization reactions

Table 3
Ethylene polymerization data with catalysts **3**–**5**/MMAO[a]

Entry	Catalyst	T_p (°C)	Activity[b]	M_w ($\times 10^{-3}$)	M_w/M_n	T_m (°C)
1	**3**	25	6570	–	–	–
2	**4**	25	10,710	–	–	–
3	**5**	25	4670	–	–	–
4	**3**	50	11,210	280	1.77	136.0
5	**4**	50	12,960	80.9	1.78	133.5
6	**5**	50	10,180	215	2.33	138.0
7	Cp_2ZrCl_2	50	2430	73.8	2.42	132.4

[a] Conditions: P(ethylene), 1 bar; [Zr], 1.0 μmol; Solvent, 50 mL of toluene; [Al]/[Zr], 1000.
[b] Activity, kg PE/(mol of Zr) h bar.

Table 4
Propylene polymerization data with catalysts **3**–**5**/MMAO[a]

Entry	Catalyst	T_p (°C)	Activity[b]	M_w ($\times 10^{-3}$)	M_w/M_n	mmmm (%)[c]	m (%)[c]
1	**3**	20	819	13.7	2.24	7.9	54.6
2	**3**	0	394	36.0	1.91	12.5	59.9
3	**4**	0	489	12.6	2.13	13.4	64.0
4	**5**	0	874	25.0	1.90	8.4	56.4

[a] Conditions: P(propylene), 1 bar; [Zr], 5.0 μmol; Solvent, 50 mL of toluene; [Al]/[Zr], 1000.
[b] Activity, kg PP/(mol of Zr)h bar.
[c] Determined by ^{13}C NMR spectroscopy.

were performed under low temperature, e.g., 0 °C, at which the concentration of propylene in solution also increases. The catalytic activities are in the range of 400–900 kg PP/(mol of Zr) h bar, and the catalyst **5** is most active in contrast to the result in ethylene polymerization. The other complexes **3** and **4** show similar activity with a slightly higher value for **4**. This fact indicates that the activity of propylene polymerization in the given catalyst systems depends largely on the steric hindrance around the metal center as similarly observed in other Waymouth-type metallocene catalyst systems [12a]. Thus the less hindered **5** is more productive than the electron-rich **3** and **4**. The molecular weights of polypropylenes are in the order of **3** > **5** > **4**. This trend is the same as is in ethylene polymerization, suggesting that chain transfer processes are also much governed by the steric factor around the metal center. The [mmmm] methyl pentad values indicative of isotactic block length of polypropylene for **3** and **4** (Entries 2 and 3) are similar and slightly increased compared with that of the polypropylene obtained at 20 °C for **3** (Entry 1). Decrease of polymerization temperature increases the [mmmm] value but does not change much. The values are still in the range of those observed in similar nonbridged zirconocene catalysts, indicating that the polypropylenes are nearly atactic [11a,17,18]. In particular, the [mmmm] value for the most active **5** is lowest. This trend in the [mmmm] values is in accordance with the report by Waymouth et al. that not only the catalyst **1** but also its mixed-Cp* derivative also produces polypropylene with a comparable [mmmm] content, while the mixed-Cp complex only gives atactic polypropylene despite its high activity [12a]. The expected stereocontrol by the restricted rotation of the biphenyl substituted ligand might not be effective in the present catalysts system as similarly observed in the case of phenyl or *para*-tolyl substituted analogue of **3**, partially supporting that the indenyl ring fragment is necessary to attain a high [mmmm] value [19]. Therefore, it can be concluded that the counterbalancing effects from both parts of cyclopentadienyl ring fragment and 2-aryl substituent in the Waymouth-type catalyst would be essential in order to produce elastomeric polypropylene.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 248935–248937 for complexes **3**, **4**, and **5**, respectively. 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 Internet: http://www.ccdc.cam.ac.uk).

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