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Ethylene-bridged pseudo-C_s symmetric *ansa*-zirconocene complexes: synthesis, structures and propylene polymerization behavior

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Abstract

The ethylene-bridged pseudo-C_s symmetric *ansa*-zirconocene complexes, (1-fluorenyl-2-cyclopentadienylethane)zirconium dichloride (**5a**) and (1-fluorenyl-2-tetramethylcyclopentadienylethane)zirconium dichloride (**5b**), were synthesized and their molecular structures have been determined by single crystal X-ray diffraction studies. The complex **5a** is very active toward propylene polymerization in the presence of methylaluminoxane (MAO), affording polypropylene with good syndiotacticity. In comparison with the known syndiotactic polypropylene catalytic system *i*Pr(fluorenyl)(cyclopentadienyl)$ZrCl_2$/MAO, **5a**/MAO system is better in thermal stability, higher in activity and lower in syndiotacticity under the identical polymerization conditions. On the other hand, **5b**/MAO system shows low activity and produces nearly atactic polypropylene with low molecular weight, which could be attributed to the increased electron density and steric bulkiness around the metal center. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Pseudo-C_s symmetry; Zirconocene; Ethylene-bridged

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1. Introduction

Metallocene complexes have been extensively investigated as catalysts for stereospecific polymerization of ethylene, propylene and other α-olefins [1]. In particular, the relationship between the structure of the metallocene catalyst and the tacticity of polypropylene is relatively well-established. Syndiotactic polypropylene, which has not been obtained as a pure form in heterogeneous catalytic systems [2], has been produced by Ewen and Razavi using C_s symmetric *i*Pr(fluorenyl)-(cyclopentadienyl)$ZrCl_2$(**6**)/MAO system [3]. In contrast to the early known homogeneous V(III) complex systems [4], this catalytic system provides syndiotactic polypropylene with not only high activity and high stereoselectivity, but also a higher molecular weight than that of its isotactic counterpart [5] via the mechanism originated from the intrinsic chirality of the catalyst [6]. On the other hand, the Si-bridged C_s symmetric analog [7] of **6** gives only atactic polypropylene, while *rac* - {(*t* - Bu)(H)C}(fluorenyl)(cyclopentadienyl)Zr - Cl_2 complex [8] with a local C_s symmetry produces syndiotactic polypropylene of which syndiospecificity is higher than that from **6**, suggesting that the perfect C_s symmetry of catalytic precursors may not be a sufficient requirement for the syndiospecific propagation reaction. Therefore, it is expected that the subtle variation of a ligand framework can cause electronic and/or steric changes on the metal center and hence significant modification of the activity of the catalysts and the stereospecificity of the resulting polypropylene. Nonetheless, only a limited number of variants of **6** were reported [9] and in particular the chemistry of ethylene-bridged pseudo-C_s symmetric analogs of **6** have not been properly reported [10]. We prepared a couple of ethylene-bridged (fluorenyl)(cyclopentadienyl)-

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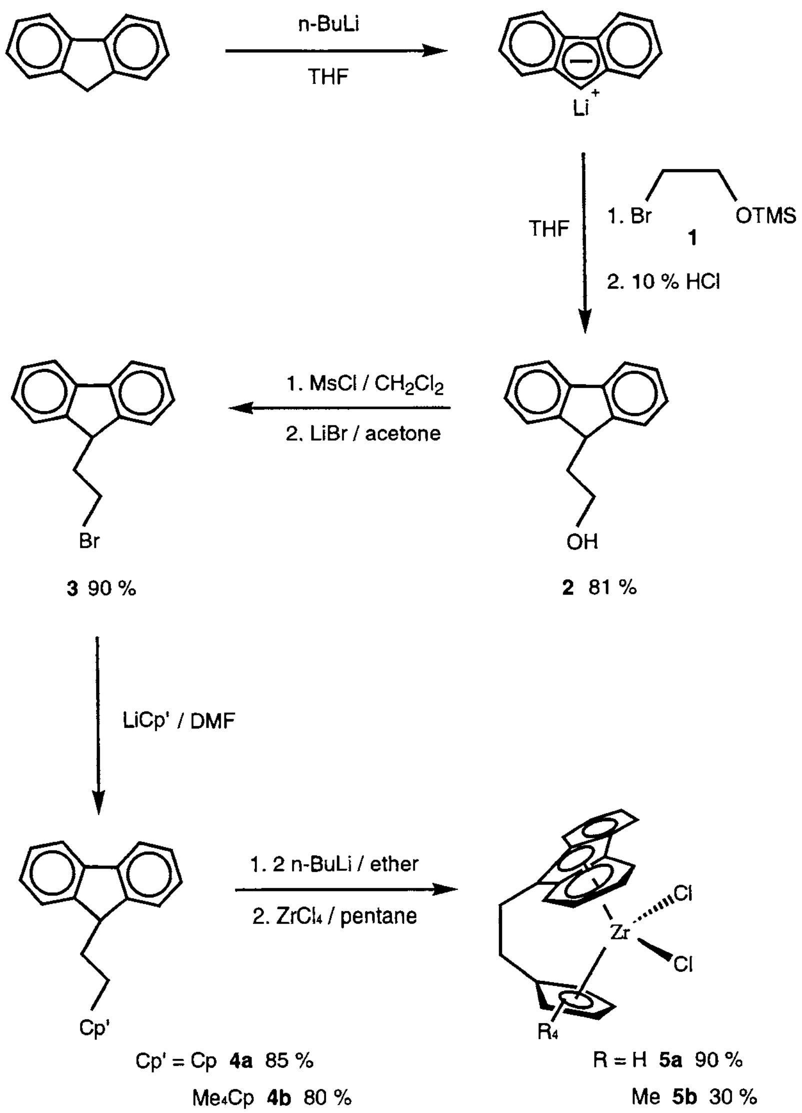

Scheme 1.

(zirconium dichloride compounds with different electronic and steric factors and studied their catalytic behavior in propylene polymerization. Reported herein are accounts of a convenient and highly affording synthetic route to ethylene-bridged ligand systems and the preparation, single crystal X-ray structures and catalytic properties of novel stereorigid propylene polymerization catalytic precursors, (1-fluorenyl-2-cyclopentadienylethane)zirconium dichloride (**5a**) and (1-fluorenyl-2-tetramethylcyclopentadienylethane)zirconium dichloride (**5b**).

2. Results and discussion

2.1. Synthesis

Synthetic routes to ethylene-bridged ligand systems and their zirconium complexes are summarized in Scheme 1. In order to introduce two different ancillary ligand groups of cyclopentadienyl and fluorenyl at the ends of the ethylene bridge, a set of stepwise reactions was performed using 2-bromoethyltrimethylsilyl ether (**1**) as a starting bridge framework.

Substitution of a fluorenyl group for a bromo group in **1** followed by acidification gave 2-(9-fluorenyl)-ethanol (**2**) as a white solid in high yield. Compound **2**, which was previously prepared by Rieger et al. from ethylene oxide [11], can be converted to 2-(9-fluorenyl)ethylbromide (**3**) in 90% yield via mesylation and treatment with LiBr [12]. The colorless product **3** is a critical intermediate in the synthesis of the desired ligands **4** since the direct reaction of the mesylation or tosylation product of **2** with the cyclopentadienyl anion leads to the undesired spiro-type 1,1′-(9-fluorenyl) cyclopropane [11,13] as a major product. The formation of the spiro product was not observed at all when compound **3** was reacted with cyclopentadienyl

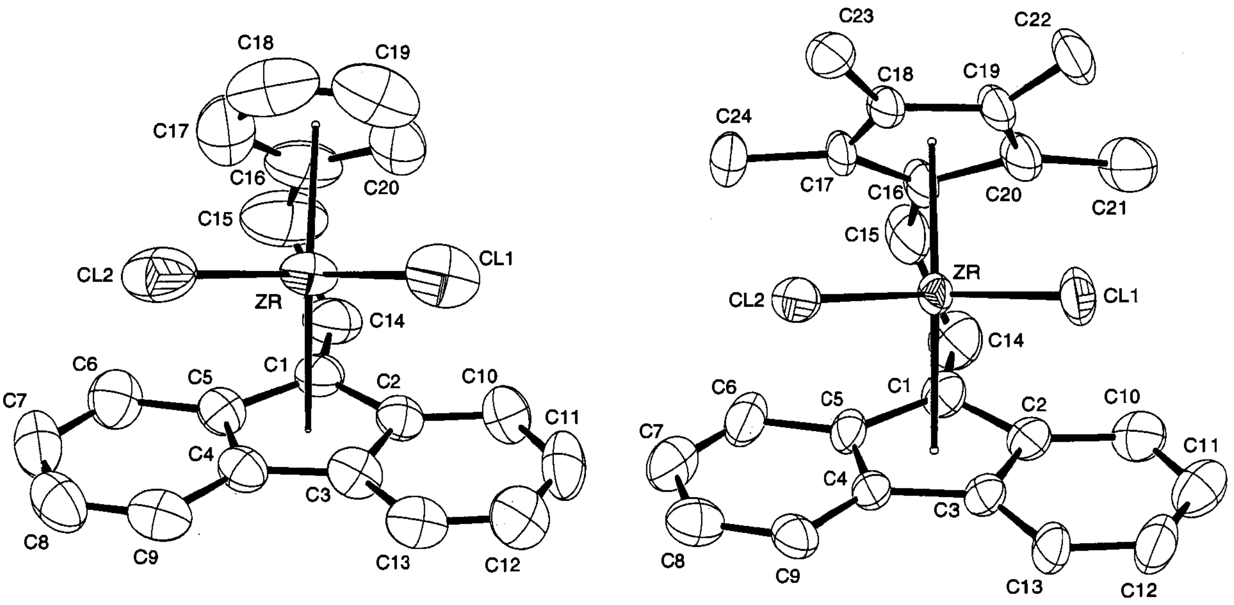

Fig. 1. Molecular structures of **5a** and **5b** (front view) showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

anions in DMF. Solvent selection is an important matter in this step because the use of THF results in minor formation of the spiro product. Straightforward metallations were effected by treating a pentane slurry of $ZrCl_4$ with an orange diethylether slurry of dilithium derivative of **4** at −78°C [14]. After workup and crystallization, the final products **5a** and **5b** were obtained as red-orange and orange crystalline solids in 90 and 30% yields, respectively. Unlike the isopropyl bridge complex **6**, the compounds **5** are rather stable in the air.

*2.2. Structures and bonding in **5a** and **5b***

The molecular structures of both zirconium complexes were determined by single crystal X-ray diffraction studies. Both compounds show the expected bent *ansa* geometry. Different views of the structures are displayed in Figs. 1 and 2. (One of the two identical structures in the unit cell is shown for **5a**.) Listed in Tables 1 and 2 are the summaries of crystallographic data and selected interatomic distances and angles.

Front views (Fig. 1) reveal the pseudo-C_s symmetric nature of the compounds with a pseudo-σ symmetric plane perpendicular to the Cl–Zr–Cl plane. Two five-membered rings of the ancillary ligands are slightly staggered owing to the conformational change induced by the ethylene bridge. A similar staggered structure has been observed for other ethylene-bridged metallocene complexes [11,15]. Torsional angles involving two methylene carbons of the ethylene bridge, which reflect the extent of the deviation from the perfect C_s symmetry as well as the degree of the increased steric bulkiness in the compounds, are 41.2 and 34.3° for **5a** and **5b**, respectively. The non-bonded repulsion interactions ([14]a, [15]c, [16]) of the equatorial chlorine atoms with the fluorenyl β-CH protons of C9 and C13 in both compounds and with β-methyl groups of C22 and C23 in **5b** would result in the ethylene bridges being stretched, leading to the decreased torsional angles for **5a** and **5b** compared with that (45.6°) found in *rac*-$Et(Ind)_2ZrCl_2$ ([15]d), in which only weaker non-bonded repulsion interactions are present. Consistent with this argument are the increased C1–C14–C15 and C14–C15–C16 angles (Table 2) from the expected angle for sp^3 hybridized carbon atoms and the larger C14–C15–C16 angle of **5b** than that of **5a**.

Metallacyclic Zr–C1–C14–C15–C16 units in both compounds adopt a δ-conformation which is isoenergic with λ-conformer owing to the achiral nature of the ligand framework ([11], [15]c,d). This indicates that in solution, both conformers would be present nearly in equal ratio, and thus the stereoselectivity of the prochiral monomer in polymerization would be decreased, particularly at high temperatures (vide infra).

Distance analysis indicates that the interaction patterns between the Zr atom and the two ancillary ligand rings in **5a**, **5b** and **6** are similar such that the cyclopentadienyl rings interact basically in pentahapto fashion, while the fluorenyl ligands deviate from the normal η^5-type, presumably due to the non-bonded interaction mentioned above. The fluorenyl ring slippage [17] of 0.281 and 0.315 Å for **5a** and **5b**, respectively, toward the bridgehead carbon atom reflects the extent of the hapticity deviation. The centroid–metal–centroid angles for **5** are expected to increase from the mono carbon-bridged analog due to the increase of the size of

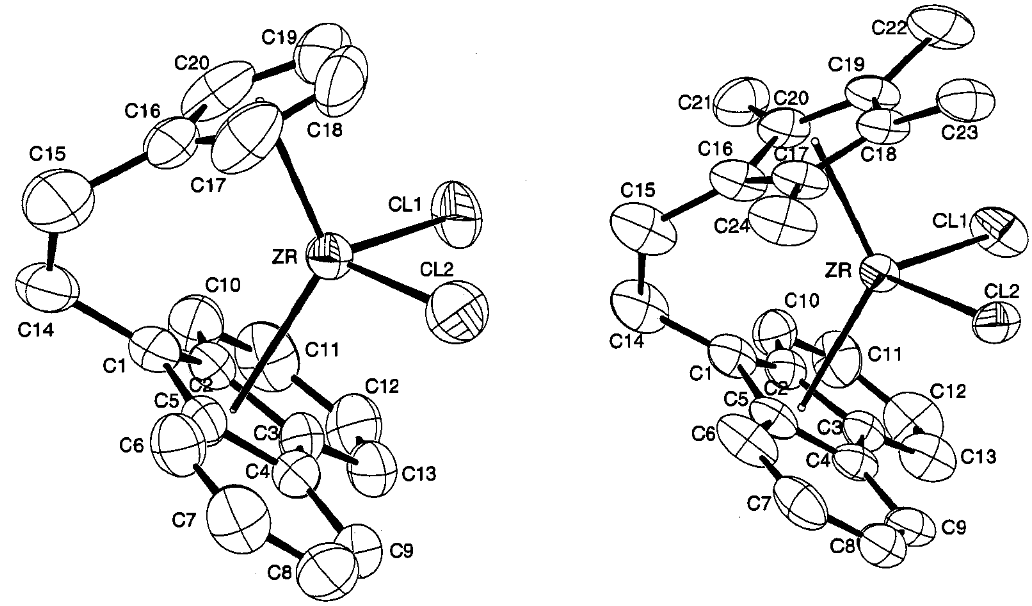

Fig. 2. Molecular structures of **5a** and **5b** (side view) showing 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity.

the bridge and the observed corresponding angles are 126.9, 128.2 and 118.6° ([14]a) for **5a**, **5b** and **6**, respectively. The foregoing structural comparison implies that the $ZrCl_2$ units in **5** are less extruded from the *ansa* ligand pocket than in **6**. This structural feature coupled with the smaller ring–ring dihedral angles in **5** (60.8 and 62.2° for **5a** and **5b**, respectively) than in **6** (72.0°) ([14]a) suggest that the extent of the steric shielding of the metal centers in **5** is larger than that in **6** and thereby explain the increased air and thermal stability of **5** compared with complex **6**.

Table 1
Crystallographic data and parameters for **5a** and **5b**

Compound	5a	5b
Formula	$C_{20}H_{16}Cl_2Zr$	$C_{24}H_{24}Cl_2Zr$
Formula weight	418.45	474.55
Temperature (K)	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	$P2_1/c$(No.14)	$P\bar{1}$(No.2)
a (Å)	13.260(2)	8.417(9)
b (Å)	15.423(2)	9.842(1)
c (Å)	16.693(2)	13.845(8)
α (°)	90.00	97.89(7)
β (°)	92.53(2)	98.25(4)
γ (°)	90.00	114.67(6)
V (Å^3)	3410.5(8)	1006.4(3)
Z	8	2
D_{calc} (g cm^{-3})	1.630	1.566
F(000)	1680	484
μ (Mo–K$_\alpha$) (mm^{-1})	0.954	0.818
Scan mode	ω-2θ	ω-2θ
2θ range (°)	4–50	4–50
Total reflections	5209	3338
Obvious reflections ($I>2\sigma(I)$)	4375	3066
Parameters refined	415	244
R_1 [a]	0.0481	0.0308
wR_2 [b]	0.1171	0.0782
Goodness-of-fit	1.185	1.061
Max. residual density (e A^{-3})	0.930	0.555

[a] $R_1=\sum||F_o|-|F_c||/\sum|F_o|$.

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

2.3. Propylene polymerizations

Propylene polymerizations of the catalytic precursors **5a** and **5b** were carried out in the presence of an MAO cocatalyst at various temperatures, and the resulting polymerization behavior was compared with that of the known catalytic system **6**/MAO under the same conditions. The polymerization data and the selected methyl sequence distributions of the resulting polypropylenes are given in Tables 3 and 4, respectively.

Among the three compounds, complex **5a** shows the highest activity with moderate syndiospecificity, while complex **5b** produces low molecular weight polypropylene with low tacticity at all temperatures. The stereospecificity–acitivity relationship for **5** is consistent with the observation that a system with a high degree of stereospecificity also shows good activity [18]. The polymerization activity of compounds **5** increases as the polymerization temperature increases and reaches maximum at 70°C, while that of the known reference **6** decreases as the polymerization temperature increases, which can be considered as a manifestation of the increased thermal stability of **5** compared with **6**.

In contrast to the activity trend, the syndiospecificity of the catalytic systems **5**/MAO is generally lower than that of **6**/MAO due to the deviation from the perfect C_s symmetry, the interconversion of the ethylene bridge

Table 2
Selected bond distances (Å) and angles (°) for **5a** and **5b**

Compound	**5a**	**5b**
Angles (°)		
CL1–ZR–CL2	97.77(7)	96.77(3)
Cp–ZR–Cf[a]	126.9(3)	128.2(9)
Cp–ZR–CL	1107.2(9)	108.2(5)
Cp–ZR–CL2	107.4(6)	106.1(9)
Cf–ZR–CL1	107.5(5)	106.8(5)
Cf–ZR–CL2	106.1(0)	106.0(2)
C1–C14–C15	112.1(5)	112.1(3)
C14C15–C16	110.4(6)	112.6(3)
C1–C14–C15–C16	41.2(8)	34.3(5)
Pl(Cp)–Pl(Cf)[b]	60.8(4)	62.2(5)
Distances (Å)		
ZR–CL1	2.43(1)	2.42(6)
ZR–CL2	2.42(0)	2.43(7)
ZR–C1	2.43(4)	2.42(7)
ZR–C2	2.55(5)	2.57(9)
ZR–C3	2.67(6)	2.71(5)
ZR–C4	2.69(7)	2.70(6)
ZR–C5	2.57(2)	2.55(9)
ZR–C16	2.47(9)	2.48(4)
ZR–C17	2.47(6)	2.51(1)
ZR–C18	2.49(3)	2.55(9)
ZR–C19	2.49(6)	2.57(0)
ZR–C20	2.47(3)	2.50(2)
ZR–Cp	2.19(0)	2.21(8)
ZR–Cf	2.28(2)	2.29(5)
C13–CL1	3.35(1)	3.43(8)
C22–CL1	—	3.27(5)
C9–CL2	3.31(5)	3.29(7)
C23–CL2	—	3.28(6)

[a] Cp, centroid of C (16, 17, 18, 19, 20); Cf, centroid of C (1, 2, 3, 4, 5).
[b] Pl, the least-square plane of each C_5 ring.

between δ- and λ-conformers and the steric factor. For **5a** and **6**, the syndiotacticity is moderate and high, respectively, at 25°C, but decreases as the polymerization temperature increases; while for **5b** the tacticity is even lower at 25°C. Since the interconversion between δ- and λ-conformers is expected to increase upon increasing the temperature, the low tacticity of **5b** for the temperature range suggests that the increased steric bulkiness that also imposes intrinsic local C_{2v} symmetry on **5b** is the most dominant factor governing the stereocontrol. On the other hand, for **5a**, the drastic decrease in tacticity observed when polymerization temperature changes from 25 to 50°C, which is consistent with the expected increased interconversion at higher temperatures, suggests that the stereocontrol is mainly affected by the interconversion between δ- and λ-conformer [11,19].

The polymers obtained with **5** and **6** show narrow molecular weight distributions near two, indicating the involvement of a single active site species in the polymerizarion reactions [20]. According to the ^{13}C-NMR spectra of methyl pentad region, all three systems do not show any evident mmmm peaks. In the case of **5a**, most stereoerrors come from mm triad and m dyad defects. The pentad ratios and triad test ([6]a) indicate that the propagation proceeds via the mixed mechanism [5] of site control and chain-end control.

Molecular weights of the polymers obtained with **5a** are similar to those obtained with **6**, ranging $1 \times 10^4 \sim 1 \times 10^5$, but in the case of **5b**, the resulting polymers have very low molecular weights and are nearly oligomeric. The nature of the low molecular weight for **5b** is rather surprising since the increased electron density on the cationic metal center due to tetramethylcyclopentadienyl ring in **5b** would slow down the β-H/Me chain transfer reactions and thus provide high molecular weight polymers [21]. However, this electronic effect seems to be more counter-balanced by the steric hindrance that imposes on the incoming monomer to cause a much slower insertion rate compared with the termination reaction [22]. Another consequence of the increased electron density is the weakening of the α-agostic stabilization [23], which in turn increases the site isomerization reaction and thus decreases the stereospecificity.

The ^{13}C-NMR end group analyses (Fig. 3) of the polymers obtained at 70°C indicate that both **5a** and **5b** catalytic systems are associated with 1,2-regioregular insertion ([6]a, [22,24,25]). No 2,1- (head-to-head, tail-to-tail) or 1,3-misinsertion was observed at all ([6]a, [22,26]). The main chain transfer reaction in **5a** is β-H elimination reaction although β-Me elimination is also involved as a minor process (Fig. 3(a)). In contrast, **5b** adopts β-Me elimination as a main chain transfer process along with a small portion of β-H elimination (Fig. 3(b)). The difference in the nature of the chain transfer is due to the different steric encumbrance, which is in accord with the fact that the chain end is located to escape from the non-bonding interaction with the more bulky ligand around the metal center [21,22,27]. In both systems, the chain transfer to Al atoms is also evident as observed from the larger isobutyl peak than the corresponding allyl peak in ^{13}C-NMR spectra [22,28].

3. Experimental

3.1. General procedure

All operations were performed under a dinitrogen atmosphere using standard Schlenk and Glove box techniques. Solvents were dried and distilled before use. THF, toluene and *n*-pentane were distilled from Na–K alloy, Et_2O from Na–benzophenone ketyl, CH_2Cl_2 from CaH_2. Anhydrous DMF (Aldrich) and acetone (Merck) were used as purchased. Chemicals were used without any further purifications after purchasing from

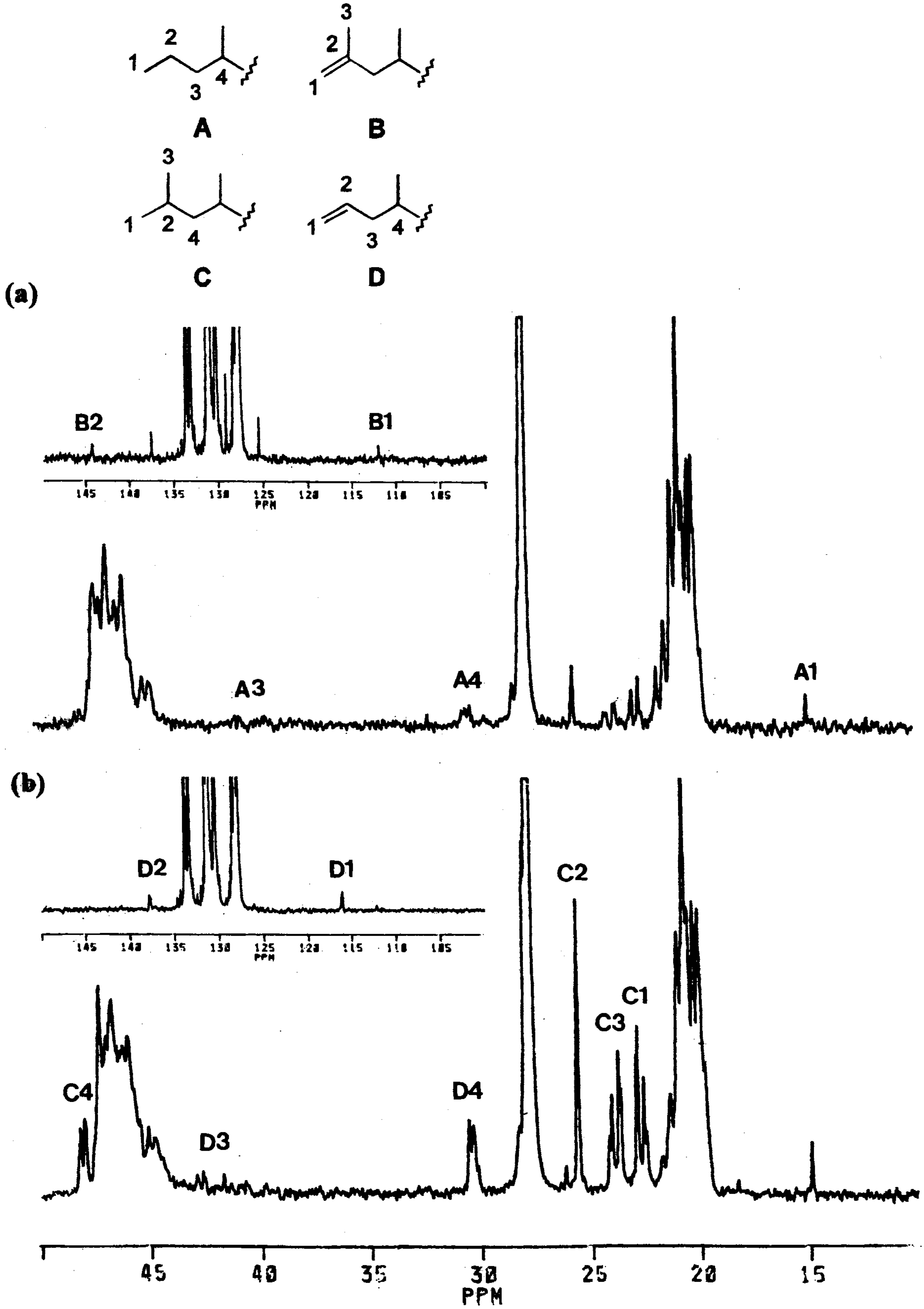

Fig. 3. ^{13}C-NMR Spectra (C_6D_6/TCB) with peak assignments for polypropylenes obtained with (a) **5a** and (b) **5b** at 70°C.

Table 3
Propylene polymerization data obtained with **5a**, **5b** and **6** at different temperatures[a]

Catalyst	T_p (°C)	Yield (g)	Activity (kg PP/mol Zr h atm)	M_w ($\times 10^3$)	M_w/M_n	rrrr (%)	T_m (°C)
5a	25	7.7	642	117	2.0	63.7	108
	50	12.5	1042	22	2.2	28.4	—
	70	26.1	2175	9.1	2.2	13.7	—
	90	18.2	1517	3.7	1.9	11.4	—
5b	25	0.9	75	n.d.[b]	n.d.	11.2	—
	50	2.1	175	2.9	1.6	11.7	—
	70	9.8	817	2.2	1.5	13.6	—
	90	3.5	292	n.d.	n.d.	n.d.	—
6	25	3.0	251	124	2.1	80.1	138
	50	1.8	150	39	1.8	61.4	103
	70	0.6	50	14	2.4	45.5	n.d.

[a] Conditions: toluene 150 ml; Cat = 10 µmol; $P_{C_3H_6} = 1.2$ atm; Al/Zr = 2000; $t_p = 1$ h.
[b] n.d, not determined.

Aldrich, Fluka and so on. **1** was prepared by the literature procedure [29] from 2-bromoethanol. Merck flash silica gel (230–400 mesh) was used for column chromatography. MAO (Akzo, 6.4 wt.% Al, $d = 0.88$) was used as toluene solution. *i*Pr(Flu)(Cp)ZrCl$_2$ (**6**) was used as a commercial product (Witco). Propylene was supplied by Yukong and used after removing residual oxygen and water by passage over the RIDOX (Fisher) column and molecular sieves (5A/13X), respectively. The ^{1}H- and ^{13}C-NMR spectra were recorded on Bruker AC 200 and Braker AM 300 spectrometers at ambient temperature, with the residual CDCl$_3$ peak as an internal standard. The ^{13}C-NMR spectra of the polymers were recorded on 15 wt.% polypropylene solution of 1,2,4-trichlrobenzene(TCB)/C$_6$D$_6$ at 80°C. MS spectra (EI-MS, JEOL JMS-SX102A) (KBSC) and elemental analyses (Carlo Erba EA 1108) were obtained at Korea Basic Science Center (KBSC). Molecular weight and molecular weight distribution of the polymers were determined by gel-permeation chromatography (GPC, Waters 150 CV+, 140°C) in TCB using polystyrene columns as a standard. Melting points of the polymers (T_m) and compounds (m.p.) were measured by differential scanning calorimetry (DSC, TA instruments DSC 2010).

*3.2. 2-(9-Fluorenyl)ethanol (**2**)*

To a solution of fluorene (8.48 g, 50 mmol) in 50 ml of THF, *n*-butyllithium (55 mmol, 2.5 M solution in hexane) was slowly added at 0°C. The reaction mixture was allowed to warm to r.t. and stirred for an additional 2 h. The red-brown solution was then added dropwise to a vigorously stirred solution of **1** in 10 ml of THF over a period of 1 h at −78°C. The reaction mixture was slowly warmed to r.t. and stirred overnight. The resulting orange solution was treated with 50 ml of 10% aqueous solution of HCl and stirred for 1 h. The yellow solution was formed after neutralization with a saturated aqueous solution of Na$_2$CO$_3$. The mixture was extracted with Et$_2$O (50 ml) and the organic layer was separated. The aqueous layer was further extracted with Et$_2$O (2 × 50 ml). The combined organic layers were dried over anhydrous MgSO$_4$, filtered and evaporated. The crude product was purified by column chromatography (eluent: hexane/ethyl acetate, 2/1) to afford a light-yellow solid. Recrystallization in pentane at −20°C gave a white crystalline solid, **2** (8.51 g, 81%). M.p. = 101°C (lit. [11] 107–108°C). ^{1}H-NMR (200.13 MHz, CDCl$_3$): δ 7.2–7.8 (m, 8H), 4.12 (t, $J = 6.0$ Hz, 1H), 3.56–3.62 (m, 2H), 2.24–2.33 (m, 2H), 1.28 (s, 1H). ^{13}C-NMR (50.32 MHz, CDCl$_3$): δ 146.74, 140.78, 126.99, 126.86, 124.31, 119.83, 59.92, 44.37, 35.59. EI-MS: *m/z* (relative intensity) 210 (M$^+$, 52), 192 (M$^+$-HOH, 100), 165 (M$^+$-C$_2$H$_4$OH, 95). Anal. Calc. for C$_{15}$H$_{14}$O: C, 85.68; H, 6.71. Found: C, 86.15; H, 6.90.

*3.3. 2-(9-Fluorenyl)ethylbromide (**3**)*

To a solution of **2** (6.30 g, 30 mmol) in CH$_2$Cl$_2$, 6.0 ml (45 mmol) of triethylamine were added. The solution was cooled to 0°C and 3.69 ml (45 mmol) of methanesulfonyl chloride (MsCl) were added dropwise via a syringe for 10 min. The reaction mixture was stirred for 1 h at this temperature and then quenched with water. The aqueous layer was extracted with CH$_2$Cl$_2$ (2 × 50 ml) and the combined organic phases were dried over anhydrous MgSO$_4$. Filtration followed by evaporation gave a red-orange oil product, which was then dissolved in 10 ml of acetone. This solution was slowly transferred via a cannula to a solution of LiBr (13 g, 150 mmol) in 100 ml of acetone at r.t. The yellow solution became a milky suspension after stirring

Table 4
^{13}C-NMR methyl sequence distributions of polypropylenes obtained with **5a**, **5b** and **6**[a]

Cat.	T_p (°C)	mmmm	mmmr	rmmr	mmrr	rmrr+mmrm	mrmr	rrrr	rrrm	mrrm	mm	mr	rr	r
5a	25	0.00	0.00	0.01	0.04	0.12	0.00	0.64	0.14	0.05	0.01	0.16	0.83	0.91
	50	0.00	0.00	0.02	0.11	0.20	0.09	0.28	0.24	0.06	0.02	0.40	0.58	0.78
	70	0.00	0.02	0.06	0.16	0.23	0.13	0.14	0.22	0.04	0.08	0.52	0.40	0.66
5b	25	0.00	0.02	0.08	0.17	0.29	0.14	0.11	0.15	0.04	0.10	0.60	0.30	0.60
	50	0.00	0.01	0.06	0.17	0.27	0.14	0.12	0.18	0.05	0.07	0.58	0.35	0.64
	70	0.00	0.01	0.05	0.14	0.24	0.13	0.14	0.20	0.09	0.06	0.51	0.43	0.68
6	25	0.00	0.00	0.01	0.02	0.04	0.02	0.80	0.05	0.06	0.01	0.08	0.91	0.95
	50	0.00	0.00	0.02	0.04	0.11	0.03	0.61	0.11	0.08	0.02	0.18	0.80	0.89
	70	0.00	0.00	0.01	0.07	0.19	0.03	0.45	0.18	0.07	0.01	0.29	0.70	0.84

[a] Triad and dyad fractions were calculated from the corresponding pentad distribution.

for 1 day. The mixture was evaporated and 100 ml of Et_2O were poured onto the resulting residue. The resulting mixture was washed with water and the organic layer was recovered. The aqueous layer was then extraced with Et_2O (2 × 50 ml) and the combined organic portions were dried, filtered and evaporated. The oily crude product was purified by column chromatography (eluent: hexane) to afford a colorless oil. Crystallization of the oil product in pentane at −40°C gave 7.4 g of **3** as a colorless needle (90%). M.p. = 52°C. ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.2–7.7 (m, 8H), 4.16 (t, $J = 6.1$ Hz, 1H), 3.30 (t, $J = 7.7$ Hz, 2H), 2.45–2.56 (m, 2H). ^{13}C-NMR (50.32 MHz, $CDCl_3$): δ 145.58, 140.85, 127.23, 126.97, 124.15, 119.90, 46.12, 36.41, 30.36. EI-MS: m/z (relative intensity) 274 and 272 (M^+, 79 each), 165 (M^+-C_2H_4Br, 100). Anal. Calc. for $C_{15}H_{13}Br$: C, 65.95; H, 4.79. Found: C, 66.24; H, 4.84.

3.4. 1-(9-Fluorenyl)-2-cyclopentadienylethane (4a)

Compound **3** (3.82 g, 14 mmol) was dissolved in 30 ml of DMF and cooled to −60°C. To which a solution of lithium cyclopentadienylide (LiCp, 1.11 g, 15.4 mmol) in 10 ml of DMF was added dropwise for 1 h. While warming to r.t., the reaction mixture was stirred for 6 h and then quenched with 30 ml of a saturated aqueous solution of NH_4Cl. The mixture was extracted with Et_2O (3 × 30 ml), and the organic phases were dried, filtered and evaporated. Purification by column chromatography (eluent: hexane) afforded 3.07 g of **4a** as a colorless oil (85%). (The ^{1}H-NMR and ^{13}C-NMR spectra were complicated by the 1:1 mixture of double bond isomers in the cyclopentadienyl ring. The ligand was further confirmed by spectral data of the corresponding zirconocene compound **5a**.) ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.9–7.4 (m, 8H), 6.5–6.1 (m, 3H), 4.16 (m, 1H), 3.03 (d, 1H), 2.91 (d, 1H), 2.46–2.33 (m, 4H). EI-MS: m/z (relative intensity) 258 (M^+, 54), 179 (M^+-CH_2Cp, 82), 178 (M^+-CH_3Cp, 100), 165 (M^+-C_2H_4Cp, 93). HR EI-MS: m/z calc. for $C_{20}H_{18}$ 258.1409. Found 258.1404.

3.5. 1-(9-Fluorenyl)-2-tetramethylcyclopentadienylethane (4b)

Treating 3.27 g (12 mmol) of **3** with lithium tetramethylcyclopentadienylide (LiCp′ = LitmCp, 1.65 g, 13.2 mmol) in a similar method to that described above, a sticky colorless oil was obtained. Further crystallization in pentane at −20°C gave 3.01 g of **4b** as a white powder (80%). (The clean ^{1}H- and ^{13}C-NMR spectra were not observed due to the serious double bond isomerizations in tmCp group. As above, the ligand nature was also confirmed by that of the corresponding zirconocene compound, **5b**.) M.p. = 112°C. ^{1}H-NMR (200.13 MHz, $CDCl_3$): δ 7.8–7.2 (m, 8H), 3.89 (m, 1H), 2.42 (m, 1H), 1.76–1.50 (br, m, 13H), 1.08–0.77 (br, m, 3H). EI-MS: m/z (relative intensity) 314 (M^+, 55), 178 (M^+-CH_3tmCp, 100), 165 (M^+-C_2H_4tmCp, 63), 136 (CH_3tmCp$^+$ = $C_5Me_5H^+$, 68). HR EI-MS: m/z calc. for $C_{24}H_{26}$ 314.2035. Found 314.2035.

3.6. [1-(η^5-Fluorenyl-2-(η^5-cyclopentadienyl)-ethane]zirconium dichloride (5a)

A solution of a ligand precursor, **4a** (1.81 g, 7 mmol) in 30 ml of Et_2O was treated with two equivalents of n-butyllithium (14 mmol, 2.5 M solution in hexane) at 0°C. Warming to r.t., the reaction mixture was stirred for 6 h. The resulting orange slurry was then rapidly transferred into a precooled flask containing a pentane slurry of one equivalent of $ZrCl_4$ (1.63 g, 7 mmol) at −78°C. Vigorous stirring continued for at least 1 h under the cooled bath. After slow warming to r.t. for 6 h, the suspension was stirred for a further 2 h at ambient temperature. The supernatant over the precipitate was then decanted. The orange powder was washed with pentane three times and dried in vacuo. Extraction with CH_2Cl_2 and filtration through a celite pad afforded a red solution. Concentration followed by cooling to −40°C gave 2.63 g of a red-orange crystal of **5a** (90%). A single crystal of **5a** for X-ray diffraction studies was obtained by recrystallization from a toluene solution at −20°C. ^{1}H-NMR (300.13 MHz, $CDCl_3$): 0 7.3–8.0 (m, 8H), 6.22 (m, 2H), 5.99 (m, 2H), 3.83–3.88 (m, 2H), 3.58–3.63 (m, 2H). ^{13}C-NMR (75.1 MHz, $CDCl_3$): δ 137.86, 128.90, 126.11, 125.64, 124.86, 123.93, 121.09, 119.25, 108.50, 102.48, 30.35, 29.27. EI-MS: m/z (relative intensity) 418 (M^+, 89), 178 (100). Anal. Calc. for $C_{20}H_{16}Cl_2Zr$: C, 57.40; H, 3.85. Found: C, 57.56; H, 3.88.

Table 5
Positional and equivalent isotropic thermal parameters[a] for non-hydrogen atoms of Et(Flu)(Cp)$ZrCl_2$ (**5a**)

Atom	x	y	z	U_{eq} [b]($Å^2$)
Zr1	0.47602(4)	−0.25809(3)	0.46523(3)	0.0393(2)
C1	10.5472(2)	−0.31790(11)	0.59004(9)	0.0688(5)
Cl2	0.31149(13)	−0.32557(12)	0.46830(12)	0.0701(5)
C1	0.5734(4)	−0.2466(4)	0.3455(3)	0.0384(12)
C2	0.6359(4)	−0.3021(4)	0.3955(3)	0.0378(12)
C3	0.5868(4)	−0.3842(4)	0.4028(3)	0.0412(13)
C4	0.4959(4)	−0.3823(4)	0.3532(3)	0.0397(12)
C5	0.4890(4)	−0.2986(4)	0.3166(3)	0.0376(12)
C6	0.4065(5)	−0.2810(4)	0.2620(3)	0.0506(15)
C7	0.3381(5)	−0.3437(5)	0.2446(4)	0.060(2)
C8	0.3449(5)	−0.4258(5)	0.2795(4)	0.061(2)
C9	0.4220(5)	−0.4464(4)	0.3333(4)	0.0512(15)
C10	0.7310(5)	−0.2887(4)	0.4355(3)	0.0495(14)
C11	0.7724(5)	−0.3572(5)	0.4799(4)	0.061(2)
C12	0.7235(5)	−0.4363(4)	0.4874(4)	0.058(2)
C13	0.6322(5)	−0.4512(4)	0.4497(3)	0.0506(15)
C14	0.6002(5)	−0.1579(4)	0.3158(3)	0.0507(15)
C15	0.5224(7)	−0.0916(5)	0.3353(5)	0.082(2)
C16	0.4868(6)	−0.1056(4)	0.4196(4)	0.063(2)
C17	0.3874(6)	−0.1193(5)	0.4371(5)	0.075(2)
C18	0.3825(8)	−0.1325(5)	0.5196(6)	0.087(3)
C19	0.4756(10)	−0.1265(5)	0.5523(4)	0.087(3)
C20	0.5426(6)	−0.1105(4)	0.4913(5)	0.072(2)
Zr2	0.00085(4)	0.03011(3)	0.27494(3)	0.0355(2)
Cl3	−0.0311(2)	0.12167(10)	0.29986(10)	0.0684(5)
Cl4	−0.12970(12)	−0.08263(13)	0.35960(9)	0.0647(5)
C21	0.1663(5)	−0.0932(5)	0.2706(3)	0.057(2)
C22	0.1265(5)	−0.1351(4)	0.3394(3)	0.054(2)
C23	0.1199(4)	−0.0735(4)	0.4023(3)	0.0448(14)
C24	0.1603(4)	0.0077(4)	0.3747(3)	0.0417(13)
C25	0.1907(4)	−0.0069(5)	0.2948(3)	0.052(2)
C26	0.2361(6)	0.0632(6)	0.2548(4)	0.079(2)
C27	0.2521(7)	0.1390(7)	0.2930(5)	0.097(3)
C28	0.2218(6)	0.1531(5)	0.3717(4)	0.077(2)
C29	0.1772(5)	0.0872(4)	0.4126(3)	0.057(2)
C30	0.0922(7)	−0.2209(4)	0.3520(4)	0.075(2)
C31	0.0566(8)	−0.2416(5)	0.4249(5)	0.086(3)
C32	0.0518(6)	−0.1811(5)	0.4878(4)	0.068(2)
C33	0.0829(5)	−0.0978(4)	0.4772(3)	0.053(2)
C34	0.1954(6)	−0.1391(7)	0.1946(4)	0.092(3)
C35	0.1392(6)	−0.1139(8)	0.1248(5)	0.106(4)
C36	0.0344(5)	−0.0841(6)	0.1382(3)	0.062(2)
C37	−0.0468(5)	−0.1340(4)	0.1657(4)	0.055(2)
C38	−0.1292(5)	−0.0780(5)	0.1703(4)	0.056(2)
C39	−0.1004(6)	0.0047(5)	0.1483(4)	0.064(2)
C40	0.0005(6)	−0.0004(5)	0.1291(4)	0.068(2)

[a] Units of each estimated S.D. in parentheses are those of the least significant digit of the corresponding parameters.

[b] The isotropic equivalent thermal parameter is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 6
Positional and equivalent isotropic thermal parameters[a] for non-hydrogen atoms of Et(Flu)(tmCp)$ZrCl_2$ (**5b**)

Atom	x	y	z	U_{eq} ($Å^2$)
Zr1	0.57838(4)	−0.17701(3)	0.25215(2)	0.02661(10)
Cl1	0.46719(12)	0.00140(10)	0.20549(7)	0.0459(2)
Cl2	0.33747(10)	−0.31628(9)	0.33169(6)	0.0413(2)
C1	0.8950(4)	−0.0930(4)	0.3196(3)	0.0363(7)
C2	0.8890(4)	0.0518(3)	0.3276(2)	0.0331(7)
C3	0.7952(4)	0.0685(3)	0.4031(2)	0.0307(6)
C4	0.7497(4)	−0.0637(3)	0.4471(2)	0.0309(6)
C5	0.8159(4)	−0.1593(3)	0.3978(2)	0.0335(7)
C6	0.7950(5)	−0.2952(4)	0.4311(3)	0.0506(10)
C7	0.7131(6)	−0.3294(4)	0.5080(3)	0.0604(12)
C8	0.6484(5)	−0.2346(5)	0.5563(3)	0.0568(11)
C9	0.6668(4)	−0.1026(4)	0.5276(3)	0.0416(8)
C10	0.9570(5)	0.1721(4)	0.2763(3)	0.0462(8)
C11	0.9329(5)	0.2994(4)	0.3017(3)	0.0568(10)
C12	0.8432(5)	0.3159(4)	0.3766(3)	0.0529(10)
C13	0.7744(5)	0.2030(4)	0.4273(3)	0.0410(8)
C14	1.0009(5)	−0.1466(5)	0.2582(3)	0.0520(10)
C15	0.8833(5)	−0.3013(5)	0.1867(3)	0.0537(10)
C16	0.6960(4)	−0.3217(4)	0.1466(2)	0.0376(7)
C17	0.5346(4)	−0.4341(4)	0.1625(2)	0.0362(7)
C18	0.3897(4)	−0.4144(4)	0.1113(2)	0.0351(7)
C19	0.4593(4)	−0.2922(4)	0.0634(2)	0.0372(7)
C20	0.6493(5)	−0.2312(4)	0.0859(2)	0.0400(8)
C21	0.7734(6)	−0.1094(5)	0.0417(3)	0.0596(11)
C22	0.3494(6)	−0.2450(5)	−0.0072(3)	0.0542(10)
C23	0.1943(5)	−0.5177(4)	0.1003(3)	0.0495(9)
C24	0.5111(6)	−0.5623(4)	0.2166(3)	0.0544(10)

[a] Units of each estimated S.D. in parentheses are those of the least significant digit of the corresponding parameters.

[b] The isotropic equivalent thermal parameter is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

3.7. *[1-(η⁵-Fluorenyl)-2-(η⁵-tetramethylcyclopentadienyl)ethane]zirconium dichloride (**5b**)*

Following the procedure described above with a ligand precursor, **4b** (2.83 g, 9 mmol) and $ZrCl_4$ (2.1 g, 9 mmol), the orange powder was obtained. Extraction, filtration and drying afforded a sticky solid, which was then solidified by rapid washing with 10 ml of cold toluene. Drying in vacuo gave 1.25 g of an orange crystal of **5b** (30%). A single crystal was obtained by recrystallization from a toluene solution at −20°C. ^{1}H-NMR (300.13 MHz, $CDCl_3$): 0 7.3–7.9 (m, 8H), 4.04–4.09 (m, 2H), 3.60–3.66 (m, 2H), 2.02 (s, 6H), 1.81 (s, 6H). ^{13}C-NMR (75.1 MHz, $CDCl_3$): δ 130.63, 128.76, 127.84, 126.6O, 124.79, 124.73, 123.43, 123.10, 122.33, 102.73, 29.47, 28.05, 12.82, 12.06. EI-MS: *m*/*z* (relative intensity) 474 (M^+, 59), 294 (100). Anal. Calc. for $C_{24}H_{24}Cl_2Zr$: C, 60.74; H, 5.10. Found: C, 60.75; H, 5.26.

3.8. Polymerizations

Into a well degassed 500 ml-glass reactor, 150 ml of toluene were placed. The temperature was adjusted to a constant (25, 50, 70, 90°C each) using a waterbath thermostat, and propylene was saturated at 1.2 atm with vigorous stirring. A toluene solution of MAO (10 ml, 20 mmol) was syringed into the reactor and then a toluene solution of 10 μmol of catalyst was immediately added. The polymerization was monitored by measuring the rate of monomer consumption using a hot-wire flowmeter (Sierra Instrument model 820) connected to a computer containing an A/D converter. After 1 h, all the reactions were quenched by the addition of methanol. The resulting polymer was precipitated by adding a MeOH/HCl solution. Filtration, washing with MeOH/HCl followed by EtOH washing and then overnight vacuum drying afforded polypropylenes. A viscous oily polymer was obtained by vacuum drying after evaporation of toluene. Catalytic activity was calculated by comparing the rate of monomer consumption with the amount of polymer obtained ($\pm 5\%$ error).

3.9. X-ray structure determination of **5a** and **5b**

An air stable single crystal of red-orange Et-(Flu)(Cp)$ZrCl_2$, **5a** (an orange single crystal of Et-(Flu)(tmCp)$ZrCl_2$, **5b**) was mounted on a glass capillary. The measurements of diffraction intensity were carried out on an Enraf-Nonius CAD-4 diffractometer using graphite-monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å). Accurate unit cell parameters and orientation matrix were determined from the least-squares fit of 25 accurately centered reflections in the range of $20° < 2\theta < 31°$ ($19° < 2\theta < 34°$). Intensity data were collected by using ω-2θ scan mode with a range of $2° < \theta < 25°$ ($2° < \theta < 25°$). Of the resulting 5209 (3338) reflections, 4375 (3066) were considered as observed ($I > 2\sigma(I)$) and used in subsequent structural analysis. All the intensity data were corrected for Lorentz and polarization effects. The structure was solved by Semi-invarient direct method (SIR '92 in MolEN) [30] and refined by full-matrix least-squares calculations (SHELXL '93) [31] with anisotropic thermal parameters for all non-hydrogen atoms. All hydrogen atoms were placed at their calculated positions derived from connected carbon atoms, and their temperature factors were refined isotropically (d(C–H) = 0.93 Å, $1.2 \times U_{eq}$(C) for **CH**, d(C–H) = 0.97 Å, $1.2 \times U_{eq}$(C) for **CH**$_2$, d(C–H) = 0.96 Å, $1.5 \times U_{eq}$(C) for **CH**$_3$). The final refinement converged at $R_1 = 0.0481$ (0.0308), $wR_2 = 0.1171$ (0.0782) and gooness-of-fit = 1.185 (1.061). The atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Tables 5 and 6.

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References

[1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem. 34 (1995) 1143. (b) A.A. Andersen, H.G. Cordes, J. Herwig, W. Kaminsky, A. Merck, R. Mottweiler, J. Pein, H. Sinn, H.J. Vollmer, Angew. Chem. 88 (1976) 689; Angew. Chem. Int. Ed. Engl. 15 (1976) 630. (c) H. Sinn, W. Kaminsky, Adv. Organomet. Chem. 18 (1980) 99. (d) L. Resconi, S. Bossi, Macromolecules 23 (1990) 4489. (e) C.J. Harlan, S.G. Bott, A.R. Barron, J. Am. Chem. Soc. 117 (1995) 6465.

[2] P. Pino, R. Mülhaupt, Angew. Chem. Int. Ed. Engl. 19 (1980) 857.

[3] J.A. Ewen, R.L. Jones, A. Razavi, J.D. Ferrara, J. Am. Chem. Soc. 110 (1988) 6255.

[4] (a) A. Zarnbelli, G. Allegra, Macromolecules 13 (1980) 42. (b) A. Zarnbelli, P. Locatelli, A. Provasoli, D.R. Ferro, Macromolecules 13 (1980) 267. (c) A. Zambelli, P. Locatelli, G. Zannoni, F.A. Bovey, Macromolecules 11 (1978) 923. (d) Y. Doi, S. Suzuki, K. Soga, Macromolecules 19 (1986) 2869.

[5] J.A. Ewen, M.J. Elder, R.L. Jones, S. Curtis, H.N. Cheng, Stud. Sur. Sci. Catal. 56 (1990) 439.

[6] (a) J.A. Ewen, J. Am. Chem. Soc. 106 (1984) 6355. (b) Y. Doi, T. Asakuru, Makromol. Chem. 176 (1975) 507. (c) Y. Doi, E. Suzuki, T. Keii, Makromol. Chem. Rapid. Commun. 2 (1981) 293. (d) R.A. Sheldon, T. Fueno, T. Tsunetsugu, J. Furukawa, J. Polym. Sci. B. 3 (1965) 23. (e) J.A. Ewen, Stud. Sur. Sci. Catal. 25 (1986) 271.

[7] Y.X. Chen, M.D. Rausch, J.C.W. Chien, J. Organomet. Chem. 497 (1995) 1.

[8] (a) R. Fierro, Z. Yu, M.D. Rausch, S. Dong, D. Alvares, J.C.W. Chien, J. Polym. Sci. A. 32 (1994) 661. (b) R. Fierro, M.D. Rausch, G.S. Herrrnan, H.G. Alt, J. Organomet. Chem. 485 (1995) 11.

[9] (a) J.A. Ewen, M.J. Elder, R.L. Jones, L. Haspeslagh, J.L. Atwood, Makromol. Chem. Macromol. Symp. 48/49 (1991) 253. (b) T.A. Herzog, W.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988. (c) M. Antberg, V. Dolle, R. Klein, J. Rohrmann, A. Winter, W. Spaleck, Stud. Sur. Sci. Catal. 56 (1990) 501.

[10] (a) K. Patsidis, S.J. Palackal, H.G. Alt, Eur. Pat. Appl., 512554 A2, 1992. (b) H.G. Alt, S.J. Palackal, K. Patsidis, M.B. Welch, R.L. Geerts, E.T. Hsieh, M.P. McDaniel, G.R. Hawley, P.D. Smith, Can. Pat. Appl. 2067525, 1992 (to Phillips Pet. Co.). (c) A. Razavi, D. Vereecke, L. Peters, D.V. Hessche, K. Den Dauw, L. Nafphiotis, Y. de Froimont, SPO 1993, p. 105. (d) A. Razavi, L. Peters, L. Nafpliotis, J. Mol. Cat. A: Chemical. 115 (1997) 129.

[11] B. Rieger, G. Jany, R. Fawzi, M. Steimann, Organometallics 13 (1994) 647.

[12] (a) F.E. Ziegler, S.I. Klein, U.K. Pati, T.F. Wang, J. Am. Chem. Soc. 107 (1985) 2730. (b) K.U. Ingold, J.C. Walton, J. Am. Chem. Soc. 109 (1987) 6937.

[13] (a) T. Kauffmann, A. Olbrich, J. Varenhort, Chem. Ber. 115 (1982) 467. (b) T. Kauffmann, M. Bisling, R. Köning, A. Rensing, F. Steinseifer, Chem. Ber. 118 (1985) 4517.

[14] (a) A. Razavi, J. Ferrara, J. Organomet. Chem. 435 (1992) 299. (b) H.G. Alt, W. Milius, J. Organomet. Chem. 472 (1994) 113.

[15] (a) F.R.W.P. Wild, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 232 (1982) 233. (b) F.R.W.P. Wild, M. Wasiucionek, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 288 (1985) 63. (c) A. Schäfer, E. Karl, L. Zsolnai, G. Huttner, H.H. Brintzinger, J. Organomet. Chem. 328 (1987) 87. (d) F. Piemontesi, I. Camurati, L. Resconi, D. Balboni et al., Organometallics 14 (1995) 1256.

[16] (a) A. Razavi, J.L. Atwood, J. Organomet. Chem. 459 (1993) 117. (b) A. Razavi, J. Atwood, J. Organomet. Chem. 491 (1995) 105.

[17] Ring slippage: distance between perpendicular projection of the metal atom on the ring L. S. plane and ring centroid. (a) J.W. Faller, R.H. Crabtree, A. Habib, Organometallics 4 (1985) 929. (b) R.N. Biagioni, I.M. Lorkovic, J. Skelton, J.B. Hartung, Organometallics 9 (1990) 547.

[18] W. Kaminsky, R. Engehausen, K. Zoumis, W. Spaleck, J. Rohrmann, Makromol. Chem. 193 (1992) 1643.

[19] (a) B. Rieger, X. Mu, D. Mallin, M.D. Rausch, J.C.W. Chien, Macromolecules 23 (1990) 3559. (b) J.C.W. Chien, R.J. Sugimoto, Polym. Sci. A: Polym. Chem. 29 (1991) 459. (c) B.J. Rieger, Organomet. Chem. 428 (1992) C33.

[20] (a) W. Kaminsky, M. Miri, H. Sinn, R. Woldt, Makromol. Chem. Rapid. Commun. 4 (1983) 417. (b) T. Tsutsui, N. Ishimaru, A. Mizuno, A. Toyota, N. Kashiwa, Polymer 30 (1989) 1350. (c) S. Miya, T. Mise, H. Yamazaki, Stud. Sur. Sci. Catal. 56 (1990) 531. (d) W. Kaminsky, K. Kulper, H.H. Brintzinger, F.R.W.P. Wild, Angew. Chem. Int. Ed. Engl. 24 (1985) 507. (e) W. Röll, H.H. Brintzinger, B. Rieger, R. Zolk, Angew. Chem. Int. Ed. Engl. 29 (1990) 279. (f) U. Stehling, J. Diebold, R. Kirsten, W. Röll, H.H. Brintzinger, S. Jüngling, R. Mülhaupt, F. Langhauser, Organometallics 13 (1994) 964.

[21] L. Resconi, R.L. Jones, A.L. Rheingold, G.P.L. Yap, Organometallics 15 (1996) 998.

[22] L. Resconi, F. Piemontesi, G. Franciscono, L. Abis, T. Fiorani, J. Am. Chem. Soc. 114 (1992) 1025.

[23] (a) M. Brookhart, L.H. Green, J. Organomet. Chem. 250 (1983) 395. (b) L.A. Castonguay, A.K. Rappé, J. Am. Chem. Soc. 114 (1992) 5832. (c) J.R. Hart, A.K. Rappé, J. Am. Chem. Soc. 115 (1993) 6159. (d) T.K. Woo, L. Fan, T. Ziegler, Organometallics 13 (1994) 2252. (e) H. Weiss, M. Ehrig, R. Ahlrichs, J. Am. Chem. Soc. 1994,116, 4919. (f) Meier, R. J.; van Doremaele, G. H. J.; Iarlori, S.; Buda, F. J. Am. Chem. Soc. 1994, 116, 7274. (g) Fan, L.; Harrison, D.; Woo, T. K.; Ziegler, T. Organometallics 14 (1995) 2018.

[24] A. Grassi, A. Zambelli, L. Resconi, E. Albizzati, R. Mazzocchi, Macromolecules 21 (1988) 617.

[25] T. Tsutsui, A. Mizuno, N. Kashiwa, Polymer 30 (1989) 428.

[26] (a) T. Tsutsui, A. Mizuno, N. Kashiwa, Makromol. Chem. 190 (1989) 1177. (b) T. Asakura, N. Nakayama, M. Demura, A. Asano, Macromolecules 25 (1992) 4876.

[27] T. Mise, A. Kageyama, S. Miya, H. Yamazaki, Chem. Lett. (1991) 1525.

[28] (a) J.C.W. Chien, A. Razavi, J. Polym. Sci. A: Polym. Chem. 26 (1988) 2369. (b) J.C.W. Chien, B.P. Wang, J. Polym. Sci. A: Polym. Chem. 26 (1988) 3089. (c) J.C.W. Chien, B.P. Wang, J. Polym. Sci. A: Polym. Chem. 28 (1990) 15. (d) L. Resconi, S. Bossi, L. Abis, Macromolecules 23 (1990) 4489.

[29] T.W. Greene, P.G.M. Wuts, Protective Groups in Organic Synthesis, Wiley, New York, 1991.

[30] MolEN, An interactive structure solution program; Enraf-Nonius: Delft, Netherlands, 1994.

[31] G.M. Sheldrick, SHELXL ‘93. Program for Crystal Structure Determination, University of Göttingen, Germany, 1993.