

## Synthesis, structure, and catalytic properties of *ansa*-zirconocenes, $\text{Me}_2\text{X}(\text{Cp})(\text{RInd})\text{ZrCl}_2$ ( $\text{X} = \text{C}, \text{Si}$ ; $\text{R} = 2\text{-}p\text{-}$ or $3\text{-}p\text{-}$ tolyl)

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### Abstract

*ansa*-Zirconocenes,  $\text{Me}_2\text{X}(\text{Cp})(3\text{-TolInd})\text{ZrCl}_2$  [ $\text{X} = \text{C}$  (**7**),  $\text{Si}$  (**8**);  $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ;  $\text{Tol} = p\text{-C}_6\text{H}_4\text{CH}_3$ ] and  $\text{Me}_2\text{Si}(\text{Cp})(2\text{-TolInd})\text{ZrCl}_2$  (**9**), have been prepared by the reactions of  $\text{ZrCl}_4$  with the corresponding dilithiated ligands in diethyl ether at  $-78^\circ\text{C}$ . The molecular structure of complex **9** has been determined by a single crystal X-ray diffraction study. Propylene polymerization has been studied for complexes **7**, **8** and **9** in the presence of methylaluminoxane (MAO). Complex **9** reveals the highest catalytic activity of 1570 kg PP/(mol Zr h atm) and the highest molecular weight of  $1.2 \times 10^6$  among the three catalysts. Complex **9** produces atactic polypropylene (PP), whereas **7** and **8** afford PP with a weak syndiotacticity at low temperature.

**Keywords:** *ansa*-Zirconocenes; Tolyindene; Propylene polymerization

### 1. Introduction

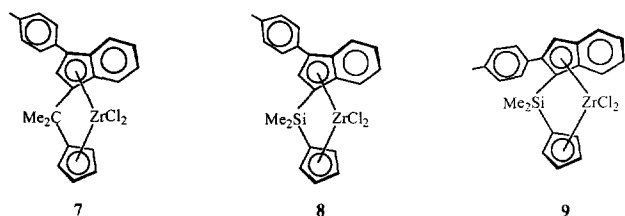
Chiral *ansa*-metallocene complexes have been extensively employed as homogeneous catalyst precursors for the highly isospecific ( $\text{C}_2$ -symmetric complex) [1,2] and syndiospecific ( $\text{C}_6$ -symmetric complex) [3–6] polymerizations of propylene. The presence of a bridging group restricts the mobility of the *ansa*-metallocene onto the growing polymer chain in an enantiomorphic site controlled process. Much of the work in the area has been concerned with how chiral, steric, and electronic properties of *ansa*-metallocenes influence the catalytic characteristics and stereoregulating ability of these catalysts by both experimental and theoretical studies. Electronic effects of bis(indenyl) catalysts, such as  $(\eta^5\text{-4,7-R}_2\text{Ind})_2\text{ZrX}_2$  and  $(\eta^5\text{-5,6-R}_2\text{Ind})_2\text{ZrCl}_2$ , have been investigated by Consiglio and coworkers [7] and Collins and coworkers [8] respectively. Spaleck et al. [2] reported that  $\text{Me}_2\text{Si}(\eta^5\text{-2,4-R}_2\text{Ind})_2\text{ZrCl}_2$ , with 2-methyl and 4-aromatic groups substituted, is a new optimized metallocene catalyst for isospecific propylene polymerization. They explained that both steric and elec-

tronic effects play an important role for the high stereospecificities and high molecular weights of the polymers. Recently, Morokuma and coworkers [9] pointed out that substituents at the 2- and 4-positions of the indenyl-based catalysts are very important to attain good stereoregulation based on combined ab initio MO–MM studies.

A highly syndiotactic  $\text{Me}_2\text{C}(\text{Cp})(\text{Flu})\text{ZrCl}_2$  (**1**, Flu = fluorenyl) catalyst [3] has been discovered by Ewen et al. Later, Rappé and coworker [10] reported molecular mechanics (MM) results which explain that, in Ewen's catalyst, the propylene coordination occurs in the same conformation (i.e. Me up or down) at alternating prochiral faces to yield syndiotactic polypropylene. In this work we wanted to utilize the previous information for syndiotactic polypropylene polymerization and try to prepare new *ansa*-metallocene complexes **7–9**. Three complexes would be sterically very similar to catalyst **1** with respect to coordination and insertion processes of propylene at the metal center, for one of the six-membered rings of the fluorenyl ligand of **1** is replaced by a *p*-tolyl (Tol) group at 2- or 3-position of the indenyl ligand (Ind). Reported herein are the synthesis of **7–9** and a structural characterization of **9** together with the

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result of propylene polymerization with 7–9/MAO (methylaluminoxane) catalyst systems.



## 2. Experimental section

### 2.1. General comments

All reactions were carried out under an inert atmosphere of argon by using either standard Schlenk or glovebox techniques. Tetrahydrofuran (THF), diethyl ether, hexane, and toluene were distilled from sodium–benzophenone under  $N_2$  atmosphere. Dichloromethane was refluxed over  $CaH_2$  and then distilled under  $N_2$  atmosphere. Silica gel (Merck, 230–400 mesh) was used for column chromatography.  $^1H$  NMR and  $^{13}C$  NMR spectra were obtained with either a Bruker AC-200 or AM-300 FT NMR spectrometer. Mass spectra were recorded on a JEOL HX 100/HX 110 spectrometer. All  $m/z$  values are referenced to  $^{35}Cl$  and  $^{90}Zr$ .

The intrinsic viscosity  $[\eta]$  of the polymer in decalin was determined using a modified Ubbelohde viscosimeter at  $135 \pm 0.1^\circ C$  [11]. Viscosity average molecular weights ( $\bar{M}_v$ ) of polymers were calculated from the Mark–Houwink equation,  $[\eta] = 1.0 \times 10^{-4} \bar{M}_v^{0.80}$  (PP).  $^{13}C$  NMR (75 MHz) spectra of the resulting polymers were recorded at  $100^\circ C$  on a Bruker AMX-300 FT NMR spectrometer. The samples were dissolved in 1,2,4-trichlorobenzene/benzene- $d_6$  (4:1 by volume) up to a concentration of 15 wt.% at  $130^\circ C$  in NMR tubes (10 mm o.d.).

### 2.2. Preparation of 1-p-tolyindene (2)

In a 500 ml three-necked flask with a reflux condenser, dry magnesium turnings (1.48 g, 61 mmol) were suspended in diethyl ether (30 ml). To this suspension were added 2–3 drops of 1,2-dibromoethane and 4-bromotoluene (7.00 ml, 57 mmol) in diethyl ether (10 ml). After 1 h, the dark green solution was transferred to a 500 ml Schlenk flask and the solvent was evaporated. The residue was dissolved in THF (30 ml). 1-Indanone (5.00 g, 38 mmol) in THF (20 ml) was added to a solution of 4-tolylmagnesium bromide in THF at  $0^\circ C$  over a 20 min period followed by the addition of

hexamethylphosphoramide (HMPA) (10 ml, 41.8 mmol). The reaction mixture was stirred at room temperature for 20 h, quenched with 15% aqueous hydrochloric acid solution (30 ml) at  $0^\circ C$ , and stirred for an additional 20 h period at room temperature to complete the dehydration of an intermediate alcohol. The solution was extracted with diethyl ether and dried over anhydrous magnesium sulfate. The crude product was purified with column chromatography over silica gel with a hexane eluent to afford **2** (6.00 g, 76%) as a colorless oil.  $^1H$  NMR ( $CDCl_3$ ,  $25^\circ C$ ):  $\delta$  7.70–7.28 (8H, m,  $C_6$  indenyl and tolyl), 6.57 (1H, t,  $J = 2.1$  Hz,  $C_5$  indenyl), 3.52 (2H, d,  $J = 2.1$  Hz,  $C_5$  indenyl), 2.45 (3H, s, tolyl  $CH_3$ ).

### 2.3. Preparation of 2-p-tolyindene (3)

Magnesium turnings (1.77 g, 72.64 mmol), 4-bromotoluene (8.41 ml, 68.1 mmol), HMPA (11.85 ml, 68.1 mmol), and 2-indanone (6.00 g, 45 mmol) were treated as described for the preparation of **2**, affording **3** (1.27 g, 29%) as a white solid.  $^1H$  NMR ( $CDCl_3$ ,  $25^\circ C$ ):  $\delta$  7.56–7.14 (9H, m, indenyl and tolyl), 3.77 (2H, s,  $C_5$  indenyl), 2.28 (3H, s, tolyl  $CH_3$ ).

### 2.4. Preparation of 2-(cyclopentadienyl)-2-(3-p-tolyl-indenyl)propane (4)

A solution of n-butyllithium (1.3 M, 6.17 ml, 8.03 mmol) in hexane was added to a solution of **2** (1.58 g, 7.64 mmol) in THF (60 ml) at  $-78^\circ C$ . The reaction mixture was allowed to warm to room temperature for 1.5 h. A THF (10 ml) solution of 6,6-dimethyl fulvene (0.89 g, 8.79 mmol) was added dropwise at room temperature. The resulting mixture was stirred overnight and then treated with a saturated solution of  $NH_4Cl$  in water (100 ml). The solution was extracted with diethyl ether and dried over anhydrous magnesium sulfate. The crude product was purified with column chromatography over silica gel with a hexane eluent to give two isomers of **4** (1.68 g, 71%) as a colorless oil.  $^1H$  NMR ( $CDCl_3$ ,  $25^\circ C$ ):  $\delta$  7.55–6.07 (12H, m,  $C_6$  indenyl and tolyl), 3.81 (1H, br s,  $C_5$  indenyl), 3.10 (2H, br s, cyclopentadienyl), 2.45 (3H, s, tolyl  $CH_3$ ), 1.36 (3H, s,  $C(CH_3)_2$ ), 1.12 (3H, s,  $C(CH_3)_2$ );  $\delta$  7.55–6.07 (12H, m,  $C_6$  indenyl and tolyl), 3.76 (1H, br s,  $C_5$  indenyl), 3.16 (2H, br s, cyclopentadienyl), 2.45 (3H, s, tolyl  $CH_3$ ), 1.40 (3H, s,  $C(CH_3)_2$ ), 1.09 (3H, s,  $C(CH_3)_2$ ) for an isomeric mixture.

### 2.5. Preparation of (cyclopentadienyl)(3-p-tolylindenyl)dimethylsilane (5)

To a solution of **2** (0.58 g, 2.8 mmol) in diethyl ether (30 ml) was added n-butyllithium (1.54 M, 2.0 ml,

3.08 mmol) in hexane at  $-78^{\circ}\text{C}$ . The resulting mixture was allowed to warm to room temperature for 2 h. After stirring for an additional 1 h, the reaction mixture was added to a solution of dichlorodimethylsilane (1.08 g, 8.37 mmol) in diethyl ether (20 ml). After stirring for 2 h, the solvent was evaporated to dryness and the resulting light orange oil was dissolved in THF (30 ml). To this light orange solution was added a solution of cyclopentadienyllithium (0.20 g, 2.8 mmol) in THF (10 ml) at  $0^{\circ}\text{C}$ . The resulting solution was gradually allowed to warm to room temperature and stirred overnight. The solvent was evaporated and the residue was dissolved in diethyl ether (30 ml). The resulting suspension was filtered and the filtrate was evaporated in vacuo to give the crude product which was purified with preparative TLC with a hexane eluent to give **5** (0.40 g, 44%) as a light green oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ):  $\delta$  7.70–7.24 (8H, m,  $\text{C}_6$  indenyl and tolyl), 6.70–6.20 (5H, m, cyclopentadienyl) 3.65 (1H, d,  $\text{C}_5$  indenyl), 2.42 (3H, s, tolyl  $\text{CH}_3$ ),  $-0.08$  (3H, s,  $\text{Si}(\text{CH}_3)_2$ ),  $-0.23$  (3H, s,  $\text{Si}(\text{CH}_3)_2$ ).

#### 2.6. Preparation of (cyclopentadienyl)(2-*p*-tolylindenyl)dimethylsilane (**6**)

Compound **2** (0.97 g, 4.72 mmol), *n*-butyllithium (1.56 M, 3.2 ml, 4.96 mmol) in hexane, dichlorodimethylsilane (1.83 g, 14.2 mmol), and cyclopentadienyllithium (0.34 g, 4.72 mmol) were treated by a procedure similar to that for the preparation of **5**, providing **6** (0.82 g, 53%) as a light green oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ):  $\delta$  7.53–7.13 (8H, m,  $\text{C}_6$  indenyl and tolyl), 6.58–6.14 (5H, m, cyclopentadienyl), 4.19 (1H, br s,  $\text{C}_5$  indenyl), 2.35 (3H, s, tolyl  $\text{CH}_3$ ),  $-0.40$  (3H, s,  $\text{Si}(\text{CH}_3)_2$ ),  $-0.46$  (3H, s,  $\text{Si}(\text{CH}_3)_2$ ).

#### 2.7. Preparation of isopropyl(cyclopentadienyl)(1-*p*-tolylindenyl)zirconium dichloride (**7**)

A solution of *n*-butyllithium (1.3 M, 3.2 ml, 4.1 mmol) in hexane was added to a diethyl ether solution (20 ml) of **4** (0.62 g, 1.99 mmol) at  $-78^{\circ}\text{C}$ . During warming to room temperature the solution changed from greenish yellow to a yellow suspension. After cooling to  $-78^{\circ}\text{C}$ , a suspension of zirconium tetrachloride (0.46 g, 1.99 mmol) in diethyl ether (20 ml) was added to the yellow suspension. Immediately after the addition the cooling bath was removed. The suspension was stirred overnight. The orange precipitate formed was filtered and washed with diethyl ether ( $3 \times 10$  ml). The orange solid was extracted with dichloromethane (20 ml) and the extract was evaporated to give **7** (0.34 g, 36%) as an orange solid.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ):  $\delta$  7.85–7.05 (8H, m,  $\text{C}_6$  indenyl and tolyl), 6.56 (1H, m, cyclopentadienyl), 6.51 (1H, m, cyclopentadienyl), 6.07 (1H, s,  $\text{C}_5$  indenyl), 5.93 (1H, m, cyclopentadienyl), 5.58 (1H, m,

cyclopentadienyl), 2.38 (3H, s, tolyl  $\text{CH}_3$ ), 2.23 (3H, s,  $\text{C}(\text{CH}_3)_2$ ), 1.95 (3H, s,  $\text{C}(\text{CH}_3)_2$ ). MS (70 eV):  $m/z$  435 ( $\text{M}^+ - \text{Cl}$ ).

#### 2.8. Preparation of dimethylsilylene(cyclopentadienyl)-(3-*p*-tolylindenyl)zirconium dichloride (**8**)

Compound **5** (1.33 g, 4.04 mmol), *n*-butyllithium (1.54 M, 5.38 ml, 8.29 mmol) and zirconium tetrachloride (0.94 g, 4.04 mmol) were treated as described for the preparation of **7**, providing **8** (1.00 g, 51%) as an orange solid.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ):  $\delta$  7.96–7.11 (8H, m,  $\text{C}_6$  indenyl and tolyl), 6.78 (2H, m, cyclopentadienyl), 6.74 (1H, s,  $\text{C}_5$  indenyl), 5.99 (1H, m, cyclopentadienyl), 5.87 (1H, m, cyclopentadienyl), 2.39 (3H, s, tolyl  $\text{CH}_3$ ), 1.08 (3H, s,  $\text{Si}(\text{CH}_3)_2$ ), 0.82 (3H, s,  $\text{Si}(\text{CH}_3)_2$ ). MS (70 eV):  $m/z$  488 ( $\text{M}^+$ ).

#### 2.9. Preparation of dimethylsilylene(cyclopentadienyl)-(2-*p*-tolylindenyl)zirconium dichloride (**9**)

Compound **6** (0.43 g, 1.29 mmol), *n*-butyllithium (1.54 M, 1.72 ml, 2.65 mmol) and zirconium tetrachloride (0.30 g, 1.29 mmol) were treated by a procedure similar to that for the synthesis of **7**, providing **9** (0.40 g, 64%) as an orange solid.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $25^{\circ}\text{C}$ ):  $\delta$  7.71–7.04 (9H, m, indenyl and tolyl), 6.89 (1H, m, cyclopentadienyl), 6.75 (1H, m, cyclopentadienyl), 5.87 (1H, m, cyclopentadienyl), 5.50 (1H, m, cyclopentadienyl), 2.40 (3H, s, tolyl  $\text{CH}_3$ ), 1.02 (3H, s,  $\text{Si}(\text{CH}_3)_2$ ), 0.51 (3H, s,  $\text{Si}(\text{CH}_3)_2$ ). MS (70 eV):  $m/z$  488 ( $\text{M}^+$ ).

#### 2.10. Crystal structure of **9**

Crystals of **9** suitable for an X-ray analysis were obtained by slow crystallization from dichloromethane at  $-20^{\circ}\text{C}$ . An orange crystal of the appropriate dimensions was sealed under  $\text{N}_2$  in a thin-walled glass capillary. Preliminary examination and data collection were performed using an Enraf–Nonius CAD4 diffractometer with graphite monochromated Mo  $\text{K}\alpha$  radiation at 298 K. Final lattice parameters were refined by least-squares refinement of 25 reflections in the range  $11.24^{\circ} < \theta < 21.40^{\circ}$ . Intensity data were collected using the  $\omega/2\theta$  scan mode,  $\omega$  scan angle =  $(0.8 + 0.35 \tan \theta)^{\circ}$ ,  $2\theta_{\text{max}} = 45^{\circ}$ . A series of psi scans monitored every 2 h indicated that no absorption correction was needed. Lorentz and polarization corrections were applied to the data. Crystallographic data and intensity data collection parameters are listed in Table 1. Calculations were carried out with the PC version of the NRCVAX program [12]. The structure was solved by direct and difference Fourier methods and refined by the full-matrix least-squares methods employing unit weights. All non-hydrogen atoms were refined with anisotropic ther-

Table 1  
Crystallographic data for complex **9**

formula	C <sub>23</sub> H <sub>22</sub> Cl <sub>2</sub> SiZr
fw	628.9
crystal system	monoclinic
space group	<i>P</i> 12 <sub>1</sub> / <i>n</i> 1
<i>a</i> (Å)	13.426(3)
<i>b</i> (Å)	11.341(2)
<i>c</i> (Å)	13.996(4)
$\beta$ (deg)	92.33(2)
<i>V</i> (Å <sup>3</sup> )	2129.3(9)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.455
temp. (K)	298
crystal size (mm <sup>3</sup> )	0.4 × 0.3 × 0.3
radiation	graphite-monochromated Mo K $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.82
scan mode	$\omega/2\theta$
$2\theta_{\max}$ (deg)	45
no. of unique reflections	2692
no. of reflections ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))	2494
no. of parameters	244
<i>R</i> <sup>a</sup>	0.072
<i>R</i> <sub>w</sub> <sup>b</sup>	0.083
GOF	4.10

<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / |F_o|$ .

<sup>b</sup>  $R_w = [\sum (|F_o| - |F_c|)^2 / \sum |F_o|^2]^{1/2}$ .

<sup>c</sup>  $GOF = [\sum (|F_o| - |F_c|)^2 / (\text{no. of reflections} - \text{no. of parameters})]^{1/2}$ .

mal parameters. Hydrogen atoms were placed in calculated positions. Refinement converged with  $R_f = 0.072$  and  $R_w = 0.083$ . The final residual values and structure refinement parameters are listed in Table 1. The atomic coordinates for the non-hydrogen atoms and selected bond distances and angles are listed in Tables 2 and 3 respectively.

### 2.11. Polymerization procedure

Solution polymerization reactions in toluene were carried out at a propylene pressure of 1.2 atm, agitating with a Teflon magnetic spinbar in a 500 ml glass reactor. Toluene (200 ml) was introduced into the reactor, the temperature was increased to the polymerization temperature, and then toluene was saturated with propylene. A toluene solution of the Zr catalyst and MAO was injected into the reactor by a tuberculin syringe, and polymerization was started. Propylene concentrations in the liquid phase were calculated with a computer program for the gas–liquid phase equilibria based on Chao–Sender correlations. After polymerization was terminated by injecting ethanol, the produced polymer was quenched by an excess of acidified methanol (ca. five times the amount of toluene used). The precipitated

Table 2  
Atomic coordinates and equivalent isotropic displacement coefficients ( $\text{\AA}^2 \times 10^3$ ) for **9**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> <sup>a</sup>
Zr	0.1852(7)	0.7782(9)	0.0441(7)	2.95(4)
Cl(1)	0.009(2)	0.7529(3)	0.069(2)	4.4(1)
Cl(2)	0.245(2)	0.6396(3)	0.166(2)	4.6(1)
Si	0.278(2)	0.9673(3)	-0.112(2)	4.0(1)
C(1)	0.2455(8)	0.9789(9)	0.0184(8)	3.4(5)
C(2)	0.150(1)	0.992(1)	0.0509(8)	3.9(5)
C(3)	0.151(1)	0.958(1)	0.1506(9)	4.7(6)
C(4)	0.2476(9)	0.917(1)	0.1743(8)	4.1(5)
C(5)	0.3061(9)	0.933(1)	0.0922(9)	4.2(5)
C(6)	0.2490(8)	0.805(1)	-0.1183(7)	3.4(5)
C(7)	0.3082(7)	0.713(1)	-0.0783(7)	3.4(5)
C(8)	0.2495(8)	0.611(1)	-0.0635(7)	3.6(5)
C(9)	0.1508(8)	0.6359(9)	-0.0993(7)	3.3(4)
C(10)	0.0650(9)	0.564(1)	-0.1065(8)	4.5(5)
C(11)	-0.0210(9)	0.612(1)	-0.1491(9)	5.1(7)
C(12)	-0.0225(9)	0.729(1)	-0.1836(8)	4.9(6)
C(13)	0.0583(8)	0.801(1)	-0.1773(8)	4.3(6)
C(14)	0.1498(7)	0.755(1)	-0.1342(7)	3.4(5)
C(15)	0.4196(7)	0.713(1)	-0.0654(8)	3.6(5)
C(16)	0.4758(8)	0.743(1)	-0.1394(8)	4.1(5)
C(17)	0.5828(9)	0.739(1)	-0.130(1)	4.9(6)
C(18)	0.6292(8)	0.704(1)	-0.046(1)	4.9(6)
C(19)	0.5713(9)	0.668(1)	0.0317(9)	4.8(6)
C(20)	0.4670(8)	0.671(1)	0.0219(9)	4.4(6)
C(21)	0.7440(9)	0.701(1)	-0.034(1)	6.2(8)
C(22)	0.194(1)	1.062(1)	-0.189(1)	6.2(7)
C(23)	0.413(1)	1.008(1)	-0.124(1)	5.6(6)

<sup>a</sup> *U*<sub>eq</sub> is defined as one-third of the trace of the orthogonalized *U*<sub>*ij*</sub> tensor.

Table 3  
Selected bond lengths and bond angles for **9** with estimated standard deviations

<i>Bond lengths (Å)</i>			
Zr–Cl(1)	2.42(3)	Zr–C(7)	2.54(1)
Zr–Cl(2)	2.43(3)	Zr–C(8)	2.59(1)
Zr–C(1)	2.45(1)	Zr–C(9)	2.60(1)
Zr–C(2)	2.47(1)	Zr–C(14)	2.54(1)
Zr–C(3)	2.58(1)	Si–C(1)	1.89(1)
Zr–C(4)	2.53(1)	Si–C(6)	1.89(1)
Zr–C(5)	2.46(1)	Zr–Cp(Cen) <sup>a</sup>	2.19(1)
Zr–C(6)	2.48(9)	Zr–Ind(Cen)	2.24(1)
<i>Bond angles (°)</i>			
Cl(1)–Zr–Cl(2)	96.8(1)	C(22)–Si–C(23)	111.2(6)
C(1)–Si–C(6)	93.5(4)	Cp(Cen)–Zr–Ind(Cen)	126.7(4)

<sup>a</sup> Cen = ring centroid.

polymer was separated from the polymerization medium by cooling to  $-30^{\circ}\text{C}$ , washed with fresh ethanol, and dried in vacuo.

### 3. Results and discussion

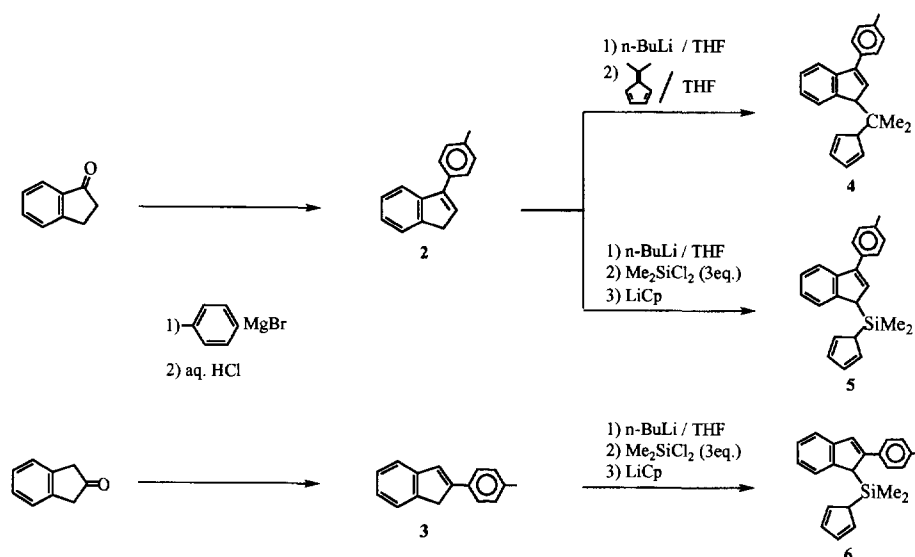
#### 3.1. Preparation of **2–9**

The *p*-tolyl substituted indenenes, 1-*p*-tolylindene (**2**) and 2-*p*-tolylindene (**3**), were prepared by an addition of 1- and 2-indanone to *p*-tolylmagnesium bromide, followed by dehydration of an alcohol intermediate with aqueous HCl [13] respectively, as shown in Scheme 1. The reaction of a lithium salt of **2** with 6,6-dimethylfulvene in THF afforded the isopropyl bridged *ansa*-ligand,  $\text{Me}_2\text{C}(\text{Cp})(3\text{-TolInd})$  (**4**), the  $^1\text{H}$  NMR spectrum of which reveals the presence of two isomers, as ex-

pected [4]. We, however, were unable to prepare 2-*p*-tolyl substituted analogue of **4** by a similar procedure, presumably due to steric reasons of the bulky 2-*p*-tolyl group for the addition to the dimethylfulvene. Reactions of a lithium salt of **2** and **3** with  $\text{Me}_2\text{SiCl}_2$  followed by treatment of LiCp produced the corresponding dimethylsilyl bridged *ansa*-ligands,  $\text{Me}_2\text{Si}(\text{Cp})(3\text{-TolInd})$  (**5**) and  $\text{Me}_2\text{Si}(\text{Cp})(2\text{-TolInd})$  (**6**) in moderate yields. The *ansa*-zirconocenes **7–9** were obtained by the reaction of the dilithio salts of ligands **4–6** with zirconium tetrachloride in diethyl ether at  $-78^{\circ}\text{C}$ . The respective  $^1\text{H}$  NMR spectrum of **7–9** shows two methyl resonances for the two inequivalent methyl groups on either carbon or silicon atom.

#### 3.2. Crystal structure of **9**

The overall molecular geometry and the atomic labelling scheme of **9** are illustrated in Fig. 1. Details of



Scheme 1.

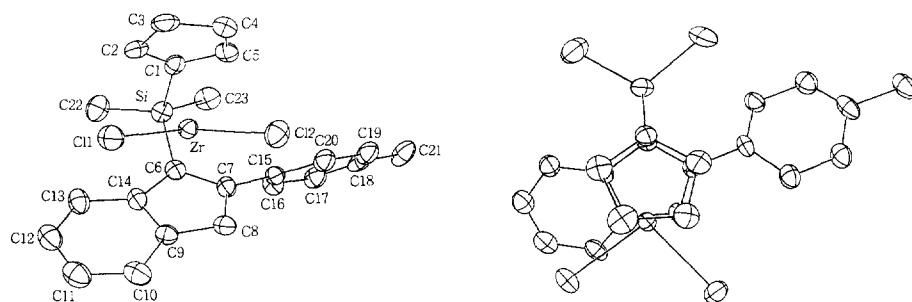


Fig. 1. Molecular structure of **9** with atomic numbering scheme (left). Projection perpendicular to ZrCl(1)Cl(2) plane (right).

the crystallographic parameters and selected bond lengths and angles are presented in Tables 1 and 3 respectively. The overall geometry of **9** is similar to that found in the parent  $\text{Me}_2\text{Si}(\text{Cp})(\text{Ind})\text{ZrCl}_2$  complex [14], adopting a distorted tetrahedral coordination in which the Cl–Zr–Cl bond angle is  $96.79(1)^\circ$  and the Cen(Cp)–Zr–Cen(2-TolInd) angle is  $126.7(4)^\circ$  (Cen = ring centroid). The Zr–Cl bond lengths are 2.423(3) and 2.430(3) Å. The Zr–Cen(Cp) and Zr–Cen(2-TolInd) lengths are 2.19(1) and 2.24(1) Å respectively. The C(1)–Si–C(6) angle is  $93.5(6)^\circ$  and the C(22)–Si–C(23) angle is  $111.2(6)^\circ$ . The *p*-tolyl substituent is oriented in the lateral sector of the opposite direction to the six-membered ring of the indenyl ligand. The dihedral angle between the cyclopentadienyl and the indenyl rings and that between the indenyl and the *p*-tolyl rings are  $60.1(4)^\circ$  and  $52.6(4)^\circ$  respectively. The Cl(1)–Zr–Cl(2) bond is slightly out of the center of Si and Zr atoms, presumably due to the steric interaction of the *p*-tolyl ring with the adjacent Cl(2) atom.

### 3.3. Propylene polymerization

Polymerization of propylene with complexes **7–9** in the presence of MAO was carried out in toluene at

various temperatures and the results are summarized in Table 4. The activities of both **7** and **8** for propylene polymerization are very low and the molecular weights of the produced polypropylene (PP) are also quite low. The  $M_n$  values with **7** and **8** at  $-30^\circ\text{C}$  are 550 and 4400 respectively. In contrast with **7** and **8**, catalyst **9** exhibits a high catalytic activity of 1570 kg PP/(mol Zr h atm) at  $30^\circ\text{C}$  and produces a high molecular weight of PP,  $1.2 \times 10^6$  ( $M_w$ ) at  $-30^\circ\text{C}$ . These polymerization results of the present metallocenes compare with those of unsubstituted metallocenes  $\text{Me}_2\text{X}(\text{Cp})(\text{Ind})\text{ZrCl}_2$  (X = C (**10**); Si (**11**)) [14,15] reported previously: the catalytic activity of **9** is higher than that of **10** and **11** by ca. two times and the molecular weight of PP produced with **9** is much higher than that with **10** and **11**, as shown in Table 4.

The different effects of the *p*-tolyl substituents in the 2- and 3-positions of the indenyl ligand in **7–9** on the catalytic performance appear to be due to the steric influences of the *p*-tolyl group. The 2-position substituted *p*-tolyl group in **9** is oriented toward the lateral sector of the bent metallocene wedge (see Fig. 1), which consequently results in less blocking of the monomer access to the metal center to show the high catalytic activity compared to **7** and **8**. The *p*-tolyl groups at the

Table 4  
Polymerization<sup>a</sup> of propylene with **7–9**/MAO catalyst systems

Metallocenes	Zr (μmol)	Al (mmol)	$T_p$ (°C)	$t_p$ (h)	A <sup>b</sup>	$\bar{M}_v^c (\times 10^{-3})$	$\bar{M}_n (\times 10^{-3})$	$\bar{M}_w (\times 10^{-3})$	MWD	<i>mm</i>	<i>mr</i>	<i>rr</i>
<b>7</b>	12	24	25	2	50							
	12	24	-30	10	10		0.55			0.10	0.42	0.48
<b>8</b>	15	30	25	1	132		0.74			0.10	0.55	0.35
	15	30	-30	3	30		4.4	7.9	1.78	0.08	0.46	0.46
<b>9</b>	15	30	25	1	1570	377				0.31	0.47	0.23
	15	30	-30	1	800	1190	620	1200	1.94	0.43	0.34	0.23
<b>10</b> [14]	10.5	21	25		700			2	2.0	0.38	0.36	0.26
<b>11</b> [14]	10.5	21	25		800			9	1.8	0.52	0.28	0.20
<b>1</b> [6]	50	125	30		1230	94						0.92

<sup>a</sup> Polymerization conditions: 1.2 atm, toluene (250 ml).

<sup>b</sup> Activity (kg PP)/(mol Zr[monomer]h).

<sup>c</sup> Calculated by the Mark–Houwink equation,  $[\eta] = 1.0 \times 10^{-4} M_v^{0.80}$ .

3-position in **7** and **8**, however, are placed on the central sector of the bent metallocene wedge and thus bring about a decreased rate of propylene insertion, low activities, and low molecular weights of PP. The higher molecular weight of PP by catalyst **9** compared to the unsubstituted systems, **10** and **11**, seems to be due to the decreased  $\beta$ -hydride elimination of the growing polymer chain for the chain termination by steric hindrance of the 2-*p*-tolyl substituent.

The stereoregularity of PP produced with each of three complexes **7–9** has been investigated by the triad analysis [16] using  $^{13}\text{C}$  NMR spectroscopy. Catalysts **7–9** have been originally designed to prepare syndiotactic PP analogous to the Ewen's catalyst [3]. Nevertheless, the stereoregularity of the polymers produced using catalysts **7**, **8**, and **9** is poor and similar to that of the  $\text{Me}_2\text{X}(\text{Cp})(\text{Ind})\text{ZrCl}_2$  system [14,15], which has been reported to produce atactic PP. Complexes **7**, **8** and **9** produced PP having  $[\text{rr}]$  populations of 0.48, 0.46 and 0.23 respectively at  $-30^\circ\text{C}$ . The catalytic activity and the molecular weight of PP produced with **9**, however, are much higher than those with Ewen's catalyst (**1**), as shown in Table 4. The *p*-tolyl group substituted at the 3-position in **7** and **8** appears to exert a greater influence on the inserting propylene than that at the 2-position in **9**, which gives the lowest value of  $[\text{rr}]$  among **7–9**. This result indicates that the steric environments of **7** and **8** for the two chloride-coordinating sites of the Zr atom seem to be quite similar in covering one site by the six-membered ring of the indenyl group and the other site by the 3-*p*-tolyl group of the indenyl ring. This structural feature of pseudo- $\text{C}_s$  symmetry may give a syndiospecific polymerization site as observed in **1**. The triad distributions, however, are not consistent with an enantiomeric site propagation model based on stereochemical control by the chirality of the catalyst, which has been mathematically derived by Ewen's coworkers [17]. We therefore consider that the weak syndio-stereospecificity for **7** and **8** at low temperature may be caused by either a site control with large errors of site isomerization or a chain end control of non-bonding interaction between a growing polymer chain and the methyl group of an inserting propylene.

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