ELSEVIER

Journal of Organometallic Chemistry 560 (1998) 47–54

Journal of Organo metallic Chemistry

Structural characterization of *ansa*-zirconocene dichloride bearing a vicinal di-*tert*-butylcyclopentadienyl ligand and high pressure polymerization of 1-hexene catalyzed by sterically hindered zirconocene complexes

Noriyuki Suzuki *, Takaya Mise, Yoshitaka Yamaguchi, Teiji Chihara, Yuji Ikegami, Hiromichi Ohmori, Akira Matsumoto, Yasuo Wakatsuki

The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan

Received 1 September 1997; received in revised form 25 February 1998

Abstract

An *ansa*-zirconocene complex having a vicinally di-*tert*-butyl-substituted cyclopentadienyl ligand, $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}t\text{-}Bu_2)ZrCl_2$ (**1**), has been synthesized and characterized by X-ray diffraction (orthorhombic, space group: *Pbca*, $a = 18.3690(8)$, $b = 18.0749(12)$, $c = 13.2039(9)$ Å, $V = 4383.9(4)$ Å^3, $Z = 8$, $R = 0.0283$, $R_w = 0.0291$). Complex **1** has a very much twisted structure due to its steric repulsion. In solution, however, the two *tert*-butyl groups are magnetically equivalent even at −80°C, indicating very fast oscillation of the bridged cyclopentadienyl unit with respect to the metal center. Complex **1** and nonbridged zirconocene dichlorides with *tert*-butyl-substituted cyclopentadienyl ligands, $(C_5H_4\text{-}t\text{-}Bu)_2ZrCl_2$ (**2**), $(C_5H_3\text{-}1,2\text{-}t\text{-}Bu_2)_2ZrCl_2$ (**3**) and $(C_5H_3\text{-}1,3\text{-}t\text{-}Bu_2)_2ZrCl_2$ (**4**), have been employed as methylaluminoxane (MAO)-activated catalysts for polymerization of 1-hexene under high pressure conditions (100–750 MPa = ca. 1000–7500 atm). Comparison with some non and methyl-substituted metallocenes are also discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zirconocene; Olefin polymerization; High pressure; 1-Hexene; *tert*-Butyl group

---

1. Introduction

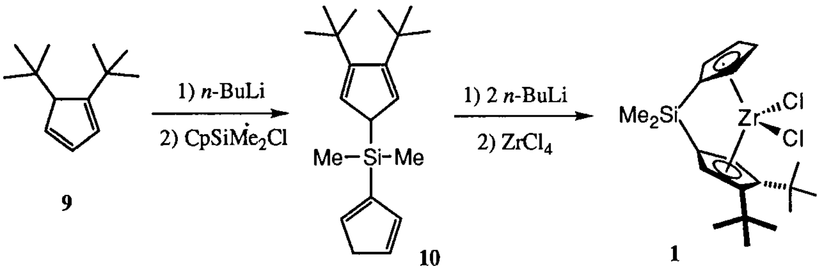
Recently we reported that the polymerization of 1-hexene by group IV metallocene dichlorides/methylaluminoxane (MAO) system was accelerated under high pressure reaction conditions [1]. One of the striking features was that the polymerization activity of zirconocene catalysts $(C_5H_{5-n}Me_n)_2ZrCl_2$–MAO increased as a function of the number of methyl groups on the cyclopentadienyl rings, i.e. in the order of $Me_0 < Me_1 < 1,2,4\text{-}Me_3 < Me_4 \ll Me_5$ under 250–500 MPa. At 500 MPa, the catalytic activity of $(C_5Me_5)_2ZrCl_2$–MAO amounted to 630 ton of polymer per mol of Zr an hour. This trend is quite unusual compared with the activities in normal pressure polymerization [2], and it might be explained in terms of electron donating property of a methyl group [3]. Under high pressure conditions, therefore, the steric hindrance around the metal center appeared to be less of a problem than in the normal pressure reactions. These observations prompted us to examine high pressure polymerization with the catalyst systems, bearing even more bulky and more electron donating alkyl substituents.

Herein we report the polymerization of 1-hexene under high pressure conditions (≤ 750 MPa) using some zirconocene complexes bearing *tert*-butyl substituents on their Cp rings. For the purpose of this study, we prepared a new *ansa*-zirconocene complex $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}t\text{-}Bu_2)ZrCl_2$ (**1**), which was

---

* Corresponding author. Fax: +81 48 4624665.

PII S0022-328X(98)00524-5



Scheme 1. Synthesis of $Me_2Si(C_5H_4)(3,4\text{-}t\text{-}Bu_2C_5H_2)ZrCl_2$ (**1**)

structurally characterized, and examined its catalytic activity. Related complexes, $(C_5H_4\text{-}t\text{-}Bu)_2ZrCl_2$ (**2**) [4], $(C_5H_3\text{-}1,2\text{-}t\text{-}Bu_2)_2ZrCl_2$ (**3**) [5] and $(C_5H_3\text{-}1,3\text{-}t\text{-}Bu_2)_2ZrCl_2$ (**4**) [6], were likewise examined. $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}Me_2)ZrCl_2$ (**5**) was also prepared and employed as a reference.

2. Results and discussion

2.1. Synthesis and structure of $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}t\text{-}Bu_2)ZrCl_2$ (1)

In the polymerization of olefins using a metallocene catalyst system, bulky substituents on the Cp rings often play an important role for controlling the direction of an approaching monomer. So far many *ansa*-zirconocene complexes bearing *tert*-butyl substituents have been reported [7]. However, to the best of our knowledge, there have been no example of *ansa*-zirconocene complexes that have two vicinal *tert*-butyl groups on their Cp rings. We have prepared an *ansa*-zirconocene complex $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}t\text{-}Bu_2)ZrCl_2$ (**1**) and examined its catalytic behavior for olefin polymerization, particularly under high pressure conditions.

Scheme 1 illustrates the preparation of **1**. The synthesis and metal-complexation of vicinal di-*tert*-butylcyclopentadiene (**9**) have been reported recently [8]. The treatment of **9** with *n*-butyllithium and then with $CpSiMe_2Cl$ gave the silylene-bridged ligand **10** in 86% yield. The Si–C bond formation occurred selectively enough that possible structural isomers were not detected. Dilithiation of **10** followed by the reaction with ZrC_4 afforded **1** as yellow crystals. The crystal structure of **1** is shown in Fig. 1. The atomic parameters and selected bond lengths and angles are listed in Tables 1 and 2, respectively. The two *tert*-butyl groups are bent out of the mean plane of the Cp ring by 9.6° (C(10)–C(13)) and 5.5° (C(11)–C(17)), which are within the range observed in other *tert*-butyl-substituted *ansa*-zirconocene complexes ([7]b–g). C(10) and C(11) in the substituted Cp ring are further from the metal (2.645(2) and 2.664(2) Å, respectively) compared with the others (2.437(3), 2.456(3) and 2.501(2) Å for C(8), C(9) and C(12), respectively). These distances are also similar to the cases of other *tert*-butyl-substituted zirconocene complexes. This is probably due to the steric repulsion between the chlorine atoms and the *tert*-butyl groups [9]. The following tendency brought about by steric congestion is noteworthy. The two chlorine atoms and the two *tert*-butyl groups are located in a staggered position. Both cyclopentadienyl rings are twisted at the Si–C(3) and Si–C(8) bonds by 14.7° and 16.6°, respectively, from the normal position perpendicular to the C(3)–Si–C(8) plane and the distance between C(4)–C(12) (4.041(4) Å) is accordingly much longer than that of C(7)–C(9) (3.107(4) Å).

In contrast to the solid-state structure, these two *tert*-butyl groups in solution were observed as one sharp singlet signal in ^{1}H-NMR spectroscopy. This signal remained singlet even at −80°C, though it was slightly broadened.

Methylation of **1** and the subsequent alkoxylation was examined with NMR spectroscopy (Scheme 2). Treatment of **1** with two equivalents of methylmagnesium bromide gave the methylated product **11** in a good yield. The methyl groups were observed as one signal in ^{1}H-NMR, even at −80°C, as were the *tert*-butyl groups. The further reaction of **11** with slightly excess *t*-BuOH cleanly gave the alkylalkoxy complex **12** [10]. The ^{1}H- and ^{13}C-NMR spectra of **12** measured at −60°C showed the presence of only one species and conformational isomers could not be distinguished. All these observation suggested that the bridged ligand in solution was oscillating faster than the ^{1}H-NMR time scale and the bulky *tert*-butoxy group attached to the metal did not slow it down [11]. Assuming a propagating polymer chain bound to the metal center has a steric effect comparable with the *tert*-butoxy group, we may infer that the bridging ligand is oscillating rapidly during the polymerization if this complex is used as a catalyst precursor. Thus, **1** can be regarded as C_s-symmetric during the polymerization [12].

The polymerization of ethylene using the combination of **1** and methylaluminoxane (Al/Zr = 10000; at 70°C, 8 atm) as a catalyst gave polyethylene in moderate activity (300 kg polymer/mol Zr an hour; $M_w = 109000$; $M_w/M_n = 4.35$).

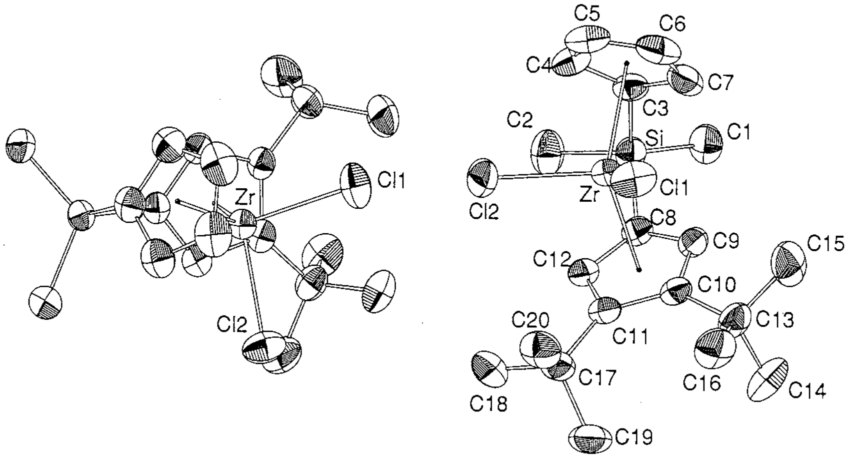


Fig. 1. Molecular structure of $Me_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}t\text{-}Bu_2)ZrCl_2$ (**1**) drawn with 50% thermal ellipsoids. Top view (left) and front view (right).

2.2. High pressure polymerization of 1-hexene by zirconocene catalysts having *tert*-butyl substituents

The polymerization reactions of 1-hexene were carried out under high pressure using various *tert*-butyl-substituted zirconocene complexes–MAO systems. We previously reported that catalytic activity of nonbridged methyl-substituted zirconocenes was remarkably enhanced under 250–500 MPa and that poly(1-hexene) of very high molecular weight was formed under such conditions [1]. The present results on nonbridged *tert*-butyl-substituted complexes **2**–**4**, however, revealed their different behavior from methyl-substituted metallocenes (Table 3). The monosubstituted zirconocene complex **2** showed no significant effect of high pressure on its catalytic activity, whereas the molecular weight of the obtained polymer was eight times larger than that of the polymer produced under normal pressure. In the case of 1,2-di-*tert*-butyl zirconocene **3**, both the catalytic activity and the molecular weight of the polymers were only slightly enhanced under high pressure. It has been reported that **4** dimerizes α-olefins selectively [13]. When the reaction was run under 500 MPa, the major product was the dimer of 1-hexene, and only traces of the trimer (< 1% to the dimer) were observed, while no tetramer or higher oligomers were detected. The catalytic activity of **4** for the dimerization of

Table 1
Atomic coordinates of **1**

Atom	*x*	*y*	*z*	B_{eqv}
Zr	0.15909(1)	0.32191(1)	0.15525(2)	2.6(0)
Cl(1)	0.08828(4)	0.22377(4)	0.23480(7)	4.5(0)
Cl(2)	0.20652(5)	0.37692(5)	0.31098(6)	4.5(0)
Si	0.23568(4)	0.41916(4)	−0.02419(5)	2.9(0)
C(1)	0.2335(2)	0.4195(2)	−0.1642(2)	4.0(1)
C(2)	0.2935(2)	0.4923(2)	0.0311(2)	4.6(1)
C(3)	0.2593(1)	0.3265(2)	0.0300(2)	3.3(1)
C(4)	0.2934(1)	0.3145(2)	0.1243(2)	3.9(1)
C(5)	0.2753(2)	0.2443(2)	0.1624(3)	4.4(1)
C(6)	0.2307(2)	0.2102(2)	0.0907(3)	4.5(1)
C(7)	0.2192(2)	0.2599(2)	0.0102(2)	3.9(1)
C(8)	0.1423(1)	0.4215(1)	0.0330(2)	2.7(1)
C(9)	0.0876(1)	0.3680(1)	0.0113(2)	2.9(1)
C(10)	0.0322(1)	0.3688(1)	0.0855(2)	2.8(1)
C(11)	0.0534(1)	0.4228(1)	0.1604(2)	2.8(1)
C(12)	0.1206(1)	0.4529(1)	0.1259(2)	2.8(1)
C(13)	−0.0388(1)	0.3250(2)	0.0629(2)	3.7(1)
C(14)	−0.0849(2)	0.3767(2)	−0.0042(3)	5.6(1)
C(15)	−0.0214(2)	0.2549(2)	0.0022(3)	5.3(1)
C(16)	−0.0839(2)	0.3000(2)	0.1538(3)	4.9(1)
C(17)	0.0141(1)	0.4551(2)	0.2539(2)	3.5(1)
C(18)	0.0595(2)	0.5188(2)	0.2990(2)	4.7(1)
C(19)	−0.0587(2)	0.4898(2)	0.2214(3)	4.9(1)
C(20)	0.0028(2)	0.3983(2)	0.3388(2)	4.6(1)

Thermal parameters are given by the equivalent temperature factors ($Å^2$).

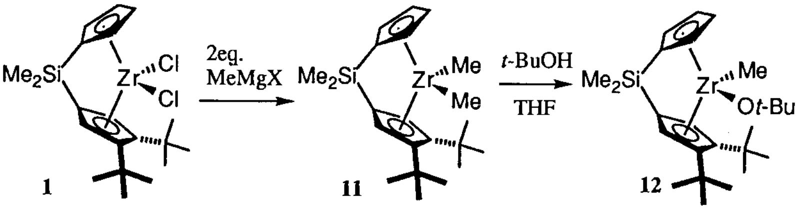
Table 2
Selected bond lengths (Å) and angles (°) for **1**

Bond length (Å)		Bond angle (°)	
Zr–Cl(1)	2.438(1)	Cl(1)–Zr–Cl(2)	97.11(3)
Zr–Cl(2)	2.445(1)	Cp(1)(c)–Zr–Cp(2)(c)	125.2
Zr–C(3)	2.477(3)	PL(1)–PL(2)[c]	64.3
Zr–C(4)	2.505(3)		
Zr–C(5)	2.556(3)	C(1)–Si–C(2)	113.9(1)
Zr–C(6)	2.556(3)	C(3)–Si–C(8)	94.5(1)
Zr–C(7)	2.478(3)	Si–C(3)–C(4)	125.3(2)
Zr–C(8)	2.437(3)	Si–C(3)–C(7)	124.1(2)
Zr–C(9)	2.456(3)	Si–C(8)–C(9)	123.3(2)
Zr–C(10)	2.645(2)	Si–C(8)–C(12)	128.2(2)
Zr–C(11)	2.664(2)		
Zr–C(12)	2.501(2)		
Zr–Cp(1)(c)[a]	2.209		
Zr–Cp(2)(c)[a]	2.236		
Zr–PL(1)[b]	2.206		
Zr–PL(2)[b]	2.220		

[a] Distances of Zr-centroid of Cp(1)(C(3)–C(7)) and Cp(2)(C(8)–C(12)).

[b] PL(*n*), the mean plane of Cp(*n*) ring.

[c] The angle between the mean plane of each Cp ring.



Scheme 2. Formation of the alkylalkoxy complex **12**

1-hexene did not increase either. The isomeric ratio of the products (2-butyloct-1-ene/5-methylundec-4(or 5)-ene) slightly changed due to high pressure (85/15 at 0.1 MPa to 71/29 at 500 MPa). These results are in a sharp contrast to the polymerization using methyl- or nonsubstituted metallocenes **6**–**8**, which were much more sensitive to the applied pressure (Table 4). Not only were the catalytic activity of **2**–**4** under atmospheric pressure lower than those of **6**–**8**, but the enhanced ratio of the activity under high pressure were also much less than those observed in **6**–**8**. The crystallographic analysis of $(C_5H_4\text{-}t\text{-Bu})_2ZrCl_2$ (**2**) showed its C_2-symmetric structure in which the two *tert*-butyl groups are directed away from each other on the opposite side of the molecule ([4]b). The cyclopentadienyl ligands of **2**, however, rotate fast in solution at r.t. as shown by Erker and coworkers [14]. This situation seems to be similar even under high pressure, since the significant stereoregularity was not observed in the polymers obtained at high pressure using **2** as the catalyst. It is known that bulky substituents on Cp rings might prevent monomers from approaching the metal center and thus, suppress its catalytic activity [2]. The present results implied that even high pressure could not overcome the large steric hindrance of *tert*-butyl groups when the Cp rings bearing them were not bridged and freely rotated.

In contrast to the nonbridged metallocenes, the results obtained with bridged metallocenes were noteworthy (Table 5). The *tert*-butyl-substituted complex **1** exhibited significant high pressure effects on both the polymerization rates and the molecular weight of the polymers. The polymerization rate was 9.3-fold greater at 250 MPa than that at atmospheric pressure, and the molecular weight was doubled at 250 MPa. The pressure effect began to decrease above 500 MPa as observed in our previous results. Distributions of the molecular weight of the polymer were close to 2 indicating that it was a single site catalyst. Although **1** are C_s-symmetric (vide supra), the polymer obtained with **1** was essentially atactic [15]. It should be noted that a significant high pressure effect was observed even in a *tert*-butyl-substituted metallocene when the Cp rings were bridged, and thus the substituents were fixed. Compared with the corresponding vicinally dimethylated metallocene **5**, although the catalytic activity of **1** was lower than that of **5**, the enhanced ratio of the activity was greater than that observed in **5** (4.4-fold at 500 MPa). The polymer of higher molecular weight was obtained with **1** rather than **5** at 100–250 MPa.

It can be concluded that *tert*-butyl groups seemed so bulky that the *tert*-butyl-substituted metallocenes showed rather lower activity for 1-hexene polymerization, even under high pressure, particularly when the substituents are not fixed by bridged structure, in spite of the electron donating character of *tert*-butyl groups. The bridged-type zirconocene with *tert*-butyl groups **1**, however, indicated the significant high pressure effect as well as the methyl-substituted analog.

3. Experimental

3.1. General

All operations were carried out under an argon atmosphere. THF and toluene were refluxed over sodium/benzophenone ketyl and distilled. 1-Hexene was distilled and stored over sodium–potassium alloy. Zirconium tetrachloride was purchased from Wako Pure Chemical Industries and sublimed before use. *n*-Butyllithium (1.63 M hexane solution) were purchased from Kanto Chemical. Methylaluminoxane was purchased from Tosoh-Akzo (MMAO-3A, Al = 5.98 wt.% in toluene solution). Other chemicals were purchased from Wako Pure Chemical Industries, Tokyo Chemical Industry and Aldrich Chemical and used without further purification. Vicinal di-*tert*-butylcyclopentadiene was prepared according to the literature ([8]a,[16]). Zirconocene complexes, $(C_5H_4\text{-}t\text{-Bu})_2ZrCl_2$ [4], $(C_5H_3\text{-}1,2\text{-}t\text{-Bu}_2)_2ZrCl_2$ [5] $(C_5H_3\text{-}1,3\text{-t-Bu}_2)_2ZrCl_2$ [6] $(C_5H_4\text{-Me})_2ZrCl_2$ [17] and $(C_5Me_5)_2ZrCl_2$ [18] were prepared by the method described in the literature. NMR spectra were recorded on a JEOL EX-270 and GSX-500 FT NMR spectrometer, GC on Hewlett Packard 5890A equipped with OV-1 fused silica column (0.25 mm × 30 m). GC-MS on a Hewlett Packard 5971A mass selective detector. Molecular weights of polyhexene were determined by GPC analysis using Shodex GPC system 11, with THF as eluent and monodispersed polystyrene as standard. Molecular weight of polyethylene was recorded on Waters 150CV Plus high-temperature GPC system at 140°C using *o*-dichlorobenzene as eluent and monodispersed polystyrene as standard.

Table 3
Polymerization of 1-hexene under high pressure using nonbridged *tert*-butyl-substituted zirconocene catalysts[a]

Run	Catalysts	Pressure (MPa)	Yield (g)	Rate[b]	M_w	M_w/M_n
1	$(C_5H_4\text{-}t\text{-}Bu)_2ZrCl_2$ **2**	0.1	0.83	420	2300	1.49
2		250	0.77	390	14 800	2.51
3		500	0.73	360	19 600	2.96
4	$(C_5H_3\text{-}1,2\text{-}t\text{-}Bu_2)_2ZrCl_2$ **3**	0.1	0.12	60	750	1.26
5		250	0.20	100	780	1.29
6		500	0.13	64	830	1.26
7	$(C_5H_3\text{-}1,3\text{-}t\text{-}Bu_2)_2ZrCl_2$ **4**	0.1	0.78	390	168	—
8		250	0.87	440	168	—
9		500	0.67	340	168	—

[a] Zr: 1.0 μmol, Al/Zr = 2000, reaction time: 2 h, r.t.

[b] kg polymer/mol Zr an hour.

3.2. Zirconocene-catalyzed polymerization of 1-hexene under high pressure

Typically, a 25 ml Teflon sample holder was charged at r.t. in a Schlenk tube with argon, 0.2 ml of a solution of the metallocene catalyst in dry toluene and a solution of MAO in toluene (Al = 2000-fold excess). After 10 min, 1-hexene (24.6 ml, 0.2 mol) was added via cannula, the sample holder was firmly closed by a screw cap and immediately cooled to −78°C. Pressure was applied by a direct piston–cylinder apparatus with a hydraulic press during warming up to r.t. After 2 h, the pressure was released, the viscous reaction mixture was transferred to a glass beaker, and MeOH (10 ml) was added. The polymer was dissolved in hexane, and separated from decomposition products of MAO by filtration. Removal of the volatiles and drying in high vacuum afforded the polymer as a colorless, viscous oil. The molecular weight was determined by GPC. When dimeric products were obtained, the reaction mixture was treated with 1 N HCl and extracted with hexane. The organic layer was analyzed by GC and MS. After drying with $MgSO_4$, the volatile was evaporated leaving a mixture of the dimer.

3.3. (2,3-Di-*tert*-butylcyclopentadien-5-yl)(cyclopentadienyl)dimethylsilane (**10**)

Cyclopentadienyldimethylchlorosilane was prepared from dimethyldichlorosilane and cyclopentadienyl sodium. It was distilled and used for the reaction immediately. To a solution of di-*tert*-butylcyclopentadiene (1.79 g, 10 mmol) in THF (20 ml) *n*-butyllithium (in hexane solution, 10 mmol) was added at 0°C. The mixture was warmed up to r.t. and stirred for 3 h. To this red solution, additional THF (15 ml) and cyclopentadienyldimethylchlorosilane (1.5 g, 9.5 mmol) was added dropwise at r.t. After stirring for 1 h, dil. HCl was added to the reaction mixture. Usual workup and column chromatography (hexane) gave the title compound (yield 86%). ^{1}H-NMR ($CDCl_3$, Me_4Si): δ −0.24 (s, 6H, $SiCH_3$), 1.37 (s, 18H, *t*-Bu), 2.98–3.1 (m, 2H), 6.34–6.7 (m, 6H). ^{13}C-NMR ($CDCl_3$, Me_4Si): δ −3.43, 32.90, 33.82, 45.14, 51.39, 129.76, 130.22, 132.81, 155.24, for other peaks of isomers, 45.75, 137.90, 142.50, 154.79. MS; $M^+ = 300$.

3.4. Dichloro[η^{10}-2,4-cyclopentadien-1-ylidene(dimethylsilylene)(3,4-di-*tert*-butyl-2,4-cyclopentadien-1-ylidene)]zirconium (**1**)

To a solution of **10** (2.24 g, 7.44 mmol) in THF (30 ml) *n*-butyllithium (hexane solution, 14.9 mmol) was added at −78°C. The mixture was warmed up to r.t. and was stirred overnight. This orange solution was added dropwise to the THF (80 ml) solution of zirconium tetrachloride (1.72 g, 7.4 mmol) at −78°C and was stirred overnight at r.t. The solvent was removed in vacuo and the orange residue was dissolved in toluene and filtered to remove lithium salts. Recrystallization from toluene solution at −30°C gave the pale yellow crystalline title compound (yield 24%). ^{1}H-NMR (CD_2Cl_2, Me_4Si): δ 0.67 (s, 6H, $SiCH_3$), 1.46 (s, 18H, *t*-Bu), 6.177 (dd, $J = 2$ Hz, 2H), 6.183 (s, 2H), 6.78 (dd, $J = 2$ Hz, 2H). ^{13}C-NMR (CD_2Cl_2, Me_4Si): δ −4.53, 32.59, 35.32, 102.85, 106.50, 118.12, 119.55, 126.11, 149.15. $C_{20}H_{30}Cl_2SiZr$ (460.67): calc. C 52.15, H 6.56; found C 52.19, H 6.61.

3.5. Dimethyl[η^{10}-2,4-cyclopentadien-1-ylidene(dimethylsilylene)(3,4-di-*tert*-butyl-2,4-cyclopentadien-1-ylidene)]zirconium (**11**)

To a solution of **1** (46 mg, 0.1 mmol) in THF (0.5 ml) methylmagnesium bromide (THF solution, 0.2 mmol) was added at −78°C. The mixture was warmed to r.t.

Table 4
Polymerization of 1-hexene under high pressure using non or methyl-substituted zirconocene catalysts[a]

Run	Catalysts	Pressure (MPa)	Zr (μmol)	Yield (g)	Rate[b]	M_w	M_w/M_n
1	$(C_5H_5)_2ZrCl_2$ **6**	0.1	0.09	0.37	2.06	3300	1.41
2		250	0.09	3.83	21.3	21 900	1.55
3		500	0.09	9.71	53.9	28 700	1.55
4	$(C_5H_4Me)_2ZrCl_2$ **7**	0.1	0.09	0.42	2.33	8100	1.49
5		250	0.09	6.31	35.06	29 500	1.45
6		500	0.09	10.97	60.94	31 000	1.43
7	$(C_5Me_5)_2ZrCl_2$ **8**	0.1	0.2	0.33	0.83	14 195	1.69
8		250	0.009	7.09	394	124 200	1.89
9		500	0.009	11.4	636	383 400	2.08

[a] See [1]. Al/Zr = 10 000, reaction time: 2 h, r.t.

[b] Ton polymer/mol Zr an hour.

and then stirred at 50°C for 1 h. ^1H-NMR spectroscopy exhibited the formation of the title compound in 92% yield. ^1H-NMR (C_6D_6/THF): δ −0.33 (s, 6H, ZrCH_3), 0.27 (s, 6H, SiCH_3), 1.37 (s, 18H, *t*-Bu), 5.73 (dd, $J=2$ Hz, 2H), 5.74 (s, 2H), 6.52 (dd, $J=2$ Hz, 2H). ^{13}C-NMR (toluene-d_8): δ 142.06, 119.63, 114.36, 114.33, 99.72, 96.28, 34.69 ($C(CH_3)_3$), 33.31 ($C(CH_3)_3$), 30.08 (ZrCH_3), −4.77 (SiCH_3).

3.6. *tert-Buthoxymethyl[η^{10}-2,4-cyclopentadien-1-ylidene(dimethylsilylene)(3,4-di-tert-butyl-2,4-cyclopentadien-1-ylidene)]zirconium* (***12***)

To a solution of **11** (0.08 mmol) in THF (0.4 ml) in an NMR tube *tert*-butyl alcohol (0.11 mmol) was added at r.t. The mixture was stirred for 1 h. ^1H-NMR spectroscopy showed the formation of the title compound in 95% yield. ^1H-NMR (C_6D_6/THF): δ 0.13 (s, 3H), 0.24 (s, 3H), 0.50 (s, 3H), 1.08 (s, 9H), 1.38 (s, 9H), 1.40 (s, 9H), 5.95 (m, 1H), 6.00 (m, 1H), 6.07 (d, $J=3$ Hz, 1H), 6.23 (m, 1H), 6.26 (d, $J=3$ Hz, 1H), 6.48 (m, 1H). ^{13}C-NMR (C_6D_6/THF): δ −7.17, −2.84, 19.50, 32.26, 33.37, 33.41, 33.41, 34.21, 77.65, 105.46, 105.83, 108.12, 110.04, 112.39, 119.63, 119.99, 121.66, 135.07, 144.17.

3.7. *Dichloro[η^{10}-2,4-cyclopentadien-1-ylidene (dimethylsilylene)(3,4-dimethyl-2,4-cyclopentadien-1-ylidene)]zirconium* (***5***) *[19]*

The title compound was prepared in a similar manner to **1** from dilithiated (2,3-dimethylcyclopentadien-5-yl)(cyclopentadienyl)dimethylsilane (3.33 g, 15.4 mmol) and zirconium tetrachloride (3.50 g, 15.0 mmol) in THF. Recrystallization from heptane gave the pale yellow crystalline title compound (yield 18%). ^1H-NMR (CD_2Cl_2, Me_4Si): δ 0.69 (s, 6H), 2.08 (s, 6H), 5.53 (s, 2H), 5.86 (dd, $J=2.3$, 2.5 Hz, 2H), 6.97 (dd, $J=2.3$, 2.5 Hz, 2H). ^{13}C-NMR (CD_2Cl_2): δ −5.09, 13.67, 104.69, 106.97, 113.75, 116.29, 127.00, 137.13. $C_{14}H_{18}Cl_2SiZr$ (376.51): calc. C 44.66, H 4.82; found C 44.81, H 4.81.

3.8. *X-ray crystallographic analysis of* ***1***

Crystals suitable for X-ray analysis were obtained from toluene/pentane solution. A pale yellow crystal of dimensions 0.6 × 0.3 × 0.2 mm^3 was used. Crystallographic data: orthorhombic, space group: *Pbca* (61), $Z=8$, $a=18.3690(8)$, $b=18.0749(12)$, $c=13.2039(9)$ Å, $V=4383.9(4)$ $Å^3$. Data were collected on an Enraf-

Table 5
Polymerization of 1-hexene under high pressure using methyl-substituted and nonsubstituted zirconocene catalysts

Run	Catalysts	Pressure (MPa)	Zr (μmol)	Al/Zr	Time (h)	Yield (g)	Rate[a]	M_w	M_w/M_n
1	$Me_2Si(C_5H_4)(C_5H_2$-3,4-t-$Bu_2)ZrCl_2$ **1**	0.1	1.0	2000	24	1.44	60	7100	1.90
2		100	1.0	2000	6	1.55	260	15 400	1.72
3		250	1.0	2000	23	13.0	560	15 500	1.74
4		500	1.0	2000	23	11.3	490	6600	1.90
5		750	1.0	2000	23	6.36	280	4500	1.92
6	$Me_2Si(C_5H_4)(C_5H_2$-3,4-$Me_2)ZrCl_2$ **5**	0.1	0.27	10000	2	0.36	670	6500	1.82
7		100	0.27	10000	2	0.89	1650	9000	1.76
8		250	0.27	10000	2	1.31	2430	9400	1.87
9		500	0.27	10000	2	1.58	2930	7700	1.78

[a] kg polymer/mol Zr an hour.

Table 6
X-ray crystallographic data for $(CH_3)_2Si(C_5H_4)(C_5H_2\text{-}3,4\text{-}t\text{-}Bu_2)ZrCl_2$ (**1**)

Formula	$C_{20}H_{30}Cl_2SiZr$
Weight	460.3
Temperature (K)	294
Crystal system	orthorhombic
Space group	*Pbca* (No. 61)
a (Å)	18.3590(9)
b (Å)	18.0749(12)
c (Å)	13.2039(8)
V (Å^3)	4383.9(4)
Z	8
D_{calc} (g cm^{-3})	1.395
Absorption coefficient (cm^{-1})	7.932
$F(000)$	1904
2θ limit (°)	$4 \leq 2\theta \leq 55$
Reflections collected	5566
Unique reflections	3955
Parameters	338
Criteria for observed	$F_0 \geq 3\sigma(F_0)$
$R(F_0)$[a]	2.83
$R_w(F_0)$[a]	2.91
Goodness-of-fit	1.53
Max shift/esd$_{max}$ (final cycle)	0.127
Final residual electron density (e Å^{-3})	0.395 and −0.511

[a] $R = (\Sigma||F_0| - |F_c||)/(\Sigma|F_0|)$, $R_w = [(\Sigma\, w(|F_0| - |F_c|)^2/(\Sigma\, w|F_0|^2)]^{1/2}$, $w = 1/\sigma(F_0)$.

Nonius CAD4 diffractometer at 295 K with a graphite monochromater using Mo–K_α radiation. A total of 5566 unique reflections were measured in the ω scan mode ($4.0° \leq 2\theta \leq 55°$). The structure was solved by direct method using MULTAN [20]. The final cycle of least-squares refinement [21] was based on 3955 observed reflections ($F \geq 3\sigma(F)$) with 338 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.0283$, $R_w = 0.0291$ ($w = 1/\sigma(F_0)$). Crystallographic data are summarized in Table 6.

Acknowledgements

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas (No. 283, 'Innovative Synthetic Reactions') from the Ministry of Education, Science, Sports and Culture, Government of Japan. One of the authors (Y. Yamaguchi) thanks Special Postdoctoral Researchers Program at The Institute of Physical and Chemical Research (RIKEN). The authors wish to thank Mr Sumio Yamamoto for his experimental assistance in the high pressure technique. The authors are grateful to Japan-Waters Ltd., for measurement of molecular weight of polyethylene with their high-temperature GPC system.

References

[1] A. Fries, T. Mise, A. Matsumoto, H. Ohmori, Y. Wakatsuki, Chem. Commun. (1996) 783–784.

[2] C. Janiak, K.C. Lange, U. Versteeg, D. Lentz, P.H.M. Budzelaar, Chem. Ber. 129 (1996) 1517–1529.

[3] It is reported that electron donating substituents on Cp rings tend to increase the catalytic activity of the group IV metallocene olefin polymerization catalysts. For example, see W. Kaminsky, Macromol. Chem. Phys. 197 (1996) 3907–3945.

[4] (a) M.F. Lappert, C.J. Pickett, P.I. Riley, Y.P.I.W., J. Chem. Soc. Dalton Trans. (1981) 805–813. (b) R.A. Howie, G.P. McQuillan, D.W. Thompson, G.A. Lock, J. Organomet. Chem. 303 (1986) 213–220.

[5] R.P. Hughes, J.R. Lomprey, A.L. Rheingold, B.S. Haggerty, G.P.A. Yap, J. Organomet. Chem. 517 (1996) 89–99.

[6] L.F. Urazowski, V.I. Ponomaryev, I.E. Nifant'ev, D.A. Lemenovskii, J. Organomet. Chem. 368 (1989) 287–294.

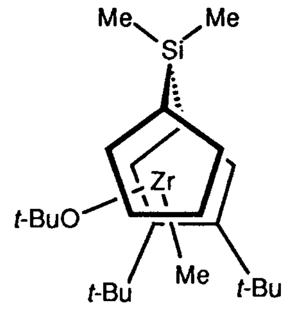
[7] (a) T. Mise, S. Miya, H. Yamazaki, Chem. Lett. (1989) 1853–1856. (b) H. Wiesenfeldt, A. Reinmuth, E. Barsties, K. Evertz, H.-H. Brintzinger, J. Organomet. Chem. 369 (1989) 359–370. (c) S. Gutmann, P. Burger, H.-U. Hund, J. Hofmann, H.-H. Brintzinger, J. Organomet. Chem. 369 (1989) 343–348. (d) L. Atovmyan, S. Mkoyan, I. Urazowski, R. Broussier, S. Ninoreille, P. Perron, B. Gautheron, Organometallics 14, (1995) 2601–2604. (e) W. Kaminsky, O. Rabe, A.-M. Schauwienold, G. U. Schupfner, J. Hanss, J. Kopf, J. Organomet. Chem. 497 (1995) 181–193. (f) J. Gräper, G. Paolucci, R.D. Fischer, J. Organomet. Chem. 501 (1995) 211–218. (g) S.T. Chacon, E.B. Coughlin, L.M. Henling, J.E. Bercaw, J. Organomet. Chem. 497 (1995) 171–180. (h) S. Miyake, Y. Okumura, S. Inazawa, Macromolecules 28 (1995) 3074–3079.

[8] (a) R.P. Hughes, A.S. Kowalski, J.R. Lomprey, Organometallic, 13 (1994) 2691–2695. (b) R.P. Hughes, J.R. Lomprey, Inorg. Chim. Acta 240 (1995) 653–656. (c) R.P. Hughes, J.R. Lomprey, A.L. Rheingold, B.S. Haggerty, G.P.A. Yap, J. Organomet. Chem. 517 (1996) 89–99.

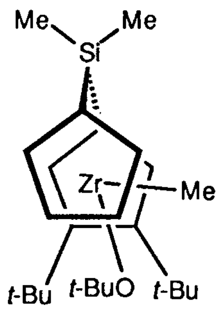
[9] In the case of the *ansa*-fluorenyl complex, $Me_2C(C_5H_4)(C_{13}H_{18})ZrCl_2$, in which two of the fluorenyl carbons are located at 2.651(7) and 2.665(7) Å from Zr, it was suggested that coordination of the fluorenyl ring was η^5-fashion rather than η^3-coordination, see A. Razavi, J. Ferrara, J. Organomet. Chem. 435 (1992) 299–310.

[10] T. Takahashi, K. Aoyagi, R. Hara, N. Suzuki, Chem. Lett. (1992) 1693–1696.

[11] It is possible that these NMR spectra represent one isomer **12-out**. However, the NMR spectra of **12** did not change at 50°C in THF in 3 h and signals assignable to the isomers were not observed.



12-out



12-in

[12] To the best of our knowledge, this is the first example of a C_s-symmetric zirconocene complex that has *tert*-butyl groups on

its Cp ring. Recently, Bercaw and coworkers reported a C_s-symmetric *ansa*-zirconocene complex that has vicinal two trimethylsilyl groups on its Cp ring. T.A. Herzog, D.L. Zubris, J.E. Bercaw, J. Am. Chem. Soc. 118 (1996) 11988–11989.

[13] (a) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10015–10031. (b) T.J. Marks, X. Yang, US Patent 5500398, Chem. 1996. (c) C. Janiak, K.C.H. Lange, P. Marquardt, Macromol. Rapid Commun. 16 (1995) 643–650.

[14] G. Erker, Pure Appl. Chem. 61 (1989) 1715–1722.

[15] Recently, Bercaw and coworkers reported that $(i\text{-Pr})_2Si(C_5H_4)[C_5H_2\text{-}3,4\text{-}(Me_3Si)_2]ZrCl_2$ of similar structure to **1** produced essentially atactic polypropylene. See [12]. Complex **5** also gave atactic polyhexene.

[16] S. Kiyooka, T. Yamashita, J. Tashiro, K. Takano, Y. Uchio, Tetrahedron Lett. 27 (1986) 5629–5632.

[17] M.F. Lappert, C.J. Pickett, P.I. Riley, Y.P.I.W., J. Chem. Soc. Dalton Trans. (1981) 805–813.

[18] J.M. Manriquez, D.R. McAlister, E. Rosenberg, A.M. Shiller, K.L. Williamson, S.I. Chan, J.E. Bercaw, J. Am. Chem. Soc. 100 (1978) 3078–3083.

[19] We previously described the preparation of **5** and the propylene polymerization with it in a patent. JP93-202124 (Kokai Tokkyo Koho); Chem. Abstr. 120: 55292y.

[20] P. Main, S.E. Hull, L. Lessinger, G. Germain, J.P. Decerq, M.M. Woolfson, MULTAN 78, University of York, 1978.

[21] T. Sakurai, K. Kobayashi, Rikagaku Kenkyusho Hokoku 55 (1979) 69.