



Ethylene polymerization and ethylene/1-octene copolymerization using group 4 half-metallocenes containing aryloxo ligands, Cp^{*}MCl₂(OAr) [M = Ti, Zr, Hf; Ar = O-2,6-R₂C₆H₃, R = ^tBu, Ph]–MAO catalyst systems

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ARTICLE INFO

Article history:

Received 13 December 2008
Received in revised form
26 December 2008
Accepted 5 January 2009
Available online 9 January 2009

Keywords:

Ethylene polymerization
Titanium
Zirconium
Hafnium
Coordination polymerization

ABSTRACT

Effect of the centered metal toward the catalytic activity as well as comonomer incorporation has been explored in ethylene (co)polymerization using a series of Cp^{*}MCl₂(O-2,6-R₂C₆H₃) [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), ^tBu (**b**), ⁱPr (**c**)] in the presence of methylaluminoxane (MAO) cocatalyst. Complexes **2a**, **3a,b** were prepared and identified, and the structures for **2–3a,b** were determined by X-ray crystallography as a distorted tetrahedral geometry around the metal center. The catalytic activity in ethylene polymerization was affected by the centered metal employed [Ti > Zr > Hf]; the complexes containing 2,6-diphenylphenoxy ligand (**1–3a**) showed higher catalytic activities than the complexes containing 2,6-di-*tert*-butylphenoxy analogues (**1–3b**). The molecular weights in the resultant polymers prepared by the Zr and the Hf analogues were lower than those prepared by the Ti–Ph (**1a**) and the Ti–ⁱPr (**1c**) analogues. Although the copolymerizations of ethylene with 1-octene afforded the copolymers with uniform molecular weight distributions (except **1b**), both the catalytic activities and the 1-octene incorporation were highly affected by the centered metal employed; the Ti–ⁱPr analogue (**1c**) seems to be the most suited in terms of both the catalytic activity and the 1-octene incorporation. The attempted copolymerization of ethylene with 2-methyl-1-pentene using **2a,b** and **3a**–MAO catalysts afforded linear polyethylene.

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1. Introduction

Design and synthesis of efficient transition metal complex catalysts for precise olefin polymerization attract considerable attention in the fields of catalysis, organometallic chemistry, and polymer chemistry [1–6]. *Nonbridged* half-metallocene type group 4 transition metal complexes of the type, Cp^{*}M(L)X₂ (Cp^{*} = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr, NR₂, NPR₃, etc.; X = halogen, alkyl), display unique characteristics as olefin polymerization catalysts, because these catalysts are effective for production of new polyolefins [4a] which are not prepared by conventional Ziegler–Natta catalysts, ordinary metallocenes [1] and/or so-called ‘constrained geometry’ (linked Cp–amide) type catalysts [2]. In particular, *nonbridged* half-titanocenes (titanium half-sandwich complexes) containing an aryloxo ligand of the type, Cp^{*}Ti(OAr)X₂ (Ar = 2,6-ⁱPr₂C₆H₃, etc.), display promising characteristics [4a,7–14]. For example, efficient catalyst precursors especially for copolymerization of ethylene with α-olefin [9], styrene [10], norbornene [11], cyclohexene [12], 2-methyl-1-pentene [13], vinylcyclohexane [14] can

be tuned by modification of the cyclopentadienyl fragment (Cp^{*}).

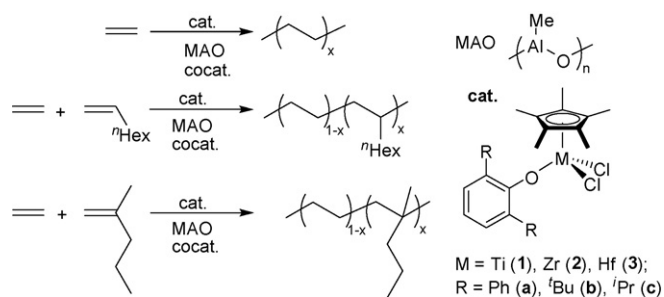
Syntheses of Cp^{*}ZrCl₂(O-2,6-^tBu₂C₆H₃) and Cp^{*}Zr(O-2,4,6-Me₃C₆H₂)₃ and their use as the catalyst precursors for ethylene polymerization in the presence of methylaluminoxane (MAO) cocatalyst were reported [15]. Moreover, synthesis of Cp^{*}TiCl₂(O-2,6-Ph₂C₆H₃) and application in cyclization (intramolecular Pauson–Khand) reaction was reported [16]. We demonstrated that the aryloxo substituent plays an important role especially toward the catalytic activity in ethylene (α-olefin) polymerization [7] as well as in copolymerization of ethylene with α-olefin [9c], 2-methyl-1-pentene [13b]. However, synthesis of a series of group 4 half-metallocenes containing aryloxo ligands and the study concerning effect of centered metal not only toward the catalytic activity in ethylene polymerization, but also toward the monomer reactivities in ethylene copolymerization have not so far been reported. In this paper, we thus explored an effect of centered metal in ethylene (co)polymerization using a series of Cp^{*}MCl₂(O-2,6-R₂C₆H₃) [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), ^tBu (**b**), ⁱPr (**c**)] in the presence of MAO cocatalyst (Scheme 1) [17,18].

2. Results and discussion

Cp^{*}ZrCl₂(O-2,6-Ph₂C₆H₃) (**2a**) could be prepared by treating Cp^{*}ZrCl₃ with Li(O-2,6-Ph₂C₆H₃) in a mixed solution of

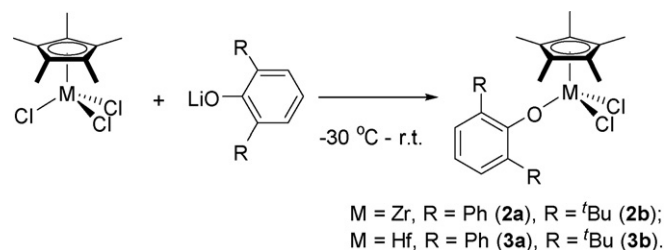
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Scheme 1.

toluene/*n*-hexane according to an analogous procedure for $\text{Cp}^*\text{ZrCl}_2(\text{O}-2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)$ (**2b**) reported previously (Scheme 2) [15]. The Hf analogues, $\text{Cp}^*\text{HfCl}_2(\text{O}-2,6\text{-}^t\text{Bu}_2\text{C}_6\text{H}_3)$ [R = Ph (**3a**), ^tBu (**3b**)], could also be prepared similarly by treating Cp^*HfCl_3 with



Scheme 2.

$\text{Li}(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ in toluene or Et_2O (Scheme 2). These complexes were identified based on ^1H , ^{13}C NMR spectra and elemental analyses. As shown in Fig. 1, the structures for **2a,b** and **3a,b** could be determined by X-ray crystallography [19], and their selected bond distances and angles are summarized in Table 1.

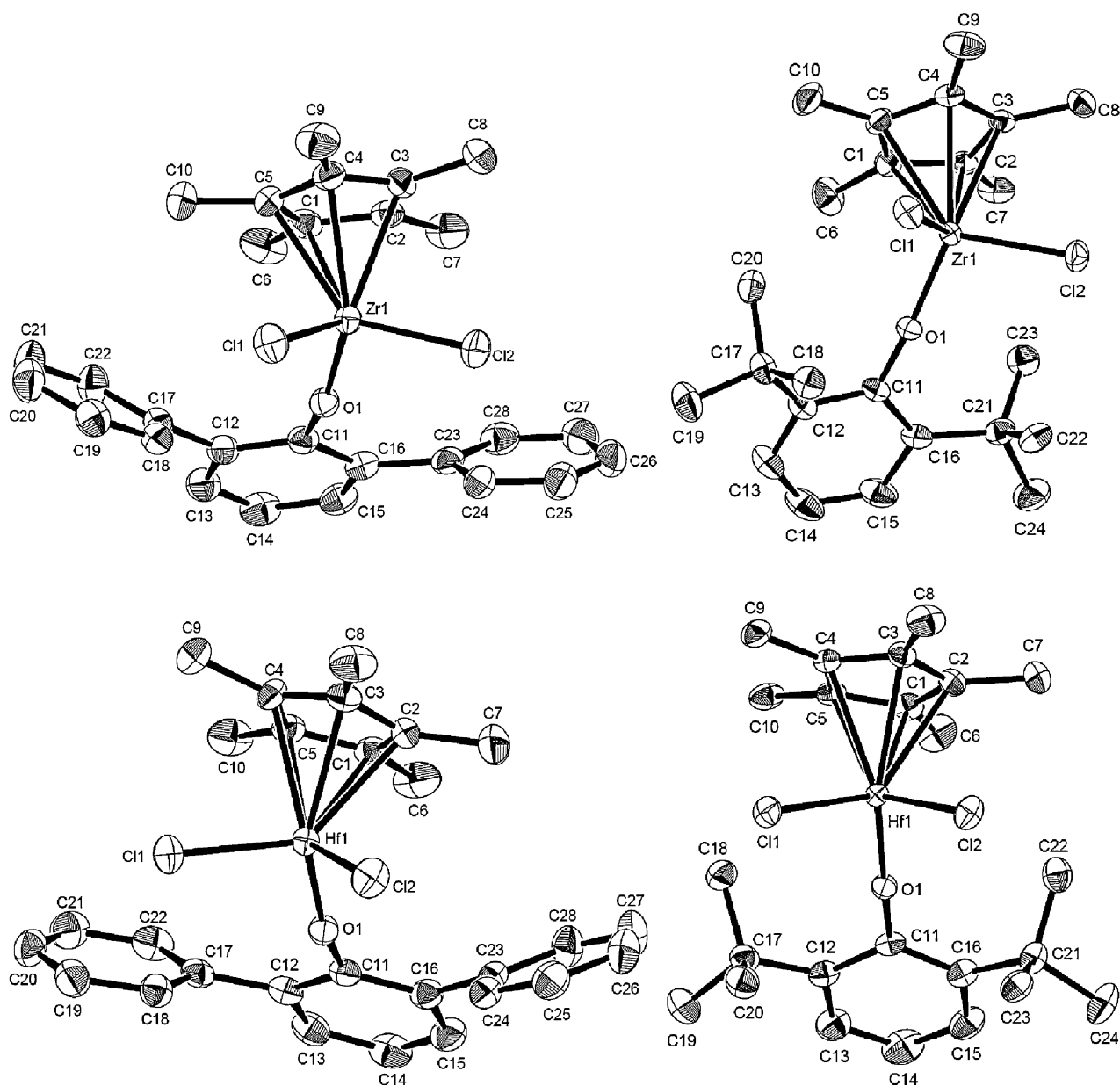


Fig. 1. ORTEP drawings for $\text{Cp}^*\text{MCl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ [top: M = Zr, R = Ph (**2a**, left), ^tBu, (**2b**, right); bottom: M = Hf, R = Ph (**3a**, left), ^tBu (**3b**, right)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity [18].

Table 1
Summary of selected bond distances (Å) and angles (°) for Cp**M*Cl₂(O-2,6-R₂C₆H₃) [*M* = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), R = ^tBu (**b**), ⁱPr (**c**)]^a.

Complex (M, R)	1a ^b (Ti, Ph)	1b ^c (Ti, ^t Bu)	1c ^d (Ti, ⁱ Pr)	2a (Zr, Ph)	2b (Zr, ^t Bu)	3a (Hf, Ph)	3b (Hf, ^t Bu)
<i>Selected bond distances</i> (Å)							
M–Cl1	2.2693(13)	2.2674(10)	2.305(2)	2.4008(4)	2.3961(3)	2.3640(7)	2.3714(6)
M–Cl2	2.2865(14)	2.2674(10)	2.239(2)	2.3881(5)	2.3963(3)	2.3751(7)	2.3710(8)
M–O	1.811(3)	1.804(2)	1.772(3)	1.9349(12)	1.9431(9)	1.9224(15)	1.9280(19)
<i>Selected bond angles</i> (°)							
M–O–C(Phenyl)	160.6(3)	155.5(2)	173.0(3)	160.99(11)	169.95(8)	160.97(14)	169.64(16)
Cl1–M–Cl2	98.70(5)	98.10(4)	103.45(5)	99.629(17)	98.234(12)	99.40(2)	98.04(2)
Cl1–M–O	104.33(10)	103.22(6)	99.1(2)	107.37(3)	103.72(2)	104.71(4)	104.60(6)
Cl2–M–O	105.20(10)	103.22(6)	104.1(2)	105.73(3)	105.52(3)	106.25(4)	103.10(5)

^a Detailed analysis conditions and results for **2a**, **b**, and **3a**, **b** are shown in the Supplementary materials.

^b Cited from reference [16].

^c Cited from reference [7].

^d Cited from reference [7].

These complexes show a rather distorted tetrahedral geometry around zirconium/hafnium, as seen in Cp**Ti*Cl₂(O-2,6-R₂C₆H₃) [R = Ph (**1a**), ^tBu (**1b**), ⁱPr (**1c**)] [7a,c,16]. The Zr–Cl bond distances [**2a**, **b**: 2.3881(5)–2.4008(4) Å] are slightly longer than the Hf–Cl bond distances [**3a**, **b**: 2.3640(7)–2.3751(7) Å], and are longer than the Ti–Cl bond distances [**1a**, **b**: 2.2674(10)–2.2865(14) Å] [7c,16], probably influenced by the atomic radii [20]. In contrast, no significant differences are observed in the Cl–M–Cl bond angles, except that the angles in the Ph analogues (**1**–**3a**) are larger than those in the ^tBu analogues (**1**–**3b**). The Zr–O bond distances [1.9349(12), 1.9431(9) Å] are also longer than the Hf–O [1.9224(15),

1.9280(19) Å] and the Ti–O [1.811(3), 1.804(2) Å] bond distances [7c,16]. The M–O–C(phenyl) bond angles in the Zr–Ph (**2a**) and the Hf–Ph analogues (**3a**) are smaller than those in the ^tBu analogues (**2**–**3b**), whereas opposite trend is observed in the Ti analogues (**1a**, **b**) [7c,16]. As reported previously [7a], the Ti–ⁱPr analogue (**1c**), which showed exceptionally high catalytic activities in ethylene (co)polymerizations, possesses large Ti–O–C(phenyl) bond angle [173.0(3)°], along with a rather short Ti–O bond distance [1.772(3) Å]; the fact suggests that these distances and angles are influenced by a combination of both the centered metal and substituent in the aryloxo group.

Table 2
Ethylene polymerization by Cp**M*Cl₂(O-2,6-R₂C₆H₃) [*M* = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), R = ^tBu (**b**), ⁱPr (**c**)]–MAO catalyst systems^a.

Run	Cat. (μmol)	MAO/mmol (Al/M × 10 ⁻³) ^b	Yield/mg	Activity/kg-PE/mol-M h	M _n ^c (× 10 ⁻⁴)	M _w /M _n ^c
1	1a (0.01)	1.0 (100)	133	79800	120	3.2
2	1a (0.01)	2.0 (200)	145	87000		
3	1a (0.01)	3.0 (300)	144	86400	67.8 ^d	3.3
4	1a (0.01)	4.0 (400)	161	96600	67.0 ^d	2.9
5	1a (0.01)	5.0 (500)	151	90600	54.4 ^d	3.4
6	1b (0.1)	1.0 (10.0)	93	5580	3.74	2.9
7	1b (0.1)	2.0 (20.0)	113	6780	2.63 ^e	2.5
8	1b (0.1)	3.0 (30.0)	127	7620	1.78 ^e	2.3
9	1b (0.1)	4.0 (40.0)	140	8400	2.67 ^e	2.4
10	1b (0.1)	5.0 (50.0)	125	7500	2.35 242	2.9 2.0
11	1c (0.01)	3.0 (300)	72	43200	189	2.4
12	2a (0.2)	1.0 (5.0)	5	200		
13	2a (0.2)	2.0 (10.0)	3	90		
14	2a (0.2)	2.5 (12.5)	85	2600	0.59	2.1
15	2a (0.2)	3.0 (15.0)	295	8850	2.31	2.2
16	2a (0.2)	4.0 (20.0)	205	6150	2.43	2.0
17	2a (0.2)	5.0 (25.0)	14	420		
18	2b (0.5)	1.0 (2.0)	181	2170	35.1	1.9
19	2b (0.5)	2.0 (4.0)	278	3340	21.3	2.3
20	2b (0.5)	3.0 (6.0)	217	2600	16.3	2.3
21	2b (0.5)	4.0 (8.0)	81	970	13.4	2.2
22	2b (0.5)	5.0 (10.0)	103	1240	13.5	2.0
23	3a (1.0)	1.0 (1.0)	20	120	0.79	2.8
24	3a (1.0)	2.0 (2.0)	24	140	0.56	2.0
25	3a (1.0)	3.0 (3.0)	108	648	0.49	2.0
26	3a (1.0)	4.0 (4.0)	125	750	0.50	1.9
27	3a (1.0)	5.0 (5.0)	86	520	0.40	2.0
28	3b (5.0)	3.0 (0.6)	65	78	2.33	4.2

^a Conditions: toluene 30 mL, MAO (prepared by removing toluene and AlMe₃ from ordinary MAO) 1–5 mmol, ethylene 6 atm, 25 °C, 10 min.

^b Molar ratio of Al/M.

^c GPC data in *o*-dichlorobenzene vs. polystyrene standards.

^d Low molecular weight shoulder was observed in small amount in the GPC trace.

^e High molecular weight shoulder was observed in small amount in the GPC trace.

Table 3Effect of temperature in ethylene polymerization by Cp^{*}MCl₂(O-2,6-R₂C₆H₃) [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), R = ^tBu (**b**), ⁱPr (**c**)]–MAO catalyst systems^a.

Run	Cat. (μmol)	MAO/mmol (Al/M × 10 ⁻³) ^b	Temperature/°C	Yield/mg	Activity/kg-PE/mol-Mh	M _n ^c (× 10 ⁻⁴)	M _w /M _n ^c
4	1a (0.01)	4.0 (400)	25	161	97000	67.0 ^d	2.9
29	1a (0.01)	4.0 (400)	40	88	52800	61.1 ^d	2.9
30	1a (0.01)	4.0 (400)	55	67	40200	40.7 ^d	3.2
9	1b (0.1)	4.0 (40.0)	25	140	8400	2.67 ^e	2.4
31	1b (0.1)	4.0 (40.0)	40	63	3780	2.54 ^e	2.2
32	1b (0.1)	4.0 (40.0)	55	82	4920	2.32 90.8	1.7 1.9
15	2a (0.2)	3.0 (15.0)	25	295	8850	2.31	2.2
33	2a (0.2)	3.0 (15.0)	40	20	600	Insoluble	
34	2a (0.2)	3.0 (15.0)	55	15	450	Insoluble	
19	2b (0.5)	2.0 (4.0)	25	278	3340	21.3	2.3
35	2b (0.5)	2.0 (4.0)	40	36	430	Insoluble	
36	2b (0.5)	2.0 (4.0)	55	37	440	Insoluble	
26	3a (1.0)	4.0 (4.0)	25	125	750	0.50	1.9
37	3a (1.0)	4.0 (4.0)	40	140	840	0.38	2.1
38	3a (1.0)	4.0 (4.0)	55	270	1620	0.41	2.0

^a Conditions: toluene 30 mL, MAO (prepared by removing toluene and AlMe₃ from ordinary MAO) 1–5 mmol, ethylene 6 atm, 25 °C, 10 min.^b Molar ratio of Al/M.^c GPC data in *o*-dichlorobenzene vs. polystyrene standards.^d Low molecular weight shoulder was observed in small amount in the GPC trace.^e High molecular weight shoulder was observed in small amount in the GPC trace.

2.1. Ethylene polymerization by Cp^{*}MCl₂(O-2,6-R₂C₆H₃)–MAO catalyst systems

Ethylene polymerizations using a series of Cp^{*}MCl₂(O-2,6-R₂C₆H₃) [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), ^tBu (**b**)] were conducted in toluene in the presence of MAO cocatalyst, and Cp^{*}TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**1c**) was also chosen for comparison. MAO white solids prepared by removing AlMe₃ and toluene from the commercially available samples [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were chosen, because it was effective for the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when **1c** and [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ were used as the catalyst precursor [9a]. The results are summarized in Tables 2 and 3.

Table 2 summarizes the results conducted at 25 °C with various Al/M molar ratios. The Ti–Ph analogue (**1a**) showed notable catalytic activity in the ethylene polymerization (runs 1–5), and the activity was somewhat higher than that by the Ti-ⁱPr analogue (**1c**, run 11) under the same conditions. As reported previously [7c], the activities by the Ti-^tBu analogue (**1b**) were lower (runs 6–10) than those by **1c** under the same conditions. The observed activities by **1a,b** were not strongly dependent upon the Al/Ti molar ratios employed, however, as exemplified in Fig. 2 (GPC charts in the result

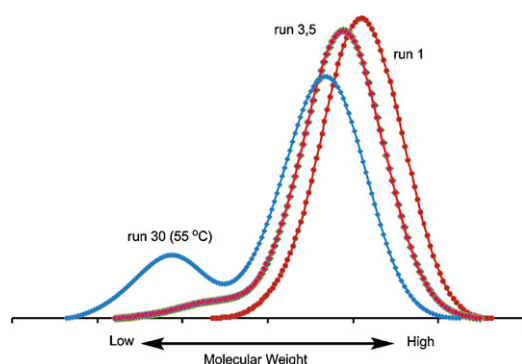


Fig. 2. GPC traces for resultant polyethylene prepared by Cp^{*}TiCl₂(O-2,6-Ph₂C₆H₃) (**1a**)–MAO catalyst.

tant polyethylene prepared by **1a**–MAO catalyst, runs 1,3,5, and 30), the Al/Ti ratio affected the molecular weight distributions in the resultant polyethylenes; peaks corresponding to trace or small amount of low molecular weight polymers were observed if the polymerizations were conducted at high Al/Ti molar ratios or at 55 °C.

The catalytic activity with a series of Cp^{*}MCl₂(O-2,6-R₂C₆H₃) (**1-3a,b**) under the optimized Al/M molar ratios increased in the order: **1a** (96600 kg-PE/mol-Ti h, run 4) » **2a** (8850, run 15), **1b** (8400, run 9) > **2b** (3340, run 19) > **3a** (750, run 26) > **3b** (78, run 28). The results suggest that the complexes containing 2,6-diphenylphenoxy ligand (**1-3a**) showed higher catalytic activities than the complexes containing 2,6-di-*tert*-butylphenoxy ligand (**1-3b**), probably due to a steric bulk around the metal center. The activity by the Zr–Ph analogue (**2a**) was sensitive toward the Al/Zr molar ratio (runs 12–17). The molecular weight in the resultant polymers prepared by the Zr and Hf analogues were lower than those prepared by Ti–Ph (**1a**) and Ti-ⁱPr (**1c**) analogues, although the polymers possessed unimodal molecular weight distributions, as seen in the polymer prepared by **1c**–MAO catalyst under the same conditions (run 11).

Table 3 summarizes the results in the ethylene polymerization employed at higher temperature. The catalytic activity by the Ti complexes (**1a,b**) decreased at higher temperature (40, 55 °C), and significant decreases in the activities were observed in case of Zr complex catalysts (**2a,b**, runs 33–36). In contrast, the activity increased at higher temperature, if the Hf–Ph complex (**3a**) was employed as the catalyst precursors (runs 37–38). The fact (temperature dependence) should be a unique contrast as effect of centered metal toward the catalytic activity.

2.2. Copolymerization of ethylene with 1-octene and 2-methyl-1-pentene by Cp^{*}MCl₂(O-2,6-R₂C₆H₃)–MAO catalyst systems

Table 4 summarizes the results in copolymerization of ethylene with 1-octene, 2-methyl-1-pentene (2M1P) using a series of Cp^{*}MCl₂(O-2,6-R₂C₆H₃) [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), ^tBu (**b**), ⁱPr (**c**)]–MAO catalyst systems. Fig. 3 shows typical ¹³C NMR spectra in the resultant polymers. As reported previously [9b,c], the Ti-ⁱPr complex (**1c**) exhibited notable catalytic activ-

Table 4
Copolymerization of ethylene with 1-octene (OC), 2-methyl-1-pentene (2M1P) by $\text{Cp}^*\text{MCl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ [$\text{M} = \text{Ti}$ (**1**), Zr (**2**), Hf (**3**); $\text{R} = \text{Ph}$ (**a**), $\text{R} = {}^t\text{Bu}$ (**b**), ${}^i\text{Pr}$ (**c**)]—MAO catalyst systems^a.

Run	Cat. (μmol)	MAO/mmol ($\text{Al}/\text{M} \times 10^{-3}$) ^b	Comonomer (mmol/mL)	Temperature/ $^\circ\text{C}$	Yield/mg	Activity/kg-PE/mol-M h	$M_n^c (\times 10^{-4})$	M_w/M_n^c	Comonomer ^d /mol%
4	1a (0.01)	4.0 (400)	–	25	161	97000	67.0 ^e	2.9	–
39	1a (0.01)	4.0 (400)	OC (1.06)	25	53	32000	4.70	1.9	27.0
40	1a (0.01)	4.0 (400)	OC (1.06)	55	Trace	–	–	–	–
41	1a (0.01)	4.0 (400)	2M1P (1.35)	25	Trace	–	–	–	–
42	1a (0.01)	4.0 (400)	2M1P (1.35)	55	222	133000	1.64	4.8	Trace
9	1b (0.1)	4.0 (40.0)	–	25	140	8400	2.67 ^f	2.4	–
43	1b (1.0)	4.0 (4.0)	OC (1.06)	25	68	410	3.86	3.8	27.8
44	1b (1.0)	4.0 (4.0)	OC (1.06)	55	127	762	3.70	3.3	34.3
45	1b (5.0)	4.0 (0.8)	2M1P (1.35)	25	99	120	1.50	5.6	Trace
11	1c (0.01)	3.0 (300)	–	25	72	43200	189	2.4	–
46 ^g	1c (0.02)	3.0 (150)	OC (1.06)	25	308	154000	12.8	2.1	27.9
47 ^h	1c (0.5)	4.5 (9.0)	2M1P (1.35)	25	705	8460	11.8	2.1	3.3
15	2a (0.2)	3.0 (15.0)	–	25	295	8850	2.31	2.2	–
48	2a (0.2)	3.0 (15.0)	OC (1.06)	25	Trace	–	–	–	–
49	2a (0.2)	3.0 (15.0)	OC (1.06)	55	431	12930	1.41	2.2	3.2
50	2a (0.2)	3.0 (15.0)	2M1P (1.35)	25	24	720	Insoluble	–	–
51 ⁱ	2a (0.1)	3.0 (30.0)	2M1P (1.35)	55	400	48000	194 ^j	2.2	None
19	2b (0.5)	2.0 (4.0)	–	25	278	3340	21.3	2.3	–
52	2b (0.5)	2.0 (4.0)	OC (1.06)	25	263	3200	26.1	2.3	9.4
53	2b (0.5)	2.0 (4.0)	OC (1.06)	55	219	2600	1.24	2.9	15.9
54	2b (0.5)	2.0 (4.0)	2M1P (1.35)	25	150	1800	6.80	1.3	None
55	2b (0.5)	2.0 (4.0)	2M1P (1.35)	55	204	2450	156	2.4	–
26	3a (1.0)	4.0 (4.0)	–	25	125	750	0.50	1.9	–
56	3a (1.0)	4.0 (4.0)	OC (1.06)	25	128	768	0.50	2.0	9.9
57	3a (1.0)	4.0 (4.0)	OC (1.06)	55	139	834	0.65	1.8	16.4
58	3a (1.0)	4.0 (4.0)	2M1P (1.35)	25	80	480	0.42	2.2	None
59	3a (1.0)	4.0 (4.0)	2M1P (1.35)	55	206	1240	0.32 ^f	2.6	–

^a Conditions: toluene 25 mL + 1-octene (OC) or 2-methyl-1-pentene (2M1P) 5 mL, MAO (prepared by removing toluene and AlMe_3 from ordinary MAO) 1–5 mmol, ethylene 6 atm, 25 $^\circ\text{C}$, 10 min.

^b Molar ratio of Al/M .

^c GPC data in *o*-dichlorobenzene vs. polystyrene standard.

^d Comonomer content in copolymer estimated by ^{13}C NMR spectra.

^e Low molecular weight shoulder was observed in small amount in the GPC trace.

^f High molecular weight shoulder was observed in small amount in the GPC trace.

^g Cited from reference [13b], polymerization 6 min.

^h Cited from reference [13a].

ⁱ Polymerization time 5 min.

^j Sample was hardly soluble even in hot *o*-dichlorobenzene.

ity in ethylene/1-octene copolymerization (run 46); the activity in the copolymerization was higher than that in the ethylene homopolymerization. The resultant polymer prepared by **1c** was high molecular weight poly(ethylene-*co*-1-octene) with unimodal molecular weight distribution. The 1-octene contents in the resultant copolymers prepared by **1a**, **1b** were very close to that prepared by **1c**, when the copolymerization was conducted under the same conditions at 25 $^\circ\text{C}$ (runs 39,43). However, the activities by **1a**, **1b** decreased upon the presence of 1-octene in the copolymerization; the M_n value in the copolymer prepared by **1a** was lower than that in the polyethylene (runs 4 vs. 39) and the resultant copolymer prepared by **1b** possessed broad molecular weight distribution.

It also turned out that the copolymerization using a series of $\text{Cp}^*\text{MCl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ (**1–2a,b**, and **3a**)—MAO catalysts afforded the copolymer, poly(ethylene-*co*-1-octene)s, with unimodal molecular weight distributions ($M_w/M_n = \text{ca. } 2$) except **1b**. However, notable increases in the activity in the copolymerization from the ethylene homopolymerization as observed by **1c** were not observed in all cases. Note that the 1-octene contents in the resultant copolymers were dependent upon the centered metal employed rather than the phenoxy substituent (Ph or ${}^t\text{Bu}$), and the Ti complexes (**1a,c**) showed better 1-octene incorporation. Both the catalytic activities and 1-octene contents in the copolymers by the Zr (**2a,b**) and the Hf (**3a**) complexes increased at higher temperatures (55 $^\circ\text{C}$, runs 49, 53, 57), whereas the extremely low catalytic activity by the Ti-Ph analogue (**1a**) was observed at 55 $^\circ\text{C}$ in the copolymerization (run 40) and the activities in the ethylene homopolymerizations

by the Zr analogues (**2a,b**) decreased at higher temperature (runs 33–34, 35–36). The Zr complex (**2b**) showed similar 1-octene incorporation to those by **3a**, however, these showed less efficient 1-octene incorporations than the Ti complexes (**1a,c**) under these conditions; **2a** showed the lowest 1-octene incorporation. No significant differences in microstructures in the resultant copolymers prepared by **1–3a** were observed, although some resonances were not seen due to the low 1-octene contents in the copolymers prepared by **2–3a** and resonances ascribed to the polymer chain ends were seen due to the low molecular weight in the copolymer by **3a**. Taking into account these results, it is thus suggested that the Ti analogues (**1a,c**) seem to be more suited as the catalyst precursors in terms of both the activity and the 1-octene incorporation in the ethylene/1-octene copolymerization; the Ti- ${}^i\text{Pr}$ analogue (**1c**) exhibits exceptionally high catalytic activity with efficient 1-octene incorporation, as reported previously [9c].

As also reported previously [13], **1c** showed moderate catalytic activity in ethylene/2M1P copolymerization, and the resultant polymer was poly(ethylene-*co*-2M1P) that possesses rather high molecular weight with uniform molecular weight distribution (run 47, $M_n = 1.18 \times 10^5$, $M_w/M_n = 2.1$, 2M1P 3.3 mol%). In contrast, the activities by the Ti-Ph (**1a**), the Ti- ${}^t\text{Bu}$ (**1b**) analogues at 25 $^\circ\text{C}$ were low (runs 41, 45). Although a significant increase in the activity was observed by **1a** at 55 $^\circ\text{C}$, the resultant polymers contained trace amount of 2M1P. Therefore, only the Ti- ${}^i\text{Pr}$ complex (**1c**) could incorporate 2M1P in the copolymerization under these copolymerization conditions.

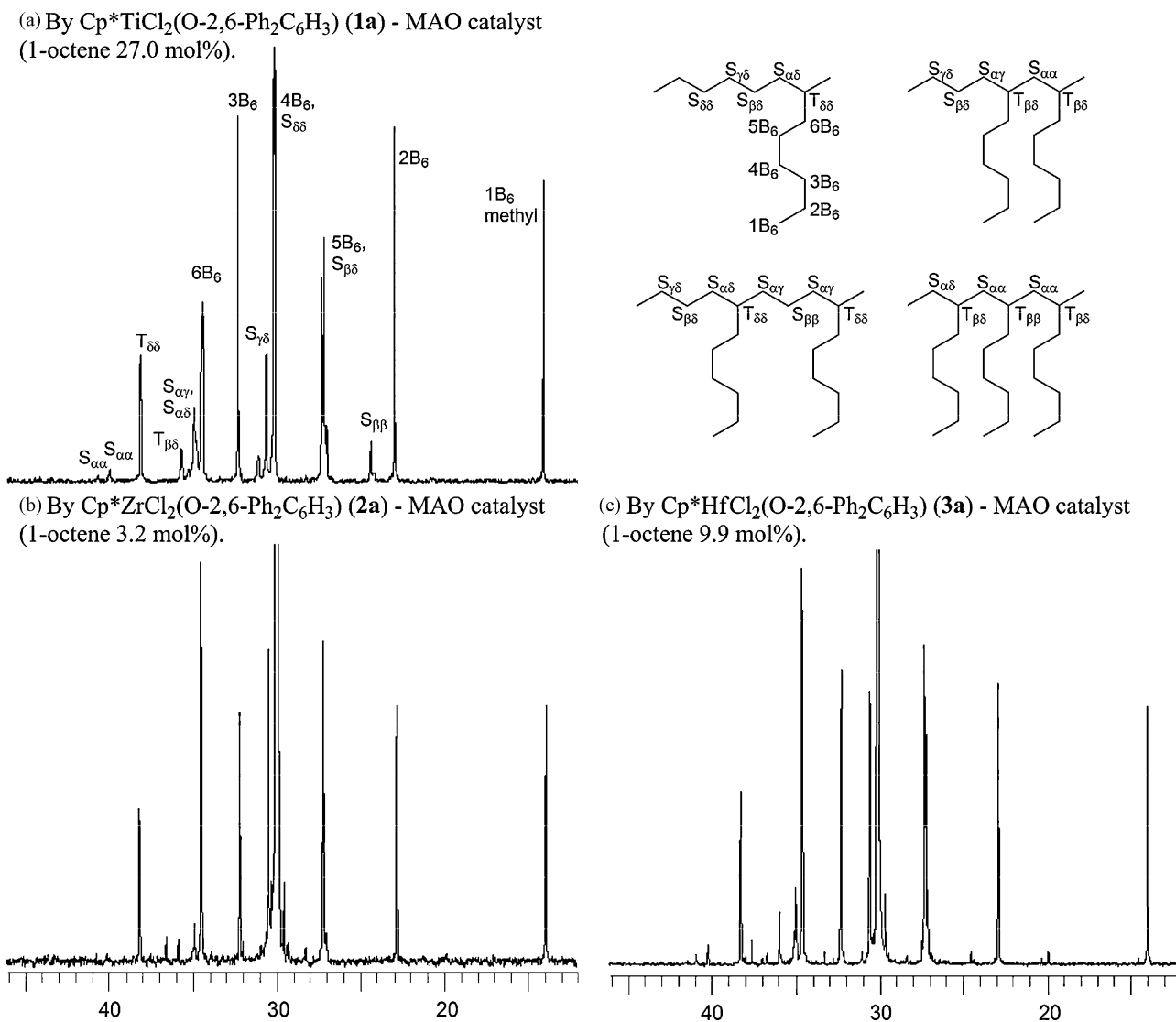


Fig. 3. ^{13}C NMR spectra (in $\text{C}_6\text{D}_6/1,2,4\text{-trichlorobenzene}$ 1/4 (v/v), at 110°C) for poly(ethylene-co-1-octene)s prepared by (a) $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)$ (**1a**), (b) $\text{Cp}^*\text{ZrCl}_2(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)$ (**2a**), and (c) $\text{Cp}^*\text{HfCl}_2(\text{O}-2,6\text{-Ph}_2\text{C}_6\text{H}_3)$ (**3a**) in the presence of MAO cocatalyst.

The polymerizations of ethylene using the Zr (**2a,b**) and the Hf (**3a**) were also explored in the presence of 2M1P, and notable increase in the activity at 55°C was observed in the polymerization using the Zr-Ph analogue (run 51). However, the resultant polymers were linear polyethylene in all cases and resonances ascribed to incorporation of 2M1P were not observed in the ^{13}C NMR spectra even in a trace amount. Taking into account of these results, the Ti-*i*Pr (**1c**) analogue should be most suited as the catalyst precursor in terms of both the catalytic activity and 2M1P incorporation.

3. Conclusion

A series of $\text{Cp}^*\text{MCl}_2(\text{O}-2,6\text{-R}_2\text{C}_6\text{H}_3)$ [Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), *t*Bu (**b**)] have been prepared and effect of the centered metal toward the catalytic activity as well as comonomer incorporation has been explored in ethylene (co)polymerization in the presence of MAO cocatalyst. Structures for **2-3a,b** were determined by X-ray crystallography as a rather distorted tetrahedral geometry around the metal center. The catalytic activity in ethylene polymerization was affected by the centered metal employed [Ti > Zr > Hf], and the complexes containing 2,6-diphenylphenoxy ligand (**1-3a**) showed higher catalytic activities than the complexes containing 2,6-di-

tert-butylphenoxy analogues (**1-3b**). The molecular weights in the resultant polymers prepared by the Zr and the Hf analogues were lower than those prepared by the Ti-Ph (**1a**) and the Ti-*i*Pr (**1c**) analogues. Although the copolymerizations of ethylene with 1-octene afforded the copolymer with uniform molecular weight distributions (except **1b**), both the activities and 1-octene incorporation were highly affected by the centered metal employed; the Ti-*i*Pr analogue (**1c**) seems to be the most suited in terms of both the catalytic activity and the 1-octene incorporation. The Ti-*i*Pr analogue (**1c**) only showed rather efficient comonomer incorporation in the copolymerization of ethylene with 2M1P. We believe that the information should be helpful for designing efficient catalyst precursors for precise, controlled olefin polymerization.

4. Experimental section

4.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. All chemicals used were of reagent grade and were purified by standard purification procedures. Anhydrous grade toluene and

n-hexane (Kanto Chemical Co., Inc.) were stored in drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Anhydrous grade dichloromethane and diethyl ether (Kanto Kagaku Co., Ltd.) were stored in drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16). Cp*TiCl₃ (Wako Pure Chemical Ind., Ltd.), Cp*ZrCl₃ (Aldrich), Cp*HfCl₃ (Aldrich) were used as received. Cp*TiCl₂(O-2,6-Ph₂C₆H₃) (**1a**) [16], Cp*TiCl₂(O-2,6-^tBu₂C₆H₃) (**1b**) [7c], Cp*TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**1c**) [7a], and Cp*ZrCl₂(O-2,6-^tBu₂C₆H₃) (**2b**) [15] were prepared according to the published procedures.

Ethylene of polymerization grade (Sumitomo Seika Chemicals, Ltd.) was used as received without further purification. 1-Octene (Wako Pure Chemical Ind., Ltd.) and 2-methyl-1-pentene (TCI Co., Ltd.) were stored in drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through alumina short column under nitrogen. Toluene and AlMe₃ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, AlMe₃, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids.

All ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ¹H and 100.53 MHz for ¹³C). All spectra were obtained in the solvent indicated at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to SiMe₄ (δ 0.00, ¹H, ¹³C). ¹³C NMR spectra for the resultant polymers [polyethylene, poly(ethylene-co-1-octene), and poly(ethylene-co-2-methyl-1-pentene)] were measured at 110 °C in C₆D₆/1,2,4-trichlorobenzene (1/4, v/v). The relaxation delay was 5.2 s, the acquisition time was 1.3 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000. Elemental analyses were performed by using a PE2400II Series (PerkinElmer Co.), and some analytical runs were performed twice to confirm the reproducibility in the independent analysis/synthesis runs. Certain C values were somewhat lower than those calculated, whereas their N, H, values were close; this is due to incomplete combustion (to form titanium carbide).

Molecular weights and molecular weight distributions for the poly(ethylene-co-2-methyl-1-pentene)s and poly(ethylene-co-1-

octene)s were measured by gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mmφ ID), ranging from <10² to <2.8 × 10⁸ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

4.2. Synthesis of Cp*ZrCl₂(O-2,6-Ph₂C₆H₃) (**2a**)

Into a toluene/*n*-hexane suspension containing Cp*ZrCl₃ 303 mg (0.910 mmol), LiO-2,6-Ph₂C₆H₃ (0.928 mmol) was added at -30 °C. The reaction mixture was warmed slowly up to room temperature, and the mixture was stirred for 5 h. The solvent was removed *in vacuo* after addition of CH₂Cl₂, and the resultant residue was extracted with hot toluene. The toluene extract was then dried *in vacuo* to give a pale yellow solid. The solid was then dissolved in a minimum amount of CH₂Cl₂ layered by a small amount of *n*-hexane. The chilled solution gave colorless crystal. Yield: 359 mg (72.7%). ¹H NMR (CDCl₃): δ 7.55 (d, 4H, *J* = 8.1), 7.44 (t, 4H, *J* = 7.5), 7.32 (t, 2H, *J* = 7.3), 7.27 (d, 2H, *J* = 7.7), 7.11 (t, 1H, *J* = 7.5), 1.57 (s, 16H). ¹³C NMR (CDCl₃): δ 154.9, 138.8, 133.3, 130.4, 130.3, 128.9, 127.1, 126.2, 122.3, 10.9. Anal. Calcd. for C₂₈H₂₈Cl₂ZrO: C, 61.97; H, 5.20; N, 0%. Found: C, 61.20; H, 5.31; N, 0%.

4.3. Synthesis of Cp*HfCl₂(O-2,6-Ph₂C₆H₃) (**3a**)

To a toluene solution (10 mL) containing Cp*HfCl₃ 506 mg (1.20 mmol), LiO-2,6-Ph₂C₆H₃ 313 mg (1.24 mmol) was added at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 12 h. The solvent was removed *in vacuo* after addition of CH₂Cl₂, and the resultant white tan residue was extracted with hot toluene. The toluene extract was then dried *in vacuo*, and the resulting white was dissolved in a minimum amount of CH₂Cl₂ layered by a small amount of *n*-hexane. The chilled solution gave colorless crystal. Yield 430 mg (56.7%). ¹H NMR (CDCl₃): δ 7.52 (dd, 4H, *J* = 7.5, 1.4), 7.41 (t, 4H, *J* = 7.5), 7.31 (tt, 2H, *J* = 7.5, 1.4), 7.26 (d, 2H, *J* = 7.4), 7.08 (t, 1H, *J* = 7.4), 1.61 (s, 15H). ¹³C NMR (CDCl₃): δ 154.9, 138.3,

Table 5
Crystal and data collection parameters [19] ^a.

Complex	2a	2b	3a	3b
Formula; formula weight	C ₂₈ H ₂₈ Cl ₂ OZr; 542.65	C ₂₄ H ₃₆ Cl ₂ OZr; 502.67	C ₂₈ H ₂₈ Cl ₂ HfO; 629.92	C ₂₄ H ₃₆ Cl ₂ HfO; 589.94
Habits	Colorless, block	Colorless, block	Colorless, block	Colorless, block
Crystal size (mm)	0.35 × 0.15 × 0.15	0.40 × 0.30 × 0.18	0.30 × 0.25 × 0.18	0.40 × 0.40 × 0.30
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2 ₁ /n (#14)	P2 ₁ /n (#14)	P2 ₁ /n (#14)	P2 ₁ /n (#14)
<i>a</i> (Å)	9.0510(3)	9.6805(4)	9.0287(3)	9.6678(3)
<i>b</i> (Å)	7.5984(2)	15.5345(5)	7.61072(18)	15.5309(4)
<i>c</i> (Å)	36.2051(10)	17.0748(5)	36.2190(8)	17.0507(4)
β (Deg)	93.0128(12)	107.1917(11)	92.9237(12)	107.1726(8)
<i>V</i> (Å ³)	2486.51(13)	2453.01(15)	2485.54(12)	2446.02(11)
<i>Z</i> value	4	4	4	4
<i>D</i> _{calcd} (g/cm ³)	1.449	1.361	1.683	1.602
<i>F</i> ₀₀₀	1112.00	1048.00	1240.00	1176.00
Temperature (K)	193	193	193	193
μ (Mo Kα) (cm ⁻¹)	6.747	6.773	44.223	44.871
No. of reflections measured	Total: 33034; Unique: 5624; <i>R</i> _{int} = 0.027	Total: 23994; Unique: 5594; <i>R</i> _{int} = 0.020	Total: 19782; Unique: 5361; <i>R</i> _{int} = 0.026	Total: 19523; Unique: 4464; <i>R</i> _{int} = 0.042
No. of observations (<i>I</i> > -3.00 δ(<i>I</i>))	4870	5117	4823	4327
No. of variables	317	289	317	289
Residuals: <i>R</i> ₁ ; <i>R</i> _w	0.0290	0.0209	0.0195	0.0261
GOF	1.004	1.009	1.006	1.008
Max (minimum) peak in final diff. map (e-Å ⁻³)	0.55 (-0.61)	0.30 (-0.35)	0.99 (-0.84)	0.80 (-2.53)

^a Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: Σw(|*F*_o| - |*F*_c|)² (*w* = Least-squares weights, Chebyshev polynomial). Standard deviation of an observation of unit weight: [Σw(|*F*_o| - |*F*_c|)²/(*N*_o - *N*_v)]^{1/2} (*N*_o = number of observations, *N*_v = number of variables).

133.4, 130.4, 130.3, 128.8, 127.1, 123.8, 122.1, 10.7. Anal. Calcd. for $C_{28}H_{28}Cl_2HfO$: C, 53.39; H, 4.48; N, 0%. Found: C, 52.62; H, 4.27; N, 0.05%.

4.4. Synthesis of $Cp^*HfCl_2(O-2,6-tBu_2C_6H_3)$ (**3b**)

Synthesis of **3b** was carried out by the same procedure as that for **1b** except that Cp^*HfCl_3 250 mg (0.595 mmol), $LiO-2,6-tBu_2C_6H_3$ 132 mg (0.622 mmol) and Et_2O as solvent were used. Yield: 94 mg (27%). 1H NMR ($CDCl_3$): δ 7.19 (d, 2H, $J = 7.7$ Hz), 6.82 (t, 1H, $J = 7.7$ Hz), 2.10 (s, 15H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$): δ 160.6, 139.2, 125.5, 124.8, 120.8, 35.3, 31.9, 12.2. Anal. Calcd. for $C_{24}H_{36}Cl_2HfO$: C, 48.86; H, 6.15; N, 0%. Found: C, 49.12; H, 6.25; N, 0.10%.

4.5. Crystallographic analysis

All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated $MoK\alpha$ radiation. Samples of single crystals (**2a,b** and **3a,b**) were prepared from CH_2Cl_2/n -hexane solution at $-30^\circ C$. The selected crystal collection parameters are summarized in Table 5, and the detailed results are described in the supporting information. All structures were solved by direct methods and expanded using Fourier techniques [21], and the non-hydrogen atoms were included but not refined. All calculations for complexes were performed using the Crystal Structure [22] crystallographic software package.

4.6. General procedure for ethylene (co)polymerization

A typical procedure (Table 2, run 3) for ethylene polymerization was performed as follows: the prescribed amounts of toluene (29.0 mL), d-MAO (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale) in the drybox, and the apparatus was then purged with ethylene. The reaction mixture was then pressurized to 5 atm (total ethylene 6 atm) soon after the addition of a toluene solution (1.0 mL) containing **1a** (0.01 μ mol). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after reaction, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH, and was then dried *in vacuo* at $60^\circ C$ for several hours. Copolymerizations of ethylene with 1-octene or 2-methyl-1-pentene were conducted in the same manner as that for ethylene polymerization except that a mixture of toluene (24.0 mL) and 1-octene or 2-methyl-1-pentene (5.0 mL) was used in place of toluene (29.0 mL).

Acknowledgements

This research was partly supported by Grant-in-Aid for Scientific Research (B) from the Japan Society for the Promotion of Science (JSPS, No. 18350055). The authors would like to express their thanks to Sumitomo Chemical Co., Ltd. for GPC analyses of some polyethylene samples. K.N. and K.I. express their thanks to Mr. Shohei Katao and Mr. Fumio Asanoma (Nara Institute of Science and Technology) for help in X-ray crystallographic analyses. K.I. thanks to JSPS for a predoctoral fellowship (18-7944). K.N. thanks to Tosoh Finechem Co. for donating MAO.

Appendix A. Appendix A. Supplementary Material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2009.01.001.

Structure reports including crystal data and crystallographic parameters for structural analyses for $Cp^*ZrCl_2(O-2,6-tBu_2C_6H_3)$

(**2a**), $Cp^*ZrCl_2(O-2,6-Ph_2C_6H_3)$ (**2b**), $Cp^*HfCl_2(O-2,6-tBu_2C_6H_3)$ (**3a**), $Cp^*HfCl_2(O-2,6-Ph_2C_6H_3)$ (**3b**). These data (including CIF files) were also deposited in Cambridge Crystallographic Data Centre as CCDC 712658–712661, respectively. The data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or e-mail deposit@ccdc.cam.ac.uk.

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