

Olefin polymerization by (cyclopentadienyl)(ketimide)titanium(IV) complexes of the type, $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ -methylaluminoxane (MAO) catalyst systems

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Abstract

Effects of substituents on cyclopentadienyl group for homopolymerization of ethylene, 1-hexene, and for ethylene/1-hexene copolymerization using a series of *nonbridged* (cyclopentadienyl)(ketimide)titanium complexes of the type, $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**1**), tBuC_5H_4 (**2**), C_5Me_5 (Cp^* , **3**), and indenyl (**4**)] have been explored in the presence of methylaluminoxane (MAO) cocatalyst. Complexes **1–3** showed the similar catalytic activities for ethylene polymerization although the activity by **4** was somewhat low, whereas the activity for 1-hexene polymerization increased in the order $\mathbf{1} > \mathbf{4} \gg \mathbf{2} > \mathbf{3}$. These complexes showed significant activities for ethylene/1-hexene copolymerization affording high molecular weight poly(ethylene-*co*-1-hexene)s with unimodal molecular weight distributions, and the activity increased in the order: $\mathbf{4} > \mathbf{1} \gg \mathbf{2}, \mathbf{3}$. The $r_{\text{E}/\text{H}}$ values in the polymerization by **1–3** at 40 °C were 0.35–0.52 which clearly indicate that the 1-hexene incorporation in the copolymerization did not proceed in a random manner. The r_{E} values by **1–3** were 6.0–6.4 and the values were independent upon the cyclopentadienyl fragment employed; the r_{E} values by **4** at 40 °C were 10.2–10.9 which were close to those by *ansa*-metallocene complex catalysts. These values were influenced by the polymerization temperature, and the 1-hexene incorporation by **1–4** became inefficient at higher temperature, although the observed activities especially by **1, 4** were highly remarkable.

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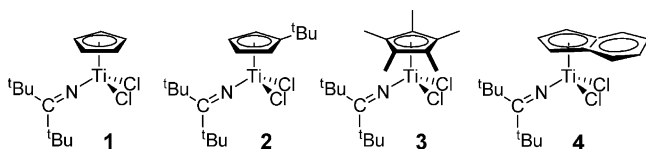
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1. Introduction

Design and synthesis of efficient transition metal complex catalysts for controlled precise olefin polymerization has attracted considerable attention in the field of catalysis, organometallic chemistry, and polymer chemistry [1,2]. *Nonbridged* half-metallocene type group 4 transition metal complexes of the type, $\text{Cp}'\text{M}(\text{L})\text{X}_2$ ($\text{Cp}' =$ cyclopentadienyl group; $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$; $\text{L} =$ anionic ligand such as OAr, NR_2 , NPR_3 , etc.; $\text{X} =$ halogen, alkyl), have attracted considerable attention (report concerning ethylene polymerization using $\text{CpTiCl}_2(\text{O}-4\text{-XC}_6\text{H}_4)\text{-Et}_2\text{AlCl}$ (classical Ziegler type) catalyst system) [3–20]. This is because that this type of complex catalyst has been expected to exhibit unique characteristics as olefin polymerization catalysts which

could produce new polymers that have never been prepared by conventional Ziegler–Natta catalysts, by ordinary metallocene type [1] and/or so-called ‘constrained geometry’ (linked Cp-amide) type catalysts [1d,e]. We reported that *nonbridged* half-titanocenes containing an aryloxo ligand of the type, $\text{Cp}'\text{Ti}(\text{OAr})\text{X}_2$ (OAr = aryloxo group), exhibited the unique characteristics [4–8]: an efficient catalyst for desired polymerization, especially for copolymerization of ethylene with α -olefin [4,5], styrene [6,7] and with norbornene [8] can be tuned by modifying the cyclopentadienyl fragment. Half-titanocenes containing anilide [17] or amide [18] ligand showed the similar characteristics that the efficient catalyst for ethylene polymerization can be modified to an efficient catalyst for syndiospecific styrene polymerization only by replacing substituent on Cp' [17b,18]. We believe that this should be one of the unique characteristics of using this type of complex catalyst for olefin polymerization.

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Scheme 1.

We have communicated recently that half-titanocenes containing ketimide ligand of the type, $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**1**), ${}^t\text{BuC}_5\text{H}_4$ (**2**), Cp^* (**3**)], showed high catalytic activities for ethylene polymerization regardless of kind of cyclopentadienyl fragment, and the catalytic activity for 1-hexene polymerization increased in the order $\mathbf{1} \gg \mathbf{2} > \mathbf{3}$ [21]. We have also shown that these complexes also showed moderate catalytic activities for syndiospecific styrene polymerization, however, the observed activities were much lower than those with Cp^*TiCl_3 under the same conditions. The observed effect in polymerization of ethylene, 1-hexene and styrene with **1–3** was quite different from those with half-titanocenes containing aryloxo [4–6], anilide [17b], and amide [18] ligands. Although syntheses of $\text{Cp}^*\text{TiX}_2(\text{N}=\text{C}'\text{Bu}_2)$, $\text{CpTiX}_2(\text{N}=\text{C}'\text{Bu}_2)$ ($\text{X} = \text{Cl}, \text{Me}$) and the reaction chemistry especially with $\text{B}(\text{C}_6\text{F}_5)_3$, $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ have been known [19] and we could also see that these complexes showed high catalytic activities for olefin polymerization [20], the observed fact that nature of anionic ancillary donor ligand plays an essential key role for both the catalytic activity and the monomer reactivity should be important for designing a better catalyst precursor for precise olefin polymerization. Since we reported previously that half-titanocenes containing amide ligand incorporated 1-hexene relatively efficiently in ethylene/1-hexene copolymerization whereas the 1-hexene incorporation was negligible if the anilide analogue was used instead [18], we thus have a strong interest to explore the effect of cyclopentadienyl fragment for ethylene/1-hexene copolymerization using a series of $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**1**), ${}^t\text{BuC}_5\text{H}_4$ (**2**), C_5Me_5 (Cp^* , **3**), indenyl (**4**), Scheme 1] in the presence of MAO cocatalyst. In this paper, we wish to introduce our explored results concerning effect of cyclopentadienyl ligand in ethylene, 1-hexene homopolymerization and ethylene/1-hexene copolymerization by **1–4**-MAO catalyst systems.

2. Results and discussion

2.1. Syntheses of $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**1**), ${}^t\text{BuC}_5\text{H}_4$ (**2**), C_5Me_5 (Cp^* , **3**), and indenyl (**4**)] and polymerization of ethylene, 1-hexene by **1–4**-MAO catalyst systems

$\text{CpTiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ (**1**) and $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ (**3**) were prepared in high yields (yield 76, 87%, respectively) according to the reported procedure [20a]. $({}^t\text{BuC}_5\text{H}_4)\text{TiCl}_2$

$(\text{N}=\text{C}'\text{Bu}_2)$ (**2**), (indenyl) $\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ (**4**) could also be isolated by the analogous procedure [by the reaction of $\text{Cp}'\text{TiCl}_3$ with $\text{Li}(\text{N}=\text{C}'\text{Bu}_2)$ in toluene], and were identified by ${}^1\text{H}$, ${}^{13}\text{C}$ NMR spectra and by elemental analyses.

Ethylene polymerizations by **1–4** were performed in toluene at 25 °C in the presence of MAO white solid [prepared by removing toluene and AlMe_3 from commercially available MAO (PMAO, Tosoh Finechem Co.)]¹, and the results are summarized in Table 1. It was revealed that complexes **1–3** exhibited the high catalytic activities, and the activities increased at higher ethylene pressure (runs 2–3) and/or upon increasing Al/Ti molar ratio. The resultant polymers were linear polyethylene in all cases confirmed by ${}^{13}\text{C}$ NMR spectra, and possessed high molecular weights with unimodal molecular weight distributions (PE by **1–3**, $M_w = 98.5\text{--}126 \times 10^4$, $M_w/M_n = 1.9\text{--}2.1$, runs 1–7). It should be noted that the observed catalytic activities by **1–3** were independent upon the substituent on Cp' , although Cp^* analogues exhibited the highest catalytic activities for ethylene polymerization by a series of $\text{Cp}'\text{TiCl}_2(\text{L})$ ($\text{L} = \text{aryloxo}, \text{amide}, \text{anilide}$)-MAO catalyst systems [4,5,17,18]. In contrast, the observed catalytic activities by the indenyl analogue **4** were lower than those by **1–3** under the same conditions (runs 8–9), and the M_w values for the resultant PE were low.

Table 2 summarizes results for 1-hexene polymerization by **1–4**-MAO catalyst systems under the conditions established in the preliminary communication [21]. It should be noted that the Cp analogue (**1**) showed much higher catalytic activity than the Cp^* (**3**), ${}^t\text{BuCp}$ (**2**) analogues, and the indenyl analogue (**4**) also showed remarkable catalytic activities. The activity as well as molecular weight for resultant poly(1-hexene)s increased in the order: $\mathbf{1} \gg \mathbf{2} > \mathbf{3}$, and the steric bulk on Cp' rather than the electronic effect thus plays an essential role especially for exhibiting the high activity. On the contrary, it is not clear at this moment why **4** exhibited the high catalytic activity, although **4** showed relatively low catalytic activity for ethylene polymerization.

2.2. Copolymerization of ethylene with 1-hexene by **1–4**-MAO catalyst systems

We reported previously that monomer incorporation in ethylene/1-hexene copolymerization using a series of half-titanocenes containing an aryloxo or amide ligand did not proceed in a random manner, and both the r_E and r_H values were dependent upon the cyclopentadienyl fragment used [5,18]. Moreover, these values were independent upon the polymerization temperature [5] although it has been known that these values were dependent upon the temper-

¹ MAO white solid was chosen as the cocatalyst, because this MAO is quite effective to prepare poly(ethylene-co-1-butene)s with narrow molecular weight distributions as well as with relatively high molecular weights if our Cp' -aryloxy titanium and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ were employed as the catalyst precursor [4b].

Table 1

Ethylene polymerization by Cp'TiCl₂(N=C'Bu₂) [Cp' = Cp (**1**), ^tBuC₅H₄ (**2**), Cp* (**3**), indenyl (**4**)]-MAO catalyst systems^a

Run	Cp'	Al/Ti ^b	Ethylene (atm)	Polymer yield (mg)	Activity ^c (×10 ⁻³)	M _w ^d (×10 ⁻⁴)	M _w /M _n ^d
1	Cp (1)	10000	4	317	9.5	98.5	1.9
2	Cp (1)	15000	4	445	13.4	96.6	1.9
3	Cp (1)	15000	6	737	22.1	98.4	1.9
4	^t BuC ₅ H ₄ (2)	10000	4	379	11.4	126	2.0
5	^t BuC ₅ H ₄ (2)	15000	4	477	14.3	99.0	2.1
6	Cp* (3)	10000	4	443	13.3	116	2.1
7	Cp* (3)	15000	4	552	16.6	104	2.2
8	Indenyl (4)	10000	4	248	7.4	55.9	2.2
9	Indenyl (4)	15000	4	255	7.7	56.1	2.1

^a Conditions: complex 0.2 μmol, toluene 40 mL, MAO white solid, 40 °C, 10 min.^b Molar ratio of Al/Ti.^c Activity in kg-PE/mol-Ti h.^d GPC data in *o*-dichlorobenzene vs. polystyrene standard.

Table 2

1-Hexene polymerization by **1–4**-MAO catalyst systems^a

Run	Cp' (μmol)	MAO (mmol) (Al/Ti) ^b	Activity ^c	M _w ^d (×10 ⁻⁴)	M _w /M _n ^d
10	Cp 1 (0.25)	2.0 (8000)	16800	61.7	1.6
11	Cp 1 (0.25)	3.0 (12000)	16600	55.2	1.8
12	^t BuC ₅ H ₄ 2 (2.5)	2.0 (800)	1310	28.5	1.7
13	^t BuC ₅ H ₄ 2 (2.5)	3.0 (1200)	1240	29.6	1.6
14	Cp* 3 (2.5)	2.0 (800)	569	13.0	1.6
15	Cp* 3 (2.5)	3.0 (1200)	539	12.0	1.6
16	Indenyl 4 (0.25)	2.0 (8000)	11900	28.1	1.7
17	Indenyl 4 (0.25)	3.0 (12000)	12700	26.6	1.7

^a Conditions: toluene 0.5 mL, 1-hexene 10 mL, MAO white solid (prepared by removing toluene and AlMe₃ from ordinary MAO), 25 °C, 20 min.^b Molar ratio of Al/Ti.^c Activity in kg-polymer/mol-Ti h.^d GPC data in THF vs. polystyrene standards.

ature if ordinary metallocene complexes were employed as the catalyst precursor [1a–d,22]. Moreover, we also reported that 1-hexene incorporation in the copolymerization was influenced by the nature of anionic donor ligand [18]. Since effects of cyclopentadienyl fragment toward the catalytic activity for ethylene, 1-hexene polymerization using Cp-ketimide complexes were quite different from those using Cp-aryloxy, Cp-amide and Cp-anilide complexes, therefore, we have a strong interest to explore the copolymerization with **1–4** in the presence of MAO.

Copolymerizations of ethylene with 1-hexene using **1–4**-MAO catalyst systems were conducted in toluene at 40 °C and the results varying the Al/Ti molar ratios and the 1-hexene concentration are summarized in Table 3. It should be noted that both **1** and **4** exhibited remarkable catalytic activities for the copolymerization and the observed activities were much higher than those for ethylene homopolymerization [activities by **1**: 13.4 (run 2) versus 162 (run 21); **4**: 7.7 (run 9) versus 58.6 (run 41), 738 (run 43)]. In addition, the activities (by **1**, **4**) increased at higher 1-hexene concentration. The observed activities by **1–4** were somewhat sensitive to the Al/Ti molar ratios (especially in **3**), and the optimized ratios depended on the cyclopentadienyl fragment employed (Fig. 1). The resultant poly(ethylene-*co*-1-hexene)s

possessed unimodal molecular weight distributions in most cases although the distributions were rather broad when **4** was used at higher Al/Ti molar ratios. It is also important to note that M_w values for the copolymer prepared by **1**, **4** were higher than those for polyethylene [ex. M_w values for poly(ethylene-*co*-1-hexene)s versus polyethylene, **1**: M_w

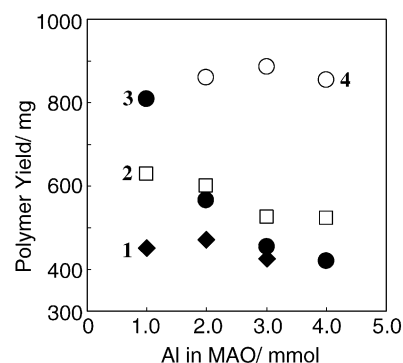


Fig. 1. Effect of aluminum cocatalyst in ethylene/1-hexene copolymerization using **1–4**-MAO catalyst systems. Conditions: complex 0.01 (**1**, **4**) or 0.2 μmol (**2**, **3**), ethylene 4 atm, 1-hexene 2.00 mmol/mL, MAO white solid, 40 °C [**1** (◆): runs 22–24, **2** (□): runs 29–32, **3** (●): runs 37–40, **4** (○): runs 45–47, Table 3].

Table 3

Ethylene/1-hexene copolymerization by Cp'TiCl₂(N=C'Bu₂) [Cp' = Cp (**1**), ⁱBuC₅H₄ (**2**), Cp* (**3**), indenyl (**4**)]-MAO catalyst systems^a
Effect of Al/Ti molar ratio and 1-hexene concentration

Run	Complex (μmol)	MAO (mmol) (Al/Ti × 10 ⁻³) ^b	1-Hexene conc. ^c (mmol/mL)	Polymer yield (mg)	Activity ^d (×10 ⁻³)	M _w ^e × 10 ⁻⁴	M _w /M _n ^e
2	1 (0.2)	3.0 (15.0)	–	445	13.4	96.6	1.9
18	1 (0.2)	3.0 (15.0)	1.00	1696	50.9	–	–
19	1 (0.01)	1.0 (100)	1.00	264	158	162	2.4
20	1 (0.01)	2.0 (200)	1.00	328	197	154	2.2
21	1 (0.01)	3.0 (300)	1.00	270	162	111	2.1
22	1 (0.01)	1.0 (100)	2.01	451	271	140	2.9
23	1 (0.01)	2.0 (200)	2.01	472	283	163	2.4
24	1 (0.01)	3.0 (300)	2.01	425	255	121	2.3
25	2 (0.2)	1.0 (5.0)	1.00	680	20.4	142	2.3
26	2 (0.2)	2.0 (10.0)	1.00	599	18.0	124	2.4
27	2 (0.2)	3.0 (15.0)	1.00	584	17.5	116	2.4
28	2 (0.2)	4.0 (20.0)	1.00	584	17.5	110	2.3
29	2 (0.2)	1.0 (5.0)	2.01	630	18.9	210	2.2
30	2 (0.2)	2.0 (10.0)	2.01	601	18.0	155	2.1
31	2 (0.2)	3.0 (15.0)	2.01	525	15.8	125	2.1
32	2 (0.2)	4.0 (20.0)	2.01	523	15.7	106	2.5
33	3 (0.2)	1.0 (5.0)	1.00	776	23.3	157	1.9
34	3 (0.2)	2.0 (10.0)	1.00	658	19.7	89.4	1.9
35	3 (0.2)	3.0 (15.0)	1.00	557	16.7	51.1	2.2
36	3 (0.2)	4.0 (20.0)	1.00	450	13.5	50.1	2.1
37	3 (0.2)	1.0 (5.0)	2.01	808	24.2	94.5	2.4
38	3 (0.2)	2.0 (10.0)	2.01	565	17.0	51.0	2.4
39	3 (0.2)	3.0 (15.0)	2.01	453	13.6	43.7	2.3
40	3 (0.2)	4.0 (20.0)	2.01	421	12.6	38.1	2.3
9	4 (0.2)	3.0 (15.0)	–	255	7.7	56.1	2.1
41	4 (0.2)	3.0 (15.0)	1.00	1952	58.6	–	–
42	4 (0.01)	2.0 (200)	1.00	708	708	120	2.3
43	4 (0.01)	3.0 (300)	1.00	738	738	103	2.6
44	4 (0.01)	4.0 (400)	1.00	728	728	108	3.0
45	4 (0.01)	2.0 (200)	2.01	860	860	89.3	2.7
46	4 (0.01)	3.0 (300)	2.01	886	886	83.6	2.8
47	4 (0.01)	4.0 (400)	2.01	855	855	71.4	3.6

^a Conditions: toluene + 1-hexene total 40 mL, ethylene 4 atm, 40 °C, 10 min (runs 18–41) or 6 min (**4**, runs 42–47), MAO white solid.

^b Molar ratio of Al/Ti.

^c Initial 1-hexene concentration mmol/mL, 1-hexene 5.0 or 10.0 mL (1.00 or 2.01 mmol/mL).

^d Activity in kg-polymer/mol-Ti·h.

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

= 111 (run 21), 121 (run 24) versus 96.6 (run 2); **4**: M_w = 103 (run 43), 83.6 (run 46) versus 56.1 (run 9)], although the resultant M_w values decreased upon increasing the Al/Ti molar ratios. Since the M_w values for the resultant copolymers were not dependent upon the Al/Ti molar ratios in the copolymerization using half-titanocenes containing an aryloxo ligand, the fact is an interesting contrast of using this type of complex for the polymerization.

Tables 4 and 5 summarize results for the copolymerization at various ethylene pressures. Although the observed catalytic activities were relatively sensitive to the Al/Ti molar ratios, the activities increased at higher ethylene pressure (Fig. 2). As shown in Fig. 2, the activity with a series of Cp'TiCl₂(N=C'Bu₂)-MAO catalyst system increased in the order (ethylene 6 atm, 1-hexene 2.01 mmol/mL): **4** > **1** >> **2**, **3**. The M_w values for resultant poly(ethylene-*co*-1-hexene)s were high, and the M_w values increased at higher ethylene pressure in most case. Moreover, the observed catalytic ac-

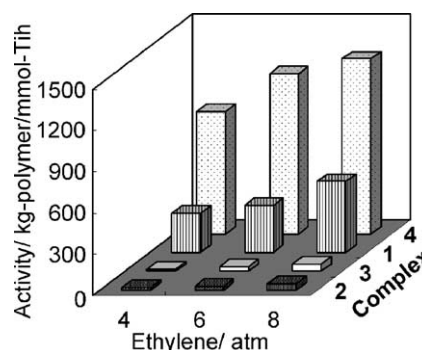


Fig. 2. Effect of ethylene pressure for the catalytic activity in ethylene/1-hexene copolymerization using **1–4**-MAO catalyst systems. Conditions: complex 0.01 (**1**, **4**) or 0.2 μmol (**2**, **3**), 1-hexene 2.00 mmol/mL, MAO white solid 2.0 (**1–3**) or 3.0 mmol (**4**), 40 °C, 10 (**1–3**) or 6 min (**4**).

Table 4

Ethylene/1-hexene copolymerization by Cp^rTiCl₂(N=C^rBu₂) [Cp^r = Cp (1), ^tBuC₅H₄ (2), Cp* (3)]-MAO catalyst systems^a
Effect of ethylene pressure

Run	Complex (μmol)	MAO (mmol) (Al/Ti × 10 ⁻³) ^b	Ethylene (atm)	1-Hexene conc. ^c (mmol/mL)	Activity ^d × 10 ⁻³	M _w ^e (×10 ⁻⁴)	M _w /M _n ^e
48	1 (0.01)	1.0 (100)	6	1.00	268	179	2.4
49	1 (0.01)	2.0 (200)	6	1.00	331	174	2.5
22	1 (0.01)	1.0 (100)	4	2.01	271	140	2.9
50	1 (0.01)	1.0 (100)	6	2.01	317	157	2.8
51	1 (0.01)	1.0 (100)	8	2.01	475	204	2.1
23	1 (0.01)	2.0 (200)	4	2.01	283	163	2.4
52	1 (0.01)	2.0 (200)	6	2.01	342	162	2.3
53	1 (0.01)	2.0 (200)	8	2.01	517	217	1.9
26	2 (0.2)	2.0 (10.0)	4	1.00	18.0	124	2.4
54	2 (0.2)	2.0 (10.0)	6	1.00	29.0	196	2.2
55	2 (0.2)	2.0 (10.0)	8	1.00	36.3	203	1.8
27	2 (0.2)	3.0 (15.0)	4	1.00	17.5	116	2.4
56	2 (0.2)	3.0 (15.0)	6	1.00	29.6	139	2.7
57	2 (0.2)	3.0 (15.0)	8	1.00	38.0	140	2.4
30	2 (0.2)	2.0 (10.0)	4	2.01	18.0	155	2.1
58	2 (0.2)	2.0 (10.0)	6	2.01	30.7	195	1.9
59	2 (0.2)	2.0 (10.0)	8	2.01	44.3	162	2.3
31	2 (0.2)	3.0 (15.0)	4	2.01	15.8	125	2.1
60	2 (0.2)	3.0 (15.0)	6	2.01	31.7	138	2.5
61	2 (0.2)	3.0 (15.0)	8	2.01	46.1	174	2.1
62	3 (0.2)	2.0 (100)	6	1.00	34.9	138	1.7
63	3 (0.2)	3.0 (15.0)	6	1.00	32.7	100	1.8
38	3 (0.2)	2.0 (10.0)	4	2.01	17.0	51.0	2.4
64	3 (0.2)	2.0 (10.0)	6	2.01	33.0	105	2.4
65	3 (0.2)	2.0 (10.0)	8	2.01	48.9	142	2.1
39	3 (0.2)	3.0 (15.0)	4	2.01	13.6	43.7	2.3
66	3 (0.2)	3.0 (15.0)	6	2.01	29.7	107	2.0
67	3 (0.2)	3.0 (15.0)	8	2.01	49.7	111	2.1

^a Conditions: toluene + 1-hexene total 40 mL, MAO white solid prepared by removing toluene and AlMe₃, 40 °C, 10 min.^b Molar ratio of Al/Ti.^c Initial 1-hexene concentration in mmol/mL.^d Activity in kg-polymer/mol-Ti h.^e GPC data in *o*-dichlorobenzene vs. polystyrene standards.

Table 5

Ethylene/1-hexene copolymerization by (indenyl)TiCl₂(N=C^rBu₂) (4)-MAO catalyst systems^a
Effect of ethylene pressure

Run	Complex (μmol)	MAO (mmol) (Al/Ti × 10 ⁻³) ^b	Ethylene (atm)	1-Hexene conc. ^c (mmol/mL)	Activity ^d (×10 ⁻³)	M _w ^e (×10 ⁻⁴)	M _w /M _n ^e
43	4 (0.01)	3.0 (300)	4	1.00	738	103	2.6
68	4 (0.01)	3.0 (300)	6	1.00	828	94.9	3.2
69	4 (0.01)	3.0 (300)	8	1.00	975	116	3.0
44	4 (0.01)	4.0 (400)	4	1.00	728	108	3.0
70	4 (0.01)	4.0 (400)	6	1.00	868	100	3.2
71	4 (0.01)	4.0 (400)	8	1.00	1030	104	3.3
46	4 (0.01)	3.0 (300)	4	2.01	886	83.6	2.8
72	4 (0.01)	3.0 (300)	6	2.01	1160	93.1	3.1
73	4 (0.01)	3.0 (300)	8	2.01	1270	138	2.3
47	4 (0.01)	4.0 (400)	4	2.01	855	71.4	3.6
74	4 (0.01)	4.0 (400)	6	2.01	1160	79.7	3.5
75	4 (0.01)	4.0 (400)	8	2.01	1260	123	2.4

^a Conditions: toluene + 1-hexene total 40 mL, MAO white solid prepared by removing toluene and AlMe₃, 40 °C, 6 min.^b Molar ratio of Al/Ti.^c Initial 1-hexene concentration in mmol/mL.^d Activity in kg-polymer/mol-Ti h.^e GPC data in *o*-dichlorobenzene vs. polystyrene standards.

Table 6

Triad sequence distributions for poly(ethylene-co-1-hexene)s prepared by Cp'TiCl₂(N=C'Bu₂) [Cp' = Cp (**1**), ^tBuC₅H₄ (**2**), Cp* (**3**), indenyl (**4**)]-d-MAO catalyst system^a

Run	Complex	1-Hexene conc. (mmol/ml)	1-Hexene content ^b (mol%)	Triads (%) ^c						Dyads (%) ^d			<i>r</i> _E ^e	<i>r</i> _H ^e	<i>r</i> _E <i>r</i> _H ^f
				EEE	HEE + EEH	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH			
21	1	1.00	25.0	38.7	29.4	6.9	19.3	5.3	0.5	53.4	43.5	3.1	6.0	0.059	0.35
26	2	1.00	24.5	38.7	29.5	7.2	18.4	4.9	1.2	53.5	42.9	3.6	6.1	0.069	0.42
34	3	1.00	25.8	38.8	28.3	7.1	18.5	6.7	0.6	52.9	43.1	4.0	6.0	0.075	0.45
43	4	1.00	19.1	54.4	22.8	3.7	14.5	4.3	0.3	65.8	31.7	2.4	10.2	0.063	0.64
	Cp*TiCl ₂ (OAr) (5) ^g	0.73	24.6	40.0	29.6	5.8	19.4	4.6	0.6	55.1	42.5	2.4	2.64	0.11	0.29
23	1	2.01	38.7	19.9	28.5	12.9	21.8	15.5	1.4	34.2	56.7	9.1	5.9	0.066	0.39
30	2	2.01	39.5	20.3	28.0	12.2	21.1	14.8	3.7	34.3	54.6	11.1	6.2	0.082	0.51
38	3	2.01	40.1	20.4	26.8	12.8	19.7	17.9	2.5	33.8	54.8	11.5	6.1	0.085	0.52
45	4	2.01	30.8	35.7	26.7	6.8	17.7	12.9	0.2	49.0	44.3	6.7	10.9	0.061	0.67
	Cp*TiCl ₂ (OAr) (5) ^h	1.45	42.6	12.2	26.0	19.2	22.2	16.8	3.6	25.2	62.8	12.0	2.29	0.13	0.31

^a Conditions, see Table 3 (toluene + 1-hexene total 40 mL, ethylene 4 atm, 40 °C, 6 or 10 min).

^b 1-Hexene content in mol% estimated by ¹³C NMR spectra [23].

^c Estimated by ¹³C NMR spectra [23].

^d [EE] = [EEE] + 1/2[EEH + HEE], [EH + HE] = [HEH] + [EHE] + 1/2{[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + 1/2[HHE + EHH].

^e *r*_E = [H]₀/[E]₀ × 2[EE]/[EH + HE], *r*_H = [E]₀/[H]₀ × 2[HH]/[EH + HE] [24].

^f *r*_E*r*_H = 4[EE][HH]/[EH + HE]².

^g Ethylene 7 atm, Cp*TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**5**) [5b].

^h Ethylene 5 atm, complex **5** [5b].

tivities by **1**, **4** increased upon increasing the 1-hexene concentration in all cases. The indenyl analogue **4** exhibited notable catalytic activities (728–1270 kg-polymer/mmol-Ti h) affording high molecular weight copolymers, although the molecular weight distributions were somewhat broad (*M*_w/*M*_n = 2.4–3.6).

2.3. Effect of cyclopentadienyl fragment on monomer reactivities and monomer sequence distributions

Table 6 summarizes triad sequence distributions, the dyads, and *r*_E*r*_H values estimated based on ¹³C NMR spectra for poly(ethylene-co-1-hexene)s prepared under the same conditions (ethylene 4 atm, 40 °C, initial 1-hexene conc. 1.00 or 2.01 mmol/mL) [23,24]. Typical ¹³C NMR spectra for resultant poly(ethylene-co-1-hexene)s are also shown in Fig. 3. The results by Cp*TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**5**) are also shown for comparison [5b]. The resultant *r*_E*r*_H values by **1–3** were 0.35–0.52, indicating that 1-hexene incorporation in the copolymerization did not proceed in a random manner. Since this can not be seen in the copolymerization with ordinary metallocene type and/or linked Cp-amide complex catalysts [5,22], but can be seen with nonbridged half-titanocenes containing an aryloxo [5], amide [18] ligand, therefore, this is one of the unique characteristics seen in the copolymerization using half-titanocene containing anionic ancillary donor ligand. The *r*_E*r*_H values estimated by **4** were 0.64–0.67 that were larger than those by **1–3**.

It should be noted that the *r*_E values by **1–3** were not influenced by the cyclopentadienyl fragment employed, and the fact is different from those observed in the copolymerization by half-titanocenes containing an

aryloxo [5], amide [18] ligand in which monomer reactivities and monomer sequence distributions were highly dependent upon substituent in both cyclopentadienyl and aryloxy/amide ligand. The *r*_E values by **1–3** are 5.9–6.2 which are somewhat larger than linked Cp-amide titanium complex like [Me₂Si(C₅Me₄)(N^tBu₂)]TiCl₂ (**6**, *r*_E = 3.42) and Cp-aryloxo titanium complex **5** (*r*_E = 2.24–2.64) under the same conditions [5b]; the *r*_H values were 0.059–0.085 which are somewhat smaller than **6** (*r*_H = 0.29) and **5** (*r*_E = 0.11–0.13) under the same conditions. These results clearly indicates that the 1-hexene incorporation by Cp-ketimide complexes of the type, Cp'TiCl₂(N=C'Bu₂), was not efficient as those by linked Cp-amide (**6**), and our Cp-aryloxo (**5**) titanium complexes under the same conditions [5b]. These results also indicate that 1-hexene incorporation in the copolymerization using half-titanocenes of the type, Cp'Ti(L)X₂, was affected by the nature of anionic donor ligand (L) employed. Although the indenyl analogue **4** exhibited remarkable catalytic activities affording high molecular weight poly(ethylene-co-1-hexene)s, the 1-hexene contents were lower than those by **1–3** under the same conditions. The *r*_E values are 10.2–10.9 that are almost similar to those by *ansa*-metallocene complex catalysts [22,25].

Table 7 summarizes effect of ethylene pressure toward the triad sequence distributions, the dyads, monomer reactivity and *r*_E*r*_H values estimated based on ¹³C NMR spectra for poly(ethylene-co-1-hexene)s [23,24]. The 1-hexene contents decreased at higher ethylene pressure, whereas *r*_E, *r*_H, and *r*_E*r*_H values did not change under these polymerization conditions. These results also suggest that the monomer reactivities and monomer sequence distribu-

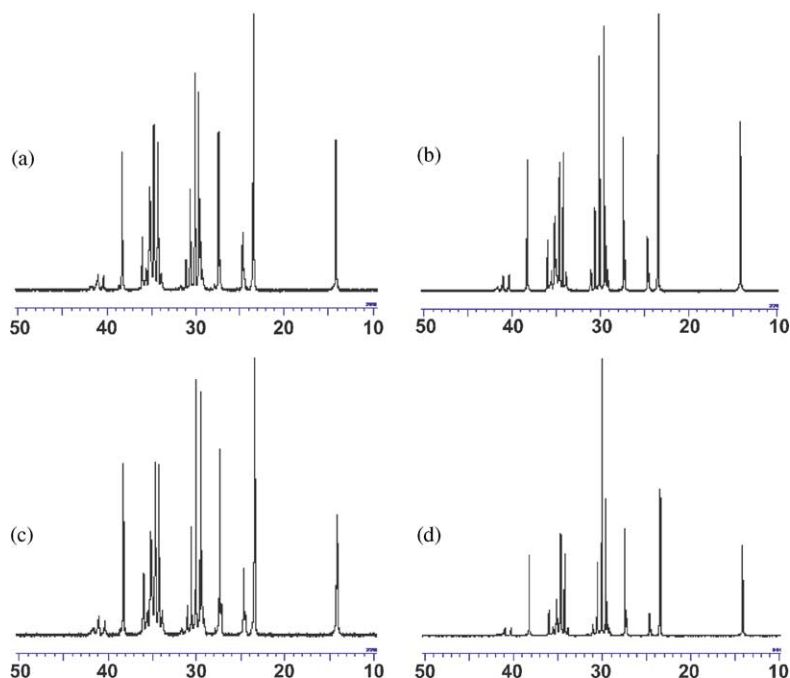


Fig. 3. Typical ^{13}C NMR spectra [in 1,3,4-trichlorobenzene/benzene- d_6 (90/10; w/w) at 130°C] for poly(ethylene-*co*-1-hexene)s prepared by **1–4**-MAO catalyst system [(a) run 23 by **1**, (b) run 30 by **2**, (c) run 38 by **3**, (d) run 45 by **4**].

tions by **1–3** were not dependent upon cyclopentadienyl fragment.

Generally, structural features of the catalyst, in particular the steric bulk of ligand, bite angle, configuration and conformation, should influence the coordination and/or insertion of monomers in transition metal catalyzed coordination polymerization reactions, and this is a distinct difference from conventional radical and ionic polymerization reactions [25]. In most cases of ethylene/ α -olefin copolymerization, espe-

cially by metallocene-type catalyst, the copolymerization proceeds in a random manner and the monomer sequences obey the first order Markov model [22,25]. We also reported that the comonomer incorporation in the copolymerization using **5** obeys first order Markov model [5b]. Since r_E and r_H values by **1–3** were not dependent upon the cyclopentadienyl fragment employed, we explored the behaviors in the copolymerization (monomer sequences in the copolymer). Table 8 summarizes the analysis results for triad sequence

Table 7

Triad sequence distributions for poly(ethylene-*co*-1-hexene)s prepared by $\text{Cp}'\text{TiCl}_2(\text{N}=\text{C}'\text{Bu}_2)$ [$\text{Cp}' = \text{Cp}$ (**1**), $^i\text{BuC}_5\text{H}_4$ (**2**), Cp^* (**3**), indenyl (**4**)]-d-MAO catalyst system^a

Effect of ethylene pressure

Run	Complex	Ethylene (atm)	1-Hexene content ^b (mol%)	Triads (%) ^c						Dyads (%) ^d			r_E^e	r_H^e	$r_E r_H^f$
				EEE	HEE + EEH	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH			
23	1	4	38.7	19.9	28.5	12.9	21.8	15.5	1.4	34.2	56.7	9.1	5.9	0.066	0.39
52	1	6	28.9	31.8	30.3	8.9	20.9	6.9	1.1	47.0	48.4	4.6	6.4	0.057	0.37
53	1	8	24.1	40.7	28.8	6.4	18.9	4.4	0.8	55.1	41.9	3.0	6.5	0.058	0.38
30	2	4	39.5	20.3	28.0	12.2	21.1	14.8	3.7	34.3	54.6	11.1	6.2	0.082	0.51
58	2	6	30.0	32.0	28.9	9.1	19.7	9.5	0.8	46.5	48.0	5.6	6.4	0.071	0.45
38	3	4	40.1	20.4	26.8	12.8	19.7	17.9	2.5	33.8	54.8	11.5	6.1	0.085	0.52
64	3	6	31.1	30.2	28.8	9.9	19.6	9.6	1.9	44.6	48.7	6.7	6.0	0.084	0.50
45	4	4	30.8	35.7	26.7	6.8	17.7	12.9	0.2	49.0	44.3	6.7	10.9	0.061	0.67
72	4	6	22.2	45.7	26.7	5.4	16.1	4.5	1.6	59.0	37.1	3.9	10.4	0.064	0.66
73	4	8	18.2	54.7	23.7	3.5	13.8	3.8	0.5	66.5	31.1	2.4	10.5	0.063	0.66

^a Polymerization conditions, see Tables 3–5 (1-hexene 10 mL, toluene 30 mL, 40°C , 6 or 10 min).

^b 1-Hexene content in mol% estimated by ^{13}C NMR spectra [23].

^c Estimated by ^{13}C NMR spectra [23].

^d $[\text{EE}] = [\text{EEE}] + 1/2[\text{EEH} + \text{HEE}]$, $[\text{EH} + \text{HE}] = [\text{HEH}] + [\text{EHE}] + 1/2\{[\text{EEH} + \text{HEE}] + [\text{HHE} + \text{EHH}]\}$, $[\text{HH}] = [\text{HHH}] + 1/2[\text{HHE} + \text{EHH}]$.

^e $r_E = [\text{H}]_0/[\text{E}]_0 \times 2[\text{EE}]/[\text{EH} + \text{HE}]$, $r_H = [\text{E}]_0/[\text{H}]_0 \times 2[\text{HH}]/[\text{EH} + \text{HE}]$ [24].

^f $r_E r_H = 4[\text{EE}][\text{HH}]/[\text{EH} + \text{HE}]^2$.

Table 8

Calculated and observed monomer sequence distribution of poly(ethylene-co-1-hexene)s prepared by **1–4**^a

Run	Complex	1-Hexene (mol%)	Method ^b	Dyads (%)			Triad sequence distribution (%)					
				EE	EH + HE	HH	EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH
	5 ^c Cp'-Ar	24.6	Exp.	55.1	42.5	2.4	40.0	29.6	5.8	19.4	4.6	0.6
			M1				39.7	30.7	5.9	19.1	4.3	0.2
			B				44.5	27.6	4.3	13.8	8.5	1.3
21	1	25.0	Exp.	53.4	43.5	3.1	38.7	29.4	6.9	19.3	5.3	0.5
			M1				37.9	30.9	6.3	19.0	5.4	0.4
			B				42.4	28.1	4.6	14.0	9.3	1.5
23	1	38.7	Exp.	34.2	56.7	9.1	19.9	28.5	12.9	21.8	15.5	1.4
			M1				18.7	31.0	12.8	21.5	13.8	2.2
			B				24.4	29.3	8.8	14.7	17.5	5.3
26	2	24.5	Exp.	53.5	42.9	3.6	38.7	29.5	7.2	18.4	4.9	1.2
			M1				38.2	30.6	6.1	18.4	6.2	0.5
			B				42.1	28.1	4.7	14.1	9.4	1.6
34	3	25.8	Exp.	52.9	43.1	4.0	38.8	28.3	7.1	18.5	6.7	0.6
			M1				37.6	30.6	6.2	18.2	6.7	0.6
			B				41.3	28.3	4.9	14.2	9.7	1.7
43	4	19.1	Exp.	65.8	31.7	2.4	54.4	22.8	3.7	14.5	4.3	0.3
			M1				53.1	25.6	3.1	13.8	4.2	0.3
			B				54.4	24.4	2.7	12.2	5.5	0.6
45	4	30.8	Exp.	49.0	44.3	6.7	35.7	26.7	6.8	17.7	12.9	0.2
			M1				33.7	30.5	6.9	17.0	10.3	1.6
			B				36.0	29.2	5.9	14.6	11.8	2.4

^a Detailed polymerization conditions, see Table 6.^b Exp. = experimental value, B = calculated value from dyads based on the Bernoullian model, M1 = calculated value from dyads based on the simple first order Markov model [28].^c Result by Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**) [5b].

distributions that are estimated from the dyads based on either the Bernoullian or the simple first order Markov model.² It turned out that the distributions in the copolymerization by **1–4**-MAO system are good agreements with those by the first order Markov model rather than those by the Bernoullian

model, as seen in the copolymerization by **5**. Although this tendency is the general characteristic feature in transition metal catalyzed olefin copolymerization, we would at least say that the last inserted monomer unit should give a great influence to insert and/or coordinate next monomer unit by choosing favored conformation.

² These calculations were made based on dyad distributions according to the following assumption: (a) calculation of triad sequence distribution according to the simple first order Markov model, $P_1(E) = P_{HE}/(P_{HE} + P_{EH})$, $P_1(H) = P_{EH}/(P_{EH} + P_{HE})$, $P_{EH} = 1 - P_{EE} = [EH]/([EE] + [EH]) = 0.5[HE + EH]/([EE] + 0.5[HE + EH])$, $P_{HE} = 1 - P_{HH} = [HE]/([EE] + [HE]) = 0.5[HE + EH]/([HH] + 0.5[HE + EH])$; $[EE] = P_2(EE) = P_1(E)P_{EE} = P_{HE}(1 - P_{EH})/(P_{HE} + P_{EH})$, $[EH + HE] = P_2(EH) + P_2(HE) = P_1(E)P_{EC} + P_1(H)P_{HE} = 2P_{EH}P_{HE}/(P_{EH} + P_{HE})$, $[HH] = P_2(HH) = P_1(H)P_{HH} = P_{EH}(1 - P_{HE})/(P_{EH} + P_{HE})$; $[EEE] = P_3(EEE) = P_1(E)P_{EE}P_{EE} = P_{HE}(1 - P_{EH})(1 - P_{EH})/(P_{HE} + P_{EH})$, $[EEH + HEE] = P_3(HEE) + P_3(EEH) = P_1(H)P_{HE}P_{EE} + P_1(E)P_{EE}P_{EH} = 2P_{EH}P_{HE}(1 - P_{EH})/(P_{EH} + P_{HE})$, $[HEH] = P_3(HEH) = P_1(H)P_{HE}P_{EH} = P_{HE}P_{HE}P_{EH}/(P_{HE} + P_{EH})$, $[EHE] = P_3(EHE) = P_{HE}P_{EH}P_{EH}/(P_{HE} + P_{EH})$, $[HHE + EHH] = P_3(HHE) + P_3(EHH) = 2P_{EH}P_{HE}(1 - P_{HE})/(P_{EH} + P_{HE})$, $[HHH] = P_3(HHH) = P_{EH}(1 - P_{HE})(1 - P_{HE})/(P_{HE} + P_{EH})$. (b) Calculation of triad sequence distribution according to the Bernoullian model, $P_1(E) = P_E = 1 - P_H = ([EE] + 0.5[EH + HE])/([EE] + [EH + HE] + [HH])$; $[EE] = P_2(EE) = P_E P_E$, $[EH + HE] = P_2(EH) + P_2(HE) = 2P_E P_H$, $[HH] = P_2(HH) = P_H P_H$, $[EEE] = P_3(EEE) = P_E P_E P_E$, $[EEH + HEE] = P_3(HEE) + P_3(EEH) = P_H P_E P_E + P_E P_E P_H = 2P_H P_E P_E$, $[HEH] = P_3(HEH) = P_H P_E P_H$, $[EHE] = P_3(EHE) = P_E P_H P_E$, $[HHE + EHH] = P_3(HHE) + P_3(EHH) = 2P_H P_H P_E$, $[HHH] = P_3(HHH) = P_H P_H P_H$.

2.4. Effect of polymerization temperature toward monomer reactivates and monomer sequence distributions

We reported that r_E and r_H values in the ethylene/1-hexene copolymerization by Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**5**) were not affected by the polymerization temperature [5], and this is an unique contrast to those using ordinary metallocene-type complex catalysts, [22], in which both r_E and r_H values are strongly influenced by the polymerization temperature. Since we assume that this is one of the unique characteristics of using nonbridged half-titanocenes for the copolymerization, we explored the temperature dependence in the copolymerization by **1–4**. The polymerization results are summarized in Table 9, and Table 10 summarizes effect of the temperature on the monomer reactivities and the monomer sequence distributions [23,24].

The catalytic activity increased at higher temperature if **1**, **3**, and **4** were employed as the catalyst, and the M_w values for resultant copolymer as well as the 1-hexene contents

Table 9

Ethylene/1-hexene copolymerization by Cp'TiCl₂(N=C'Bu₂) [Cp' = Cp (**1**), ^tBuC₅H₄ (**2**), Cp* (**3**), indenyl (**4**)]-MAO catalyst systems^a
Effect of temperature

Run	Complex (μmol)	MAO (mmol) (Al/Ti × 10 ⁻³) ^b	Temperature (°C)	Activity ^c (× 10 ⁻³)	M _w ^d (× 10 ⁻⁴)	M _w /M _n ^d
76	1 (0.01)	3.0 (300)	25	114	169	2.4
21	1 (0.01)	3.0 (300)	40	162	111	2.3
77	1 (0.01)	3.0 (300)	60	223	101	2.6
78	2 (0.2)	2.0 (10.0)	25	17.0	202	2.3
26	2 (0.2)	2.0 (10.0)	40	18.0	124	2.4
79	2 (0.2)	2.0 (10.0)	60	14.4	102	2.6
80	3 (0.2)	2.0 (10.0)	25	12.6	113	2.6
34	3 (0.2)	2.0 (10.0)	40	19.7	89.4	1.9
81	3 (0.2)	2.0 (10.0)	60	25.0	50.5	2.4
82	4 (0.01)	3.0 (300)	25	638	148	2.3
43	4 (0.01)	3.0 (300)	40	738	103	2.6
83	4 (0.01)	3.0 (300)	60	585	90.9	2.4

^a Reaction conditions: toluene + 1-hexene total 40 mL, 1-hexene 5.0 mL (1.00 mmol/mL), MAO white solid prepared by removing toluene and AlMe₃, 6 (by **4**) or 10 min (by **1–3**).

^b Molar ratio of Al/Ti.

^c Activity in kg-polymer/mol-Ti h.

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

decreased at higher temperature in all cases whereas *M_w* values for the copolymer by **5** were not influenced by both the polymerization temperature and the Al/Ti molar ratios [5b]. These suggest that dominant chain transfer reactions in the copolymerization by **1–4** were different from that by **5**.

Noteworthy is that *r_E* value by **1–3** increased at higher temperature (*r_E* = 4.5, 6.0, 8.4 at 25, 40, 60 °C, respectively), although the *r_Er_H* values were unchanged under these conditions. These are similar observation that can be

seen in the copolymerization using ordinary metallocene type complex catalysts [22], but are quite different from those using half-titanocenes containing an aryloxo ligand [5]. The *r_E* value by **4** also increased at higher temperature (*r_E* = 7.4, 10.2, 14.9 at 25, 40, 60 °C, respectively), and the *r_Er_H* values seemed increasing. We do not have clear reason why the indenyl analogue **4** exhibit different behavior from **1** to **3**, we believe, these are unique characteristics of using this type of complexes as the catalysts for this copolymerization. These results clearly indicate that complexes **1–4**

Table 10

Temperature dependence toward the triad sequence distributions for poly(ethylene-*co*-1-hexene)s prepared by Cp'TiCl₂(N=C'Bu₂) [Cp' = Cp (**1**), ^tBuC₅H₄ (**2**), Cp* (**3**), indenyl (**4**)]-d-MAO catalyst system^a

Run	Complex	Temperature (°C)	1-Hexene content ^b (mol%)	Triads (%) ^c						Dyads (%) ^d			<i>r_E</i> ^e	<i>r_H</i> ^e	<i>r_Er_H</i> ^f
				EEE	HEE + EEH	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH			
76	1	25	26.9	34.5	30.7	7.9	20.5	5.2	1.2	49.9	46.4	3.8	4.5	0.079	0.35
21	1	40	25.0	38.7	29.4	6.9	19.3	5.3	0.5	53.4	43.5	3.1	6.0	0.059	0.35
77	1	60	23.0	42.5	28.8	5.7	18.1	4.9	0.1	56.8	40.6	2.5	8.4	0.041	0.34
78	2	25	28.4	34.4	29.1	8.0	19.5	7.2	1.6	49.0	45.8	5.2	4.4	0.11	0.49
26	2	40	24.5	38.7	29.5	7.2	18.4	4.9	1.2	53.5	42.9	3.6	6.1	0.069	0.42
79	2	60	24.7	41.4	27.8	6.2	17.8	6.7	0.2	55.3	41.2	3.5	8.1	0.057	0.46
80	3	25	26.2	39.1	27.6	7.1	18.6	7.5	0.1	52.9	43.2	3.9	5.1	0.086	0.44
34	3	40	25.8	38.8	28.3	7.1	18.5	6.7	0.6	52.9	43.1	4.0	6.0	0.075	0.45
81	3	60	25.8	39.0	28.0	7.2	17.7	7.2	0.9	53.0	42.5	4.5	7.5	0.07	0.53
82	4	25	20.1	49.5	25.8	4.6	15.0	5.0	Trace	62.4	35.0	2.6	7.4	0.070	0.52
43	4	40	19.1	54.4	22.8	3.7	14.5	4.3	0.3	65.8	31.7	2.4	10.2	0.063	0.64
83	4	60	16.2	58.5	22.5	2.8	12.5	3.5	0.2	69.8	28.2	2.0	14.9	0.046	0.68

^a Polymerization conditions, see Table 8 (1-hexene 5 mL, toluene + 1-hexene total 40 mL, ethylene 4 atm, 40 °C, 6 or 10 min, MAO white solid).

^b 1-Hexene content in mol% estimated by ¹³C NMR spectra [23].

^c Estimated by ¹³C NMR spectra [23].

^d [EE] = [EEE] + 1/2[EEH + HEE], [EH + HE] = [HEH] + [EHE] + 1/2{[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + 1/2[HHE + EHH].

^e *r_E* = [H]₀/[E]₀ × 2[EE]/[EH + HE], *r_H* = [E]₀/[H]₀ × 2[HH]/[EH + HE] [24].

^f *r_Er_H* = 4[EE][HH]/[EH + HE]².

may not be suited as the catalyst for the copolymerization at higher temperature due to the inefficient 1-hexene incorporation, although **1**, **4** exhibited the remarkable catalytic activities.

We have shown that (cyclopentadienyl)(ketimide)titanium(IV) complexes of the type, $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$, exhibited remarkable catalytic activities especially for copolymerization of ethylene with 1-hexene. Although the 1-hexene incorporations by **1–4** were not efficient as those by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**), the M_w values for the resultant copolymers were high. Based on results shown in this paper, it was revealed that the 1-hexene incorporation in the ethylene/1-hexene copolymerization and effect of cyclopentadienyl fragment for the catalytic activities in olefin polymerizations using nonbridged half-titanocenes of the type, $\text{Cp}^*\text{Ti}(\text{L})\text{X}_2$ (L = anionic ancillary ligand), were affected by the nature of anionic ancillary ligand employed.

3. Experimental

3.1. General procedure

All experiments were carried out under nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. Anhydrous grade of toluene (Kanto Chemical Co., Inc.) was stored in a Schlenk tube in the drybox in the presence of molecular sieves. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used as received. 1-Hexene of reagent grade (Wako Chemical Co. Ltd.) was stored in the drybox in the presence of molecular sieves, and was used without further purification. Toluene and AlMe_3 in the commercially available methylaluminoxane [PMAO-S, 9.5 wt.% (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 °C for removing toluene, AlMe_3 , and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Syntheses of $\text{CpTiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**1**), $\text{Cp}^*\text{TiCl}_2(\text{N}=\text{C}^t\text{Bu}_2)$ (**3**) were according to the previous report [19,20].

Molecular weight and molecular weight distribution for polyethylene and poly(ethylene-co-1-hexene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm φ i.d.), ranging from <10² to <2.8 × 10⁸ M_w) at 140 °C using *o*-dichlorobenzene containing 0.05 % (w/v) 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Molecular weights and molecular weight distributions for resultant polypropylene, poly(1-hexene)s were measured by GPC (Shimadzu SCL-10A with RID-10A detector) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min).

HPLC grade THF was used for GPC and were degassed prior to use, and GPC columns (ShimPAC GPC-806, 804 and 802, 30 cm × 8.0 mm φ, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from <10² to 2 × 10⁷ MW) were calibrated versus polystyrene standard samples.

All ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ¹H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me₄Si. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. ¹³C NMR spectra for polyethylene, poly(1-hexene)s, and poly(ethylene-co-1-hexene)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ¹³C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 10,000. The analysis samples of polyethylene, poly(ethylene-co-1-hexene)s were prepared by dissolving polymers in a mixed solution of 1,3,4-trichlorobenzene/benzene-d₆ (90/10; w/w), and the spectrum was measured at 130 °C. The samples for poly(1-hexene)s were measured in CDCl₃. Elemental analyses were performed by using PE2400II Series (Perkin-Elmer Co.).

3.2. Synthesis of (^tBuC₅H₄)TiCl₂(N=C^tBu₂) (**2**)

Synthetic procedure for **2** was the same as that for **1**, except that (^tBuC₅H₄)TiCl₃ (1.00 g, 3.63 mmol) was used in place of CpTiCl₃ (LiN=C^tBu₂ 535 mg, 3.63 mmol, toluene 25 mL). The resultant solid, after passing through Celite pad and removal of toluene, was dissolved in a minimum amount of Et₂O and was layered by *n*-hexane. The solution gave pale-red microcrystals upon standing. Yield 710 mg (52%). ¹H NMR (CDCl₃): δ 6.44 (t, 2H, J = 5.2 Hz, ^tBuC₅H₄), 6.40 (t, 2H, J = 5.6 Hz, ^tBuC₅H₄), 1.39 (s, 9H, (CH₃)₃CCp), 1.28 (s, 18H, N=C(CH₃)₃). ¹³C NMR (CDCl₃): δ 203.8, 148.8, 114.7, 115.6, 46.7, 31.1, 30.3. Anal. Calcd. for C₁₈H₃₁Cl₂N₂Ti: C, 56.68; H, 8.22; N, 3.68. Found: C, 56.79; H, 8.50; N, 3.58.

3.3. Synthesis of (indenyl)TiCl₂(N=C^tBu₂) (**4**)

Synthetic procedure for **4** was the same as that for **1**, except that (indenyl)TiCl₃ (1.00 g, 3.75 mmol) was used in place of CpTiCl₃ (LiN=C^tBu₂ 553 mg, 3.75 mmol, toluene 12 mL). The resultant solid, after passing through Celite pad and removal of toluene, was dissolved in a minimum amount of toluene and was layered by *n*-hexane. Yield 818 mg (59%). ¹H NMR (CDCl₃): δ 7.77, 7.61–7.68, 7.43–7.46, 7.36–7.39, 7.29–7.31 (m, Ind), 6.82 (t, Ind), 6.51 (d, Ind), 1.24 (s, 18H, (CH₃)₃C–). ¹³C NMR (CDCl₃): δ 206.1 (C = N), 127.4, 125.6, 119.1, 112.1, 109.2 (Ind), 47.4 (CCH₃), 30.1 (C(CH₃)₃). Anal. Calcd. for C₁₈H₂₅Cl₂N₂Ti: C, 57.78; H, 6.73; N, 3.74. Found: C, 57.55; H, 6.79; N, 3.67.

3.4. Ethylene polymerization, ethylene/1-hexene copolymerization

The typical reaction procedure for ethylene polymerization (run 1, Table 1) is as follows. Toluene (39 mL), and d-MAO solid (116 mg, 2.0 mmol) were added into the autoclave (100 mL scale stainless steel) in the drybox, and the reaction apparatus was then placed in an oil bath preheated at 40 °C, and was filled with ethylene (1 atm). A toluene solution (1.0 mL) containing **1** (0.2 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (ethylene total 4 atm). The mixture was magnetically stirred for 10 min, ethylene remained was purged after the 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. Basic experimental procedure in the ethylene/1-hexene copolymerization was the same as that in ethylene homopolymerization except that a certain amount of 1-hexene was added in place of toluene partially (total amount 29 mL).

The 1-hexene contents and the monomer sequence distributions in the resultant poly(ethylene-co-1-hexene)s were estimated by the previous report using ¹³C NMR spectra of copolymer. The calculation of r_E and r_H values are based on dyads by the following equations ($[H]_0$ and $[E]_0$ are the initial monomer concentrations, respectively):

$$r_E = \left[\frac{H_0}{E_0} \right] \times 2 \left[\frac{EE}{EH + HE} \right],$$

$$r_H = \left[\frac{E_0}{H_0} \right] \times 2 \left[\frac{HH}{EH + HE} \right]$$

The initial monomer concentrations, especially for ethylene were estimated by using the equation quoted by Kissin, and ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported previously [24].

3.5. 1-Hexene polymerization

Typical procedure for 1-hexene polymerization was as follows: prescribed amount of MAO and 1-hexene (10.0 mL) were added to a round bottom flask (25 mL) in the drybox, and the polymerization was started by the addition of a toluene solution (0.5 mL) containing the catalyst (0.25 or 2.5 μmol). The reaction mixture was stirred for 20 min (or 5, 10 min) at 25 °C, and the polymerization was terminated with the addition of EtOH. The reaction product was extracted with CHCl₃ which was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na₂SO₄, and chloroform and 1-hexene remained was then removed in vacuo. The resultant poly(1-hexene)s possessed atactic stereoregularity with favored repeated 1,2-insertion mode.

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