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Effect of ketimide ligand for ethylene polymerization and ethylene/norbornene copolymerization catalyzed by (cyclopentadienyl)(ketimide)titanium complexes–MAO catalyst systems: Structural analysis for $Cp^*TiCl_2(N{=}CPh_2)$

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Dedicated in honor of Professor Dr. Gerhard Erker on the occasion of his 60th birthday.

Abstract

Ligand effects on the catalytic activity [and norbornene (NBE) incorporation] for both ethylene polymerization and ethylene/NBE copolymerization using half-titanocenes (titanium half-sandwich complexes) containing ketimide ligand of type $Cp'TiCl_2[N{=}C(R^1)R^2]$ [$Cp' = Cp$ (**1**), C^5Me^5 (Cp^*, **2**); $R^1,R^2 = {}^tBu,{}^tBu$ (**a**), ${}^tBu$,Ph (**b**), Ph,Ph (**c**)]–methylaluminoxane (MAO) catalyst systems have been investigated. $CpTiCl_2[N{=}C({}^tBu)Ph]$ (**1b**) $CpTiCl_2(N{=}CPh_2)$ (**1c**), and $Cp^*TiCl_2(N{=}CPh_2)$ (**2c**) were prepared and identified; the structure of $Cp^*TiCl_2(N{=}CPh_2)$ (**2c**) was determined by X-ray crystallography. The catalytic activity for ethylene polymerization increased in the order: **1a** > **1b** > **1c**, suggesting that an electronic nature of the ketimide ligand affects the activity. However, molecular weight distributions for resultant (co)polymers prepared by **1b**,**c** and by **2c**–MAO catalyst systems were bi- or multi-modal, suggesting that the ketimide substituent plays a key role in order for these (co)polymerizations to proceed with single catalytically-active species. $CpTiCl_2(N{=}C{}^tBu_2)$ (**1a**) exhibited both remarkable catalytic activity and efficient NBE incorporation for ethylene/NBE copolymerization.

Keywords: Titanium; Polymerization; Homogeneous catalysis; Ethylene; Norbornene; Copolymerization

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, $Cp'M(L)X_2$ (Cp' = cyclopentadienyl group; M = Ti, Zr, Hf; L = anionic ligand such as OAr, NR_2, and NPR_3; X = halogen, alkyl), display unique characteristics as olefin polymerization catalysts, because these catalysts are effective for production of new polyolefins [4] which are not prepared by conventional Zigler-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, $Cp'Ti(OAr)X_2$ ($Ar = 2,6\text{-}{}^iPr_2C_6H_3$, etc.), displayed the promising characteristics [4,7–14]. 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 Cp'.

Half-titanocenes containing ketimide ligand of the type, $Cp'TiCl_2(N{=}C{}^tBu_2)$ [15–21], also exhibited high catalytic activities for ethylene polymerization. The complexes also showed catalytic activities for syndiospecific styrene

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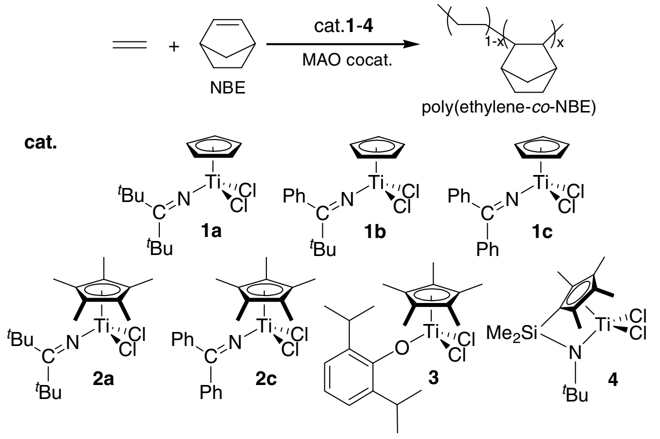

Scheme 1.

polymerization, but the observed activities were much lower than those with Cp*TiCl$_3$ under the same conditions [17]. We also reported that both CpTiCl$_2$(N=C^{t}Bu$_2$) and (indenyl)TiCl$_2$(N=C^{t}Bu$_2$) exhibited remarkable catalytic activities (ca. activity 728–1270 kg-polymer/mmol-Ti h, ethylene 4–8 atm, 1-hexene 2.01 mmol/mL in toluene, MAO cocatalyst) as well as efficient 1-hexene incorporation for ethylene/1-hexene copolymerization [18]. More recently, we reported that ethylene/styrene copolymerization by Cp*TiCl$_2$(N=C^{t}Bu$_2$)–MAO catalyst system proceeded in a living manner [19]. Moreover, we communicated that CpTiCl$_2$(N=C^{t}Bu$_2$) exhibits both remarkable catalytic activity and efficient norbornene (NBE) incorporation for ethylene/NBE copolymerization, and the NBE incorporation by Cp′TiCl$_2$(X)(X = N=C^{t}Bu$_2$, O-2, 6-^{i}Pr$_2$C$_6$H$_3$; Cp′ = Cp, C$_5$Me$_5$, indenyl) was related to the calculated coordination energy after ethylene insertion [20].

Although syntheses of Cp′TiX$_2$(N=C^{t}Bu$_2$) (X = Cl, Me) and the reaction chemistry especially with B(C$_6$F$_5$)$_3$, [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] [15] as well as their use as the catalyst precursors for ethylene (co)polymerizations [18,20] were known, however, there are few reports concerning effect of the ketimide substituents on the activity (and comonomer incorporations) in ethylene (co)polymerizations. In this paper we thus prepared various half-titanocenes containing ketimide ligands of type, Cp′TiCl$_2$[N=C(R^1)R^2] [Cp′ = Cp (**1**), C$_5$Me$_5$ (Cp∗, **2**); R^1,R^2 = ^{t}Bu, ^{t}Bu (**a**), ^{t}Bu,Ph (**b**), Ph,Ph (**c**)], and explored effect of the ketimide substituents for ethylene polymerization and ethylene/NBE copolymerization (Scheme 1). Structure of Cp*TiCl$_2$(N=CPh$_2$) (**2c**) was also determined by X-ray crystallography.

2. Results and discussion

2.1. Syntheses of Cp′TiCl$_2$[N=C(R^1)R^2] [Cp′ = Cp (1), C$_5$Me$_5$ (Cp*, 2); R^1,R^2 = ^{t}Bu,^{t}Bu (a), ^{t}Bu,Ph (b), Ph,Ph (c)], and structural analysis for Cp*TiCl$_2$(N=CPh$_2$)

Cp′TiCl$_2$(N=C^{t}Bu$_2$) [Cp′ = Cp (**1a**), Cp*(**2a**)] were prepared by reaction of Cp′TiCl$_3$ with Li(N=C^{t}Bu$_2$) in toluene according to the reported procedure [15a]. CpTiCl$_2$[N=C(^{t}Bu)Ph] (**1b**), CpTiCl$_2$(N=CPh$_2$) (**1c**), and Cp*TiCl$_2$(N=CPh$_2$) (**2c**) were prepared similarly in moderate yields (69–93%) from Cp′TiCl$_3$ by treating with Li[N=C(^{t}Bu)Ph] [22] or Li(N=CPh$_2$) [23] in toluene. The resultant complexes were identified by ^{1}H and ^{13}C NMR spectra and elemental analyses.

The structure of Cp*TiCl$_2$(N=CPh$_2$) (**2c**) was determined by X-ray crystallography (Fig. 1), and the selected bond distances and angles are summarized in Table 1. The structure showed that **2c** has a distorted tetrahedral geometry around the titanium metal center. Ti–N(ketimide) distance (1.828 Å) is close to those in **2a** (1.844 Å) [21a], (indenyl)TiCl$_2$(N=C^{t}Bu$_2$) (1.814 Å) [21a]. The distance is shorter than those in a series of Cp′TiCl$_2$-[N(R^1)R^2] (Cp′ = Cp*, 1, 3-Me$_2$C$_5$H$_3$; R^1,R^2 = Me,Cy, Cy,Cy, 1.861–1.873 Å) [24] and that in (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(SiMe$_3$)(2,6-Me$_2$C$_6$H$_3$)] (1.898 Å) [25]. The Ti–N dis-

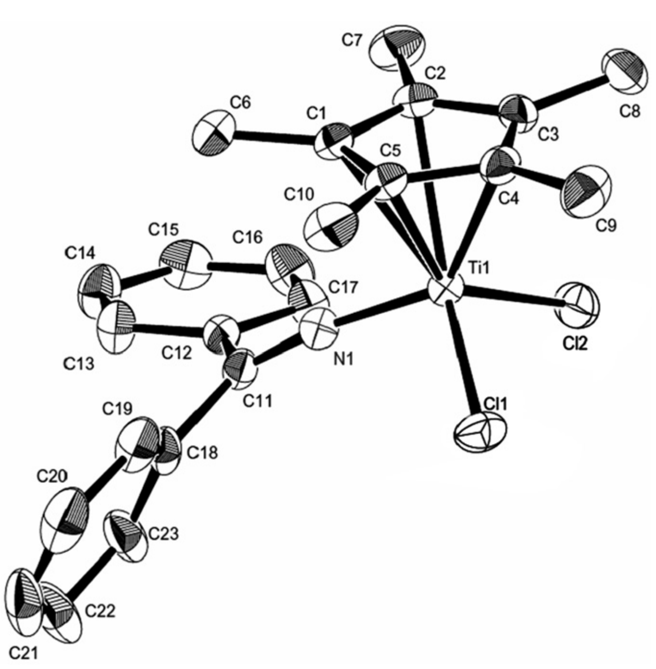

Fig. 1. ORTEP drawings for Cp*TiCl$_2$(N=CPh$_2$) (**2c**). Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for Cp*TiCl$_2$(N=CPh$_2$) (**2c**)

Bond distances in Å			
Ti(1)–Cl(1)	2.2844(8)	Ti(1)–Cl(2)	2.2735(10)
Ti(1)–N(1)	1.827(2)	Ti(1)–Cp$^{cent.}$	2.024
Ti(1)–C(1)	2.361(2)	Ti(1)–C(2)	2.351(2)
C(11)–C(12)	1.495(3)	C(11)–C(18)	1.491(3)
N(1)–C(11)	1.276(3)		
Bond angles in °			
Cl(1)–Ti(1)–Cl(2)	102.53(3)	Ti(1)–N(1)–C(11)	170.5(2)
Cl(1)–Ti(1)–N(1)	102.44(7)	N(1)–C(11)–(12)	120.4(2)
Cl(2)–Ti(1)–N(1)	105.27(7)	N(1)–C(11)–(18)	121.2(2)
Ti(1)–Cp^{plane}	89.826	C(12)–C(11)–C(18)	118.3(2)

tance is also shorter than that in $Cp_2Zr(N{=}CPh_2)_2$ (2.058–2.063 Å) [26]. The N(1)–C(11) distance (1.276 Å) in **2c** is close to those in **2a** (1.266 Å) [21a], $Cp_2Zr(N{=}CPh_2)_2$ (1.259 and 1.266 Å) [26], and is comparable to those in a series of (arylimido)(ketimide)vanadium complexes (1.250–1.270 Å) [27]. Ti–N(ketimide)–C bond angle, [Ti(1)–N(1)–C(11) = 170.58°], in **2c** is slightly larger than those in **2a** (166.4°) [21a], (indenyl)$TiCl_2(N{=}C^tBu_2)$ (167.6°) and $Cp_2Zr(N{=}CPh_2)_2$ (164.1°, 163.7°) [26]; the angle is within a range of those in a series of (arylimido)(ketimide)vanadium complexes (169.4–177.3°) [27]. These results strongly suggest that strong π-donation of the nitrogen atom to Ti would be thus present.

2.2. *Ethylene polymerization catalyzed by* $Cp'TiCl_2[N{=}(R^1)R^2]$ [$Cp' = Cp$ (**1**), *C_5Me_5 (Cp^*, 2); $R^1,R^2 = {}^tBu,{}^tBu$ (a), ${}^tBu$,Ph (b), Ph,Ph (c)]–MAO catalyst systems*

Ethylene polymerizations by **1**–**2**–MAO catalyst systems were performed in toluene at 25 °C, and $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**) was also chosen for comparison [7]. MAO white solid [prepared by removing toluene and $AlMe_3$ from the commercially available MAO (PMAO, Tosoh Finechem Co.)] was chosen as the cocatalyst, because this MAO is effective for preparing poly(ethylene-*co*-1-butene)s with narrow molecular weight distributions as well as with relatively high molecular weights when **3** and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**) were employed as the catalyst precursors [9a,10]. The results under the optimized Al/Ti ratios are summarized in Table 2.

As reported previously, **2a** showed the remarkable catalytic activity affording high molecular weight linear polyethylene (PE) with unimodal molecular weight distribution (run 4), and the Cp analogue (**1a**) also showed the high catalytic activity (run 1). The observed activities by **1a**, **2a** are in the similar level to that by the Cp^*-aryloxo analogue (**3**). The catalytic activities with a series of $CpTiCl_2[N{=}C(R^1)R^2]$–MAO catalyst systems increased in the order: **1a** (5880 kg-PE/mol-Ti h, $R^1R^2 = {}^tBu,{}^tBu$, run 1) > **1b** (90.0 kg-PE/mol-Ti h, $R^1R^2 = {}^tBu$,Ph, run 2) > **1c** (56.4 kg-PE/mol-Ti h, R^1R^2 = Ph,Ph, run 3). The same trend was observed between **2a** and **2c**, and the activities by the Cp^* analogues were higher than that by the Cp analogues (ex. $R^1R^2 = {}^tBu,{}^tBu$, runs 1 and 4; $R^1R^2 = {}^tBu$,Ph, runs 3 and 5). These results would suggest that an electronic nature of the ketimide ligand affects the catalytic activity. However, the molecular weight distributions for the resultant PEs prepared by **1b**–**c**, **2c**–MAO catalyst systems were multi-modal, consisting of a mixture of high and low molecular weight polymers. The complexes with the ketimide ligand containing two *tert*-Bu substituents, $Cp'TiCl_2(N{=}C^tBu_2)$, were thus effective for the ethylene polymerization to give polymers with unimodal molecular weight distributions, in other words, to proceed with sole catalytically-active species.

2.3. *Copolymerization of ethylene with norbornene (NBE) catalyzed by $Cp'TiCl_2[N{=}(R^1)R^2]$ [$Cp' = Cp$ (1), C_5Me_5 (Cp^*, 2); $R^1,R^2 = {}^tBu,{}^tBu$ (**a**), ${}^tBu$,Ph (**b**), Ph,Ph (**c**)]–MAO catalyst systems*

As communicated previously [20], **1a** showed notable both catalytic activity and norbornene (NBE) incorporation for ethylene/NBE copolymerization in the presence of MAO, and it is possible to prepare high molecular weight poly(ethylene-*co*-NBE)s with high NBE contents (>50 mol%) as well as with unimodal molecular weight distributions. The copolymerization results by **1a**–MAO catalyst system under various conditions are summarized in Table 3, and the results by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**)–MAO catalyst systems under the same conditions are also shown for comparison.

The copolymerization by **1a**–MAO catalyst system proceeded at remarkable rate, and the activity (calculated based on the polymer yields vs. amount of **1a** charged) after 20 min was the same as that after 30 min (runs 13 and 14), suggesting that no distinct decrease in the activity was seen under these conditions. The activity increased upon increasing the initial NBE concentration [5880 kg-PE/mol-Ti h (run 1) vs. 40200 kg-polymer/mol-Ti h (run 12)], whereas the activities by **3**, **4**–MAO catalyst systems decreased upon increasing the NBE concentration (runs

Table 2
Ethylene polymerization by $Cp'TiCl_2[N{=}C(R^1)R^2]$ [$Cp' = Cp$ (**1**), Cp^* (**2**); $R^1,R^2 = {}^tBu,{}^tBu$ (**a**), ${}^tBu$,Ph (**b**), Ph,Ph (**c**)] or $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**)–MAO catalyst systems [a]

Run	Complex (μmol)	Cp′	$R^1;R^2$	Yield (mg)	Activity[b]	$M_n \times 10^{-4}$ [c]	M_w/M_n [c]
1	**1a** (0.1)	Cp	${}^tBu;{}^tBu$	98	5880	45.2	2.30
2	**1b** (5.0)	Cp	${}^tBu$;Ph	75	90.0	Multi-modal[d]	
3	**1c** (5.0)	Cp	Ph;Ph	47	56.4	Multi-modal[d]	
4	**2a** (0.05)	Cp*	${}^tBu;{}^tBu$	164	19680	42.2	2.45
5	**2c** (5.0)	Cp*	Ph;Ph	105	126	Multi-modal[d]	
6	**3** (0.2)	Cp*	–	280	8400	65.2	1.90

[a] Conditions: toluene 50 mL, MAO white solid (prepared by removing $AlMe_3$, toluene from PMAO, MAO: methylaluminoxane) 3.0 mmol, ethylene 4 atm, 25 °C, 10 min.

[b] Activity in kg-PE/mol-Ti h.

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

[d] Multi-modal molecular weight distributions [$M_n = 4.16 \times 10^4$, $M_w/M_n = 21.1$ (run 3); $M_n = 9.91 \times 10^3$, $M_w/M_n = 25.9$ (run 5)].

Table 3
Copolymerization of ethylene with norbornene (NBE) by $CpTiCl_2(N{=}C^tBu_2)$ (**1a**), $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**), $[Me_2Si(C_5Me_4)(N\,{}^tBu)]TiCl_2$ (**4**)–MAO catalyst systems [a]

Run	Complex (μmol)	NBE (mmol/mL)[b]	Ethylene (atm)	Temperature (°C)	Time (min)	Activity × 10^{-3}[c]	$M_n \times 10^{-4}$[d]	M_w/M_n[d]	NBE (mol%)[e]
7	**3** (0.2)	0.2	4	25	10	6.54	57.9	1.61	8.2
8	**3** (0.2)	1.0	4	25	10	2.64	29.6	1.46	21.7
9	**4** (0.50)	0.2	4	25	10	2.46	21.1	1.88	9.6
10	**4** (0.50)	1.0	4	25	10	2.00	12.8	2.15	26.5
11	**1a** (0.02)	0.2	4	25	10	21.6	70.6	1.85	17.8
12	**1a** (0.02)	1.0	4	25	10	40.2	71.9	2.92	40.7
13	**1a** (0.02)	1.0	4	25	20	60.2	53.4	2.11	41.5
14	**1a** (0.02)	1.0	4	25	30	59.7	61.3	2.18	41.0
15	**1a** (0.02)	1.0	4	40	10	48.9	62.0	2.37	45.9
16	**1a** (0.02)	1.0	4	60	10	194	47.5	2.20	51.2
17	**1a** (0.02)	1.0	4	80	10	133	33.8	2.34	61.7
18[f]	**1a** (0.01)	2.5	2	25	10	90.0	32.3	2.09	58.8[g]
19[f]	**1a** (0.01)	5.0	2	25	10	85.8	34.0	2.00	65.8[g]
20[f]	**1a** (0.02)	10.0	2	25	10	31.5	44.4	2.01	73.5[g]

[a] Conditions: toluene 50 mL, MAO white solid (prepared by removing $AlMe_3$, toluene from PMAO) 3.0 mmol.

[b] Initial NBE concentration in mmol/mL.

[c] Activity in kg-polymer/mol-Ti h.

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

[e] NBE content in mol% estimated by ^{13}C NMR spectra.

[f] Ethylene 2 atm, toluene 10 mL.

[g] Glass transition temperature measured by DSC were 185 (run 18), 202 (run 19), 214 (run 20) °C, respectively.

7–10). The NBE contents in the copolymers prepared by **1a** were higher than those prepared by **3**, **4** under the same conditions. Note that both the activity (by **1a**) and the NBE contents in the copolymer increased at higher temperature (runs 15–17, 40–80 °C), and the resultant copolymers possessed large M_n values with unimodal molecular weight distributions ($M_n = 3.38\text{–}6.20 \times 10^5$, $M_w/M_n = 2.20\text{–}2.37$). The increases in the NBE contents at higher temperatures (45.9–61.7 mol%) would be due to an decrease in the ethylene concentration in toluene.

The efficient syntheses of high molecular weight copolymers with high NBE contents (58.8–73.5 mol%) could thus be achieved upon increasing the NBE concentration at low ethylene pressure (2 atm, runs 18–20), and glass transition temperature (T_g) for the resultant copolymers increased linearly upon increasing the NBE content (ex. 185, 202, and 214 °C at the NBE contents in the copolymers are 58.8, 65.8, and 73.3 mol%, respectively). Note that the activities at higher NBE/ethylene feed ratios (ethylene 2 atm, NBE 2.5–5.0 mmol/mL, runs 18 and 19) were higher than those at lower NBE/ethylene feed ratios (ethylene 4 atm, NBE 1.0 mmol/mL, runs 12–14), although the activity decreased upon increasing the NBE concentration (runs 18–20). The observed facts are unique contrast to those in the copolymerization using ordinary metallocenes or linked half-titanocenes.

It is known that microstructures for poly(ethylene-*co*-NBE)s prepared by **3**, **4** estimated by ^{13}C NMR spectra possesses few NBE repeat units and contained both *meso* and *racemo* alternating ethylene-NBE sequences as well as isolated NBE units (33.0–33.5 ppm) [11,28], and the NBE dyads were also observed as a tiny trace. In contrast, as shown in Fig. 2, resonances ascribed to NBE dyads (resonances ascribed to the NBE repeating units) were observed for the copolymers prepared by **1a**, and the microstructures thus possessed a mixture of two and/or three NBE repeat units (including dyads, triads) in addition to alternating, isolated NBE sequences (Fig. 2b). The intensity of resonances ascribed to NBE dyads, triads increased upon increasing the NBE contents (Fig. 2c).

The results for ethylene/NBE copolymerization by half-titanocenes containing various ketimide ligands, $Cp'TiCl_2[N{=}(R^1)R^2]$ [$Cp' = Cp$ (**1**), C_5Me_5 (Cp^*, **2**); $R^1,R^2 = {}^tBu,{}^tBu$ (**a**), ${}^tBu$,Ph (**b**), Ph,Ph (**c**)], MAO catalyst systems under the same conditions are summarized in Table 4. $Cp^*TiCl_2(N{=}C^tBu_2)$ (**2a**) showed high catalytic activities, but the activity decreased upon increasing the NBE concentration (runs 25 and 26); the NBE contents for the resultant copolymers prepared by **2a** were lower than those by **1a** under the same conditions. The observed trend is somewhat similar to that seen in the copolymerization by **3**–MAO catalyst system.

The ethylene/NBE copolymerization by using **1b**,**c** and **2c**–MAO catalyst systems were conducted to explore effect of the ketimide substituents toward both the activity and NBE incorporation. However, the observed catalytic activities were lower than those by $Cp'TiCl_2(N{=}C^tBu_2)$ (**1a**, **2a**)–MAO catalyst systems. The resultant polymers possessed bimodal molecular weight distributions consisting of low and high molecular weight polymers. The order in the activity was somewhat different that for ethylene polymerization; **1c** showed higher catalytic activity than **1b**, and we have no clear reason to explain the observed results at this moment.

We reported effect of the ketimide substituent on the activity for ethylene polymerization using VCl_2(N-2,6-

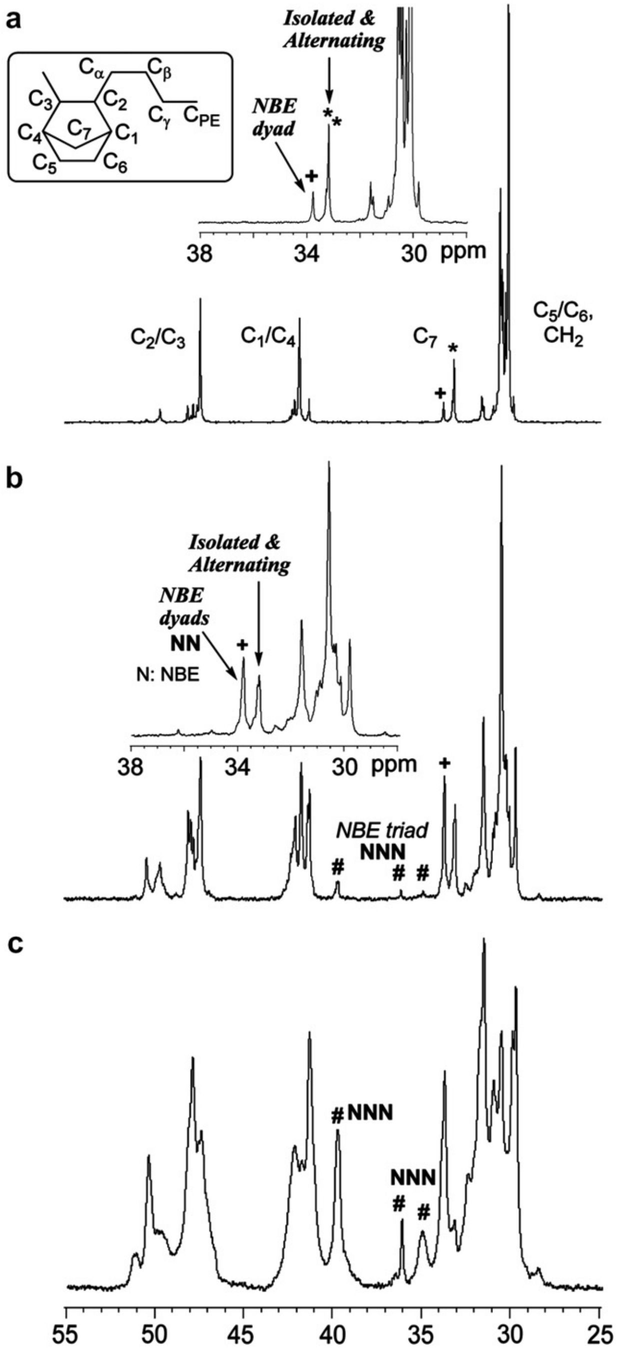

Fig. 2. ^{13}C NMR spectra for poly(ethylene-*co*-NBE)s prepared by **1a**–MAO catalyst system. NBE contents: (a) 17.8 (run 11), (b) 40.7 (run 12), (c) 58.8 mol% (run 18).

$Me_2C_6H_3$)[N=C(R^1)^{t}Bu] [R^1 = ^{t}Bu (**5a**), CH_2SiMe_3 (**5b**)]–MAO catalyst systems [29]. The activity by **5b** at 25 °C was higher than that by **5a** [activity 985 kg-PE/mol-V h vs. 666 kg-PE/mol-V h, ethylene 8 atm in toluene], but the activity by **5b** decreased at 50 °C whereas increase in the activity was observed in **5a** [543 kg-PE/mol-V h vs. 743 kg-PE/mol-V h]. We speculated that two *tert*-butyl group in **5a** may be necessary to improve the stability of V–N=C bond under these conditions, especially minimizing the reaction of **5a**,**b** with MAO (or $AlMe_3$ contaminated) to give another catalytically-active species. We also found that **5a** showed much higher catalytic activity than **5b** for ring-opening metathesis polymerization of NBE in the presence of MeMgBr/PMe_3 [30], and speculated that a stability of V–N=C bond toward the MeMgBr might affect the catalytic activity. It is also reported that imino (ArN=CH–Ar′) group in zirconium complexes containing two phenoxy-imine, [N-(3-*tert*-butylsalicylidene)anilinato], ligand was reacted with Al^iBu_3 to afford another zirconium complexes containing phenoxy-amide ligands [31]. Taking into account the above facts, it is thus assumed that the observed difference in the activity between **1a** and **1b**,**c** might be due to the stability of imino group, N=C(R^1)R^2, toward the Al cocatalyst in the reaction mixture.

We have prepared half-titanocenes containing various ketimide ligands of type, Cp′$TiCl_2$[N=C(R^1)R^2] [Cp′ = Cp (**1**), C_5Me_5 (Cp*, **2**); R^1,R^2 = ^{t}Bu,Ph (**b**), Ph,Ph (**c**)], and the structure of **2c** was determined by X-ray crystallography. The catalytic activities for ethylene polymerization by **1b**,**c**, **2c**–MAO catalyst systems were lower than those reported by **1a**, **2a**–MAO catalyst systems [17,18], and the resultant polymers possessed multi-modal molecular weight distributions. Although **1a**–MAO catalyst system showed both notable catalytic activities and efficient norbornene (NBE) incorporations for ethylene/NBE copolymerization, the observed activities for the copolymerization by **1b**,**c**, **2c**–MAO catalyst systems were low and the resultant polymers consisted of a mixture of high and low molecular weight polymers. Although the polymerization results by **1b**,**c** and by **2c**–MAO catalyst systems were not promising, however, the results presented here should afford important information for designing efficient catalysts with half-titanocenes for precise olefin polymerization.

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, hexane (Kanto Chemical Co., Inc.) were stored in a Schlenk tube in the drybox in the presence of molecular sieves (a mixture of 3A 1/16, 4A 1/8, and 13X 1/16). Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used as received. All chemicals used were reagent-grades and purified by standard purification procedures. Toluene and $AlMe_3$ in the commercially available MAO [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 Cp$TiCl_2$(N=C^tBu_2) (**1a**), Cp*$TiCl_2$(N=C^tBu_2) (**2a**) were according to the previous report [15a].

Table 4
Copolymerization of ethylene with norbornene (NBE) by $Cp'TiCl_2[N{=}C(R^1)R^2]$ [Cp′ = Cp (**1**), Cp* (**2**); R^1,R^2 = ^{t}Bu,^{t}Bu (**a**), ^{t}Bu,Ph (**b**), Ph,Ph (**c**)]–MAO catalyst systems[a]

Run	Complex (μmol)	NBE (mmol/mL)[b]	Activity[c]	$M_n^d \times 10^{-4}$	M_w/M_n^d	NBE (mol%)[e]
1	**1a** (0.10)	–	5880	45.2	2.30	–
11	**1a** (0.02)	0.2	21600	70.6	1.85	17.8
12	**1a** (0.02)	1.0	40200	71.9	2.92	40.7
2	**1b** (5.0)	–	90.0	Multi-modal		
21	**1b** (5.0)	0.2	106	151	2.24	
				0.19	5.80	
22	**1b** (5.0)	1.0	161	2.06[g]	1.71	
3	**1c** (5.0)	–	56.4	Multi-modal[f]		
23	**1c** (5.0)	0.2	154	110	2.63	
				6.60	2.84	
24	**1c** (5.0)	1.0	389	8.37	2.75	
				1.89	2.14	
4	**2a** (0.05)	–	19680	42.2	2.45	–
25	**2a** (0.05)	0.2	31700	52.3	2.47	12.7
26	**2a** (0.05)	1.0	22200	97.0	2.04	20.3
5	**2c** (5.0)	–	126	Multi-modal[f]		
27	**2c** (5.0)	0.2	245	1.40[h]	6.09	
28	**2c** (5.0)	1.0	Trace	–	–	

[a] Conditions: toluene 50 mL, ethylene 4 atm, 25 °C, 10 min, MAO white solid (prepared by removing $AlMe_3$, toluene from PMAO) 3.0 mmol.
[b] Initial NBE concentration in mmol/mL.
[c] Activity in kg-polymer/mol-Ti h.
[d] GPC data in *o*-dichlorobenzene vs. polystyrene standards.
[e] NBE content in mol% estimated by ^{13}C NMR spectra.
[f] Multimodal molecular weight distributions [$M_n = 4.16 \times 10^4$, $M_w/M_n = 21.1$ (run 3); $M_n = 9.91 \times 10^3$, $M_w/M_n = 25.9$ (run 5)].
[g] A trace amount of peak ascribed to high molecular weight polymer (PE) was seen in the GPC trace.
[h] High molecular weight shoulder peak was observed in the GPC trace.

Li[N=C(^{t}Bu)Ph] [22] or Li(N=CPh_2) [23] were prepared according to the reported procedures. Elemental analyses were performed by using PE2400II Series (Perkin–Elmer Co.), and some analysis runs were employed twice to confirm the reproducibility in the independent analysis/synthesis runs.

Molecular weights and molecular weight distributions for polyethylene and poly(ethylene-*co*-norbornene)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∅ ID), ranging from $<10^2$ to $<2.8 \times 10^8$ MW at 140 °C using *o*-dichlorobenzene containing 0.05 wt/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.

All ^1H and ^{13}C 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 in the drybox, and all chemical shifts are given in ppm and are referenced to Me_4Si. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. ^{13}C NMR spectra for poly(ethylene-*co*-norbornene)s and polyethylene were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) 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. 6000. The analysis samples of polyethylene, poly(ethylene-*co*-norbornene)s were prepared by dissolving polymers in a mixed solution of 1,3,4-trichlorobenzene/benzene-d_6 (90/10 wt), and the spectrum was measured at 130 °C.

3.1.1. Synthesis of $CpTiCl_2[N{=}C(^tBu)Ph]$ (1b)

To a toluene solution (10 mL) containing $CpTiCl_3$ (439 mg, 2.0 mmol) was added Li[N=C(^{t}Bu)Ph] (351 mg, 2.1 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature (25 °C), and the mixture was then stirred for additional 4 h. The solution was filtered through Celite pad, and the solvent was removed *in vacuo*. The residue was then dissolved in minimal amount of CH_2Cl_2 and the solution was covered with *n*-hexane. The chilled solution (−30 °C) yielded 602 mg (88%) of the titled complex as red microcrystals. ^1H NMR ($CDCl_3$): δ 1.32 (s, 9H, CH_3C), 6.55 (s, 5H, *Cp*), 7.36 (m, 3H, *Ph*), 7.43 (m, 2H, *Ph*). ^{13}C NMR ($CDCl_3$): δ 29.1, 45.4, 117.3, 127.1, 128.2, 129.7, 138.3, 196.1. Anal. Calc. for $C_{16}H_{19}Cl_2NTi$: C, 55.85; H, 5.57; N, 4.07. Found (1): C, 55.69; H, 5.24; N, 3.83%. Found (2): C, 55.47; H, 5.39; N, 3.88%.

3.1.2. Synthesis of $CpTiCl_2(N{=}CPh_2)$ (1c)

The titled compound was synthesized according to the same procedure as for **1b** except that $CpTiCl_3$ (230 mg, 1.05 mmol) and Li(N=CPh_2) (206 mg, 1.10 mmol) in place of Li[N=C(^{t}Bu)Ph] were used. Yield 250 mg (69%). ^1H NMR ($CDCl_3$): δ 6.65 (s, 5H, *Cp*), 7.43 (t, 4H, *meta*), 7.52 (t, 2H, *para*), 7.60 (d, 4H, *ortho*). ^{13}C NMR ($CDCl_3$): δ 117.3, 128.5, 130.3, 131.9, 136.7, 181.9.

*3.1.3. Synthesis of Cp**TiCl$_2$(N=CPh$_2$) (**2c**)*

Titled compound was synthesized according to the same procedure as for **1b** except that Cp*TiCl$_3$ (246 mg, 0.92 mmol) and Li(N=CPh$_2$) (206 mg, 1.10 mmol) was used in place of CpTiCl$_3$ and Li[N=C(^{t}Bu)Ph], respectively. Yield 371 mg (93%). ^{1}H NMR (CDCl$_3$): δ 2.11 (s, 15H, CH_3), 7.40 (t, 4H, *meta*), 7.47 (t, 2H, *para*), 7.62 (d, 4H, *ortho*). ^{13}C NMR (CDCl$_3$): δ 13.2, 128.4, 129.5, 131.1, 137.0, 180.2. Anal. Calc. for $C_{23}H_{25}Cl_2NTi$: C, 63.62; H, 5.80; N, 3.23. Found (1): C, 3.31; H, 5.63; N, 3.16%. Found (2): C, 63.29; H, 5.55; N, 3.27%.

*3.1.4. Crystallographic analysis for Cp**TiCl$_2$(N=CPh$_2$) (**2c**)*

All measurements were performed on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The selected crystal collection parameters are listed in Table 5, and the detailed results were described in the reports attached below. All structures were solved by direct method and expanded using Fourier techniques [32], and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations for complex **2c** were performed using the Crystal Structure [33,34] crystallographic software package.

3.1.5. Ethylene polymerization, ethylene/norbornene copolymerization

The typical reaction procedure for ethylene polymerization (Table 2, run 1) is as follows. Toluene (49 mL), and d-MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale stainless steel) in the drybox, and was filled with ethylene (1 atm). A toluene solution (1.0 mL) containing **1a** (0.1 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/norbornene copolymerization was the same as that in ethylene homopolymerization except that norbornene was added in toluene in the drybox.

Table 5

Crystal and data collection parameters for Cp*TiCl$_2$(N=CPh$_2$) (**2c**)[a]

Complex	Cp*TiCl$_2$(N=CPh$_2$) (**2c**)
Formula; formula weight	$C_{23}H_{25}Cl_2NTi$; 434.26
Habits; crystal size (mm)	Red, platelet; $0.80 \times 0.30 \times 0.10$
Crystal system	Orthorhombic
Space group	*Pbca* (#61)
a (Å); b (Å); c (Å)	8.5825(18); 18.048(6); 28.745(6)
V (Å^3)	4452.6(18)
Z value	8
D_{calcd} (g/cm^3)	1.296
F_{000}	1808.00
Temperature (K)	243
λ (Mo Kα) (Å)	0.71075
Number of reflections measured: (R_{int})	Total: 40434, unique: 5091 (0.042)
Number of observations ($I > 3.00\sigma(I)$)	3121
Number of variables	269
Residuals: R_1; wR_2	0.0.369; 0.0945
GOF	1.018
Maximum (minimum) peak in final difference map (e Å^3)	0.29 (−0.26)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares on F^2. Function minimized: $\sum w(|F_o| - |F_c|)^2$ {w = least squares weights, $1/[0.0008F_o^2 + 1.0000\sum(F_o^2)]/(4F_o^2)$}. Standard deviation of an observation of unit weight: $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$ (N_o = number of observations, N_v = number of variables).

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Appendix A. Supplementary material

CIF file and structure report for structural determination for Cp*TiCl$_2$(N=CPh$_2$) (**2c**). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2007.04.043.

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