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Olefin Polymerization by Half-Titanocenes Containing η^2-Pyrazolato Ligands−MAO Catalyst Systems

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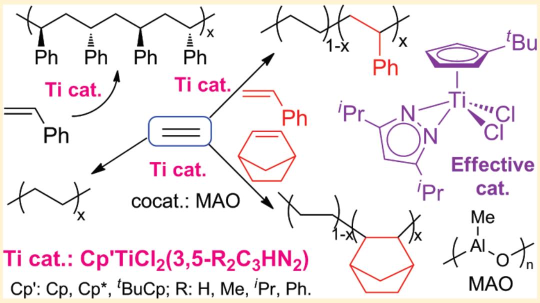
Supporting Information



ABSTRACT: A series of half-titanocenes containing pyrazolato ligands, $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ (**1a**−**d**, **2a**−**c**, **3a**−**c**) [Cp′ = Cp (**1**), Cp* (**2**), *tert*-BuC_5H_4 (*tert*-BuCp, **3**); R = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)], have been employed as the catalyst precursors for ethylene polymerization, syndiospecific styrene polymerization, and copolymerization of ethylene with 1-hexene, styrene, and norbornene (NBE) in the presence of MAO cocatalyst. The Cp* analogues, especially **2a**,**b**, exhibited high catalytic activities for ethylene polymerization affording the polymer with unimodal molecular weight distributions, whereas the Cp analogue (especially **1b**,**c**) and the *tert*-BuCp analogues (**3a**−**c**) exhibited high catalytic activities for syndiospecific styrene polymerization. The ethylene/styrene copolymerization using the *tert*-BuCp−diisopropyl analogue (**3c**) −MAO catalyst system proceeds in a living manner, irrespective of the styrene concentration employed (in toluene at 25 °C), and the same system exhibited relatively high catalytic activity for the ethylene/NBE copolymerization with highly efficient NBE incorporation.

INTRODUCTION

Design of efficient molecular catalysts for precise olefin polymerization attracts considerable attention in the field of organometallic chemistry, catalysis, and of polymer chemistry.[1−7] Half-titanocenes containing anionic donor ligands of type, $Cp'TiX_2(Y)$ (Cp′ = cyclopentadienyl group, X = halogen, alkyl, Y = aryloxo, ketimide, phosphinimide etc.), exemplified in Chart 1, are promising candidates,[5,7−10,12] especially in terms of syntheses of new polymers by ethylene copolymerizations as demonstrated by using the aryloxo and the ketimide analogues.[5b,c,8−11] We already demonstrated that efficient catalyst for the desired ethylene copolymerizations with styrene,[8,9] norbornene (NBE)[10,11] or other cyclic olefins[12] can be tuned by the ligand modifications (Cp′, Y). It was also demonstrated that the anionic donor ligand strongly affects the comonomer incorporation and the copolymerization behavior.[5b,c,8−10] It was also suggested that the NBE incorporation by $Cp'TiCl_2(Y')$ (Y′ = $N{=}C^tBu_2$, O-2,6-$^iPr_2C_6H_3$) −MAO catalyst systems was related to the calculated coordination energy to the cationic titanium(IV) alkyl species after ethylene insertion.[10b,c] Therefore, exploring the role of anionic donor ligand should be important for designing the efficient catalysts for precise olefin copolymerization directed toward synthesis of new polymers by incorporation of new comonomers that cannot be achieved by the conventional catalysts.[5c,9b,12a]

We recently reported that half-titanocenes containing η^2-pyrazolato ligands, $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ (**1a**−**d**, **2a**−**c**) [Cp′ = Cp (**1**), Cp* (**2**); R = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)], exhibited from moderate to high catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO) cocatalyst affording polymers with unimodal molecular weight distributions,[13] whereas the resultant polymers by half-titanocenes containing pyrrolides, $Cp'TiCl_2(Y)$ [Cp′ = Cp, Cp*; Y = C_4H_4N, 2,5-$Me_2C_4H_2N$, 2,4-$Me_2C_4H_2N$, 2,4-Me_2-3-EtC_4HN], conducted under the same conditions possessed bimodal molecular weight distributions (Scheme 1).[14] These results suggest that the pyrazolato analogues should be more effective than the pyrrolide analogues in terms of stability in the polymerization. Since, as described above, the ligand modification plays an important role for the desired (co)polymerizations, we thus focused on the pyrazolato analogue and explored in more details.[15]

In this paper, we wish to present our explored results in ethylene polymerization, syndiospecific styrene polymerization, and copolymerization of ethylene with 1-hexene, styrene, NBE using various (cyclopentadienyl)(pyrazolato)titanium(IV) dichloride complexes, $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ (**1a**−**d**, **2a**−**c**, **3a**−**c**) [Cp′ = Cp (**1**), Cp* (**2**), *tert*-BuC_5H_4 (**3**); R = H (**a**), Me

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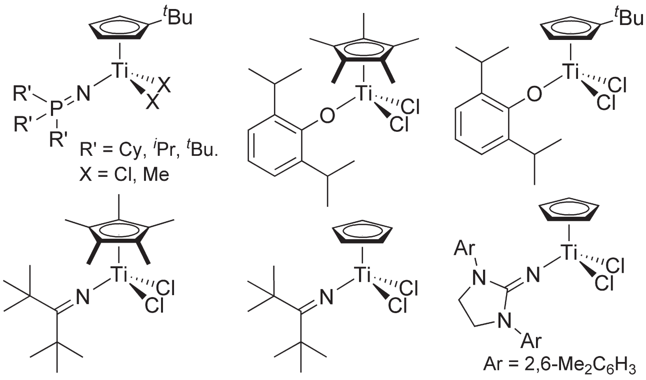
(**b**), ^{i}Pr (**c**), Ph (**d**)], in the presence of MAO (Scheme 2). Through this research, we wish to demonstrate that precise tuning of the ligand substituents plays an essential role for the desired copolymerization with better comonomer incorporation as well as for the better control in this catalysis.

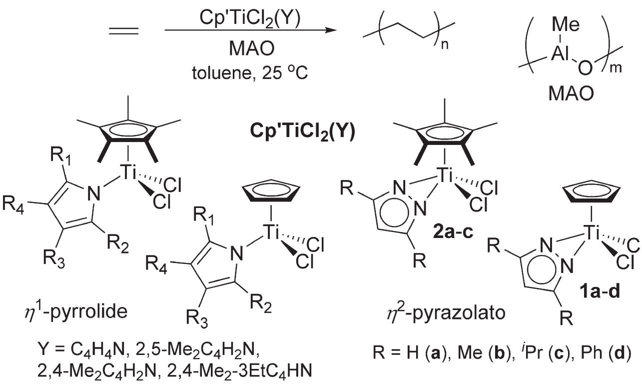
■ RESULTS AND DISCUSSION

1. Syntheses of Cp′–Pyrazolato Titanium(IV) Dichloride Complexes and Their Structural Analyses. A series of *tert*-BuCp analogues, (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) (**3a**–**c**), could be prepared from the trichloride analogue, (*tert*-BuC$_5$H$_4$)TiCl$_3$, according to the previous report (Scheme 3) for syntheses of the Cp (**1a**–**d**) and the Cp* analogues (**2a**–**c**), and the complexes were identified by NMR spectra and elemental analysis. As described below, structures for complexes **3b**, **c** were determined by X-ray crystallography.[16] We focused on the *tert*-BuCp in this study, because the *tert*-BuCp–aryloxo analogue, (*tert*-BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_3$HN$_2$), exhibited better both styrene and norbornene incorporations in the ethylene copolymerizations.[9a,b,10a,10b]

Chart 1. **Typical Reported Half-Titanocenes Effective for Olefin Polymerization**[5]



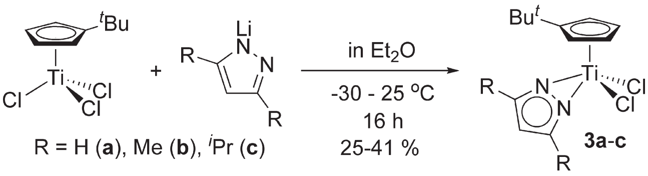
Scheme 1



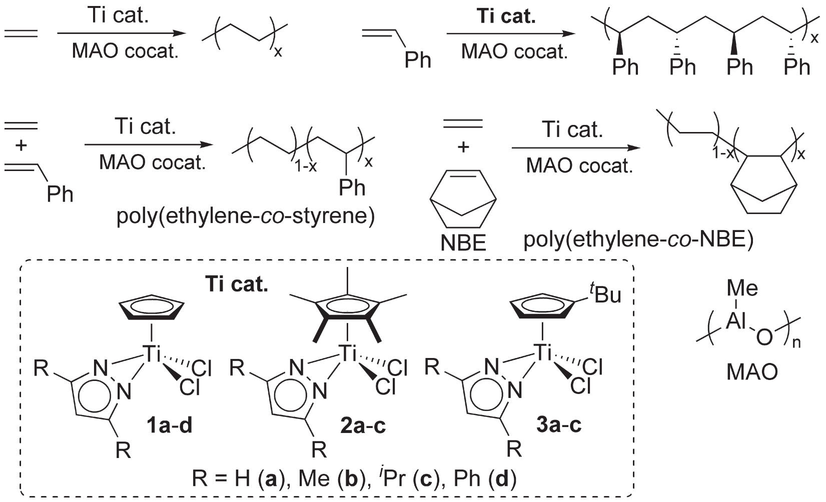
Yellow (**3b**) or orange (**3c**) microcrystals that are suitable for X-ray crystallographic analyses were grown from the chilled CH$_2$Cl$_2$ solution (−30 °C) layered by *n*-hexane, and suitable yellow or orange microcrystals of CpTiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (**1c**), CpTiCl$_2$(3,5-Ph$_2$C$_3$HN$_2$) (**1d**), and Cp*TiCl$_2$(3,5-^{i}Pr$_2$-C$_3$HN$_2$) (**2c**), that were not determined in the previous report,[13] were also obtained under similar conditions. The structures of **1c**, **d** and **2c** are shown in Figure 1, and the selected bond distances and angles are summarized in Table 1;[16] the structures of **3b**,**c** are shown in Figure 2, and the selected bond distances and angles are summarized in Table 2.[16]

In all cases (**1a**–**d**, **2a**–**c**, **3b**,**c**), the pyrazolato ligands are coordinated in η^2-*N*,*N*′ fashion with relatively similar Ti–N bond lengths [1.9895(14)–2.0366(19) Å], which are comparable with most of the reported Ti complexes bearing η^2-*N*,*N*′-coordinated pyrazolato ligands.[13,17] As described previously,[13] the Ti–N bond distances are significantly longer than those in (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] [1.898(2) Å],[18] Cp*TiCl$_2$[N(Me)(cyclohexyl)] [1.870(3) Å],[19] and in Cp*TiCl$_2$(N=CPh$_2$) [1.827 (2) Å],[20] and the distances are relatively close to the estimated value (2.02 Å) for a titanium–nitrogen single bond according to Pauling's covalent radii.[21] The

Scheme 3



Scheme 2



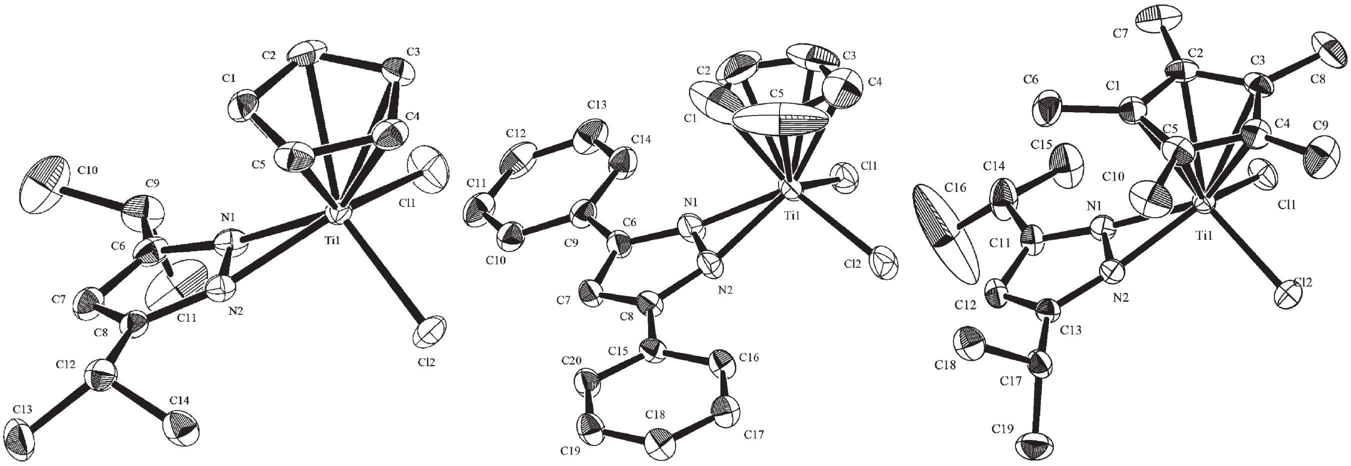


Figure 1. Ortep drawings for $CpTiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (**1c**, left), $CpTiCl_2(3,5\text{-}Ph_2C_3HN_2)$ (**1d**, middle), and $Cp^*TiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (**2c**, right). Thermal ellipsoids are drawn at 50% probability level, and H atoms were omitted for clarity. The structural analysis reports including CIF files are shown in the Supporting Information.[16]

Table 1. Selected Bond Distances (Å) and Angles (deg) for $CpTiCl_2(C_3H_3N_2)$ (1a),[13] $CpTiCl_2(3,5\text{-}Me_2C_3HN_2)$ (1b),[13] $CpTiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (1c), $CpTiCl_2(3,5\text{-}Ph_2C_3HN_2)$ (1d), and $Cp^*TiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (2c).[a]

Cp′;R	Cp; H (**1a**)[13]	Cp; Me (**1b**)[13]	Cp; ^{i}Pr (**1c**)	Cp; Ph (**1d**)	Cp*; ^{i}Pr$_2$ (**2c**)
			Bond Distances (Å)		
Ti(1)−Cl(1), Ti(1)−Cl(2)	2.3018(7), 2.2904(7)	2.2760(16), 2.3146(10)	2.3093(5), 2.2763(4)	2.2895(8), 2.2867(8)	2.3153(8), 2.2857(8)
Ti(1)−N(1), Ti(1)−N(2)	2.023(2), 2.0159(19)	2.022(3), 2.007(3)	2.0021(13), 2.0106(12)	2.020(2), 2.012(2)	2.028(2), 2.0366(19)
Ti(1)−C(1), Ti(1)−C(3)	2.330(2), 2.333(4)	2.332(5), 2.321(7)	2.3423(15), 2.3494(15)	2.356(6), 2.347(5)	2.360(3), 2.384(3)
N(1)−N(2)	1.363(2)	1.396(4)	1.3763(18)	1.372(3)	1.375(3)
N(1)−C(6), N(2)−C(8)	1.341(3), 1.385(4)	1.335(4), 1.335(5)	1.343(2), 1.3372(19)	1.347(3), 1.347(3)	N(1)−C(11) 1.344(3), N(2)−C(13) 1.339(3)
C(6)−C(7), C(7)−C(8)	1.385(4), 1.336(3)	1.407(5), 1.373(4)	1.393(2), 1.404(2)	1.400(4), 1.399(3)	C(11)−C(12) 1.392(4), C(12)−C(13) 1.401(4)
			Bond Angles (deg)		
Cl(1)−Ti(1)−Cl(2)	95.48(2)	96.63(5)	97.735(19)	96.15(3)	95.51(3)
N(1)−Ti(1)−N(2)	39.07(5)	40.56(12)	40.12(5)	39.78(8)	39.54(8)
Cl(1)−Ti(1)−N(1), Cl(1)−Ti(1)−N(2)	92.25(4), 123.40(5)	93.93(11), 120.86(11)	90.51(4), 127.48(3)	93.59(7), 123.18(7)	93.53(6), 126.04(6)
Cl(2)−Ti(1)−N(1), Cl(2)−Ti(1)−N(2)	121.03(6), 91.65(6)	125.65(9), 90.35(8)	117.16(4), 93.61(4)	123.92(6), 91.81(6)	121.19(6), 92.72(6)

[a] The structure reports including CIF file are shown in the Supporting Information.[16]

N−N distances [1.363(2)−1.396(4) Å] and the N(1)−Ti(1)−N(2) bite angles [39.07(5)−40.56(12)°] in the pyrazolato ligands are also similar to those in the other η^2-*N,N*′-pyrazolato titanium complexes.[13,17] The coordination spheres around the Ti possess an approximate tetrahedral geometry, if center of the nitrogen−nitrogen bond in the pyrazolato ligand is considered as a monodentate ligand. As a result of η^2-*N,N*′-coordination of the pyrazolato ligand, the Cl(1)−Ti−Cl(2) bond angles (in **1a**−**d**, **2a**−**c**, and **3b**,**c**) were constrained [93.823(16)° (**3b**), 98.23(2)° (**3c**)], although, as described below, the angle was affected by the substituents in both Cp′ and the pyrazolato ligand. On the basis of these results, these complexes would be considered as 14e complexes (by 3e donation with the pyrazolato ligand) rather than 16e complexes (by 5e donation).

Although both the bond distances and the angles are affected by the substituents in both Cp′ and the pyrazolato ligand, apparent trends as explained by electronic or steric influences were not observed. For example, the Cl−Ti−Cl bond angle in the Cp analogues increased in the order: 95.48(2)° (**1a**)[13] < 96.15(3)° (**1d**) < 96.63(5)° (**1b**)[13] < 97.735(19)° (**1c**), whereas the angle in the Cp* analogues and the *tert*-BuCp analogues increased in the order: 93.823(16)° (**3b**) < 95.51(3)° (**2c**) < 95.684(18)° (**2a**)[13] < 97.24(3)° (**2b**)[13] < 98.23(2) (**3c**). The N(1)−N(2) bond distances (Å) in in the Cp analogues increased in the order 1.363(2) (**1a**)[13] < 1.372(3) (**1d**), 1.3763(18) (**1c**) < 1.396(4) (**1b**)[13], whereas the distance in the Cp* analogues and the *tert*-BuCp analogues increased in the order 1.3679(18) (**2a**)[13] < 1.370(2) (**3c**), 1.3744(18) (**3b**), 1.375(3) (**2c**) < 1.381(5) (**2b**)[13]. Although we explored the differences or trends by comparison of these data (bond angles and distances) on the basis of the crystallographic analysis results, the reason for the observed difference can be only assumed as the result of combination of both electronic and steric effect.

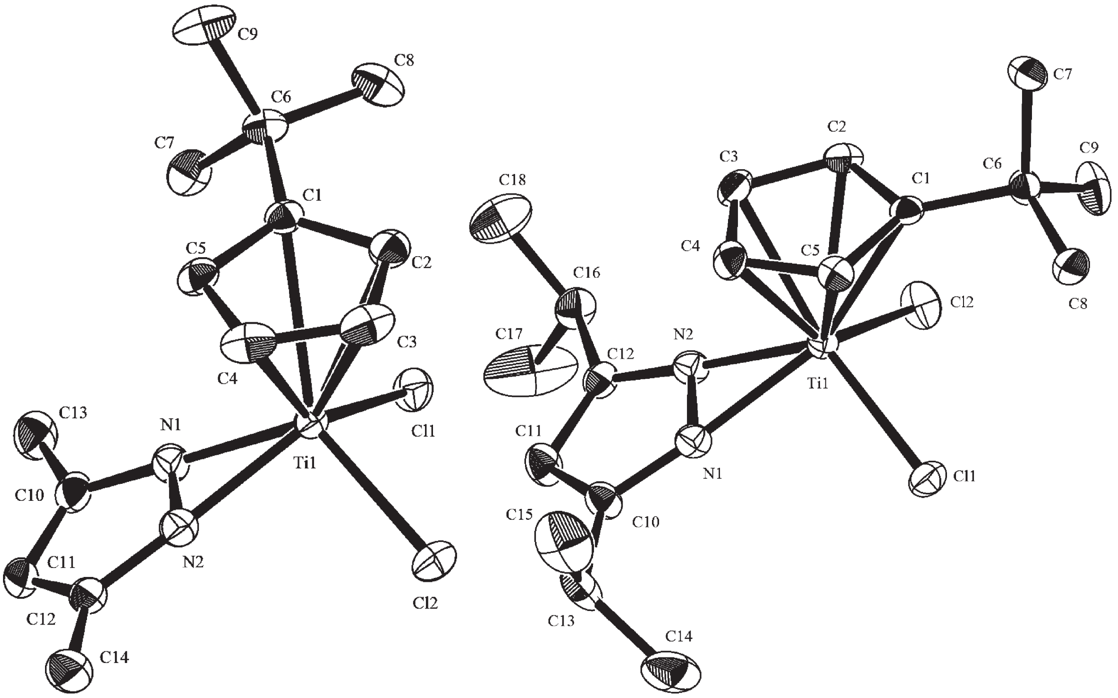


Figure 2. Ortep drawings for (*tert*-BuC_5H_4)$TiCl_2$(3,5-$Me_2C_3HN_2$) (**3b**, left) and (*tert*-BuC_5H_4)$TiCl_2$(3,5-$^iPr_2C_3HN_2$) (**3c**, right). Thermal ellipsoids are drawn at 50% probability level, and H atoms were omitted for clarity. The structural analysis reports including CIF files are shown in the Supporting Information.[16]

Table 2. Selected Bond Distances (Å) and Angles (deg) for (*tert*-BuC_5H_4)$TiCl_2$(3,5-$Me_2C_3HN_2$) (3b) and (*tert*-BuC_5H_4)$TiCl_2$(3,5-$^iPr_2C_3HN_2$) (3c).[a]

	(*tert*-BuC_5H_4)$TiCl_2$(3,5-$Me_2C_3HN_2$) (**3b**)	(*tert*-BuC_5H_4)$TiCl_2$(3,5-$^iPr_2C_3HN_2$) (**3c**)
	Bond Distances (Å)	
Ti(1)−Cl(1), Ti(1)−Cl(2)	2.3053(4), 2.3051(4)	2.2979(6), 2.2902(6)
Ti(1)−N(1), Ti(1)−N(2)	2.0031(14), 1.9895(14)	2.0269(16), 2.0077(16)
Ti(1)−C(1)	2.4186(14)	2.4337(18)
Ti(1)−C(2), Ti(1)−C(3)	2.3783(16), 2.3418(16)	2.370(2), 2.315(2)
N(1)−N(2)	1.3744(18)	1.370(2)
N(1)−C(10), N(2)−C(12)	1.347(2), 1.336(2)	1.344(2), 1.339(2)
C(10)−C(11), C(11)−C(12)	1.396(2), 1.390(2)	1.397(2), 1.396(3)
	Bond Angles (°)	
Cl(1)−Ti(1)−Cl(2)	93.823(16)	98.23(2)
N(1)−Ti(1)−N(2)	40.27(5)	39.70(6)
Cl(1)−Ti(1)−N(1), Cl(1)−Ti(1)−N(2)	92.22(3), 124.09(4)	91.27(5), 123.39(5)
Cl(2)−Ti(1)−N(1), Cl(2)−Ti(1)−N(2)	120.95(3), 91.85(4)	120.73(4), 90.78(5)

[a] The structure repots including CIF file are shown in the Supporting Information.[16]

2. Ethylene Polymerization and Ethylene/1-Hexene Copolymerization Using Cp′−Pyrazolato Titanium(IV) Dichloride Complexes−MAO Catalyst Systems. Ethylene polymerizations using Cp′$TiCl_2$(3,5-$R_2C_3HN_2$) [**1a**−**d**, **2a**−**c**, **3a**−**c**; Cp′ = Cp (**1**), Cp* (**2**), *tert*-BuC_5H_4 (**3**); *R* = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)] were conducted in toluene at 25 °C in the presence of MAO. MAO white solid (d-MAO) prepared by removing $AlMe_3$ and toluene from the commercially available samples (PMAO-S, 6.8 wt % in toluene, Tosoh Finechem Co.) was chosen in this study, because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when the Cp*$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) was used as the catalyst precursor.[22] Table 3 summarized the results using **3a**−**c**−MAO catalyst systems under various Al/Ti molar ratios. Since the polymerization data by **1a**−**d**, **2a**−**c**−MAO catalyst systems in the previous report[13] were collected under a certain Al/Ti molar ratio (2.0 or 3.0 mmol without full optimization), the polymerizations under various Al/Ti molar ratios were also conducted in this study (Figure 3).[23]

The catalytic activity in ethylene polymerization using **3a**−**c** − MAO catalyst systems (under optimized Al/Ti molar ratio) increased in the order: 490 kg-PE/mol-Ti·h

Table 3. Ethylene Polymerization by (*tert*-Bu-C_5H_4)$TiCl_2$-(3,5-$R_2C_3HN_2$) [*R* = H (a), Me (b), ^{i}Pr (c)] - MAO Catalyst Systems[a]

run	complex (μmol)	MAO/ mmol	yield/ mg	activity[b]	M_n[c] × 10^{-3}	M_w/M_n[c]
1	**3a** (1.0)	1.0	82	490	10.4	2.28
2	**3a** (1.0)	2.0	114	680	13.5	2.20
3	**3a** (1.0)	3.0	128	770	12.5	2.10
4	**3a** (1.0)	4.0	268	1610	12.3	2.00
5	**3a** (1.0)	5.0	91	550	9.52	2.45
6	**3b** (1.0)	1.0	45	270	6.25	5.30[d]
7	**3b** (1.0)	2.0	72	430	5.78	3.94
8	**3b** (1.0)	3.0	81	490	6.94	3.37
9	**3b** (1.0)	4.0	65	390	8.64	2.74
10	**3b** (1.0)	5.0	64	380	5.82	4.16
11	**3c** (1.0)	1.0	179	1070	546	1.85
12	**3c** (1.0)	2.0	133	800	473	1.67
					3.20	3.65
13	**3c** (1.0)	3.0	131	800	499	1.54
					5.71	2.63
14	**3c** (1.0)	4.0	124	740	418	1.70
					7.92	2.00
15	**3c** (1.0)	5.0	126	760	410	1.57
					6.37	2.30

[a] Polymerization conditions: toluene 30 mL, ethylene 6 atm, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] High molecular weight shoulder was observed in small amount in the GPC trace.

(**3b**) < 1070 (**3c**) < 1610 (**3a**). These results suggest that the activity was affected by substituent in the pyrazolato ligand. The resultant polymers by **3a**,**b** possessed low molecular weights with unimodal distributions in most cases (runs 1−10, M_n = 5780−13500), whereas the resultant polymer by **3c** under the optimized conditions possessed relatively high molecular weight with unimodal distribution (run 11, M_n = 5.46 × 10^5, M_w/M_n = 1.85).

The selected polymerization results by **1a**−**d**, **2a**−**c**, **3a**−**c** under the optimized conditions are summarized in Table 4. The catalytic activities were affected by the cyclopentadienyl fragment (Cp′), and the Cp* analogues (**2a**−**c**, activity: 3060−9600 kg-PE/mol-Ti·h, runs 27−30) exhibited higher catalytic activities than the Cp analogues (**1a**−**d**, activity: 1200−1700 kg-PE/mol-Ti·h) and the *tert*-BuCp analogues (490−1610 kg-PE/mol-Ti·h). Moreover, the molecular weights in the resultant polymers were also affected by the Cp′ employed; the M_n values in the resultant PE by **1a**−**d** were higher than those by **2a**−**c**, **3a**−**c**. In terms of both the activity and the M_n value in the resultant PE, the Cp* analogues, especially **2a**,**b**, seem to be suited for the ethylene polymerization.

Table 5 summarized results for ethylene/1-hexene copolymerization by Cp′$TiCl_2$(3,5-$R_2C_3HN_2$) (**1a**−**d**, **2a**−**c**, **3a**−**c**) − MAO catalyst systems under the optimized Al/Ti molar ratios (conducted for the ethylene polymerization).[24] Although the Cp* analogues (**2a**−**c**) exhibited high catalytic activities for the ethylene polymerization (runs 27−30, Table 4), the activities drastically decreased when the polymerizations were conducted in the presence of 1-hexene (runs 35−37). The activities by the Cp (**1a**−**d**) and the *tert*-BuCp analogues (**3a**,**b**) were also lower than those in the ethylene polymerization. In contrast, the activity in the copolymerization by the *tert*-BuCp−diisopropyl analogue (**3c**) was relatively close to that in the ethylene polymerization; the resultant polymer contained 1-hexene with relatively high molecular weight as well as with unimodal molecular weight distribution.[24]

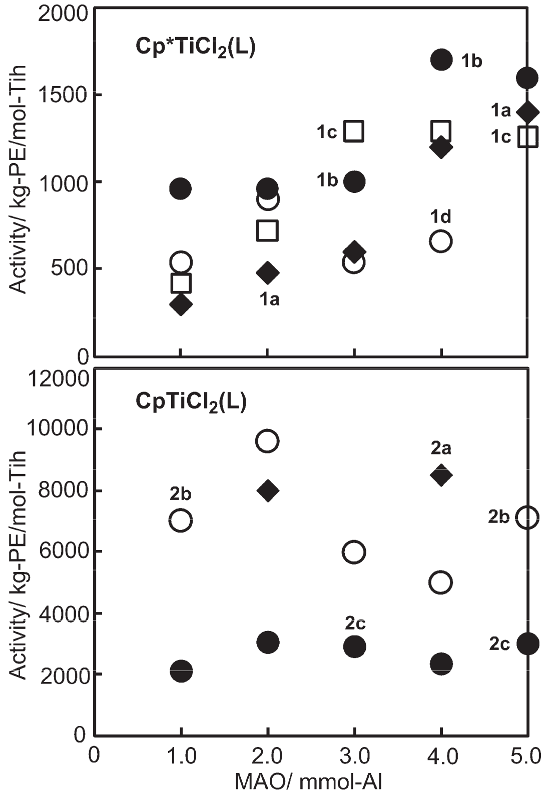


Figure 3. Effect of Al/Ti molar ratios toward the catalytic activity in ethylene polymerization catalyzed by Cp*$TiCl_2$(3,5-$R_2C_3HN_2$) (**1a**−**d**), Cp*$TiCl_2$(3,5-$R_2C_3HN_2$) (**2a**−**c**) [*R* = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)] in the presence of d-MAO (ethylene 6 atm in toluene, 25 °C, 10 min). Detailed data are shown in the Supporting Information.[23]

The resultant polymers prepared by the Cp analogues (**1a**−**d**) and the Cp* analogues (**2b**,**c**) except **2a** possessed broad molecular weight distributions, suggesting that several catalytically active species would be generated under these conditions. The resultant polymers prepared by **2a**, **3a** possessed low molecular weights with unimodal molecular weight distributions (runs 35, 38) as well as with moderate 1-hexene contents (15.5, 15.7 mol %). On the basis of microstructure analyses in the poly(ethylene-*co*-1-hexene)s prepared by **2a**, **3a**, **3c**−MAO catalyst systems (Table 6, estimated by the ^{13}C NMR spectra),[24] it is clear that these copolymerizations proceeded in a random manner (1-hexene incorporations were random in these catalyzes) due to that the $r_E \cdot r_H$ values were close to 1. The r_E values by **2a**, **3a** were 11.7,11.6, respectively, and the values were much larger that those by the Cp*−aryloxo analogue (2.70)[25] and the Cp′−ketimide analogues (4.5).[26] Moreover, the r_E value by **3c** in the copolymerization was 22.7, and the values was larger than those by the ordinary linked zirconocenes [r_E = 8.2−18.9 by linked bis(indenyl)zirconium complexes in ethylene/1-octene copolymerization].[27] These results thus suggest that the present catalysts showed less efficient 1-hexene incorporations, although the r_E values were affected by the ligand sets employed. The results also indicate that precise modifications of both Cp′ and the pyrazolato ligands are important for the copolymerization to proceed with uniform catalytically active species as well as with moderate comonomer incorporation.

3. Syndiospecific Styrene Polymerization and Ethylene/Styrene Copolymerization Using Cp′–Pyrazolato Titanium(IV) Dichloride Complexes–MAO Catalyst Systems. We previously demonstrated in the Cp′–aryloxo,[9a] Cp′–amide’ and the phenoxy–imine[15n] analogues that efficient catalyst precursors for the syndiospecific styrene polymerization can be tuned from the efficient catalyst precursors for the ethylene polymerization by modification of the cyclopentadienyl fragment. For example, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ is the effective catalyst precursor for the ethylene polymerization, whereas $(tert\text{-}BuC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ is the effective catalyst precursor for the syndiospecific styrene polymerization.[9a] We thus conducted styrene polymerization using a series of Cp′–pyrazolato analogues (**1a**–**d**, **2a**–**c**, **3a**–**c**) in the presence of MAO (at 25 °C), and the results conducted under certain Al/Ti molar ratios (shown in Table 4) are summarized in Table 7.

As demonstrated previously,[9a,15n,19] both the Cp and the *tert*-BuCp analogues (runs 41–44, 48–50) showed higher catalytic activities than the Cp* analogues (runs 45–47), affording syndiotactic polymers with almost perfect tacticity.[24] The fact clearly supports that unique characteristics by using the nonbridged half-titanocenes of this type, as described above, can also be observed in the present catalysts. The resultant polymers possessed relatively high molecular weights with unimodal molecular weight distributions in all cases, suggesting that these polymerizations proceeded with uniform catalytically active species. The activities were also affected by the pyrazolato substituent; the placement of methyl or isopropyl group (**1b**, **3a**,**b**) seems effective for exhibiting the high activity.

On the basis of the above homopolymerization results, the (co)polymerizations using a series of Cp′–pyrazolato analogues (**1a**–**d**, **2a**–**c**, **3a**–**c**) were conducted under ethylene pressure, and the results are summarized in Table 8. Although these complexes afforded syndiotactic polystyrene with unimodal distributions, unfortunately, the resultant polymers prepared by the Cp analogues (**1a**–**d**) and the Cp* analogues (**2a**–**c**) were a mixture of polyethylene (PE) and syndiotactic polystyrene (SPS) or PE confirmed by both NMR spectra and the DSC thermograms after careful fractional separation of all polymer samples.[24] The ratios of PE and SPS were highly dependent upon the initial molar ratios of monomers (ethylene, styrene).[28] Although the resultant polymers conducted by using **3a**,**b**–MAO catalyst systems were mixtures of PE and SPS or SPS, the resultant polymers prepared by the *tert*-BuCp–diisopropyl analogue (**3c**) were poly(ethylene-*co*-styrene)s exclusively with relatively narrow molecular weight distributions (runs 67, 68, Table 8). The fact clearly suggests that precise tuning of both Cp′

Table 4. Selected Data for Ethylene Polymerization by $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ [Cp′ = Cp (1), Cp* (2), *tert*-Bu-C_5H_4 (3); R = H (a), Me (b), ^{i}Pr (c), Ph (d)] –MAO Catalyst Systems[a]

run	complex (μmol)	MAO/mmol	yield/mg	activity[b]	M_n[c] × 10^{-3}	M_w/M_n[c]
16	**1a** (0.2)	2.0	16	480	insoluble[d]	
17[e]	**1a** (0.1)	2.0	9	540	1310	2.31
18	**1a** (0.2)	5.0	47	1400	insoluble[d]	
19	**1b** (0.1)	2.0	16	960	insoluble[d]	
20[e]	**1b** (0.1)	2.0	13	780	1240	2.29
21	**1b** (0.1)	4.0	29	1700	insoluble[d]	
22	**1c** (0.2)	2.0	24	720	insoluble[d]	
23[e]	**1c** (0.1)	2.0	14	840	974	3.07
					3.6	2.04
24	**1c** (0.2)	4.0	43	1290	insoluble[d]	
25	**1d** (0.2)	2.0	30	900	insoluble[d]	
26[e]	**1d** (0.1)	2.0	20	1200	895	3.03
27	**2a** (0.1)	2.0	132	8000	49.6	1.67
28[e]	**2a** (0.1)	2.0	150	9000	35.2	2.17
29	**2b** (0.1)	2.0	160	9600	56.9	1.73
30	**2c** (0.1)	2.0	51	3060	36.6	8.15[f]
4	**3a** (1.0)	4.0	268	1610	12.3	2.00
8	**3b** (1.0)	3.0	81	490	6.94	3.37
11	**3c** (1.0)	1.0	179	1070	546	1.85

[a] Polymerization conditions: toluene 30 mL, ethylene 6 atm, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Insoluble for GPC measurement. [e] Cited from reference.[13] [f] High molecular weight shoulder was observed in small amount in the GPC trace.

Table 5. Copolymerization of Ethylene with 1-Hexene by $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ [Cp′ = Cp (1), Cp* (2), *tert*-Bu-C_5H_4 (3); R = H (a), Me (b), ^{i}Pr (c), Ph (d)] –MAO Catalyst Systems[a]

run	complex (μmol)	MAO/mmol	yield/mg	activity[b]	M_n[c] × 10^{-3}	M_w/M_n[c]	content[d]/ mol %
31	**1a** (2.5)	5.0	140	340	2.33	5.39	
32	**1b** (2.5)	4.0	91	220	2.88	3.99	
33	**1c** (2.5)	4.0	113	270	4.79	5.86	
34	**1d** (2.5)	2.0	81	190	5.82	8.82	
35	**2a** (1.0)	2.0	86	520	5.46	2.87	15.5
36	**2b** (1.0)	2.0	36	200	8.82	3.21	
37	**2c** (1.0)	2.0	44	260	33.1	7.49	
38	**3a** (2.5)	4.0	69	170	5.41	2.17	15.7
39	**3b** (2.5)	3.0	47	110	3.56	9.53[e]	
40	**3c** (1.0)	1.0	229	1370	492	2.15	8.9

[a] Conditions: toluene 25 mL, 1-hexene 5 mL, ethylene 6 atm, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] 1-Hexene content (mol %) estimated by ^{13}C NMR spectra.[24] [e] High molecular weight shoulder was observed in small amount in the GPC trace.

Table 6. Monomer Sequence Distributions of Poly(ethylene-*co*-1-hexene)s Prepared by Copolymerization of Ethylene (E) with 1-Hexene (H) by Cp′TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) [Cp′ = Cp* (2), *tert*-Bu-C$_5$H$_4$ (3); R = H (a), ^{i}Pr (c)] −MAO Catalyst Systems[a]

			triad sequence distribution[c] (%)						dyad[d]					
run	complex	content[b]/ mol %	EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH	$r_E \cdot r_H$[e]	r_E[f]	r_H[f]
35	**2a**	15.5	61.3	21	2.2	11.2	4.3	–	71.8	26.1	2.1	0.90	11.7	0.077
38	**3a**	15.7	61.3	20.6	2.4	11.2	4.5	–	71.5	26.2	2.3	0.94	11.6	0.081
40	**3c**	8.9	77.6	12.1	1.4	7.5	1.4	–	83.7	15.6	0.7	0.98	22.7	0.043

[a] For detailed polymerization conditions, see Table 5. [b] 1-Hexene content (mol %) estimated by ^{13}C NMR spectra.[24] [c] Estimated by ^{13}C NMR spectra. [d] [EE] = [EEE] + $^1/_2$[EEH + HEE], [EH] = [HEH] + [EHE] + $^1/_2${[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + $^1/_2$[HHE + EHH]. [e] $r_E \cdot r_H$ = 4[EE][HH]/[EH + HE].[2] [f] r_E = {[H]$_0$/[E]$_0$} × 2[EE]/[EH + HE], r_H = {[E]$_0$/[H]$_0$} × 2[HH]/[EH + HE], [E]$_0$ and [H]$_0$ are the initial monomer concentrations.

Table 7. Syndiospecific Styrene Polymerization by Cp′TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) [Cp′ = Cp (1), Cp* (2), ^{t}BuCp (3); R = H (a), Me (b), ^{i}Pr (c), Ph (d)] −MAO Catalyst Systems[a]

run	complex (μmol)	MAO/ mmol	yield[b]/ mg	activity[c]	M_n[d] × 10^{-4}	M_w/ M_n[d]
41	**1a** (0.3)	5.0	72	1440	2.55	2.06
42	**1b** (0.3)	4.0	158	3160	1.65	2.19
43	**1c** (0.3)	4.0	126	2520	1.99	1.98
44	**1d** (0.3)	2.0	90	1780	2.60	1.85
45	**2a** (0.5)	2.0	83	990	4.29	1.96
46	**2b** (0.5)	2.0	85	1020	2.54	1.88
47	**2c** (0.5)	2.0	107	1280	1.98	1.98
48	**3a** (0.2)	4.0	108	3240	4.20	2.01
49	**3b** (0.2)	3.0	113	3390	4.77	1.90
50	**3c** (0.2)	1.0	74	2220	4.25	2.05

[a] Polymerization conditions: complex in toluene 1.0 mL, styrene 10 mL, d-MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 10 min. [b] Polymer yield based on acetone insoluble fraction. [c] Activity = kg-SPS/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

and pyrazolato substituent plays an important role for the effective catalyst in this catalysis.

Table 9 summarizes results for ethylene/styrene copolymerization using the *tert*-BuCp−diisopropyl analogue (**3c**) −MAO catalyst system under various conditions. Importantly, the M_n values increased over the time course as well as upon increasing the polymer yields consistently with relatively narrow molecular weight distributions (M_w/M_n = 1.22−1.64). The activity initially decreased upon increasing the styrene concentration (runs 67−70 vs 68−76) but kept constant upon further increase (runs 77−79). The styrene contents in the resultant copolymers were low (1.4−6.0 mol %), but the content increased upon increasing the styrene concentration. Resonances ascribed to the isolated styrene incorporation were thus observed in the ^{13}C NMR spectra.[24]

As shown in Figure 4, the M_n values increased linearly upon increasing the polymer yields in all cases, and, as described above, the M_w/M_n values did not change significantly under these conditions. The first order relationship between the M_n values and the polymer yields clearly indicate that the degree of chain transfer from Ti-alkyl to Al-alkyl was negligible and that the copolymerization proceeded in a living manner, as demonstrated by the Cp*TiCl$_2$(N=C^{t}Bu$_2$)−MAO catalyst system.[9c,d] Since the resultant polymers prepared in both the ethylene polymerization and the styrene polymerization possessed unimodal molecular weight distributions with certain chain transfers (runs 11 and 50, M_w/M_n = 1.85, 2.05, respectively), also since resonances corresponding to the styrene repeating units were not observed in the resultant poly(ethylene-*co*-styrene)s, the facts thus suggest that a certain degree of the styrene insertion inhibited the chain transfer in this catalysis.[9d]

4. Ethylene/Norbornene Copolymerization Using Cp′−Pyrazolato Titanium(IV) Dichloride Complexes−MAO Catalyst Systems. It has been known that certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV−vis region along with humidity-, and heat-resistance (high glass transition temperature, T_g).[29] The copolymerization of ethylene with cyclic olefins, especially norbornene (NBE), seems promising, because the desired properties (T_g, etc.) can be tuned by their compositions (cyclic olefin contents etc.) as well as their microstructures.[29,30] On the basis of our previous results,[10,30] we explored the ethylene/NBE copolymerization using the Cp′−pyrazolato analogues (**1a**−**d**, **2a**−**c**, **3a**−**c**) in the presence of MAO (in toluene at 25 °C). The results are summarized in Table 10.[24,31]

In contrast to the results in the copolymerization of 1-hexene, styrene, these copolymerizations using the Cp analogues (**1a**−**d**) and the *tert*-BuCp−diisopropyl analogue (**3c**), proceeded with relatively high catalytic activities; apparent increases in the activities upon the presence of NBE were observed by **1a**,**c**, and by **3c** under these conditions (ethylene 5 atm, NBE 0.5 mmol/mL at 25 °C). However, the resultant polymers prepared by **1b**-**d** possessed relatively broad molecular weight distributions; the resultant polymers prepared by the Cp* analogues (**2a**−**c**) also possessed broad molecular weight distributions containing high molecular weight shoulders in their GPC traces. In contrast, both **1a** and **3c** exhibited remarkable catalytic activities, affording high molecular weight polymers with unimodal molecular weight distributions (runs 80, 89).

On the basis of the results shown in Table 10, the polymerizations using **1a**,**3c**−MAO catalyst systems were conducted under various conditions, and the results are summarized in Table 11.[24] The catalytic activity by **1a** increased upon increasing the initial NBE concentration (run 90 vs run 80), but decreased at higher NBE concentration (runs 91−92); the resultant copolymers with low NBE contents possessed high molecular weights (runs 80, 90) but the M_n value decreased drastically upon increasing the NBE content (runs 91, 92). The resultant copolymers prepared by **1a** possessed unimodal but rather broad molecular weight distributions. On the basis of both the melting temperatures (T_m) and the glass transition temperatures (T_g) in the resultant copolymers,[10,30,31] it seems likely that the resultant polymers would be a mixture of two copolymers with different compositions; an additional T_g curve was thus observed as a tiny

Table 8. Copolymerization of Ethylene with Styrene by $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ [Cp′ = Cp (1), Cp* (2), ^{t}BuCp (3); R = H (a), Me (b), ^{i}Pr (c), Ph (d)] −MAO Catalyst Systems[a]

run	complex (μmol)	styrene/ mL	MAO/ mmol	yield[b]/ mg	activity[c]	THF soluble content[d]/ wt %	THF insoluble content[d]/ wt %	T_m[e]/ °C	composition (%)[f]	M_n[g] × 10^{-4}	M_w/M_n[g]
51	**1a** (1.0)	5	5.0	42	250	trace	>99	128.3	PE	1.89	2.4
52	**1a** (4.0)	10	5.0	249	370	>99	trace	121.2, 258.8	PE (3);SPS (97)	7.08	2.33
53	**1b** (1.0)	5	4.0	66	400	trace	>99	128	PE	1.66	2.72
54	**1b** (4.0)	10	4.0	214	320	>99	trace	118.9, 258.0	PE (1); SPS (99)	6.74	2.35
55	**1c** (1.0)	5	4.0	45	270	trace	>99	128.5	PE	1.96	2.53
56	**1c** (8.0)	10	4.0	77	60	>99	trace	122.0, 258.0	PE (9); SPS (91)	3.52	1.90
57	**1d** (1.0)	5	2.0	31	190	trace	>99	127.0, 260.3	PE (95); SPS (5)	4.01	1.97
58	**1d** (8.0)	10	2.0	257	190	>99	trace	120.9, 257.8	PE (3); SPS (97)	6.89	2.5
59	**2a** (2.0)	5	2.0	54	160	trace	>99	125.5	PE (or E−S)	0.78	2.34
60	**2a** (4.0)	10	2.0	53	80	>99	trace	103.0, 266.2	PE or E−S (17); SPS (83)	6.33	2.29
61	**2c** (4.0)	5	2.0	53	80	trace	>99	125.2	PE (or E-S)	1.28	2.79
62	**2c** (6.0)	10	2.0	22	20	>99	trace	108.9, 265.3	PE or E−S (39); SPS (61)	5.11	2.21
63	**3a** (6.0)	5	4.0	50	50	>99	trace	124.8, 265.9	PE (1); SPS (99)	1.37	2.47
64	**3a** (10)	10	4.0	282	170	>99	trace	266.4	SPS	2.95	2.13
65	**3b** (6.0)	5	3.0	16	20	>99	trace	114.0, 264.1	PE or E−S (6); SPS (94)	2.09	1.86
66	**3b** (10)	10	3.0	44	30	>99	trace	266.8	SPS	3.48	1.86
67	**3c** (1.0)	5	1.0	33	200	>99	trace	117.1	E−S	9.61	1.46
68	**3c** (2.0)	10	1.0	13	40	>99	trace	107.9	E−S	3.72	1.34

[a] Conditions: toluene + styrene total 30 mL, ethylene 4 atm, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 10 min. [b] Polymer yield based on acetone insoluble fraction. [c] Activity = kg-polymer/mol-Ti·h. [d] Ratios on the basis of a mixture of PE, SPS, and copolymer. (THF soluble or insoluble fraction). [e] Melting temperature (T_m) by DSC thermograms of the polymers as the acetone insoluble fractions (mixture of THF soluble/insoluble fractions). [f] Ratios estimated by ^{13}C NMR spectra. [g] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Table 9. Ethylene/Styrene Copolymerization by (*tert*-BuC_5H_4)$TiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (3c) −MAO Catalyst System[a]

run	complex (μmol)	styrene/mL	time/min	yield[b]/mg	activity[c]	M_n[d] × 10^{-4}	M_w/M_n[d]	T_m[e]/°C	content[f]/mol %
67	1.0	5	10	33	200	9.61	1.46	117.1	1.4
69	1.0	5	20	69	210	13.8	1.46		
70	1.0	5	30	97	190	18.1	1.64	116.0	1.4
68	2.0	10	10	13	40	3.72	1.34	107.9	4.1
71	2.0	10	15	23	50	5.14	1.35		
72	2.0	10	20	29	40	5.71	1.36		
73	2.0	10	25	35	40	6.69	1.35		
74	2.0	10	30	42	40	7.50	1.38	105.8	4.4
75	2.0	10	35	50	40	8.35	1.38		
76	2.0	10	40	66	50	9.80	1.32		
77	4.0	15	10	36	50	3.21	1.42	104.5	5.3
78	4.0	15	20	51	40	4.58	1.30		
79	4.0	15	30	73	40	7.35	1.22	100.3	6.0

[a] Conditions: toluene + styrene total 30 mL, ethylene 4 atm, 25 °C, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO) 1.0 mmol. [b] Polymer yield based on acetone insoluble and THF soluble fractions. [c] Activity = kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Melting temperature by DSC thermograms. [f] Styrene content (mol %) estimated by ^{1}H NMR spectra.[24]

trace in the DSC thermograms of the resultant copolymers prepared by **1a** under high NBE concentrations (runs 91,92).[24] In contrast, it should be noted that the resultant copolymers prepared by **3c** possessed high molecular weights with unimodal molecular weight distributions; the DSC thermograms clearly indicate that the resultant polymer possessed uniform compositions and the T_g value increased linearly upon increasing the NBE content.[24] Therefore, the *tert*-BuCp−diisopropyl analogue (**3c**) is the most suited as the catalyst precursor for exhibiting high catalytic activity with efficient NBE incorporation.

Figure 5 shows selected ^{13}C NMR spectra (in 1,2,4-trichlorebenzene-C_6D_6 at 110 °C) for poly(ethylene-*co*-NBE)s prepared by **3c**−MAO catalyst system.[24,10a,10b,31] The resultant polymers with relatively high NBE contents (runs 89,95) possessed resonances ascribed to both alternating and two NBE repeat units, and the ratio of the latter resonances increased in the copolymer with higher NBE content; resonances ascribed to three NBE repeat units (35 ppm etc.) were also observed in the copolymers with high NBE contents (runs 95,96). Since **3c** afforded NBE homopolymer in the absence of ethylene (run 97), these results suggest that it is possible for **3c** to prepare the copolymer with high NBE content.

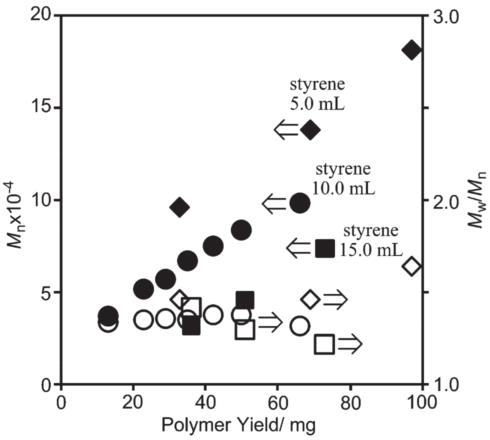


Figure 4. Plots of M_n, M_w/M_n vs polymer yields in ethylene/styrene copolymerization by (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (**3c**) −MAO catalyst system (ethylene 4 atm, 25 °C). Conditions: styrene/toluene =5.0/25.0 mL (♦, ◇), 10.0/20.0 mL (●, ○), 15.0/15.0 mL (■, □). Detailed results are shown in Table 9.

Table 10. Copolymerization of Ethylene with Norbornene (NBE) by Cp′TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) [Cp′ = Cp (1), Cp* (2), ^{t}BuCp (3); R = H (a), Me (b), ^{i}Pr (c), Ph (d)] −MAO Catalyst Systems[a]

run	complex (μmol)	MAO/ mmol	yield/ mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]
80	**1a** (0.15)	5.0	153	6120	82.8	2.77
81	**1b** (0.3)	4.0	90	1800	71.9	3.59
82	**1c** (0.3)	4.0	181	3620	77.2	3.53
83	**1d** (0.3)	2.0	156	3120	76.8	3.54
84	**2a** (0.5)	2.0	150	1810	3.74	4.56[d]
85	**2b** (1.0)	2.0	144	860	3.39	5.09[d]
86	**2c** (1.0)	2.0	181	1090	3.24	5.82[d]
87	**3a** (2.5)	4.0	149	360	–	–
88	**3b** (2.5)	3.0	69	110	–	–
89	**3c** (0.25)	1.0	215	5170	126	2.32

[a] Conditions: toluene 30 mL, NBE 0.5 mmol/mL, d-MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), ethylene 5 atm, 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] High molecular weight shoulder was observed in small amount in the GPC trace.

Figure 6 shows plots of NBE contents in the copolymers vs initial monomer molar ratios, [E]$_0$/[NBE]$_0$ (*E* = ethylene, NBE = norbornene), in the copolymerization using (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (**3c**) −MAO catalyst system. The data by CpTiCl$_2$(N=C^{t}Bu$_2$) (Cp−Ket), which showed the most efficient NBE incorporation among various half-titanocenes,[10c] and by [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC)[10a] are also added for comparison. Note that **3c** showed the better NBE incorporation than the Cp−ketimide analogue as well as CGC under these conditions. Although the catalytic activities by **3c** (ex. 3470 kg-polymer/mol-Ti·h, ethylene 5 atm, NBE 1.0M, run 95) were not so high as that by the Cp−ketimide analogue (activity =40200 kg-polymer/mol-Ti·h, ethylene 4 atm, NBE 1.0 M at 25 °C), the facts clearly indicate that **3c** is one of the promising candidate as the efficient catalysts in the ethylene/NBE copolymerization in terms of efficient NBE incorporation. The facts also indicate that the efficient catalyst precursor(s) for the desired copolymerization can be tuned by the precise ligand modifications (substituents on both Cp′ and the anionic donor ligand). We believe that the fact observed here is one of the unique characteristics for using this type of complexes, nonbridged half-titanocenes, as the catalyst for olefin polymerization.

CONCLUDING REMARK

A series of half-titanocenes containing pyrazolato ligands, Cp′TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) (**1a**−**d**, **2a**−**c**, **3a**−**c**) [Cp′ = Cp (**1**), Cp* (**2**), *tert*-BuC$_5$H$_4$ (**3**); R = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)], have been employed as the catalyst precursors for ethylene polymerization, syndiospecific styrene polymerization, and copolymerization of ethylene with 1-hexene, styrene and with norbornene (NBE) in the presence of MAO cocatalyst. The results through this study are summarized as follows.

(1) A series of half-titanocenes containing pyrazolato ligands (**1a**−**d**, **2a**−**c**, **3a**−**c**), especially **3a**−**c**, have been prepared and identified. On the basis of X-ray crystallographic analyses, it was revealed that the pyrazolato ligands are coordinated in η^2-*N*,*N*′ fashion with relatively similar Ti−N bond lengths and that both the bond distances and the angles are influenced by the ligand substituents (Cp′ and pyrazolato).

(2) These complexes exhibited from moderate to high catalytic activity for ethylene polymerization; the Cp* analogues, especially **2a**,**b**, exhibited high catalytic activities (8000−9600 kg-PE/mol-Ti·h, ethylene 6 atm in toluene

Table 11. Copolymerization of Ethylene with Norbornene (NBE) by CpTiCl$_2$(3,5-C$_3$H$_3$N$_2$) (1a), (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (3c) −MAO Catalyst Systems[a]

run	complex (μmol)	NBE/mol/L	ethylene/atm	MAO/mmol	yield/mg	activity[b]	M_n[c] × 10^{-4}	M_w/M_n[c]	T_g (T_m)[d]/°C	content[e]/mol %
90	**1a** (0.3)	0.1	5	5.0	88	1760	91.9	2.41	36.6 (119.8)	
80	**1a** (0.15)	0.5	5	5.0	153	6120	82.8	2.77	43.8 (108.6)	25.5
91	**1a** (0.3)	1.0	5	5.0	142	2840	5.44	1.67	130.3	42.6
92	**1a** (1.0)	0.5	2	5.0	42	250	1.58	2.33	160.5	50.4
93	**3c** (0.5)	0.1	5	1.0	184	2210	158	1.71	−6.7 (57.9)	11.3
89	**3c** (0.25)	0.5	5	1.0	215	5170	126	2.32	87	37.2
94	**3c** (0.25)	0.75	5	1.0	182	4370	83.3	2.39	104.6	40.6
95	**3c** (0.25)	1.0	5	1.0	145	3470	89.2	2.63	117.6	43.9
96	**3c** (1.0)	0.5	2	1.0	186	1120	53.8	2.57	145.1	50.1
97[f]	**3c** (1.0)	0.5	0	1.0	14	10				100

[a] Conditions: toluene 30 mL, d-MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Glass transition (or melting) temperature by DSC thermograms. [e] Comonomer content estimated by ^{13}C NMR spectra. [f] Time 60 min.

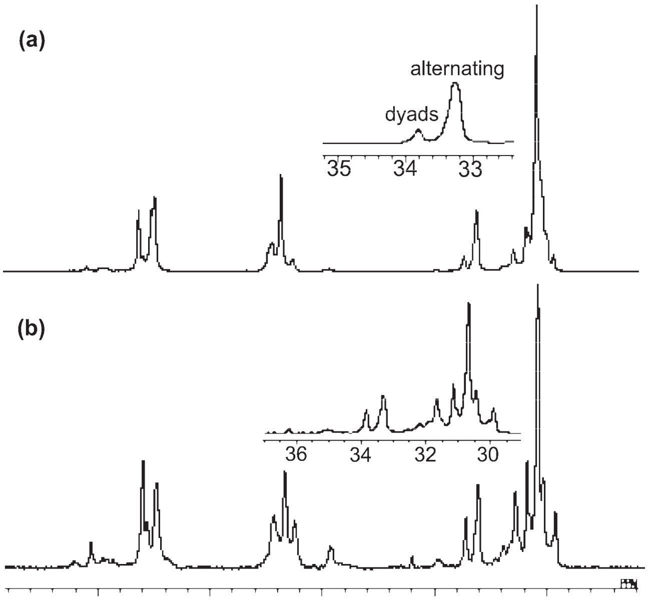


Figure 5. ^{13}C NMR spectra in the poly(ethylene-*co*-NBE)s prepared by **3c** − MAO catalyst system (in 1,2,4-trichlorobenzene/C_6D_6 at 110 °C, Table 11). Conditions: NBE 0.5 M in toluene, MAO 1.0 mmol, 25 °C, 10 min, (a) ethylene 5 atm (**3c**, 0.25 μmol, run 89); (b) ethylene 2 atm (**3c**, 1.0 μmol, run 95).

at 25 °C) affording the polymer with unimodal molecular weight distributions. However, the activities decreased upon the presence of 1-hexene, except in the copolymerization by **3c**. The ethylene/1-hexene copolymerizations by **2a**,**3a**,**c**−MAO catalyst systems afforded the copolymers with unimodal molecular weight distributions, but the 1-hexene incorporations were not so efficient as those by the Cp′−aryloxo analogues, exemplified as Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$),[25] and the Cp′−ketimide analogues, exemplified as CpTiCl$_2$(N=C^{t}Bu$_2$).[26]

(3) Both the Cp analogue (especially **1b**,**c**) and the *tert*-BuCp analogues (**3a**−**c**) exhibited high catalytic activities for syndiospecific styrene polymerization, and the facts indicate that the efficient catalyst precursors for the ethylene polymerization can be tuned for the efficient catalyst precursors for the syndiospecific styrene polymerization by simple replacement of the cyclopentadienyl fragment, as previously demonstrated by the Cp−aryloxo,[9a] amide,[19] and phenoxy−imine[15n] analogues.

(4) The ethylene/styrene copolymerization using the *tert*-BuCp−diisopropyl analogue (**3c**) −MAO catalyst system proceeds in a living manner, irrespective of the styrene concentration employed (in toluene at 25 °C). Although the styrene incorporation is no so efficient as that in the Cp*−ketimide analogues,[9c,d] the present results are still one of the limited examples in the successful living copolymerization. It was suggest that a certain degree of the styrene insertion inhibited the chain transfer in this catalysis.[9d]

(5) The *tert*-BuCp−diisopropyl analogue (**3c**) −MAO catalyst system exhibited relatively high catalytic activity for the ethylene/NBE copolymerization with efficient NBE incorporation, affording high molecular weight copolymers with unimodal molecular weight distributions. The efficiency in the NBE incorporation by **3c** is higher than that by the Cp−ketimide analogue, CpTiCl$_2$(N=C^{t}Bu$_2$),[10c] and it is thus clear that **3c** is one of the promising catalyst precursors for the copolymerization, especially in terms of efficient NBE incorporation.

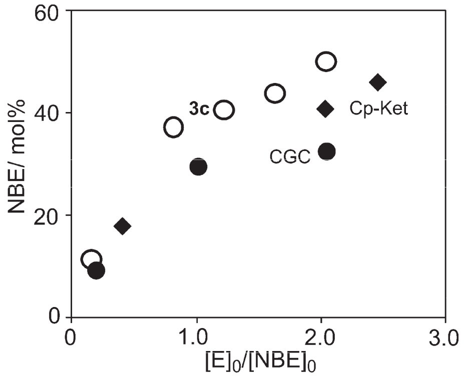


Figure 6. Plots of NBE content in poly(ethylene-*co*-NBE)s vs molar ratios of the initial concentration, [NBE]$_0$/[E]$_0$, in ethylene/NBE copolymerization by (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (**3c**) − MAO catalyst system. Detailed results are shown in Table 11, and the data by CpTiCl$_2$(N=C^{t}Bu$_2$) (Cp−Ket),[10c] [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]-TiCl$_2$ (CGC)[10a] are cited from our previous reports.

These results clearly suggest that the Cp′−pyrazolato analogues presented here are one of the good catalyst precursors for the ethylene (co)polymerization. Moreover, it is also demonstrated that the precise ligand modifications of both cyclopentadienyl fragment and the anionic donor ligand (substuents in the pyrazolato ligand) are the key for the successful (co)polymerization with remarkable catalytic activity as well as with efficient comonomer incorporation. As emphasized previously,[5b,c] this is one of the unique characteristics for using nonbridged half-titanocenes as the catalyst for olefin polymerization, and we believe that the facts introduced here should be important for designing the more efficient catalyst for the precise olefin polymerization. We are exploring the more efficient catalysts by modification of the anionic donor ligands and we hope that we will establish the origin of the ligand effect for the efficient comonomer incorporation in the near future.

■ EXPERIMENTAL SECTION

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade tetrahydrofuran, diethyl ether, *n*-hexane, dichloromethane, and toluene (Kanto Chemical Co., Inc.) were transferred into bottles containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and were used without further purification. Reagent grade pyrazole, 3,5-dimethylpyrazole, 3,5-diisopropylpyrazole, 3,5-diphenylpyrazole were purchased from Wako Pure Chemical Ind., Ltd., and were used as received. (*tert*-BuC$_5$H$_4$)TiCl$_3$ was prepared according to our previous report.[22b] CpTiCl$_2$(3,5-R$_2$C$_3$HN$_2$) [**1a**−**d**; R = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)], Cp*TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) (**2a**−**c**) were also prepared according to our previous report.[13] Li(C$_3$H$_3$N$_2$), Li(3,5-Me$_2$-C$_3$HN$_2$), Li(3,5-^{i}Pr$_2$−C$_3$HN$_2$) were prepared according to our previous report.[13] Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received.

Table 12. Crystal Data and Collection Parameters of $CpTiCl_2(3,5\text{-}^iPr_2C_3HN_2)$ (1c), $CpTiCl_2(3,5\text{-}Ph_2C_3HN_2)$ (1d), $Cp^*TiCl_2(3,5\text{-}^iPr_2C_3HN_2)$ (2c), $(tert\text{-}BuC_5H_4)TiCl_2(3,5\text{-}Me_2C_3HN_2)$ (3b), $(tert\text{-}BuC_5H_4)TiCl_2(3,5\text{-}^iPr_2C_3HN_2)$ (3c)

	1c	1d[a]	2c[b]	3b	3c
formula	$C_{14}H_{20}N_2Cl_2Ti$	$C_{20}H_{11}Cl_2N_2Ti$	$C_{19}H_{26}Cl_2N_2Ti$	$C_{14}H_{20}N_2Cl_2Ti$	$C_{18}H_{28}N_2Cl_2Ti$
formula weight	335.13	398.13	401.23	335.13	391.24
crystal color, habit	yellow, block	orange, block	orange, block	yellow, block	orange, block
crystal size (mm)	0.28 × 0.20 × 0.14	0.25 × 0.15 × 0.10	0.20 × 0.12 × 0.10	0.10 × 0.10 × 0.03	0.12 × 0.10 × 0.07
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	$P2_1/c$ (no. 14)	*Pbca* (no. 61)	$P2_1/c$ (no. 14)	$P-1$ (no. 2)	$C2/c$ (no. 15)
a (Å)	12.4924(2)	14.6060(3)	6.6940(3)	6.6559(4)	30.9170(8)
b (Å)	15.1082(3)	12.1974(3)	17.8966(7)	10.1468(5)	10.5621(3)
c (Å)	25.6216(5)	20.7330(4)	17.2184(7)	11.8754(6)	12.0811(3)
α (deg)				88.7370(15)	
β (deg)	96.8486(7)		93.321(2)	83.4290(16)	92.5986(9)
γ (deg)				79.4303(15)	
V (Å^3)	4801.25(15)	3693.7(2)	2059.3(2)	783.22(7)	3941.00(18)
Z value	12	8	4	2	8
D_{calcd} (g/cm^3)	1.391	1.432	1.294	1.421	1.319
F_{000}	2088.00	1608.00	840.00	348.00	1648.00
temp (K)	123	123	123	123	123
μ(Mo Kα) (cm^{-1})	8.567	7.561	6.777	8.753	7.061
no. of reflections measured	38 819	28 278	16 689	6448	14 607
no. of observations ($I > 2.00\sigma(I)$)	8747	3362	3734	2844	3594
no. of variables	515	221	235	173	209
R1 ($I > 2.00\sigma(I)$)	0.0256	0.0382	0.0346	0.0247	0.0283
wR2 ($I > 2.00\sigma(I)$)	0.0660	0. 1054	0.1039	0.0701	0.0748
goodness of fit	1.050	1.051	1.099	1.126	1.097

[a] For analysis of **1d**, five hydrogen atoms on the cyclopentadienyl ligand were eliminated due to partially disordered carbons in the cyclopentadienyl ligand (probably due to rapid rotation). [b] For analysis of **2c**, four hydrogen atom on the isopropyl group (C16 and C14) were eliminated due to a disordered methyl carbon (probably due to flexible nature). The structure reports including CIF files are shonw in the Supporting Information.[16]

Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.).

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNMLA400 spectrometer (399.65 MHz, ^1H; 100.40 MHz, ^{13}C). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to residual solvent peaks. Molecular weights and molecular weight distributions for the polyethylene samples were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm ×7.8 mm i.d.), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05% w/v 2,6-di-*tert*-butyl-*p*-cresol. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Synthesis of (tert-BuC$_5$*H*$_4$*)TiCl*$_2$*(C*$_3$*H*$_3$*N*$_2$*) (**3a**).* Into an Et_2O solution (10 mL) containing ($tert$-BuC_5H_4)$TiCl_3$ (274 mg, 1.0 mmol), Li($C_3H_3N_2$) (85 mg, 1.15 mmol)[13] was added at −30 °C. The reaction mixture was stirred for 16 h at 25 °C followed by addition of a small amount of CH_2Cl_2 (0.5 mL). The reaction mixture was filtered through a Celite pad using a glass filter. The filtercake was washed with Et_2O, and the combined filtrate and the washings were taken to dryness under reduced pressure to give a solid red residue. The residue was dissolved in a minimum amount of CH_2Cl_2 and layered with hexane. The chilled solution (−30 °C) afforded red microcrystals. Yield: 77 mg (25%). ^1H NMR (C_6D_6): δ 1.00 (s, 9H, *tert*-Bu), 6.06 (t, 2H, J = 1.75 Hz, *tert*-BuC_5*H*$_4$), 6.20 (t, 2H, J = 1.75 Hz, *tert*-BuC_5*H*$_4$), 6.30 (s, 1H, NCHC*H*), 7.22 (s, 1H, NC*H*CH). ^{13}C NMR (C_6D_6): δ 30.9 (*tert*-Bu), 34.1 (*tert*-Bu), 119.3, 119.6, 120.9, 121.2, 150.8. Anal. Calcd for $C_{12}H_{16}Cl_2N_2Ti$: C, 46.94; H, 5.25; N, 9.12. Found: C, 47.27; H, 5.49; N, 9.06.

(tert-BuC$_5$*H*$_4$*)TiCl*$_2$*(3,5-Me*$_2$*-C*$_3$*HN*$_2$*) (**3b**).* The synthetic procedure of **2** was the same as that for **1** except that lithium salt of 3,5-dimethylpyrazole (118 mg, 1.15 mmol) was used in place of Li($C_3H_3N_2$). Yield: 136 mg (41%). ^1H NMR ($CDCl_3$): δ 1.01 (s, 9H, *tert*-Bu), 2.02 (s, 6H, *Me*), 5.97 (s, 1H, NCC*H*), 6.18 (t, 2H, J = 1.75 Hz, *tert*-BuC_5*H*$_4$), 6.32 (t, 2H, J = 1.75 Hz, *tert*-BuC_5*H*$_4$). ^{13}C NMR ($CDCl_3$): δ 12.6 (*Me*), 30.9 (*tert*-Bu), 33.9 (*tert*-Bu), 118.8, 119.7, 120.5, 147.0, 149.9. Anal. Calcd for $C_{14}H_{20}Cl_2N_2Ti$: C, 50.18; H, 6.02; N, 8.36. Found: C, 50.57; H, 6.10; N, 8.32.

(tert-BuC$_5$*H*$_4$*)TiCl*$_2$*(3,5-*^{i}*Pr*$_2$*C*$_3$*HN*$_2$*) (**3c**).* The synthetic procedure of **3** was the same as that for **1** except that lithium 3,5-diisproplylpyrazolato (182 mg, 1.15 mmol) was used in place of Li($C_3H_3N_2$). Yield: 136 mg (35%). ^1H NMR ($CDCl_3$): δ 1.15 (s, 9H, *tert*-Bu), 1.21 (d, 12H, J = 4.25 Hz, *Me*), 2.86 (sep, 2H, J = 4.25 Hz, C*H*Me$_2$), 6.08 (t, 2H, J = 1.75 Hz, *tert*-BuC_5*H*$_4$), 6.26 (s, 1H, NCC*H*), 6.36 (t, 2H, J = 1.75 Hz, *tert*-BuC_5*H*$_4$). ^{13}C NMR ($CDCl_3$): δ 23.0 (CH*Me*$_2$), 28.0 (CHMe$_2$), 31.0 (*tert*-BuC_5H_4), 34.2 (*tert*-BuC_5H_4), 114.9, 119.1, 119.6, 150.4, 157.6. Anal. Calcd for $C_{18}H_{28}Cl_2N_2Ti$: C, 55.26; H, 7.21; N, 7.16. Found: C, 55.72; H, 7.66; N, 7.17.

Crystallographic Analysis. Yellow or orange block microcrystals which are suited for the crystallographic analysis were grown from the chilled CH_2Cl_2 solution layered by *n*-hexane (−30 °C). All measurements were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The selected crystal collection parameters are listed in Table 12, and the detailed results were described in the reports in the Supporting Information. All structures were solved by direct methods[32] and expanded using Fourier techniques,[33] and the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the Crystal Structure[34] crystallographic software package except for refinement, which was performed using SHELXL-97.[35] Detailed analysis data including the collection parameters, CIF files, and the structure reports are shown in the Supporting Information. Five hydrogen atoms in the cyclopentadienyl ligand in **1d** were not placed on the analysis due to disordered carbons on the Cp; four hydrogen atoms in the isopropyl group were not placed in the analysis of **2c** due to a disordered methyl carbon in an isopropyl group in the pyrazolato ligand.

Ethylene Polymerization. Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Solvent (29.0 mL) and prescribed amount of MAO white solid, prepared by removing toluene and $AlMe_3$ from commercially available MAO (PMAO-S, Tosoh Finechem Co.), were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of complex via a syringe, the reaction apparatus was pressurized to 5 atm (total 6 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo*.

Syndiospecific Polymerization of Styrene. Styrene (10 mL) and the prescribed amount of MAO solid were added into the round-bottom flask in the drybox at room temperature (25 °C). A toluene solution (1.0 mL) containing prescribed amount of complex was then added into the autoclave, and the mixture was magnetically stirred for 10 min. The mixture was then taken out from the drybox, and was quickly terminated by adding EtOH (ca. 3 mL). 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*. According to the previous report,[9a] the resultant polymer mixture was separated into two fractions, and atactic polystyrene prepared only by MAO itself was extracted with acetone; syndiotactic polystyrene prepared by titanium complexes—MAO catalyst was isolated as the acetone insoluble fraction.

Copolymerization of Ethylene with 1-Hexene, Styrene, Norbornene. Experimental procedures for the copolymerization of ethylene with norbornene were the same as those for the ethylene polymerization described above except that prescribed amount of norbornene was added into an autoclave. Experimental procedures for the ethylene/1-hexene and ethylene/styrene copolymerizations were the same as those for the ethylene polymerizations except that a prescribed amount of 1-hexene or styrene was charged and the total volume of toluene and 1-hexene was set to 30 mL.

According to the previous report,[9] the resultant polymer mixture in the ethylene/styrene copolymerization might be separated into three fractions, and atactic polystyrene which was prepared only by MAO was extracted with acetone. Poly(ethylene-*co*-styrene) was extracted with tetrahydrofuran (THF), and polyethylene and/or syndiotactic polystyrene which were the byproduct in this reaction was separated as THF insoluble fraction. The basic experimental procedure is as follows:

The polymer sample obtained in the copolymerization experiment was added into a round-bottom flask containing acetone equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate acetone soluble and insoluble fraction. The acetone insoluble fraction was then dried *in vacuo*, and was added into a round-bottom flask containing THF equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate THF soluble and insoluble fractions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. (i) Detailed ethylene polymerization data using $Cp'TiCl_2(3,5\text{-}R_2C_3HN_2)$ [Cp′ = Cp (**1**), Cp* (**2**), ^{t}BuCp (**3**); R = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)] and MAO catalyst systems, (ii) NMR and DSC data in the copolymerization of ethylene with 1-hexene, styrene and with norbornene, and (iii) structural analysis reports in .cif format for $CpTiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (**1c**), $CpTiCl_2(3,5\text{-}Ph_2C_3HN_2)$ (**1d**), $Cp^*TiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (**2c**), (*tert*-BuC_5H_4)$TiCl_2(3,5\text{-}Me_2\text{-}C_3HN_2)$ (**3b**), and (*tert*-BuC_5H_4)$TiCl_2(3,5\text{-}{}^iPr_2C_3HN_2)$ (**3c**). This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) Recent selected reviews, see: (a) Gibson, V. C.; Spitzmesser, S. K. *Chem. Rev.* **2003**, *103*, 283. (b) Bolton, P. D.; Mountford, P. *Adv. Synth. Catal.* **2005**, *347*, 355.(c) Mason, A. F.; Coates, G. W. In *Macromolecular Engineering*, Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Eds.; Wiley-VCH: Weinheim, Germany, 2007, Vol. 1, p 217.

(2) *Frontiers in Metal-Catalyzed Polymerization* (special issue). Gladysz, J. A., Ed.; *Chem. Rev.* **2000**, *100* (4). For example: (a) Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169. (b) Alt, H. G.; Köppl, A. *Chem. Rev.* **2000**, *100*, 1205. (c) Chen, E. Y.-X.; Marks, T. J. *Chem. Rev.* **2000**, *100*, 1391.

(3) *Metallocene complexes as catalysts for olefin polymerization* (special issue). Alt, H. G., Ed.; *Coord. Chem. Rev.* **2006**, *250* (1−2), 1.

(4) *Metal-catalysed Polymerisation* (special issue). Milani, B.; Claver, C. Eds; *Dalton Trans.* **2009**, (41), 8769.

(5) Reviewing articles, accounts for half-metallocenes, see: (a) Stephan, D. W. *Organometallics* **2005**, *24*, 2548. (b) Nomura, K.; Liu, J.; Padmanabhan, S.; Kitiyanan, B. *J. Mol. Catal. A* **2007**, *267*, 1. (c) Nomura, K. *Dalton Trans.* **2009**, 8811. (d) Nomura, K.; Liu, J. *Dalton Trans.* **2011** in press. Related typical half-titanocenes containing monodentate or multidentate mono anionic donor (with mono or multi neutral donor) ligands were shown in ref 5b.

(6) Selected reviewing articles for living polymerization, see: (a) Coates, G. W.; Hustad, P. D.; Reinartz, S. *Angew. Chem., Int. Ed.* **2002**, *41*, 2236. (b) Domski, G. J.; Rose, J. M.; Coates, G. W.; Bolig, A. D.; Brookhart, M. *Prog. Polym. Sci.* **2007**, *32*, 30.

(7) Recent examples for syndiotactic polystyrene and the related chemistry, see: (a) Schellenberg, J. *Prog. Polym. Sci.* **2009**, *34*, 688. (b) *Syndiotactic Polystyrene - Synthesis, Characterization, Processing, and Applications*, Schellenberg, J., Ed.; John Wiley & Sons, Inc.: New York, 2010. Mason, A. F.; Coates, G. W. In *Macromolecular Engineering*, Matyjaszewski, K.; Gnanou, Y.; Leibler, L., Eds.; Wiley-VCH: Weinheim, Germany, 2007, Vol. 1, p 217.

(8) (a) Nomura, K. In *Syndiotactic Polystyrene - Synthesis, Characterization, Processing, and Applications*, Schellenberg, J., Ed.; John Wiley & Sons, Inc.: New York, 2010; p 60. (b) Nomura, K. *Catal. Surv. Asia* **2010**, *14*, 33.

(9) (a) Nomura, K.; Komatsu, T.; Imanishi, Y. *Macromolecules* **2000**, *33*, 8122. (b) Nomura, K.; Okumura, H.; Komatsu, T.; Naga, N. *Macromolecules* **2002**, *35*, 5388. (c) Zhang, H.; Nomura, K. *J. Am. Chem. Soc.* **2005**, *127*, 9364. (d) Zhang, H.; Nomura, K. *Macromolecules* **2006**, *39*, 5266. (e) Zhang, H.; Byun, D.-J.; Nomura, K. *Dalton Trans.* **2007**, 1802.

(10) (a) Nomura, K.; Tsubota, M.; Fujiki, M. *Macromolecules* **2003**, *36*, 3797. (b) Wang, W.; Tanaka, T.; Tsubota, M.; Fujiki, M.; Yamanaka, S.; Nomura, K. *Adv. Synth. Catal.* **2005**, *347*, 433. (c) Nomura, K.; Wang, W.; Fujiki, M.; Liu, J. *Chem. Commun.* **2006**, 2659.

(11) Selected examples for ethylene/norbornene copolymerization usind linked Cp′−amide titanium complex catalysts, see: (a) Hasan, T.; Ikeda, T.; Shiono, T. *Macromolecules* **2004**, *37*, 8503. (b) Hasan, T.; Ikeda, T.; Shiono, T. *Macromolecules* **2005**, *38*, 1071. (c) Cai, Z.; Nakayama, Y.; Shiono, T. *Macromolecules* **2006**, *39*, 2031. (d) Shiono, T.; Sugimoto, M.; Hasan, T.; Cai, Z.; Ikeda, T. *Macromolecules* **2008**, *41*, 8292. (e) Cai, Z.; Harada, R.; Nakayama, Y.; Shiono, T. *Macromolecules* **2010**, *43*, 4527.

(12) (a) Wang, W.; Fujiki, M.; Nomura, N. *J. Am. Chem. Soc.* **2005**, *127*, 4582. (b) Liu, J.; Nomura, K. *Adv. Synth. Catal.* **2007**, *349*, 2235.

(13) Saeed, I.; Katao, S.; Nomura, K. *Inorg. Chem.* **2009**, *48*, 5011.

(14) Saeed, I.; Katao, S.; Nomura, K. *Organometallics* **2009**, *28*, 111.

(15) Selected initial examples for nonbridged half-metallocenes containing mono anionic bidentate or multidentate donor ligands:[5b] (a) Richter, J.; Edelmann, F. T.; Noltemeyer, M.; Schmidt, H. -G.; Schmulinson, M.; Eisen, M. S. *J. Mol. Catal. A* **1998**, *130*, 149. (b) Doherty, S.; Errington, R. J.; Jarvis, A. P.; Collins, S.; Clegg, W.; Elsegood, M. R. J. *Organometallics* **1998**, *17*, 3408. (c) Sita, L. R.; Babcock, R. *Organometallics* **1998**, *17*, 5228. (d) Kim, Y.; Hong, E.; Lee, M. H.; Kim, J.; Han, Y.; Do, Y. *Organometallics* **1999**, *18*, 36. (e) Vollmerhaus, R.; Shao, P.; Taylor, N. J.; Collins, S. *Organometallics* **1999**, *18*, 2731. (f) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958. (g) Keaton, R. J.; Jayaratne, K. C.; Henningsen, D. A.; Koterwas, L. A.; Sita, L. R. *J. Am. Chem. Soc.* **2001**, *123*, 6197. (h) Kim, Y.; Han, Y.; Hwang, J.-W.; Kim, M. W.; Do, Y. *Organometallics* **2002**, *21*, 1127. (i) Huang, J.; Lian, B.; Qian, Y.; Zhou, W.; Chen, W.; Zheng, G. *Macromolecules* **2002**, *35*, 4871. (j) Taberneroa, V.; Cuenca, T.; Herdtweck, E. *J. Organomet. Chem.* **2002**, *663*, 173. (k) Bott, R. K. J.; Hughes, D. L.; Schormann, M.; Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **2003**, *665*, 135. (l) Yasumoto, T.; Yamagata, T.; Mashima, K. *Organometallics* **2005**, *24*, 3375. (m) Dove, A. P.; Xie, X. J.; Waymouth, R. M. *Chem. Commun.* **2005**, 2152. (n) Zhang, H.; Katao, S.; Nomura, K.; Huang, J. *Organometallics* **2007**, *26*, 5967.

(16) Structure reports including CIF files for CpTiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (**1c**), CpTiCl$_2$(3,5-Ph$_2$C$_3$HN$_2$) (**1d**), Cp*TiCl$_2$(3,5-^{i}Pr$_2$C$_3$HN$_2$) (**2c**), (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-Me$_2$C$_3$HN$_2$) (**3b**), (*tert*-BuC$_5$H$_4$)TiCl$_2$(3,5-^{i}Pr$_2$-C$_3$HN$_2$) (**3c**) are shown in the Supporting Information.

(17) (a) Guzei, I. A.; Baboul, A. G.; Yap, G. P. A.; Rheingold, A. L.; Schlegel, H. B.; Winter, C. H. *J. Am. Chem. Soc.* **1997**, *119*, 3387. (b) Guzei, I. A.; Winter, C. H. *Inorg. Chem.* **1997**, *36*, 4415. (c) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Inorg. Chem.* **1999**, *38*, 1871. (d) Yélamos, C.; Heeg, M. J.; Winter, C. H. *Organometallics* **1999**, *18*, 1168. (e) Mösch-Zanetti, N. C.; Krätzer, R.; Lehmann, C.; Schneider, T. R.; Usón, I. *Eur. J. Inorg. Chem.* **2000**, *2*, 13. (f) Yélamos, C.; Gust, K. R.; Baboul, A. G.; Heeg, M. J.; Schlegel, H. B.; Winter, C. H. *Inorg. Chem.* **2001**, *40*, 6451.

(18) Nomura, K.; Fujii, K. *Organometallics* **2002**, *21*, 3042.

(19) Nomura, K.; Fujii, K. *Macromolecules* **2003**, *36*, 2633.

(20) Nomura, K.; Yamada, J.; Wang, W.; Liu, J. *J. Organomet. Chem.* **2007**, *692*, 4675.

(21) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(22) (a) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K.; Imai, A. *Organometallics* **1998**, *17*, 2152. (b) Nomura, K.; Naga, N.; Miki, M.; Yanagi, K. *Macromolecules* **1998**, *31*, 7588.

(23) Detailed ethylene polymerization data using Cp′TiCl2(3,5-R2C3HN2) [**1a**−**d**, **2a**−**c**, **3a**−**c**; Cp′ = Cp (**1**), Cp* (**2**), tBuCp (**3**); R = H (**a**), Me (**b**), iPr (**c**), Ph (**d**)] −MAO catalyst systems are shown in the Supporting Information.

(24) Selected ^{1}Hand ^{13}C NMR spectra and DSC thermograms in the resultant (co)polymers in the (co)polymerization of ethylene with 1-hexene, styrene and with norbornene using Cp′TiCl$_2$(3,5-R$_2$C$_3$HN$_2$) [**1a**−**d**, **2a**−**c**, **3a**−**c**; Cp′ = Cp (**1**), Cp* (**2**), ^{t}BuCp (**3**); R = H (**a**), Me (**b**), ^{i}Pr (**c**), Ph (**d**)] −MAO catalyst systems are shown in the Supporting Information.

(25) Nomura, K.; Oya, K.; Imanishi, Y. *J. Mol. Catal. A* **2001**, *174*, 127.

(26) Nomura, K.; Fujita, K.; Fujiki, M. *J. Mol. Catal. A* **2004**, *220*, 133.

(27) (a) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 735. (b) Suhm, J.; Schneider, M. J.; Mülhaupt, R. *J. Mol. Catal. A* **1998**, *128*, 215.

(28) Although melting temperatures in the resultant polymers (acetone insoluble fractions, mixture of THF soluble/insoluble fractions) were somewhat low compared to polyethylene, we could not observe the incorporation of styrene in the ^{13}C NMR spectra (probably due to the low percentage of the THF insoluble fraction).

(29) For example, see: (a) Kaminsky, W. *Angew. Makromol. Chem.* **1994**, *223*, 101. (b) Cherdron, H.; Brekner, M.-J.; Osan, F. *Angew. Makromol. Chem.* **1994**, *223*, 121. (c) Kaminsky, W.; Beulich, I.; Arndt-Rosenau, M. *Macromol. Symp.* **2001**, *173*, 211.(d) Dragutan, V.; Streck, R. *Catalytic Polymerization of Cycloolefins*; Studies in Surface Science and Catalysis 131; Elsevier: Amsterdam, 2000.

(30) Nomura, K. *Chin. J. Polym. Sci.* **2008**, *26*, 513.

(31) Microstructure analyses and the NBE contents in the resultant copolymers were estimated by the ^{13}C NMR spectra according to the following previous reports.[10a,b](a) Provasoli, A.; Ferro, D. R.; Tritto, I.; Boggioni, L. *Macromolecules* **1999**, *32*, 6697. (b) Tritto, I.; Marestin, C.; Boggioni, L.; Zetta, L.; Provasoli, A.; Ferro, D. R. *Macromolecules* **2000**, *33*, 8931. (c) Tritto, I.; Marestin, C.; Boggioni, L.; Sacchi, M. C.; Brintzinger, H.-H.; Ferro, D. R. *Macromolecules* **2001**, *34*, 5770. (d) Tritto, I.; Boggioni, L.; Jansen, J. C.; Thorshaug, K.; Sacchi, M. C.; Ferro, D. R. *Macromolecules* **2002**, *35*, 616. (e) Thorshaug, K.; Mendichi, R.; Boggioni, L.; Tritto, I.; Trinkle, S.; Friedrich, C.; Mü1lhaupt, R. *Macromolecules* **2002**, *35*, 2903. (f) Tritto, I.; Boggioni, L.; Ferro, D. R. *Macromolecules* **2004**, *37*, 9681.

(32) *SIR92*:Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(33) *DIRDIF99*; Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. The DIRDIF-99 program system, Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1999.

(34) CrystalStructure 3.8: Crystal Structure Analysis Package, Rigaku and Rigaku Americas; The Woodlands TX, 2000−2007.

(35) *SHELX97*; Sheldrick, G. M., 1997.