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Effect of Cyclopentadienyl and Amide Fragment in Olefin Polymerization by *Nonbridged* (Amide)(cyclopentadienyl)titanium(IV) Complexes of the Type $Cp'TiCl_2[N(R^1)R^2]$−Methylaluminoxane (MAO) Catalyst Systems

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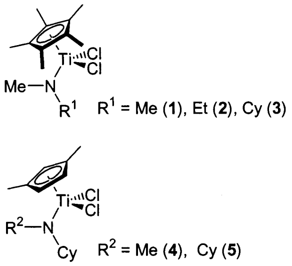
ABSTRACT: $Cp^*TiCl_2[N(Me)R^1]$ [R^1 = Me (**1**), Et (**2**), Cy (**3**), Cp^* = C_5Me_5, Cy = cyclohexyl], and (1,3-$Me_2C_5H_3$)$TiCl_2[N(Cy)R^2]$ [R^2 = Me (**4**), Cy (**5**)] have been prepared from the reaction of $Cp'TiCl_3$ (Cp' = cyclopentadienyl) with the corresponding lithium amide in toluene or *n*-hexane. The structures for **3**, **4**, and **5** have been determined by X-ray crystallography. The catalytic activity for ethylene polymerization in the presence of d-MAO [prepared by removing toluene and $AlMe_3$ from ordinary methylaluminoxane (MAO) solution] increased in the order: **3** (4540 kg-PE/mol-Ti·h, in toluene, ethylene 6 atm, 25 °C, 10 min) $\gg$ **5** (2000 kg-PE/mol-Ti·h) > **2** (1680), **1** (1600), and **4** (1520). In particular, **3** exhibited the highest catalytic activity, suggesting both electronic and steric factors play a role. On the other hand, **4** exhibited the highest catalytic activity for syndiospecific styrene polymerization, and the results clearly show that efficient catalyst for the desired polymerization can be modified only by replacing the substituent on Cp′. **3** exhibited better 1-hexene incorporation than **1**, affording poly(ethylene-*co*-1-hexene) with high molecular weight. **4** exhibited both the highest catalytic activity and efficient 1-hexene incorporation, and the 1-hexene incorporation as well as the monomer sequence distributions were affected by the substituents on both cyclopentadienyl and amide ligands. On the other hand, $Cp^*TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (**6**) showed poor 1-hexene incorporation under the same conditions, affording the copolymer with relatively low molecular weight. The resultant r_Er_H values by **3** and **4** were 0.38−0.48, which showed that these copolymerizations did not proceed in a random manner that can be seen in ordinary metallocene and linked half-metallocene catalysts.

Introduction

Olefin polymerization by homogeneous transition metal complex catalysts attracts particular attention in the field of organometallic chemistry, catalysis, as well as of polymer chemistry. Many reports have thus been reported concerning this topic especially using early transition metal complexes.[1] Among them, *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, NPR_3, $N{=}CR_2$ etc.; X = halogen, alkyl)[2−14] have attracted considerable attention, because this type of catalyst has been expected to exhibit unique characteristics as olefin polymerization catalysts that would be different from those by ordinary metallocene type and/or so-called “constrained geometry” type catalysts.[15]

We have already demonstrated the utility of (cyclopentadienyl)(aryloxy)titanium(IV) complex catalyst of the type $Cp'Ti(OAr)X_2$ (OAr = aryloxy group) for olefin polymerization.[3] We also reported that this catalyst can be tuned to the effective catalyst for both styrene and ethylene/styrene copolymerization only by replacing the Cp′ fragment.[16] Although syntheses of (amide)(cyclopentadienyl)titanium(IV) complexes have been known,[14,17−18] however, reports concerning olefin polymerization with this type of complexes as the catalysts have been limited so far.[14] Therefore, we have an interest to explore the possibility of this series of complexes, especially the effect of substituents on both cyclopentadienyl and amide groups for olefin polymerization.[19,20] In this paper, we wish to introduce syntheses of a series of (amide)(cyclopentadienyl)titanium(IV) complexes of the type $Cp^*TiCl_2[N(Me)R^1]$ [R^1 = Me (**1**), Et (**2**), Cy(**3**)] and (1,3-$Me_2C_5H_3$)$TiCl_2[N(Cy)R^2]$ [R^2 = Me (**4**), Cy (**5**)] (Chart 1) and their use in catalysts for ethylene, propylene, 1-hexene, and styrene polymerization as well as for ethylene/1-hexene copolymerization.

Chart 1



Results and Discussion

1. Syntheses of $Cp^*TiCl_2[N(Me)R^1]$ [Cp^* = C_5Me_5, R = Me (1), Et (2), Cy (3), Cy = cyclohexyl] and (1,3-$Me_2C_5H_3$)$TiCl_2[N(Cy)R^2]$ [R^2 = Me (4), Cy (5)]. **1** could be prepared in relatively high yield (86%) by the reaction of Cp^*TiCl_3 with $LiNMe_2$ in hexane at room temperature (for 20 h). This is the established procedure reported by Serano et al.[17] and later by Okuda et al.[14] **2** could also be isolated by the analogous procedure, but

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the yield was not so high as that for **1** due to the difficulty for isolating the desired complex as the pure form from the reaction mixture. On the other hand, an attempt to prepare **3** under the same conditions for **1** was not successful, and $\mathrm{Cp^*TiCl_3}$ could be recovered from the reaction mixture exclusively. In addition, the attempt in toluene at room temperature for 2 days recovered the starting compounds, although this is also an analogous procedure for preparing $\mathrm{Cp^*TiCl_2(N^iPr_2)}$.[18] Therefore, we explored the possibility to isolate the desired complex, **3**.

It was found that **3** could be isolated in a moderate yield (43%) if $\mathrm{Cp^*TiCl_3}$ was treated with 1.2 equiv of LiN(Me)Cy in toluene at 50 °C for 20 h. On the other hand, $\mathrm{Cp^*TiCl_3}$ was recovered as the major isolated compound if the reaction was performed at 80 or 100 °C, and these are probably due to the decomposition of lithium amide under these conditions. In addition, the attempts by the reaction of $\mathrm{Cp^*TiCl_3}$ with HN(Me)Cy or $\mathrm{Me_3SiN(Me)Cy}$ in toluene (for 2 days at 100 °C) were not successful, and the starting compound was thus recovered. The conditions described above [$\mathrm{Cp^*TiCl_3}$ with LiN(Me)Cy in toluene at 50 °C for 20 h] have thus been only one positive result for isolating **3**. Since **3** was easily soluble in hexane than $\mathrm{Cp^*TiCl_3}$, **3** could be isolated by a fractional crystallization at chilled temperature (−30 °C). **3** could be identified by ^{1}H and ^{13}C NMR spectra, elemental analysis, and by X-ray crystallography. **4** and **5** were also prepared by the same procedure for **3**, and were identified similarly.

2. Crystal Structures for 3—5. The orange needle (**3**), orange platelet (**4**), and red prism (**5**) microcrystals were grown from the concentrated hot hexane solution upon standing at room temperature in the drybox, and their structures were determined at −30 °C.

The molecular structure for **3** is shown in Figure 1, and the selected bond distances and angles are summarized in Table 1. The crystal structure shows it to be a tetrahedral geometry around the titanium metal center. Three substituents [titanium atoms and carbon atoms in methyl and in cyclohexyl groups (C11 and C12)] are placed perpendicular to the plane of the cyclopentadienyl ring, and this geometry is somewhat different from that in $\mathrm{Cp^*Ti(CH_2Ph)_2(NMe_2)}$ reported previously.[14] Ti−N bond distance (1.87 Å) in **3** was the same as that in $\mathrm{Cp^*TiCl_2(N^iPr_2)}$[18] and was somewhat shorter than that (1.89 Å) in $\mathrm{Cp^*Ti(CH_2Ph)_2(NMe_2)}$. Since the observed value was shorter than the estimated value (2.02 Å) for titanium−nitrogen single bond according to Pauling's covalent radii,[21] and the observed value was thus consistent with the presence of titanium−nitrogen double bond. Ti−Cl bond distances (2.30 Å) were somewhat longer than those in $\mathrm{Cp^*TiCl_2(N^iPr_2)}$ (2.27, 2.29 Å), and relatively wide bond angle of Cl−Ti−Cl (101.2°) in **3** compared to that in $\mathrm{Cp^*TiCl_2(N^iPr_2)}$ (99.2°) was also observed.

The molecular structure for **4** is shown in Figure 2, and the selected bond distances and angles are summarized in Table 2. The structure for **5** is also shown in Figure 3, and the selected data are summarized in Table 3. The crystal structure for **4** show it to be a tetrahedral geometry around the titanium metal center, and the basic structure for **5** is also the same as that for **4**. Three substituents [titanium atoms and carbon atoms in methyl and in cyclohexyl groups (C8 and C9)] in **4** are placed perpendicular to the plane of the cyclopentadienyl ring, and three substituents [titanium atoms and carbon atoms in two cyclohexyl groups (C8 and C14)] in **5** are also placed perpendicular to the plane of the cyclopentadienyl ring. These geometries are the same as that in **3**, but are different from that in $\mathrm{Cp^*Ti(CH_2Ph)_2(NMe_2)}$.[14] Ti−N bond distances (1.86 Å in **4**, 1.87 Å in **5**) were the same as those in **3** and $\mathrm{Cp^*TiCl_2(N^iPr_2)}$,[18] and the values was somewhat shorter than that (1.89 Å) in $\mathrm{Cp^*Ti(CH_2Ph)_2(NMe_2)}$. These values are also consistent with the presence of titanium−nitrogen double bond. No distinct difference in Ti−Cl bond distances (2.29−2.31 Å) from those in reported values were observed, and relatively wide bond angles of Cl−Ti−Cl (102.6° in **4**, 101.0 in **5**) compared to that in

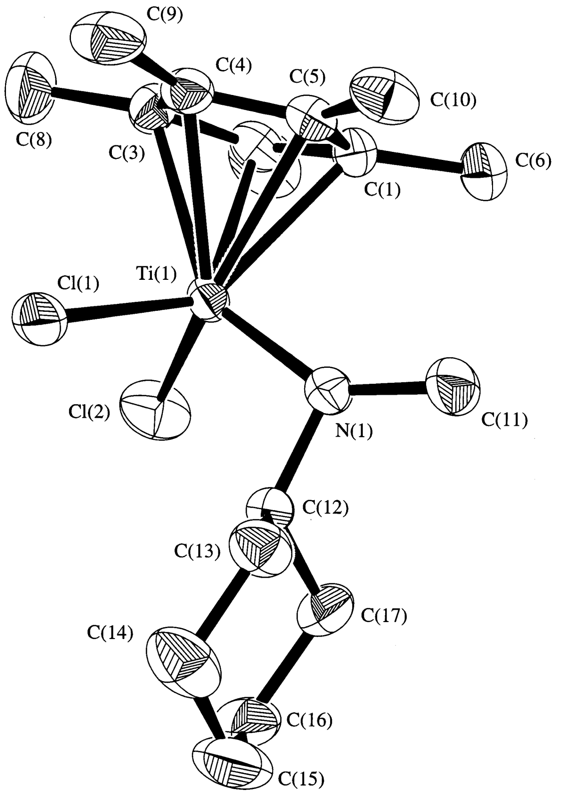

Figure 1. Ortep drawing for $\mathrm{(C_5Me_5)TiCl_2[N(Me)Cy]}$ (**3**). Thermal ellipsoids are drawn at a 50% probability level, and hydrogen atoms were omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for $\mathrm{(C_5Me_5)TiCl_2[N(Me)Cy]}$ (3)[a]

Bond Distances (Å)			
Ti−Cl(1)	2.302(1)	Ti−Cl(2)	2.304(1)
Ti−N(1)	1.870(3)	Ti−C(1) in Cp	2.394(3)
Ti−C(2) in Cp	2.372(3)	Ti−C(3) in Cp	2.365(4)
C(1)−C(2)	1.403(5)	C(1)−C(5)	1.426(5)
C(1)−C(6)	1.499(5)	C(2)−C(7)	1.507(6)
C(3)−C(8)	1.505(6)	N(1)−C(11) in Me	1.457(5)
N(1)−C(12) in Cy	1.491(4)	C(12)−C(13)	1.523(6)
C(13)−C(14)	1.525(6)	C(14)−C(15)	1.515(9)
C(12)−C(17)	1.530(5)		

Bond Angles (deg)			
Cl(1)−Ti−Cl(2)	101.2(5)	Cl(1)−Ti−N(1)	105.6(1)
Cl(2)−Ti−N(1)	104.3(1)	Cl(1)−Ti(1)−C(1)	140.99(9)
Cl(1)−Ti−C(2)	129.3(1)	Cl(1)−Ti−C(3)	94.86(10)
Cl(1)−Ti−C(4)	84.08(9)	Cl(2)−Ti−C(1)	107.89(9)
Cl(2)−Ti−C2)	84.58(9)	Cl(2)−Ti−C(3)	96.9(1)
N(1)−Ti−C(1)	91.0(1)	N(1)−Ti−C(2)	121.5(1)
N(1)−Ti−C(3)	146.5(1)	Ti−N(1)−C(11)	143.2(3)
Ti−N(1)−C(12)	103.7(2)	C(11)−N(1)−C(12)	113.1(4)
C(13)−C(12)−C(17)	111.7(3)	C(12)−C(13)−C(14)	109.8(4)

[a] For detailed conditions and collected data, see the Supporting Information.

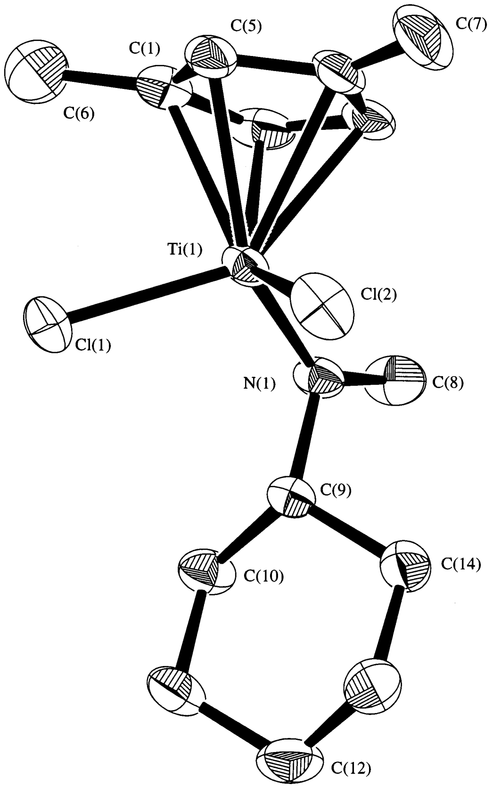

Figure 2. Ortep drawing for (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(Me)Cy] (**4**). Thermal ellipsoids are drawn at a 50% probability level, and hydrogen atoms were omitted for clarity.

Table 2. Selected Bond Distances (Å) and Bond Angles (deg) for (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(Me)Cy] (4)[a]

Bond Distances (Å)			
Ti−Cl(1)	2.2858(8)	Ti−Cl(2)	2.2816(9)
Ti−N(1)	1.861(2)	Ti−C(1) in Cp	2.373(3)
Ti−C(2) in Cp	2.317(3)	Ti−C(3) in Cp	2.319(3)
C(1)−C(2)	1.400(4)	C(1)−C(5)	1.402(4)
C(1)−C(6)	1.486(5)	C(4)−C(7)	1.472(4)
N(1)−C(8) in Me	1.451(3)	N(1)−C(9) in Cy	1.475(3)
C(9)−C(10)	1.518(3)	C(10)−C(11)	1.516(4)
C(11)−C(12)	1.507(4)	C(9)−C(14)	1.516(4)
Bond Angles (deg)			
Cl(1)−Ti−Cl(2)	102.56(4)	Cl(1)−Ti−N(1)	105.93(7)
Cl(2)−Ti−N(1)	105.18(7)	Cl(1)−Ti−C(1)	84.92(8)
Cl(2)−Ti−C(4)	84.96(9)	N(1)−Ti−C(1)	117.9(1)
N(1)−Ti−C(4)	118.81(10)	N(1)−Ti−C(5)	142.78(10)
C(8)−N(1)−C(9)	114.8(2)	Ti−N(1)−C(8)	139.6(2)
Ti−N(1)−C(9)	105.5(2)	N(1)−C(9)−C(10)	112.7(2)
N(1)−C(9)−C(14)	112.3(2)	C(10)−C(9)−C(14)	111.9(2)

[a] For detailed conditions and collected data, see the Supporting Information.

Cp*TiCl$_2$(N^{i}Pr$_2$) (99.2°) was also observed. The observed bond distances and bond angles in both **4** and **5** are thus concluded to be almost identical as those in **3**.

3. Polymerization of Ethylene, Propylene, and 1-Hexene. Ethylene polymerizations were performed in toluene at 25 °C in the presence of d-MAO white solid [prepared by removing toluene and AlMe$_3$ from commercially available MAO (PMAO, Tosoh Finechem Co.)]. d-MAO was chosen as the cocatalyst, because this MAO was quite effective to prepare ethylene/α-olefin copolymers with narrow molecular weight distributions as well as with relatively high molecular weights if our Cp′−aryloxytitanium and [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ were employed as the catalyst precursor.[3a,b] The results are summarized in Table 4.

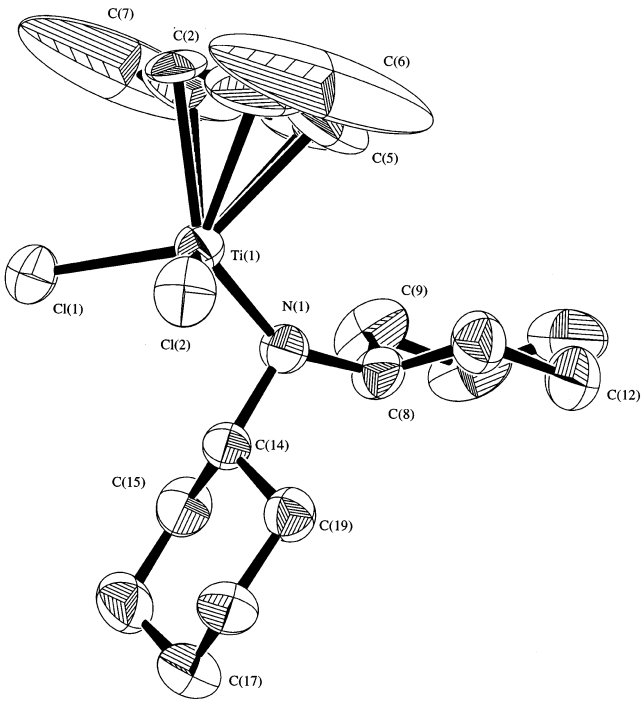

Figure 3. Ortep drawing for (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(NCy)$_2$ (**5**). Thermal ellipsoids are drawn at a 50% probability level, and hydrogen atoms were omitted for clarity.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(NCy)$_2$ (5)[a]

Bond Distances (Å)			
Ti−Cl(1)	2.309(2)	Ti−Cl(2)	2.296(2)
Ti−N(1)	1.873(3)	Ti−C(1) in Cp	2.39(1)
Ti−C(2) in Cp	2.362(5)	Ti−C(3) in Cp	2.356(6)
C(1)−C(2)	1.32(2)	C(1)−C(5)	1.15(2)
C(1)−C(6)	1.44(2)	C(3)−C(7)	1.36(2)
N(1)−C(8)	1.482(5)	N(1)−C(14)	1.505(6)
C(8)−C(9)	1.521(7)	C(9)−C(10)	1.558(8)
C(8)−C(13)	1.523(8)	C(14)−C(15)	1.529(6)
C(14)−C(15)	1.529(6)	C(14)−C(19)	1.532(6)
Bond Angles (deg)			
Cl(1)−Ti−Cl(2)	100.99(6)	Cl(1)−Ti−N(1)	108.0(1)
Cl(2)−Ti−N(1)	106.0(1)	Cl(1)−Ti−C(1)	123.8(4)
Cl(2)−Ti−C(4)	129.3(3)	N(1)−Ti−C(1)	125.4(5)
N(1)−Ti−C(2)	143.5(2)	N(1)−Ti−C(3)	114.2(4)
C(8)−N(1)−C(14)	111.4(3)	Ti−N(1)−C(8)	148.0(3)
Ti−N(1)−C(14)	100.7(2)	N(1)−C(8)−C(9)	112.6(4)
N(1)−C(8)−C(13)	112.2(4)	C(9)−C(8)−C(13)	113.7(5)
N(1)−C(14)−C(15)	113.4(4)	N(1)−C(14)−C(19)	112.6(3)
C(15)−C(14)−C(19)	112.4(4)		

[a] For detailed conditions and collected data, see the Supporting Information.

It was revealed that **1** exhibited moderate catalytic activity in the presence of d-MAO, and the initial catalytic activity slightly decreased if the ordinary MAO was used in place of d-MAO. The activity further decreased significantly at 50 °C in the presence of MAO [activity: 1410 kg-PE/mol-Ti·h (run 3) vs 180 kg-PE/mol-Ti·h (run 5)], and this would be due to the similar observation reported by Okuda et al.[14] that **1** exhibited low activity for ethylene polymerization (at 50 °C in toluene). The decrease in the activity by **1** under these conditions would be due to the dissociation of amide ligand from the metal center by AlMe$_3$, and would generate the same active species from Cp*TiCl$_3$, which is an efficient catalyst for syndiospecific styrene polymerization not for ethylene polymerization.

Table 4. Ethylene Polymerization by $Cp^*TiCl_2[N(Me)R^1]$−MAO [R^1 = Me (1), Et (2), Cy(3)] and $(1,3\text{-}Me_2C_5H_3)TiCl_2[N(Cy)R^2]$−MAO [$R^2$ = Me (4), Cy (5)] Catalyst Systems[a]

run no.	catal (μmol)	Al cocatal	Al/Ti[b] molar ratio	temp (°C)	yield (mg)	activity (kg-PE/mol-Ti·h)
1	**1** (2.0)	d-MAO[c]	1500	25	522	1570
2	**1** (2.0)	d-MAO[c]	1500	25	533	1600
3	**1** (2.0)	MAO	1500	25	470	1410
4	**1** (2.0)	MAO	1500	25	477	1430
5	**1** (2.0)	MAO	1500	50	60.0	180
6	**2** (2.0)	d-MAO[c]	1500	25	559	1680
7	**2** (2.0)	d-MAO[c]	1500	25	548	1640
8	**3** (1.0)	d-MAO[c]	3000	25	567	3400
9	**3** (1.0)	d-MAO[c]	3000	25	599	3590
10	**3** (1.0)	d-MAO[c]	3000	25	664	3980[d]
11	**3** (0.5)	d-MAO[c]	6000	25	360	4320
12	**3** (0.5)	d-MAO[c]	6000	25	378	4540
13	**4** (1.0)	d-MAO[c]	3000	25	254	1520
14	**4** (1.0)	d-MAO[c]	3000	25	247	1480
15	**5** (1.0)	d-MAO[c]	3000	25	333	2000

[a] Polymerization conditions: toluene, 30 mL; d-MAO, 3.0 mmol (Al); ethylene, 6 atm; 10 min. [b] Molar ratio of Al/Ti. [c] d-MAO was prepared by removing toluene and $AlMe_3$ from commercially available MAO. [d] GPC data vs polystyrene standard in *o*-dichlorobenzene: $M_w = 1.65 \times 10^4$, $M_w/M_n = 2.88$, and $M_w = 6.79 \times 10^5$, $M_w/M_n = 1.99$ (small amount).

Table 5. Polymerization of Propylene and 1-Hexene by (1−5)−MAO Catalyst Systems[a]

run no.	catal (μmol)	monomer	temp (°C)	yield (mg)	activity[b]	M_n[c]	M_w/M_n[c]
16	**1** (10.0)	1-hexene	25	292	29.2	926[d]	1.16
17	**2** (10.0)	1-hexene	25	181	18.1	928[e]	1.17
18	**3** (10.0)	1-hexene	25	175	17.5	886[f]	1.17
19	**4** (10.0)	1-hexene	25	386	38.6	2.86×10^4	1.73
20	**5** (10.0)	1-hexene	25	386	38.6	1.90×10^4	1.73
21	**5** (2.0)	propylene	0	860	2580	39.9[g]	2.23
22	**5** (10.0)	propylene	25	1042	625	13.0[g]	3.10

[a] Conditions (propylene polymerization): toluene, 30 mL; d-MAO, 3.0 mmol (Al/Ti = 500, molar ratio); propylene, 7 atm; 30 min. Conditions (1-hexene polymerization): catalyst, 2.0 μmol/mL of 1-hexene; 60 min; room temperature. [b] Activity in kg-polymer/mol-Ti·h. [c] GPC data in THF vs polystyrene standard. [d] High molecular weight PH was also observed in a small amount. $M_n = 1.54 \times 10^4$, $M_w/M_n = 1.33$. [e] High molecular weight PH was also observed in a small amount. $M_n = 1.36 \times 10^4$, $M_w/M_n = 1.38$. [f] High molecular weight PH was also observed in a small amount. $M_n = 1.51 \times 10^4$, $M_w/M_n = 1.33$. [g] Small amount of low molecular weight polymer was also observed on GPC trace.

It should be noteworthy that **3** exhibited notable catalytic activity for ethylene polymerization, although the activity was not improved if **2** was employed in place of **1** under the same conditions. The observed activity by **3** apparently increased at lower concentration conditions. In addition, as depicted in Table 4, the results presented here were reproducible in all cases. The resultant polymer possessed bimodal molecular weight distributions consisted of a mixture of low and high molecular weight polyethylene [run 10, $M_w = 1.65 \times 10^4$, $M_w/M_n = 2.88$ and $M_w = 6.79 \times 10^5$, $M_w/M_n = 1.99$ (small amount)], and these results are the same as those in ethylene polymerization using (cyclopentadienyl)(aryloxy)titanium(IV) complexes.[3a,b] Distinct differences in the ratios between high and low molecular weight polymers were not observed with a series of these catalysts. The reason for the bimodal molecular weight distribution is not clear at this moment, probably due to the poor solubility of polyethylene in the reaction mixture, as assumed previously.[3a] It was also revealed that dimethylcyclopentadienyl analogue **4** and **5** showed relatively high catalytic activity for ethylene polymerization.

The activity observed here, especially by **3**, should be promising, because the activity can be tuned only by replacing of one methyl group on amide ligand in **1** into cyclohexyl group. An assumption that introduction of electron-donating substituents into the amide group increases the activity can be thus considered, because the observed activity by **3** was higher than that reported by $Cp^*TiCl_2[N(SiMe_3)(2,6\text{-}Me_2C_6H_3)]$ under the same conditions (1080 kg-PE/mol-Ti·h).[19] We also assume that the effect of increased steric bulk with cyclohexyl group would also be considered, because the dissociation of amide ligand by aluminum would be disturbed by the steric bulk of cyclohexyl fragment.

Table 5 summarizes results for 1-hexene polymerization by (**1**−**5**)−d-MAO catalyst system (1-hexene = 10 mL, at 25 °C). Although $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, which exhibits the highest catalytic activity for both ethylene and 1-hexene polymerization among the series of $Cp'TiCl_2(OAr)$, showed the high catalytic activity (728 kg-PH/mol-Ti·h) affording high molecular weight poly(1-hexene) ($M_n = 41.5 \times 10^4$, $M_w/M_n = 1.62$),[3c] **3** showed the low catalytic activity (17.5 kg-PH/mol-Ti·h) and the resultant poly(1-hexene) possessed low molecular weight oligomer ($M_n = 886$, $M_w/M_n = 1.17$) containing high molecular weight polymer in a small amount. These results were somewhat the same as those observed in 1-hexene polymerization with a series of (anilide)(cyclopentadienyl)titanium complex catalysts.[19] On the other hand, **4** and **5** exhibited relatively higher catalytic activities (38.6 kg-PH/mol-Ti·h) than **1-3**, affording high molecular weight polymers with narrow polydispersities (runs 19−20), and the effect of steric bulk would be thus considered. Since not only lower catalytic activities were observed but also the resultant polymer possessed low molecular weight in all cases if a series of (anilide)(cyclopentadienyl)titanium(IV) complexes were used as the catalysts (1.2−6.1 kg-PH/mol-Ti·h)[19] under the same conditions, the results observed here are remarkable contrasts between anilide and amide ligand. It is thus assumed that both electronic and steric effect play a role for the high activity.

Results for propylene polymerization by **5**−d-MAO catalyst system are also summarized in Table 5. High catalytic activity was observed if the polymerization was performed at 0 °C (2580 kg-PP/mol-Ti·h), and the observed catalytic activity decreased if the polymerization was performed at 25 °C. The observed activity at 25 °C (625 kg-PP/mol-Ti·h) was somewhat lower than that for ethylene polymerization (2000 kg-PE/mol-Ti·h), but also higher than that for 1-hexene polymerization (38.6 kg-PH/mol-Ti·h), and effect of steric bulk of hydrogen, methyl, and *n*-butyl branch would be thus considered as the probable reason for these difference. The resultant polypropylene possessed bimodal molecular weight distributions consisted of high and low molecular weight polymers, and possessed atactic stereoregularity.

4. Polymerization of Styrene. We have recently shown in our reports using (cyclopentadienyl)(aryloxy)titanium(IV) complex catalysts that the efficient catalyst for both ethylene polymerization and ethylene/α-olefin copolymerization can be modified toward the efficient catalyst for both styrene homopolymerization and ethylene/styrene copolymerization only by replacing sub-

Table 6. Styrene Polymerization by (1−5)−d-MAO System[a]

run no.	catal (μmol)	MEK soluble[b] yield (mg)	MEK insoluble[c] yield (mg)	activity[d]	M_n[e] × 10^{-4}	M_w/M_n[e]
23	**1** (10.0)	22	69	41.4	3.81	3.78
24	**2** (10.0)	16	49	29.4	7.92	1.91
25	**3** (10.0)	13	54	32.4	14.7	1.99
26	**4** (10.0)	23	309	185.4	12.0	2.07
27	**5** (10.0)	20	40	24.0	50.5	1.50
28	none[f]	34				

[a] Polymerization conditions: styrene, 5 mL (containing 10 μmol of catalyst); d-MAO, 5.0 mmol (Al/Ti = 500, molar ratio); 25 °C; 10 min. [b] Atactic polystyrene (APS). [c] Syndiotactic polystyrene (SPS). [d] Activity = kg-SPS/mol-Ti·h. [e] GPC data in THF vs polystyrene standard. [f] Polymerization with d-MAO (3.0 mmol), $M_n = 2.03 \times 10^4$, $M_w/M_n = 2.07$.

stituent on the Cp′ groups.[16] Since it is expected from the above results that the series of Cp′−amide analogue should be also effective for styrene polymerization, also since the catalytically active species for styrene polymerization should be still under discussion in this research field, we thus explored the possibility.[22]

Table 6 summarizes results for styrene polymerization by (**1**−**5**)−d-MAO catalyst systems. Since d-MAO itself gave low molecular weight atactic polystyrene as 2-butanone-soluble (methyl ethyl ketone, MEK) fraction,[16,22] the polymerization with d-MAO was also carried out for comparison (run 28). Since the yields (13−23 mg, runs 23−27) in MEK soluble fraction by (**1**−**5**)−d-MAO catalysts were lower than that by d-MAO (MEK soluble product only, 34 mg), it is thus clear that the products by catalysts **1**−**5** were in MEK-insoluble fraction. The resultant polymer as MEK-insoluble fraction was found to be a perfect syndiotactic polystyrene confirmed by ^{13}C NMR spectrum. It is thus concluded that **1**−**5** catalyze styrene polymerization to afford the syndiotactic polymer exclusively.

It was revealed that **4** exhibited the highest catalytic activity among **1**−**5**, and these results clearly show that substituent in Cp′ directly affects the catalytic activity. The result also clearly shows that the efficient catalyst can be modified by a replacement of substituent on Cp′. We believe that the present observation would be one of the unique characteristics for using nonbridged half-metallocene type titanium catalyst for precise olefin polymerization.

5. Copolymerization of Ethylene with 1-Hexene by (1—5)—d-MAO Catalyst Systems. Copolymerizations of ethylene with 1-hexene using **1** and **3**−**5** as catalysts were performed in toluene in the presence of d-MAO. $Cp^*TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$− (**6**) d-MAO catalyst[19] was also chosen for comparison. Polymerization results are summarized in Table 7,[23,24] and the typical ^{13}C NMR spectra for poly(ethylene-*co*-1-hexene)s prepared by **1**−, **3**−, and **4**−d-MAO catalyst systems are shown in Figure 4. As depicted in Table 7 (runs 32−33, 35−36, and 39−40), these polymerization results were reproducible.

It was revealed that these complexes (**1** and **3**−**5**) exhibited relatively high catalytic activities, and the resultant poly(ethylene-*co*-1-hexene)s possessed relatively high molecular weights in all cases. It is interesting to note that **3** exhibited better 1-hexene incorporation than **1**, although **3** possessed a bulky cyclohexyl group in the amide ligand.[25] The observed catalytic activities by **3** were, however, lower than those observed in ethylene polymerization (as shown in Table 4), and the activity decreased under both high 1-hexene concentration and low ethylene pressure conditions (run 34) probably due to the steric bulk of cyclohexyl group especially for 1-hexene incorporation. The observed catalytic activities were almost same as those in the ethylene polymerization if **1** was used as the catalyst, and this may also suggest the above assumption for the decreased activity by **3**. Bimodal molecular weight distributions for the resultant poly(ethylene-*co*-1-hexene) was observed if **1** was used as the catalyst under the specified conditions. Tiny amount of low molecular weight peak was also observed in the GPC traces in the copolymer prepared by **3** under certain conditions, and the trend (and the ratio of high and low molecular weight polymers prepared by **1** and **3**) was somewhat dependent upon 1-hexene concentration, ethylene pressure, time course, and Al/Ti molar ratio.[26] These are probably due to the deactivation of initial catalytically active species which are generated by **1** or **3** with the reaction of MAO, and then affording another catalytically active species.

It was also revealed that **4** exhibits both the highest catalytic activities (2040 kg-polymer/mol-Ti·h) and efficient 1-hexene incorporation under the same conditions, and both the activity and 1-hexene content increased upon the increase in the initial 1-hexene concentration. **5** also showed both high catalytic activities and efficient 1-hexene incorporation, and the resultant copolymers possessed high molecular weights with unimodal molecular weight distributions. It is thus concluded that **4** is the most suited catalyst for both high activity and efficient 1-hexene incorporation.

On the other hand, it is important to note that 1-hexene incorporation as well as the observed catalytic activity was low if $Cp^*TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (**6**), that exhibited relatively high catalytic activity for ethylene polymerization,[19] was chosen as the catalyst. The catalytic activity as well as the molecular weight for resultant poly(ethylene-*co*-1-hexene) decreased under high 1-hexene concentration conditions (runs 41−43). Chain end analysis for the resultant copolymer was performed not only because the observed results were somewhat different from those by **1**−**5**, but also because the resultant copolymer possessed low molecular weight. As shown in Figure 4, the dominant chain transfer process is the alkyl transfer from the metal center to aluminum although d-MAO (excess amount of $AlMe_3$ was removed from the commercially available MAO) was used as the cocatalyst in this case, and peaks corresponding to the chain transfer by β-hydrogen elimination were not observed.[23] Since it is clear that the catalytic activity and 1-hexene incorporation depended upon the nature of substituents in the amide (anilide) ligand, this should be a remarkable contrast between Cp′−anilide and Cp′−amide type catalyst. We can at least say from these results that both electronic (anilide vs amide) and steric bulk directly affect the 1-hexene incorporation.

Table 8 summarizes triad sequence distributions, the dyads, and r_Er_H values calculated based on ^{13}C NMR spectra for poly(ethylene-*co*-1-hexene)s.[23,24] The resultant r_Er_H values by **3** and **4** were 0.38−0.48, clearly indicating that these copolymerizations did not proceed in a random manner that can be seen in the copolymerization with ordinary metallocene type and/or linked Cp−amide complex catalysts. On the other hand, r_Er_H

Table 7. Copolymerization of Ethylene with 1-Hexene by 1−5 and Cp*$TiCl_2[N(2,6-Me_2C_6H_3)(SiMe_3)]$− (6) d-MAO System[a]

run no.	catal (μmol)	Al/Ti[b]	ethylene (atm)	1-hexene (mL)	yield (mg)	activity[c]	1-hexene content[d]	M_n[e] × 10^{-4}	M_w/M_n[e]
29	**1** (3.0)	1000	6	10	574	1150		40.7	1.84
								0.62	1.31
30	**1** (1.0)	4000	8	10	379	2270	12.0	37.8[f]	1.82
31	**3** (3.0)	1000	6	10	557	1110	22.2	30.3[f]	2.02
32	**3** (1.0)	3000	8	10	165	990	15.2	30.1[f]	1.90
33	**3** (1.0)	3000	8	10	171	1030		33.3[f]	1.97
34	**3** (1.0)	3000	4	10	61	366	28.9	15.1[f]	1.96
35	**4** (3.0)	1000	6	3	668	1340	18.9	67.5[f]	2.07
36	**4** (3.0)	1000	6	3	685	1370			
37	**4** (3.0)	1000	6	10	1017	2030	36.9	80.0[f]	2.09
38	**4** (1.0)	3000	4	10	425	2550	39.2	56.5	1.88
39	**5** (3.0)	1000	6	10	519	1040	36.1	27.6	2.23
40	**5** (3.0)	1000	6	10	508	1020			
41	**6** (10.0)	500	6	10	38	22.8	*g*	0.66	1.46
42	**6** (10.0)	500	6	5	42	25.2	*g*	1.25	1.42
43	**6** (10.0)	500	6	3	74	44.4	*g*	1.21	1.65

[a] Polymerization conditions: toluene + 1-hexene, total 30 mL; 10 min; 25 °C; d-MAO (prepared by removing toluene and $AlMe_3$). [b] Molar ratio of Al/Ti. [c] Activity in kg-polymer/mol-Ti·h. [d] 1-Hexene content (mol %) in copolymer estimated by ^{13}C NMR spectra. [e] GPC data in *o*-dichlorobenzene vs polystyrene standard. [f] Trace amount of low molecular weight peak was also observed, and the GPC traces are shown in the Supporting Information. [g] Small amount of 1-hexene content.

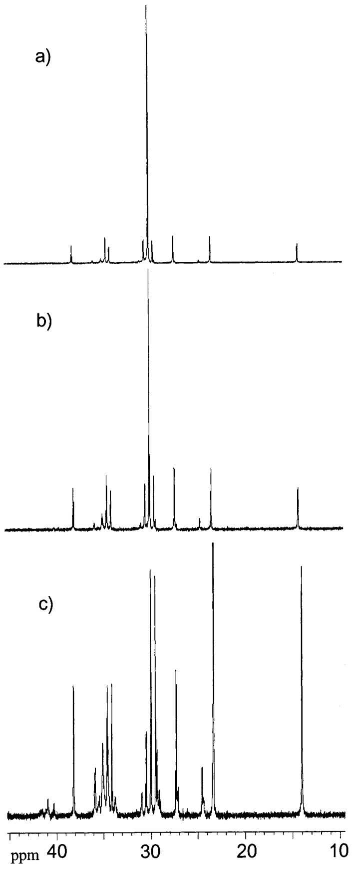

Figure 4. ^{13}C NMR spectra (10−45 ppm, in benzene-d_6 and 1,3,5-trichlorobenzene at 130 °C) for poly(ethylene-*co*-1-hexene)s prepared by (a) **1**−MAO (run 30, ethylene 8 atm, 1-hexene 10 mL), (b) **3**−MAO (run 32, ethylene 8 atm, 1-hexene 10 mL), and (c) **4**−MAO (run 37, ethylene 6 atm, 1-hexene 10 mL) catalyst systems.

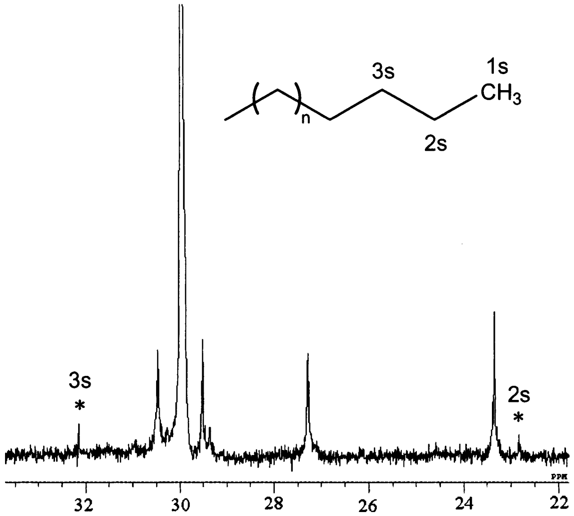

Figure 5. ^{13}C NMR spectrum for poly(ethylene-*co*-1-hexene) (extended chart at 22-33 ppm) prepared by the **6**−MAO catalyst system (run 42). The full spectrum is shown in the Supporting Information.

value calculated by **1** was 1.19, suggests that the copolymerization took place in a random manner.[27] One probable possibility for explaining the observed difference might be a disproportionation of **1** affording the same catalytically active species generated from $Cp^*_2TiCl_2$.

The observed triad sequence distributions and dyads distributions by **3**−**5** were strongly dependent upon substituents in both cyclopentadienyl and amide fragment (runs 32 and 34 vs 35, and run 37 vs 39, Table 8). Since we also reported in a study concerning ethylene/1-hexene copolymerization using a series of (cyclopentadienyl)(aryloxy)titanium complexes−MAO catalyst systems[3e,f] that $r_E r_H$ values, monomer reactivities, and monomer sequence distributions were highly dependent upon substituent in both cyclopentadienyl and aryloxy ligand, we thus believe that this is one of the unique characteristics for using nonbridged half-metallocene type catalyst for olefin polymerization.

We have shown that the efficient catalyst for desired polymerization, such as ethylene, 1-hexene, and styrene homopolymerization as well as ethylene/1-hexene copolymerization, can be modified by a replacement of substituent on both cyclopentadienyl and amide ligands. Although a precise design for both electronic and steric bulk can be thus required, we believe that the unique characteristics described above can be seen for using *nonbrodged* half-metallocene type titanium complex catalysts for precise olefin polymerization.

Table 8. Triad Sequence Distributions for Poly(ethylene-*co*-1-hexene)s Prepared by (1−5)−d-MAO System[a]

run no.	catal	1-hexene[b] (mol %)	triad sequence distribution[c] (%)						dyads[d] (%)			
			EEE	EEH + HEE	HEH	EHE	EHH + HHE	HHH	EE	EH + HE	HH	r_Er_H[e]
30	**1**	12.0	70.7	15.8	1.5	8.9	3.1	trace	78.6	19.9	1.5	1.19
31	**3**	28.9	32.4	28.8	9.9	18.8	9.5	0.6	46.8	47.8	5.4	0.44
32	**3**	22.2	43.6	27.8	6.4	17.2	4.7	0.3	57.5	39.9	2.6	0.38
34	**3**	15.2	59.1	21.9	3.8	13.0	2.0	0.2	70.0	28.8	1.2	0.41
35	**4**	18.9	51.5	24.9	4.7	14.6	3.9	0.4	63.9	33.7	2.4	0.54
37	**4**	36.9	21.1	28.6	13.4	20.3	13.9	2.7	35.4	54.9	9.7	0.46
38	**4**	39.2	20.4	28.6	11.8	21.5	13.8	3.9	34.7	54.5	10.8	0.50
39	**5**	36.1	29.9	24.7	9.3	17.5	18.6	trace	42.3	48.4	9.3	0.67

[a] Polymerization conditions: see Table 7. [b] 1-Hexene content in mol % estimated by ^{13}C NMR spectra. [c] Calculated by ^{13}C NMR spectra. [d] [EE] = [EEE] + $^1/_2$[EEH + HEE], [EH + HE] = [HEH] + [EHE] + $^1/_2${[EEH + HEE] + [HHE+EHH]}, [HH] = [HHH] + $^1/_2$[HHE+EHH]. [e] r_Er_H = 4[EE][HH]/[EH + HE]^2.

Experimental Section

General Procedure. All experiments were carried out under nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Toluene for polymerization was distilled in the presence of sodium and benzophenone under nitrogen atmosphere, and was stored in a Schlenk tube in the drybox in the presence of molecular sieves. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd.) and was used as received. Propylene for polymerization was of polymerization grade (Takachiho Co. Ltd.) and was used as received. 1-Hexene of reagent grade (Wako Chemical Co. Ltd.) was stored in the drybox in the presence of molecular sieves, and was used without further purification. Toluene and AlMe$_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness under reduced pressure (at ca. 50 °C for removing toluene, AlMe$_3$, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Cp*TiCl$_2$NMe$_2$ (**1**) was prepared according to the previous reports.[14,17]

Molecular weight and molecular weight distribution for polyethylene and poly(ethylene-*co*-1-hexene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH$_{HR}$-H HT x 2) 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. Molecular weights and molecular weight distributions for resultant polypropylene, poly(1-hexene), and polystyrene were measured by GPC (Shimadzu SCL-10A with RID-10A detector, column: ShimPAC GPC-806, -804, and -802) in THF vs polystyrene standard.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me$_4$Si. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. ^{13}C NMR spectra for polyethylene, polypropylene, polystyrene, and poly(ethylene-*co*-1-hexene)s 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. 10000. The analysis samples were prepared by dissolving polymers in a mixed solution of 1,3,5-trichlorobenzene/benzene-d_6 (90/10 wt), and the spectrum was measured at 130 °C. The samples for polypropylene, poly(1-hexene), and polystyrene were measured in CDCl$_3$.

Synthesis of Cp*TiCl$_2$[N(Me)Et] (2). **2** was prepared by the analogous procedure reported for **1**[14,17] except that LiNMeEt was used in place of LiNMe$_2$. Yield: 42%. ^{1}H NMR (C$_6$D$_6$): δ 0.90 (t, 3H, J = 6.8 Hz), 1.89 (s, 15H, C$_5$*Me*$_5$), 3.10 (s, 3H, N−C*H*$_3$), 3.85 (q, 2H, J = 6.8 Hz, N−C*H*$_2$CH$_3$). ^{13}C NMR (C$_6$D$_6$): δ 128.4, 51.9, 45.9, 45.7, 13.1, 12.8, 12.6. Cp*TiCl$_2$(NMe$_2$) (**1**), ^{1}H NMR (C$_6$D$_6$): δ 1.83 (s, 15H, C$_5$*Me*$_5$), 3.20 (s, 3H, N−C*H*$_3$). ^{1}H NMR (CDCl$_3$): δ 2.16 (s, 15H, C$_5$*Me*$_5$), 3.53 (s, 3H, N−C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 129.0, 49.5, 49.2, 13.6, 13.2, 12.7, 12.2.

Synthesis of Cp*TiCl$_2$[N(Me)Cy] (3). Into a sealed tube equipped with Kontes three-way bulb was added a toluene solution (30 mL) containing Cp*TiCl$_3$ (924 mg, 3.19 mmol) LiNMeCy (456 mg, 3.83 mmol) at room temperature. The reaction mixture was then placed in an oil bath warmed at 50 °C and stirred for 20 h. After the reaction, dichloromethane was added into the reaction mixture, and the solution was evaporated in vacuo. The resultant solid was extracted with *n*-hexane (ca. 80 mL) at room temperature, and the extract was concentrated to 50 mL and was then placed in the freezer (−30 °C). The pale yellow microcrystals were collected as the first crop (410 mg), and the second crop (70 mg) could be collected from the concentrated mother liquor at −30 °C. Yield: 43%. These are basically analytically pure, but may contain Cp*TiCl$_3$ in some experimental runs. ^{1}H NMR (C$_6$D$_6$): δ 0.76−0.95, 1.03−1.15, 1.35−1.55, 1.74 (dd or m, 4H), 1.94 (s, 15H, C$_5$Me$_5$), 3.17 (s, 3H, N−CH$_3$), 5.32 (m, 1H). ^{13}C NMR (C$_6$D$_6$): δ 134.0, 60.9, 40.9, 29.2, 26.9, 26.0, 12.9. Anal. Calcd for C$_{17}$H$_{29}$Cl$_2$NTi: C, 55.76; H, 7.98; N, 3.83. Found (1): C, 55.68; H, 7.70; N, 3.94. Found (2): C, 55.90; H, 7.80, N, 3.80. The sample for X-ray crystallography was prepared from the orange needles obtained from the concentrated hot hexane solution when it was allowed to stand at room temperature in the drybox.

Synthesis of (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(Me)Cy] (4). Synthetic procedure for **4** was the same as that for **3** except that (1,3-Me$_2$C$_5$H$_3$)TiCl$_3$ (802 mg, 3.24 mmol), LiN(Me)Cy (463 mg, 3.89 mmol) were used. After the reaction, the reaction mixture was evaporated in vacuo, and the resultant solid was extracted with *n*-hexane (ca. 80 mL) and was then concentrated up to ca. 50 mL. The chilled solution (−30 °C) gave orange microcrystals (570 mg), and the concentrated mother liquor gave the second crop (100 mg). Yield: 64%. ^{1}H NMR (CDCl$_3$): δ 0.84−0.88, 1.01−1.12, 1.24−1.34, 1.47−1.56, 1.68−1.76 (dd or m, 10H), 2.20 (s, 6H, Cp-C*H*$_3$), 3.16 (s, 3H, N−C*H*$_3$), 5.45 (m, 1H), 6.17 (s, 1H, Cp-H), 6.28 (s, 2H, Cp-H). ^{13}C NMR (CDCl$_3$): δ 133.8, 120.2, 118.0, 61.4, 44.8, 28.8, 26.6, 25.6, 16.8. Anal. Calcd for C$_{14}$H$_{23}$Cl$_2$NTi: C,51.88; H, 7.15; N, 4.32. Found: C, 51.50; H, 7.12; N, 4.18. The sample for X-ray crystallography was prepared from orange platelet microcrystals obtained from the concentrated hot hexane solution when allowed to stand at room temperature in the drybox.

Synthesis of (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(NCy$_2$) (5). The synthetic procedure for **5** was the same as that for **3** except that (1,3-Me$_2$C$_5$H$_3$)TiCl$_3$ (740 mg, 2.99 mmol) and LiNCy$_2$ (672 mg, 3.83 mmol) were used. After the reaction, the reaction mixture was evaporated in vacuo, and the resultant solid was extracted with *n*-hexane (ca. 80 mL) and was then concentrated up to ca. 50 mL. The chilled solution (−30 °C) gave orange microcrystals (435 mg), and the concentrated mother liquor gave the second crop (150 mg). Yield: 50%. ^{1}H NMR (CDCl$_3$): δ 0.84−0.88, 1.14−1.19, 1.20−1.28, 1.347−1.46, 1.58−1.76, 1.85−1.88 (dd or m, 20H), 2.20 (s, 6H, Cp-C*H*$_3$), 4.29(m or broad, 2H), 6.36 (s, 1H, Cp-H), 6.48 (s, 2H, Cp-H). ^{13}C NMR (CDCl$_3$): δ 133.7, 121.1, 115.2, 62.9, 33.4, 26.8, 25.7, 17.0. The sample for X-ray crystallography was prepared from the red prism

Table 9. Crystal and Data Collection Parameters for $(C_5Me_5)TiCl_2[N(Me)Cy]$ (3), $(1,3\text{-}Me_2C_5H_3)TiCl_2[N(Me)Cy]$ (4), and $(1,3\text{-}Me_2C_5H_3)TiCl_2(NCy_2)$ (5)[a]

	3	4	5
formula	$C_{34}H_{58}Cl_4N_2Ti_2$	$C_{14}H_{23}Cl_2NTi$	$C_{19}H_{31}Cl_2NTi$
fw	732.46	324.15	392.27
habits	orange, needle	orange, platelet	red, prism
cryst size (mm)	0.80 × 0.21 × 0.17	0.80 × 0.67 × 0.33	0.80 × 0.80 × 0.50
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_12_12_1$ (No. 19)
a (Å)	8.1771(4)	13.8739(6)	11.0294(4)
b (Å)	28.245(2)	6.7380(1)	12.5162(5)
c (Å)	16.317(2)	18.0293(2)	14.6992(4)
β (deg)	90.249(3)	108.786(1)	
V (Å^3)	3768.6(4)	1595.63(7)	2029.2(1)
Z value	4	4	4
D_{calcd} (g/cm^3)	1.291	1.349	1.284
F_{000}	1552.00	680.00	832.00
temp (K)	243	243	243
λ(Mo Kα) (Å)	0.710 69	0.710 69	0.710 69
2θ range (deg)	5.0−55.0	5.9−54.9	2.8−55.0
no. of reflcns meas			
tot.; unique	31051; 8016	14011; 3569	18507; 2632
R_{int}	0.060	0.049	0.050
no. of observns ($I > -10.00\delta(I)$)	8016	3569	2632
no. of variables	379	163	209
residuals: R_1; R_w	0.050; 0.135	0.049; 0.157	0.059; 0.172
GOF	1.15	1.86	1.92
max peak in final diff map (e/Å^3)	0.66	0.42	0.62
min peak in final diff map (e/Å^3)	-0.67	-0.63	-0.52

[a] Diffractometer: Rigaku RAXIS-RAPID imaging plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma\omega(F_o^2 - F_c^2)^2$. Least-squares weights: $w = 1/\delta^2(F_o^2)$; p-factor, 0.05.

microcrystals obtained from the concentrated hot hexane solution when allowed to stand at room temperature in the drybox.

Ethylene, Propylene Polymerization, and Ethylene/1-Hexene Copolymerization. The typical reaction procedure (run 1, Table 4) is as follows. Toluene (29 mL), and MAO solid [174 mg, prepared from ordinary MAO (Tosoh Finechem Co. PMAO-S) by removing toluene and $AlMe_3$] were added into the autoclave (100 mL scale stainless steel) in the drybox. The reaction apparatus was then filled with ethylene (1 atm), and the autoclave was then placed into a water bath. **1** (2.0 μmol) in toluene (1.0 mL) was then added into the autoclave, the reaction apparatus was then immediately pressurized to 5 atm, and the mixture was magnetically stirred for 10 min. After the above procedure, the ethylene remaining was purged, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer (white precipitate) was collected on a filter paper by filtration, and was adequately washed with EtOH and water and then dried in vacuo for several hours. The polymerization of propylene was also performed in the same manner. The copolymerization of ethylene with 1-hexene was performed in the same manner except that 1-hexene was also added into the autoclave in advance.

1-Hexene Polymerization. A prescribed amount of MAO was added to a round-bottom flask (25 mL) in the drybox, and the polymerization was started by the addition of a 1-hexene solution (5.0 mL) containing the catalyst (10.0 μmol). The reaction mixture was stirred for 30 min at room temperature, and the polymerization was terminated with the addition of EtOH. The reaction product was extracted with $CHCl_3$ which was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na_2SO_4, and the chloroform and 1-hexene remaining was then removed in vacuo.

Polymerization of Styrene. MAO was added into a round-bottom flask (25 mL) containing a styrene solution (5.0 mL) of the titanium complex (10.0 μmol) in the drybox, and the reaction mixture was stirred for 10 min at room temperature. The polymerization was terminated with the addition of ethanol containing HCl, and the resultant white solid was filtered and was then dried in vacuo (at 60 °C for 6 h). The resultant solid was then separated into two fractions by washing with methyl ethyl ketone (MEK) as the extraction solvent.

Crystallographic Analysis for 3—5. The orange needle (**3**), orange platelet (**4**), and red prism (**5**) microcrystals were grown from the concentrated hot hexane solution upon standing at room temperature in the drybox, and the structures were determined at −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 9. All structures were solved by direct method and expanded using Fourier techniques.[28] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan[29] crystallographic software package of the Molecular Structure Corporation. The detailed results are described in the Supporting Information.

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Supporting Information Available: Text and tables gving detailed crystallographic analysis data for **3**, **4**, and **5** and figures showing GPC traces and ^{13}C NMR spectra for poly(ethylene-*co*-1-hexene)s prepared by the **1**−**6**−d-MAO catalyst system (see Table 7 in the text). This material is available free of charge via the Internet at http://pubs.acs.org.

Note Added after ASAP Posting

This article was released ASAP on 3/5/2003. Changes were made in the wording of the title and the correct version was posted on 3/19/2003.

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(25) A most plausible assumption for explaining this observation would be due to the fact that the structures, especially geometries around the nitrogen atom determined by X-ray crystallography (**3** and dibenzyl analogue for **1**), were different between these two complexes, but this discussion might not be appropriate at this moment because these geometries might be changed if the dichloro (for **1**) or cationic alkyl analogues were compared. Although the reason for the observed difference is not clear at this moment, we can at least say that the *monomer reactivity can be directly modified by the amide fragment.*

(26) Resultant poly(ethylene-*co*-1-hexene)s possessed unimodal molecular weight distributions as shown in Table 7. However, low molecular weight shoulders were somewhat observed in the GPC traces if Cp*TiCl$_2$(NMe$_2$) (**1**) and Cp*TiCl$_2$[N(Me)-Cy] (**3**) (especially **1**) were employed as the catalyst precursor under specified conditions. The ratios for high and low molecular weight polymers were dependent upon the polymerization conditions such as ethylene pressure, 1-hexene concentration, time course, and Al/Ti molar ratio and the catalyst concentrations. Although the exact reason is not clear even at this moment, we assume that the stability for the initial catalytically active species would be due to the steric bulk of amide ligand because the dissociation of the amide ligand by the reaction with aluminum would be disturbed by the increased steric bulk. For evaluation of r_Er_H values, we carefully chose better samples that possess almost unimodal polydispersities.

(27) One assumption for explaining the observed difference in the copolymerization behavior between **1** and **3**−**4** was due to that disproportionation of **1** gave the catalytically active species derived from Cp*$_2$TiCl$_2$. The disproportionation might be disturbed if a cyclohexyl group was introduced (corresponds to **3**) in place of a methyl group. Although the possibility concerning a plausible assumption for the observed difference in the 1-hexene incorporation between **1** and **3** described in ref 25 would be still retained, the difference in the 1-hexene incorporation would be explained by this assumption.

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