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Synthesis of Nonbridged (Anilide)(cyclopentadienyl)titanium(IV) Complexes of the Type Cp′TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(R)] and Their Use in Catalysis for Olefin Polymerization

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(Anilide)(cyclopentadienyl)titanium(IV) complexes of the type Cp′TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)-(R)] (**8a-d**: Cp′ = C$_5$Me$_5$ (Cp*), 1,3-Me$_2$C$_5$H$_3$, Cp; R = SiMe$_3$, Si^{t}BuMe$_2$) have been prepared by the reaction of Cp′TiCl$_3$ with the corresponding lithium anilide in toluene. The structure of (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (**8b**) has been determined by X-ray crystallography. These complexes exhibited high catalytic activities for ethylene polymerization in the presence of methylaluminoxane (MAO); especially Cp*TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (**8a**) exhibited the highest catalytic activity (1080 kg of PE/((mol of Ti) h), ethylene 6 atm at 25 °C), whereas the analogous zirconium complex Cp*ZrCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (**9a**) showed a lower activity (637 kg of PE/((mol of Ti) h)) under the same conditions. The activity by Cp′TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] for the ethylene polymerization increased in the order Cp* > 1,3-Me$_2$C$_5$H$_3$, Cp. The molecular weight for the resultant polyethylene depended upon the cyclopentadienyl fragment used. The low catalytic activity was observed for propylene polymerizations by **8a**; the resultant polymer was atactic and possessed high molecular weight with narrow polydispersity.

Introduction

Olefin polymerization by homogeneous transition-metal complex catalysis has attracted particular attention in the field of organometallic chemistry, catalysis, and polymer chemistry. Many contributions have thus been made concerning this topic, especially using early-transition-metal complexes.[1] Among them, *nonbridged* half-metallocene 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$_3$; X = halogen, alkyl)[2−20] 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" (hybrid "half-metallocene") type catalysts.[21−30] In addition, the synthesis of this type is not complicated (shorter synthetic steps with relatively

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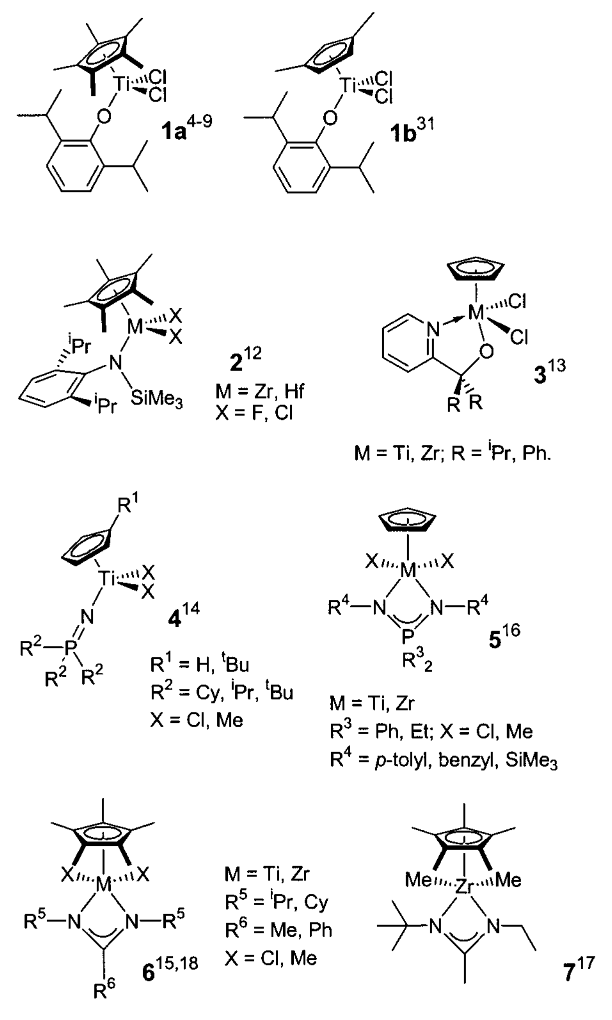
Chart 1



high yield), and the ligand modification sterically and/or electronically should be thus easier especially than the ordinary bridged half-metallocene type complexes. There are several examples that have already been known as efficient catalyst precursors for ethylene or 1-hexene homopolymerization, and these (**1**−**7**) are listed in Chart 1. However, only a few reports concerning ligand effects in ethylene/α-olefin copolymerization and/or concerning detailed polymerization behavior with these complexes have been published.

We have reported that the nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complex−MAO catalyst system, especially **1a**, exhibited exceptionally high catalytic activity not only for ethylene polymerization but also for ethylene/α-olefin copolymerization.[4,5,8,9] Moreover, the efficient catalyst precursor toward both styrene homopolymerization and ethylene/styrene copolymerization could be transferred only by replacing the substituent on the Cp′ groups (from **1a** to **1b**).[31]

With regard to the relevance to the above Cp−aryloxy−titanium chemistry, we thus have a strong interest for exploring the possibility of nonbridged (anilide)(cyclopentadienyl)titanium(IV) complexes as the olefin polymerization catalyst. The synthesis of analogous zirconium and hafnium complexes (**2**) has already been reported by Roesky et al.,[12] but reports concerning the synthesis and catalytic activity for olefin polymerization with related titanium complexes have not been reported so far. One related report, by Teuben and Linden,[32] is known for the synthesis of $CpTiCl_2(NHPh)$ from $CpTiCl_3$ with $Me_3SiN(H)Ph$, but this complex readily decomposes to give the bridged imido dimer $[CpTiCl]_2(\mu\text{-}PhN)_2$ upon heating (Scheme 1). Therefore, we first examined the possibility of preparing a series of titanium(IV) complexes of this type, explored their thermal stability, and performed an X-ray crystallographic analysis. In this paper, we wish to introduce our results concerning the synthesis of various complexes of this type, $Cp'TiCl_2[N(2,6\text{-}Me_2C_6H_3)(R)]$ (R = $SiMe_3$ and Cp′ = Cp* (**8a**), $1,3\text{-}Me_2C_5H_3$ (**8b**), Cp (**8c**); R = Si^tBuMe_2 and Cp′ = Cp (**8d**; Chart 2), and the effect of both cyclopentadienyl and anilide groups on olefin polymerization.[33]

Scheme 1

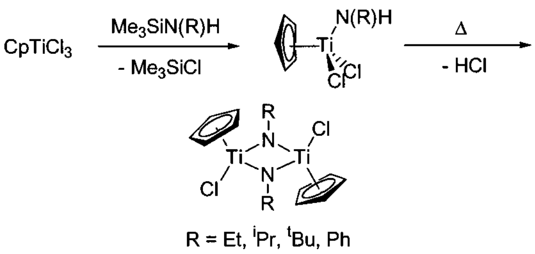
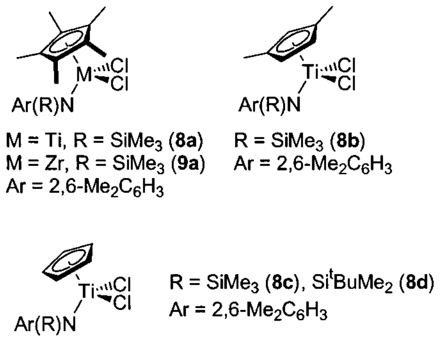


Chart 2



Results and Discussion

1. Syntheses of $Cp'TiCl_2[N(2,6\text{-}Me_2C_6H_3)(R)]$ (8, Cp′ = Cp*, $1,3\text{-}Me_2C_5H_3$, Cp; R = $SiMe_3$, Si^tBuMe_2) and $Cp^*ZrCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (9a). $Cp^*TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (**8a**) could be prepared in relatively high yield (78%) by the reaction of Cp^*TiCl_3 with $LiN(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ in toluene under reflux conditions (12 h), although **8a** could not be isolated from the mixture if the reaction was performed at room temperature or at 50 °C (Cp^*TiCl_3 was recovered instead). This is the related method for preparing (amide)(cyclopentadienyl)titanium(IV) complexes of the

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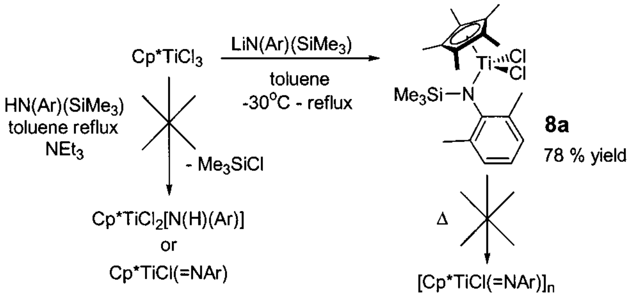
[33] We have also found that the $Cp^*TiCl_2[NMe(Cy)]$−MAO catalyst exhibited remarkable catalytic activity for ethylene polymerization: Nomura, K. Unpublished results.

Scheme 2



type Cp′TiCl$_2$(NR$_2$),[34−36] especially for preparing Cp*TiCl$_2$(N^{i}Pr$_2$),[35] although the reaction was complete at room temperature in the reported case. Furthermore, the attempt of a reaction in Et$_2$O at room temperature, which has been a known method for the synthesis of the analogous zirconium/hafnium complex Cp*MCl$_2$[N(2,6-^{i}Pr$_2$C$_6$H$_3$)(SiMe$_3$)] (M = Zr, Hf),[12] was not successful and Cp*TiCl$_3$ was thus recovered. On the other hand, the analogous zirconium complex Cp*ZrCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (**9a**) could be isolated in high yield according to a previous report on preparing Cp*ZrCl$_2$[N(2,6-^{i}Pr$_2$C$_6$H$_3$)(SiMe$_3$)].[12] This is an interesting contrast between titanium and zirconium/hafnium complexes of this type. In addition, Cp*TiCl$_3$ was recovered as the sole isolated compound from the reaction mixture if reactions of Cp*TiCl$_3$ with HN(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$) in place of the lithium salt under various conditions were attempted (Scheme 2). **8a** could be identified by ^{1}H and ^{13}C NMR and elemental analysis.

It turned out that **8a** was thermally stable under refluxing conditions in toluene for longer than 12 h, and elimination of Me$_3$SiCl was not observed under these conditions. This is a remarkable contrast to the fact that the reaction of CpTiCl$_3$ with Me$_3$SiN(H)Ph at room temperature gave CpTiCl$_2$N(H)Ph quantitatively, accompanying the elimination of Me$_3$SiCl, then afforded the imido-bridged dimer [CpTiCl]$_2$(μ-PhN)$_2$ upon heating, as shown in Scheme 1.[32] The observed difference might be explained by the steric bulk of the substituents on the anilide group at the 2,6-positions that would disturb the elimination of Me$_3$SiCl.

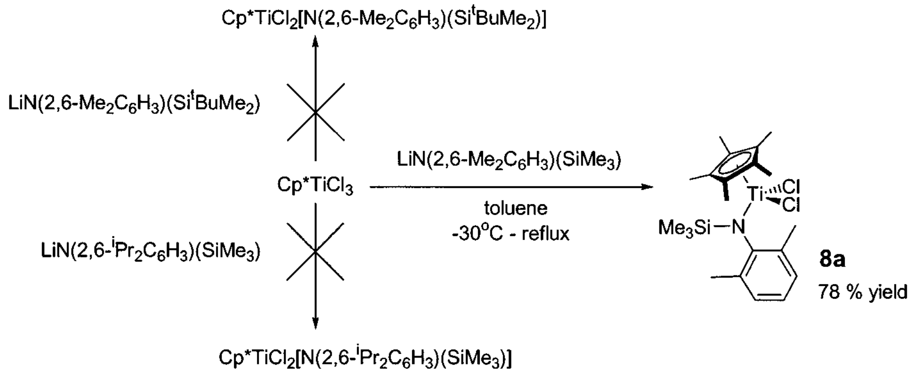
The reaction of Cp*TiCl$_3$ with LiN(2,6-^{i}Pr$_2$C$_6$H$_3$)(SiMe$_3$) in place of LiN(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$) was attempted under the same conditions for **8a**, but the ^{1}H NMR spectrum for the reaction mixture after removal of the solvent (which was then quickly washed with cold hexane and dried in vacuo) showed the starting compound including decomposed compounds or some impurities (Scheme 3). The reaction in xylene at 130 °C for 2−4 days was also attempted, but the desired complex, Cp*TiCl$_2$[N(2,6-^{i}Pr$_2$C$_6$H$_3$)(SiMe$_3$)], or related products could not be isolated. These results are also interesting in contrast with the synthesis of analogous zirconium and hafnium complexes that were prepared in high yield under mild conditions (room temperature in Et$_2$O). Attempts to prepare Cp*TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(Si^{t}BuMe$_2$)] from the reaction of Cp*TiCl$_3$ with LiN(2,6-Me$_2$C$_6$H$_3$)(Si^{t}BuMe$_2$) under analogous conditions for **8a** (toluene reflux for 3 days) failed, and Cp*TiCl$_3$ was recovered instead.

Although the reaction under reflux conditions of toluene was absolutely necessary to prepare **8a**, (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (**8b**) could be isolated in high yield by a similar reaction at 50 °C for 12 h after stirring the reaction mixture at room temperature. In addition, CpTiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (**8c**), and CpTiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(Si^{t}BuMe$_2$)] (**8d**) could also be isolated in high yields by the reaction of CpTiCl$_3$ with LiN(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$) and LiN(2,6-Me$_2$C$_6$H$_3$)(Si^{t}BuMe$_2$), respectively, in toluene at room temperature. The formation of (bridged or monodentate) imido derivatives (e.g. CpTiCl(=N-2,6-Me$_2$C$_6$H$_3$)) was not observed under these conditions. These compounds were also identified by ^{1}H and ^{13}C NMR spectra and elemental analyses.

2. Crystal Structure of (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(SiMe$_3$)] (8b). Since attempts to prepare Cp*TiCl$_2$[N(2,6-^{i}Pr$_2$C$_6$H$_3$)(SiMe$_3$)] and/or Cp*TiCl$_2$[N(2,6-Me$_2$C$_6$H$_3$)(Si^{t}BuMe$_2$)] were not successful, even though the analogous zirconium complex Cp*ZrCl$_2$[N(2,6-^{i}Pr$_2$C$_6$H$_3$)(SiMe$_3$)] was easily prepared in diethyl ether under mild conditions, the structure determination for the titanium complexes of this type by X-ray crystallography was thus explored to observe the difference among these complexes. Yellow prismatic microcrystals were grown from the concentrated hot hexane solution containing **8b** by gradual cooling upon standing in the drybox, and the structure could be determined if the measurement was done at −30 °C. The attempt at room temperature failed due to the gradual decomposition of the crystal of **8b** during the analysis run.

The molecular structure of **8b** is shown in Figure 1, and selected bond distances and angles are summarized in Table 1. The X-ray structure of **8b** shows it to have a tetrahedral geometry around the titanium metal center, and remarkable differences in the structural

Scheme 3



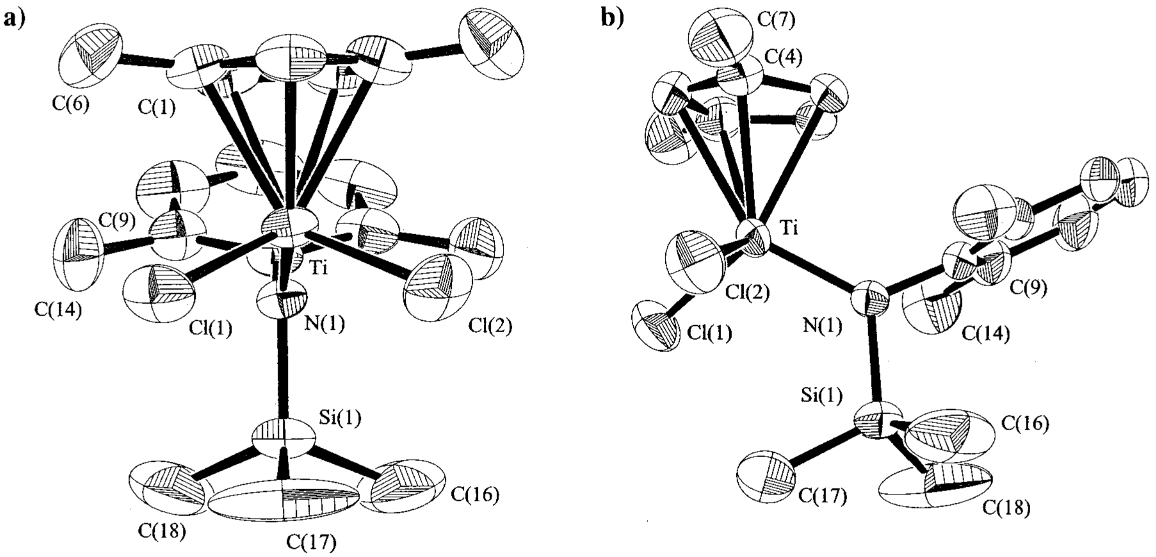


Figure 1. Ortep drawings for (1,3-$Me_2C_5H_3$)$TiCl_2$[N(2,6-$Me_2C_6H_3$)($SiMe_3$)] (**8b**). Thermal ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Bond Angles (deg) for (1,3-$Me_2C_5H_3$)$TiCl_2$[N(2,6-$Me_2C_6H_3$)($SiMe_3$)] (8b)[a]

Bond Distances			
Ti−Cl(1)	2.2770(9)	Ti−Cl(2)	2.2662(9)
Ti−N(1)	1.898(2)	Ti−C(1) in Cp	2.387(3)
Ti−C(2) (Cp)	2.307(2)	Ti−C(3) in Cp	2.326(3)
Si(1)−N(1)	1.806(2)	Si(1)−C(16) ($SiMe_3$)	1.830(5)
N(1)−C(8) (phenyl)	1.442(3)	C(1)−C(2)	1.402(4)
C(1)−C(5)	1.417(5)		
Bond Angles			
Cl(1)−Ti−Cl(2)	103.25(4)	Cl(1)−Ti−N(1)	105.17(7)
Cl(1)−Ti−C(1)	83.63(8)	Cl(1)−Ti−C(2)	108.14(9)
Cl(2)−Ti−N(1)	105.07(7)	N(1)−Si(1)−C(16)	111.2(2)
N(1)−Si(1)−C(17)	114.6(2)	N(1)−Si(1)−C(18)	110.6(2)
C(16)−N(1)−C(17)	106.8(4)	Ti−N(1)−Si(1)	120.6(1)
Ti−N(1)−C(8)	111.6(2)	Ti−C(2)−C(1)	75.8(2)
Ti−C(2)−C(3)	73.2(1)	Ti−C(3)−C(4)	76.0(2)

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

features compared to the hafnium complex Cp*$HfCl_2$[N(2,6-$^iPr_2C_6H_3$)($SiMe_3$)][12] were not observed. The position of substituents around the nitrogen atom was also found to be the same as that in the analogous hafnium complex, the aryl group was positioned close to the cyclopentadienyl group, and a plane consisting of nitrogen and the three substituents (Ti, Si in $SiMe_3$, and carbon atoms in the aryl groups) is placed perpendicular to the plane of the cyclopentadienyl ring. The Ti−N bond distance (1.90 Å) in **8b** was somewhat shorter than that in hafnium (2.05 Å), and the Ti−Cl bond distances (2.27−2.28 Å) were somewhat shorter than those in hafnium (2.36−2.38 Å). The observed Ti−N bond distance (1.90 Å) was the same as that in Cp*Ti(CH_2Ph)$_2$(NMe_2) (1.89 Å)[36] or somewhat longer than that in Cp$TiCl_2$[N($SiMe_3$)$_2$] (1.88 Å)[37] or Cp*$TiCl_2$(N^iPr_2) (1.87 Å),[35] despite the electron-withdrawing nature of the aryl group. The observed value was shorter than the estimated value (2.02 Å) for a titanium−nitrogen single bond according to Pauling's covalent radii[38] and was consistent with the presence of a titanium−nitrogen double bond. No distinct differences were observed for N−C (in phenyl) and N−Si bond distances between these complexes. This structural result clearly explains the reason it is difficult to prepare Cp*$TiCl_2$[N(2,6-$^iPr_2C_6H_3$)($SiMe_3$)], because the desired complex was sterically hindered in the case of titanium.

3. Ethylene Polymerization by the 8− and 9−MAO Catalyst Systems. Ethylene polymerization by **8a** was conducted in toluene (ethylene at 6 atm) by using a 100 mL autoclave. MAO white solid, which was prepared by removing toluene and $AlMe_3$ contaminated in the commercially available MAO (PMAO-S, Tosoh Finechem Co.), was chosen as the cocatalyst, because this MAO was effective in preparing ethylene/α-olefin copolymers with narrow molecular weight distributions as well as with relatively high molecular weights if our Cp′−aryloxy titanium species and [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$ were employed as the catalyst precursors.[5,8−9] The results are summarized in Table 2.

It turned out that **8a** exhibited high catalytic activity for ethylene polymerization and that the activity could be optimized by varying the Al/Ti molar ratio. The activity was, however, very sensitive to the polymerization temperature, and the value decreased at both 40 and 0 °C. The decrease in the activity at 40 °C would be probably due to the partial decomposition of catalytically active species, because a lower activity was observed if the polymerization was carried out at 60 °C (run 9). A decrease in the activity was, on the other hand, not observed at 0 °C after 60 min (runs 6 and 7). The polymerization with an analogous zirconium complex (**9a**) was also carried out; the optimized catalytic activity was lower than that by **8a**, and a significant decrease in the activity was observed at 40 °C. Since **8a** itself is stable under reflux conditions in toluene as described above, one probable reason for the decrease

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Table 2. Ethylene Polymerization by the $Cp^*MCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (M = Ti (8a), Zr (9a))−MAO Catalyst System[a]

run no.	cat. (amt/μmol)	Al/Ti[b]	temp/°C	time/min	yield/mg	activity[c]/(kg of PE/((mol of Ti) h))
1	**8a** (1.0)	1000	25	30	207	414 (69.0)
2	**8a** (1.0)	2000	25	30	361	722 (120)
3	**8a** (1.0)	3000	25	30	435	870 (145)
4	**8a** (1.0)	5000	25	30	451	902 (150)
5	**8a** (2.0)	1000	25	10	360	1080 (180)
6	**8a** (2.0)	1000	0	10	23	69 (11.5)
7	**8a** (2.0)	1000	0	60	173	87 (14.5)
5	**8a** (2.0)	1000	25	10	360	1080 (180)
8	**8a** (2.0)	1000	40	10	113	338 (56.3)
9	**8a** (2.0)	1000	60	10	78	235 (39.2)
10	**9a** (3.0)	1000	25	30	717	478 (79.7)
11	**9a** (1.0)	3000	25	30	319	637 (106)
12	**9a** (1.0)	3000	40	30	200	40 (6.7)

[a] Polymerization conditions: toluene 30 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from commercially available MAO), ethylene 6 atm. [b] Molar ratio of Al/Ti. [c] In parentheses, the activity is displayed as kg of PE/((mol of Ti) h atm).

in the activity would be the thermal stability of the catalytically active species under these polymerization conditions, containing an excess amount of MAO.

Table 3 summarizes results for the ethylene polymerization with various Cp′−anilide titanium complexes. The observed catalytic activity with a series of $Cp'TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ complexes at 25 °C increased in the order (MAO cocatalyst in toluene) Cp′ = Cp* (**8a**, 902 kg of PE/((mol of Ti) h)) > 1,3-$Me_2C_5H_3$ (**8b**, 104 kg of PE/((mol of Ti) h)), Cp (**8c**, 113 kg of PE/((mol of Ti) h)). On the basis of these results, it would be suggested that the introduction of an electron-donating group into the cyclopentadienyl ring increases the catalytic activity as previously reported in Cp′−aryloxy titanium complexes,[5] although there are several factors such as the stability of the catalytically active species and/or the percentage of the *actual* catalytically active species, because these complexes are used as the catalyst *precursor* and do not act as the catalyst itself. The activity by $CpTiCl_2[N(2,6\text{-}Me_2C_6H_3)(Si^tBuMe_2)]$ (**8d**) seemed somewhat higher than $CpTiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (**8c**) under the same conditions, and this trend is similar to that observed for ethylene polymerization with a series of $[1,8\text{-}C_{10}H_6(NR)_2]TiCl_2$ (R = $SiMe_3$, Si^tBuMe_2, Si^iPr_3)−MAO catalyst systems.[39] The observed effect of the amide ligand on the activity would be thus explained by the assumption that the stability of catalytically active species, especially the stability of the N−alkylsilyl bond in solution under these reaction conditions,[37] affects the observed catalytic activity.

The resultant polymer was linear in all cases confirmed by ^1H and ^{13}C NMR, but the molecular weight for the resultant polyethylene depended upon the substituent on the cyclopentadienyl group. The resultant polymer from **8a** possessed poor solubility in hot *o*-dichlorobenzene and so was not suited for a conventional GPC analysis (in *o*-dichorobenzene at 140 °C), but the polymer was completely soluble in 1,3,5-trichlorobenzene at 150 °C.[40] This result suggests that the resultant polymer from **8a** possessed extremely high molecular weight. On the other hand, the resultant polymer from **8b** possessed relatively low molecular weight with unimodal polydispersity. Moreover, the resultant polymer from the Cp analogues **8c** and **8d** gave a mixture consisting of polyethylene with multimodal molecular weight distributions (insoluble in acidified ethanol) and oligomeric oil (soluble in acidified ethanol and could be extracted with chloroform). From the analysis of the GC chromatogram as well as GC-MS, these oligomers consisted of linear $C_{14}-C_{30}$ hydrocarbons. In addition, the ^1H NMR spectrum reveals that the resultant oligomer consisted of a mixture of linear alkanes (71.5 mol %) and olefins (28.5 mol %) (Figure 2b). Olefinic double bonds were also observed by the ^1H NMR spectrum for the ethanol-insoluble sample (Figure 2a). One probable assumption for producing a mixture of oligomer and high-molecular-weight polyethylene by **8c**,**d** would be that several catalytically active species were present under these polymerization conditions. Although the polymerization by **8c**,**d** afforded a mixture of low- and high-molecular-weight products, these results clearly suggest that the nature of the cyclopentadienyl fragment directly affects the molecular weight in these catalyses.

4. Polymerization of Propylene and 1-Hexene by the 8a−MAO Catalyst System. Table 4 summarizes the results for propylene polymerization with the **8a**−MAO catalyst system. The catalytic activity increased at the lower temperature of 0 °C, and the activity also increased at higher propylene pressure. The resulting polymer possessed extremely high molecular weight

Table 3. Ethylene Polymerization by the $Cp'TiCl_2[N(2,6\text{-}Me_2C_6H_3)(R)]$−MAO Catalyst System (R = $SiMe_3$ and Cp′ = Cp* (8a), 1,3-$Me_2C_5H_3$ (8b), Cp (8c); R = Si^tBuMe_2 and Cp′ = Cp (8d))[a]

run no.	cat. (amt/μmol)	Al/Ti[b]	temp/°C	yield[c]/mg	activity[d]/(kg of PE/((mol of Ti) h))	$10^{-4}M_w$[e]	M_w/M_n[e]
3	**8a** (1.0)	3000	25	435	870 (145)	insoluble[f]	
4	**8a** (1.0)	5000	25	451	902 (150)	insoluble[f]	
8	**8a** (2.0)	1000	40	113	338 (56.3)	insoluble[f]	
13	**8b** (10.0)	500	25	518	104 (17.3)	0.19	2.00
14	**8b** (10.0)	500	25	484	97 (16.2)	0.19	2.00
15	**8b** (10.0)	500	40	140	28 (4.7)	0.18	2.01[g]
16	**8c** (10.0)	500	25	567 (373)	113 (18.8)	34.2[h]	198
17	**8c** (10.0)	500	25	525 (335)	105 (17.5)	63.9[h]	297
18	**8d** (10.0)	500	25	684 (477)	137 (22.8)		
19	**8d** (10.0)	500	40	257 (183)	51 (8.5)	28.4[i]	96.1

[a] Polymerization conditions: toluene 30 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from commercially available MAO), ethylene 6 atm, 25 °C, 30 min (run 8, 10 min). [b] Molar ratio of Al/Ti. [c] The yield of low-molecular-weight oligomer oil is given in parentheses (soluble in acidified ethanol and extracted with chloroform; see the Experimental Section). [d] In parentheses, the activity is displayed as kg of PE/((mol of Ti) h atm). [e] GPC data (acidified ethanol-insoluble portion) in *o*-dichlorobenzene vs polystyrene standard. [f] The resulting polyethylene was insoluble in hot *o*-dichlorobenzene (but soluble in 1,3,5-trichlorobenzene at 145−150 °C). [g] High-molecular-weight PE was also observed in a trace amount. [h] Mixture of high- and low-molecular-weight polymers. [i] Bimodal molecular weight distribution consisted of $M_w = 5.01 \times 10^5$, 2.19×10^3.

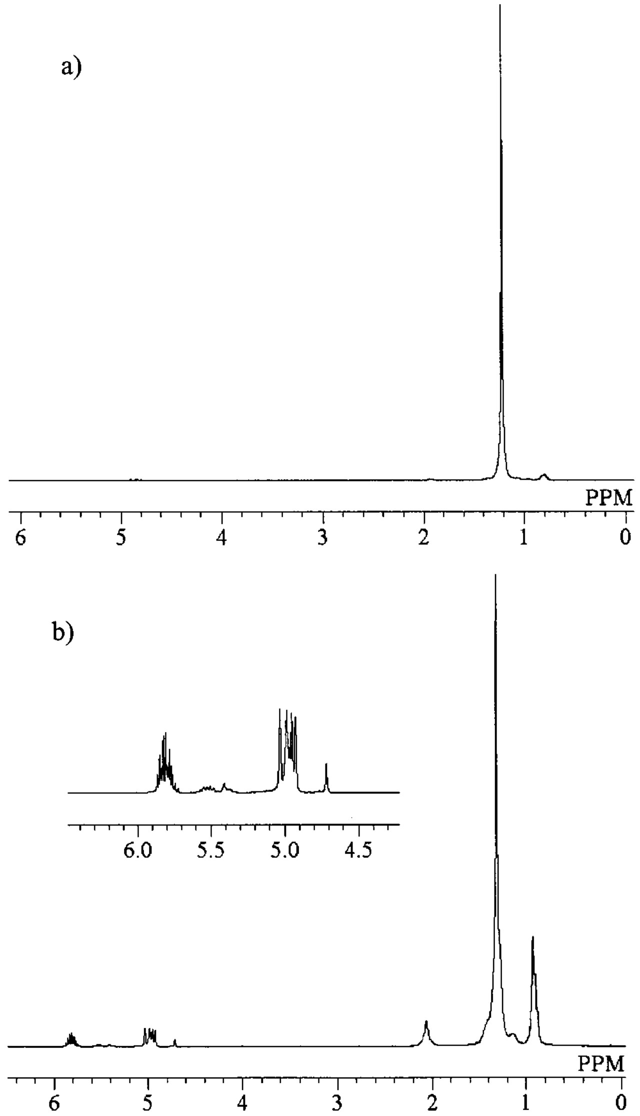

Figure 2. ^{1}H NMR spectra (in $CDCl_3$) for polyethylene prepared by the $CpTiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (**8c**)−MAO catalyst system (Table 3, run 17): (a) EtOH-insoluble fractio; (b) EtOH-soluble fraction.

Table 4. Polymerization of Propylene by the $Cp^*TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (8a)−MAO Catalyst System[a]

run no.	propylene press./atm	temp/°C	yield/mg	activity[b]/(kg of PP/((mol of Ti) h)))	$10^{-4}M_w$[c]	M_w/M_n[c]
20	5	0	41.8	13.9 (2.78)		
21	5	40	26.5	8.83 (1.77)		
22	7	0	200.4	51.0 (7.29)	91.3	1.77
23	7	25	53	17.7 (2.53)	185[d]	1.40[d]
24	7	25	51	17.0 (2.43)		
25	7	40	12.3	4.10 (0.59)		

[a] Polymerization conditions: **8a** 6.0 μmol, toluene 30 mL, d-MAO (prepared by removing toluene and $AlMe_3$ from commercially available MAO) 3.0 mmol (Al/Ti = 500), 30 min. [b] In parentheses, the activity is displayed as kg of PP/((mol of Ti) h atm). [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] Low-molecular-weight polypropylene was observed: $M_n = 7.08 \times 10^4$, $M_w/M_n = 1.60$, $M_n = 5.16 \times 10^3$, $M_w/M_n = 1.09$.

Table 5. Polymerization of 1-Hexene by the $Cp'TiCl_2[N(2,6\text{-}Me_2C_6H_3)(R)]$−MAO Catalyst System ($R = SiMe_3$ and $Cp' = Cp^*$ (8a), $1,3\text{-}Me_2C_5H_3$ (8b), Cp (8c); $R = Si^tBuMe_2$ and $Cp' = Cp$ (8d))[a]

run no.	complex (amt/μmol)	yield/mg	activity/(kg of PH/((mol of Ti) h)	M_n[b]	M_w/M_n[b]
26	**8a** (20.0)	121.5	6.08	967[c]	1.18
27	**8b** (10.0)	14	1.4	932[d]	1.07
28	**8c** (10.0)	12	1.2	965[e]	1.10
29	**8d** (10.0)	36	3.6	769[f]	1.09

[a] Polymerization conditions: catalyst 2.0 μmol/mL of 1-hexene, 1-hexene 5 mL (run 26, 10 mL), 60 min, room temperature, d-MAO (prepared by removing toluene and $AlMe_3$ from commercially available MAO), molar ratio of Al/Ti 500. [b] GPC data in THF vs polystyrene standard. [c] High-molecular-weight PH was also observed in a small amount. $M_n = 4.61 \times 10^4$, $M_w/M_n = 1.80$. [d] High-molecular-weight PH was also observed in a small amount. $M_n = 2.34 \times 10^4$, $M_w/M_n = 1.32$. [e] High-molecular-weight PH was also observed in a small amount. $M_n = 8.38 \times 10^5$, $M_w/M_n = 1.53$. [f] High-molecular-weight 1-hexane oligomer was also observed in a small amount. $M_n = 4.82 \times 10^3$, $M_w/M_n = 1.15$.

with narrow molecular weight distributions ($M_w = (91.3-185) \times 10^4$, $M_w/M_n = 1.40-1.77$), and these results were in good correspondence with those for ethylene polymerization by **8a**, in which extremely high molecular weight polyethylene could be prepared. On the basis of the ^{13}C NMR spectrum (in C_6D_6/1,3,5-trichlorobenzene), the resultant polypropylene possessed regioregularity but did not have stereoregularity, and the atactic polymer was thus obtained.[41]

Polymerization of 1-hexene was also employed, and the results are summarized in Table 5. The observed catalytic activity by **8a** was low (6.08 kg of PH/((mol of Ti) h)), and lower catalytic activities were found for **8b**−**d**. In addition, the resultant poly(1-hexene)s possessed low molecular weights with narrow molecular weight distributions in all cases. The results observed here are in interesting contrast with those using the $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$−MAO catalyst system, which exhibited remarkably high catalytic activity and afforded high-molecular-weight poly(1-hexene) with narrow molecular weight distribution ($M_n = 69.5 \times 10^4$, $M_w/M_n = 1.62$) under similar conditions.[6] As expected, the resultant polymer does not have a stereoregularity.[41]

We have shown that (anilide)(cyclopentadienyl)titanium(IV) complexes of the type $Cp'TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ should be candidates for effective catalyst precursors especially for ethylene polymerization. However, we do not have an exact reason why a significant difference (catalytic activity, molecular weight) can be observed, especially in 1-hexene polymerization between Cp′−aryloxy and Cp′−anilide titanium catalyst systems. Although our present attempts to find titanium catalysts more active than $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ for olefin polymerization were not very successful, the facts observed here should be very important for designing effective catalyst precursors for precise olefin polymerization. We are doing more research with these catalysts, especially for ethylene-based copolymerization, and these results will be introduced soon.

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(39) Nomura, K.; Naga, N.; Takaoki, K. *Macromolecules* **1998**, *31*, 8009.

(40) K.N. expresses his thanks to Mr. G. Uematsu (Tosoh Co.) for helpful comments concerning the analysis of polyethylene prepared by **8a**.

(41) For the ^{13}C NMR spectrum (in $CDCl_3$), see the Supporting Information.

Experimental Section

General Procedures. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene for polymerization was distilled in the presence of sodium and benzophenone under a nitrogen atmosphere and was stored in a Schlenk tube in the drybox. 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 removed and dried in vacuo in the drybox and used as the white solid.

The molecular weight and molecular weight distribution of the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a 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 calibration with standard polystyrene samples.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^1H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me_4Si. All spectra were obtained in the solvent indicated at 25 °C unless otherwise noted. ^{13}C NMR spectra for polyethylene and polypropylene 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. 10 000. The polymer solution for polyethylene prepared by the **8a**−MAO catalyst system was prepared by dissolving the polymers in a mixed solution of 1,3,5-trichlorobenzene and benzene-d_6 (90/10 wt), and the spectrum was measured at 130 °C. The samples for polyethylene prepared by the **8c**−MAO catalyst system were measured at room temperature in $CDCl_3$. The sample for polypropylene prepared by the **8a**−MAO catalyst system was also measured at room temperature in $CDCl_3$. Molecular weights and molecular weight distributions for the resultant polypropylene and poly(1-hexene) were measured by GPC (Shimazu SCL-10A with RID-10A detector, ShimPAC GPC-806, 804, and 802 columns) in THF vs polystyrene standard.

Synthesis of $Cp^*TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (8a). Into a sealed tube equipped with a Kontes three-way bulb was added Cp^*TiCl_3 (500 mg, 1.727 mmol) in toluene (30 mL) in the drybox. $LiN(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (344 mg, 1.727 mmol) was then added at −30 °C, and the reaction mixture was warmed slowly to room temperature and was placed into an oil bath preheated at 110 °C. After the reaction (12 h), the mixture was filtered through a Celite pad, the solution was evaporated in vacuo, and the resultant solid was extracted with *n*-hexane (ca. 80 mL) at room temperature. The extract was concentrated and placed in the freezer (−30 °C). The pale yellow microcrystals were collected as the first crop (602 mg) from the chilled solution. Yield: 78%. ^1H NMR ($CDCl_3$): δ 7.01 (d, $J = 7.6$ Hz, 2H, phenyl), 6.88 (t, $J = 8.0$ Hz, 1H, phenyl), 2.12 (s, 6H, CH_3−phenyl), 1.86 (s, 15H, C_5Me_5), 0.22 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 155.7, 131.9, 130.2, 128.2, 124.1, 21.3 (Cp*), 12.9 (CH_3−Ph), 3.7 ($SiMe_3$). Anal. Calcd for $C_{21}H_{33}Cl_2NSiTi$: C, 56.51; H, 7.45; N, 3.14. Found (1): C, 57.05; H, 7.70; N, 3.30. Found (2): C, 57.06; H, 7.35; N, 3.51.

Synthesis of $(1,3\text{-}Me_2C_5H_3)TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (8b). Into a sealed tube equipped with a Kontes three-way bulb was added $(1,3\text{-}Me_2C_5H_3)TiCl_3$ (100 mg, 0.404 mmol) in toluene (10 mL) in the drybox. $LiN(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (1.0 equiv with respect to titanium) was then added at −30 °C, and the reaction mixture was warmed slowly to room temperature and placed into an oil bath preheated at 50 °C. After the reaction (12 h), the mixture was filtered through a Celite pad, the solution was evaporated in vacuo, and the resultant solid was extracted with *n*-hexane (ca. 10 mL) at room temperature. The extract was concentrated to half-volume and placed in the freezer (−30 °C). The pale yellow microcrystals were collected as the first crop (105 mg) from the chilled solution. The second crop (30 mg) was collected from the chilled solution of the concentrated mother liquor. Yield: 83% (135 mg). ^1H NMR ($CDCl_3$): δ 7.07 (d, $J = 7.2$ Hz, 2H, phenyl), 6.94 (t, $J = 7.4$ Hz, 1H, phenyl), 6.02 (s, 1H, Cp), 5.49 (s, 2H, Cp), 2.26 (s, 6H, CH_3−phenyl), 2.17 (s, 15H, C_5Me_5), 0.28 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 159.3, 136.6, 128.4, 124.5, 123.0, 121.1, 20.6, 17.5, 2.8. Anal. Calcd. for $C_{18}H_{27}Cl_2NSiTi$: C, 53.48; H, 6.73; N, 3.46. Found: C, 53.16; H, 6.68; N, 3.63. $(1,3\text{-}Me_2C_5H_3)TiCl_3$ was prepared according to the procedures given in our previous paper.[5]

Synthesis of $CpTiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (8c). Into a round-bottom flask containing $CpTiCl_3$ (100 mg, 0.456 mmol) in toluene (10 mL) was added $LiN(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (91 mg, 0.456 mmol) at −30 °C. The stirred reaction mixture was warmed slowly to room temperature, and the mixture was then stirred for 12 h. The solution was then filtered through a Celite pad, and the filtrate was placed in a rotary evaporator to remove toluene. The resultant solid was extracted with *n*-hexane, and the chilled (−30 °C) concentrated solution gave the first crop as yellow needles. Yield: 126 mg (73%). ^1H NMR ($CDCl_3$): δ 7.08 (d, $J = 7.2$ Hz, 2H, phenyl), 6.95 (t, $J = 7.6$ Hz, 1H, phenyl), 6.30 (s, 5H, Cp), 2.16 (s, 6H, CH_3−phenyl), 0.31 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 160.0, 128.5, 128.1, 124.9, 121.1, 20.6, 2.7. Anal. Calcd for $C_{16}H_{23}Cl_2NSiTi$: C, 51.08; H, 6.16; N, 3.72. Found: C, 51.0; H, 5.96; N, 3.59.

Synthesis of $CpTiCl_2[N(2,6\text{-}Me_2C_6H_3)(Si^tBuMe_2)]$ (8d). The synthetic procedure for preparing **8d** was the same as that for **8c** from $CpTiCl_3$ (266 mg, 0.752 mmol), except that $LiN(2,6\text{-}Me_2C_6H_3)(Si^tBuMe_2)$ (1.0 equiv with respect to titanium; 320 mg was used in this case) was added in place of $LiN(2,6\text{-}Me_2C_6H_3)(SiMe_3)$. Orange microcrystals were collected from the chilled hexane solution. Yield: 81% (341 mg). ^1H NMR ($CDCl_3$): δ 7.06 (d, $J = 7.2$ Hz, 2H, phenyl), 6.96 (t, $J = 7.6$ Hz, 1H, phenyl), 6.25 (s, 5H, Cp), 2.23 (s, 6H, CH_3−phenyl), 0.74 (s, 6H, $SiMe_2{}^t\mathit{Bu}$), 0.31 (s, 9H, $Si\mathit{Me}_2{}^tBu$). ^{13}C NMR ($CDCl_3$): δ 158.9, 128.7, 128.4, 125.3, 121.6, 27.5, 22.8, 21.9, 0.3. Anal. Calcd for $C_{16}H_{23}Cl_2NSiTi$: C, 54.56; H, 6.99; N, 3.35. Found: C, 54.70; H, 6.85; N, 3.41.

Synthesis of $Cp^*ZrCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (9a). The synthesis of **9a** was according to the analogous procedure for the synthesis of $Cp^*ZrCl_2[N(2,6\text{-}{}^iPr_2C_6H_3)(SiMe_3)]$ reported by Roesky.[12] A round-bottom flask containing Cp^*ZrCl_3 (250 mg, 0.751 mmol) was cooled to −30 °C. $LiN(2.6\text{-}Me_2C_6H_3)(SiMe_3)$ (150 mg, 0.752 mmol) was then added and the reaction mixture was warmed to room temperature, and the solution was stirred for 24 h. The solvent was then removed in vacuo after the reaction, and the resultant solid was extracted with hexane at room temperature. The extract was concentrated to ca. 3 mL and was placed in the freezer (−30 °C). The pale yellow microcrystals were collected as the first crop (288 mg) from the chilled solution. Yield: 78%. ^1H NMR ($CDCl_3$): δ 7.02 (d, $J = 7.2$ Hz, 2H, phenyl), 6.84 (t, $J = 7.4$ Hz, 1H, phenyl), 2.17 (s, 6H, CH_3−phenyl), 1.82 (s, 15H, C_5Me_5), 0.21 (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ 150.0, 131.8, 128.4, 126.5, 123.1, 21.2 (Cp*), 11.6 (CH_3−Ph), 3.0 ($SiMe_3$).

Polymerization Procedures. Ethylene polymerizations were conducted in a 100 mL stainless steel autoclave. The typical reaction procedure (run 4, Table 2) is as follows.

Toluene (29.5 mL) and d-MAO solid (290 mg, prepared from ordinary MAO (Tosoh Finechem Co. PMAO-S) by removing toluene and $AlMe_3$) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm) and the autoclave was placed into an oil bath. **8a** (1.0 μmol) in toluene (0.5 mL) was then added into the autoclave, the reaction apparatus was immediately pressurized to 5 atm, and the mixture was magnetically stirred for 30 min. After the above procedure, the ethylene that remained 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. In polymerization by **8c**,**d** (runs 16−19), the EtOH solution was then added to chloroform. The chloroform extract was then washed with water and dried over Na_2SO_4. The solution was placed in a rotary evaporator, and the low-boiling compounds such as $CHCl_3$ and toluene were removed in vacuo. Polymerization of propylene was also performed in the same manner.

Polymerization of 1-hexene was performed as follows: 1-hexene (5 mL) and the prescribed amount of MAO were added to a round-bottom flask (25 mL) connected to three-way valves under N_2, and the polymerization was started by the addition of a toluene solution (2.5 mL) containing the catalyst (5.0 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 $CHCl_3$, and the extract 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 that remained were then removed in vacuo.

Crystallographic Analysis for 8b. The yellow prismatic microcrystal was grown from the concentrated hot hexane solution containing **8b** upon standing at room temperature in the drybox, and the structure could be determined if the measurement was done 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 6. All structures were solved by direct methods and expanded using Fourier techniques.[42] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. All calculations were performed using the teXsan[43] crystallographic software package of Molecular Structure Corp. Detailed results are described in the Supporting Information.

Table 6. Crystal and Data Collection Parameters for $(1,3\text{-}Me_2C_5H_3)TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (8b)[a]

formula	$C_{18}H_{27}Cl_2NSiTi$
fw	404.31
habits	yellow, prism
cryst size (mm)	0.80 × 0.80 × 0.33
cryst syst	triclinic
space group	$P\bar{1}$ (No. 2)
a (Å)	8.887(1)
b (Å)	10.298(2)
c (Å)	13.081(1)
α (deg)	94.823(6)
β (deg)	101.545(4)
γ (deg)	114.807(6)
V (Å^3)	1045.5(2)
Z	3
D_{calcd} (g/cm^3)	1.926
F_{000}	636.00
temp (K)	243
λ(Mo Kα) (Å)	0.71069
2θ range (deg)	4.4−54.7
no. of rflns measd: total; unique	9207; 4662
R_{int}	0.056
no. of observns ($I > -10.00\delta(I)$)	4662
no. of variables	208
residuals: R1; wR2	0.062; 0.172
GOF	2.21
max (min) peak in final diff map (e/Å^3)	0.40 (−0.47)

[a] Conditions: diffractometer, Rigaku RAXIS-RAPID imaging plate; structure solution, direct methods; refinement, full-matrix least squares; function minimized, $\sum w(F_o^2 - F_c^2)^2$; least-squares weights, $w = 1/\delta^2(F_o^2)$; p factor, 0.05.

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Supporting Information Available: Figures giving the ^{13}C NMR spectrum (in $CDCl_3$) for polypropylene prepared by the **8a**−MAO catalyst system (Table 3, run 17) and selected GPC traces for polyethylene summarized in Table 3 and tables giving detailed crystallographic analysis data for **8b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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