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Half-Titanocence Anilide Complexes $Cp'TiCl_2[N(2,6\text{-}R^1{}_2C_6H_3)R^2]$: Synthesis, Structures and Catalytic Properties for Ethylene Polymerization and Copolymerization with 1-Hexene

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A number of new half-sandwich titanium(IV) complexes of the type $[Cp'TiCl_2\{N(2,6\text{-}R^1{}_2C_6H_3)R^2\}]$ [R^1 = *i*Pr (**1**, **2**, **4**), Me (**3**, **5**); R^2 = Me (**1**, **3**, **4**, **5**), Bn (**2**); Cp′ = Cp (**1**, **2**, **3**), Cp* (**4**, **5**)] have been synthesized by the reaction of $[Cp'TiCl_3]$ with the lithium salts of the corresponding anilide in toluene or diethyl ether. All titanium complexes were characterized by ^1H and ^{13}C NMR spectroscopy and elemental analyses. The molecular structures of complexes **1**, **4**, and **5** were determined by single-crystal X-ray diffraction analysis. When activated with $Al\textit{i}Bu_3$ and $Ph_3CB(C_6F_5)_4$, complexes **1**–**5** exhibited reasonable catalytic activity in ethylene polymerization, producing high- or ultra-high-molecular-weight polyethylene. It was found that complex **4** shows the highest catalytic activity in ethylene polymerization and complexes **1**–**3** produced ultra-high-molecular-weight ($M_\eta > 3\times10^6\,g\,mol^{-1}$, viscosity-average molecular weight) polyethylene. The copolymerization of ethylene with 1-hexene catalyzed by these complexes in the presence of $Al\textit{i}Bu_3/Ph_3CB(C_6F_5)_4$ was also investigated. Complexes **4** and **5** with the pentamethylcyclopentadienyl ligand were found to show higher catalytic activity in ethylene/1-hexene copolymerization and produced poly(ethylene-co-1-hexene)s with much higher molecular weights and co-monomer incorporation than their cyclopentadienyl analogues **1**–**3** under similar conditions. The co-monomer incorporation abilities of complexes **4** and **5** are relatively high in comparison with other half-sandwich titanium catalyst systems.

Introduction

Group 4 metallocene catalysts have attracted intense interest in recent decades due to their unique properties and advantages as olefin polymerization catalysts.[1–6] Much research effort has been focused on the development of new homogeneous metallocene catalysts for producing a variety of high-performance polyolefin materials and understanding the relationship between the structure and catalytic properties of a given catalyst with respect to polymer chain composition and architecture.[7–10] In particular, a large number of new metallocene catalysts have been developed for the copolymerization of ethylene with α-olefins,[11] cycloolefins,[12] dienes,[13] and polar monomers.[14] Several metallocenes are known to be good catalysts for the copolymerization of different olefins. The *ansa*-zirconocene complex $[Ph_2C(Cp)(Flu)ZrCl_2]$[15] in combination with $(Me_2PhNH)[B(C_6F_5)_4]/Al\textit{i}Bu_3$ has been reported to produce ethylene/1-hexene random copolymers with high molecular weights. Constrained geometry titanium complexes (CGC)[2,3,16] have been found to exhibit excellent catalytic performance in the copolymerization of ethylene with a variety of co-monomers. The so-called PHENICS complexes[17] (phenoxy-induced complex of Sumitomo) have also been reported to be good catalysts in ethylene copolymerization with α-olefins. Nonbridged (cyclopentadienyl)(aryloxy)titanium catalyst systems[18] have also been systematically studied by Nomura and co-workers and been found to show good catalytic activity and efficient co-monomer incorporation in ethylene/α-olefin copolymerization. Similar nonbridged half-sandwich catalysts, (cyclopentadienyl)(amide)titanium complexes $[Cp'TiCl_2(NR^1R^2)]$ (R^1, R^2 = alkyl)[19] and (cyclopentadienyl)(anilide)titanium complexes $[Cp'TiCl_2\{N(2,6\text{-}R^1{}_2C_6H_3)R^2\}]$ (R^1 = Me, R^2 = $SiMe_3$ or $Si\textit{t}BuMe_2$)[20] have also been synthesized and explored as catalysts for ethylene polymerization and copolymerization with 1-hexene. The results indicated that the (cyclopentadienyl)(anilide)titanium complexes exhibit extremely low catalytic activity and co-monomer incorporation ability in ethylene/1-hexene copolymerization upon activation with methylaluminoxane (MAO). From a structural point of view, this type of catalyst may show similar catalytic performance to the nonbridged (cyclopentadienyl)(aryloxy)titanium catalyst systems. In view of the very limited research carried out on this type of complex in olefin polymerization, especially in ethylene/α-olefin copolymerization, it is of interest to develop more titanium(IV) complexes of this type with a less bulky anilide ligand and explore their catalytic performance in ethylene/α-olefin copo-

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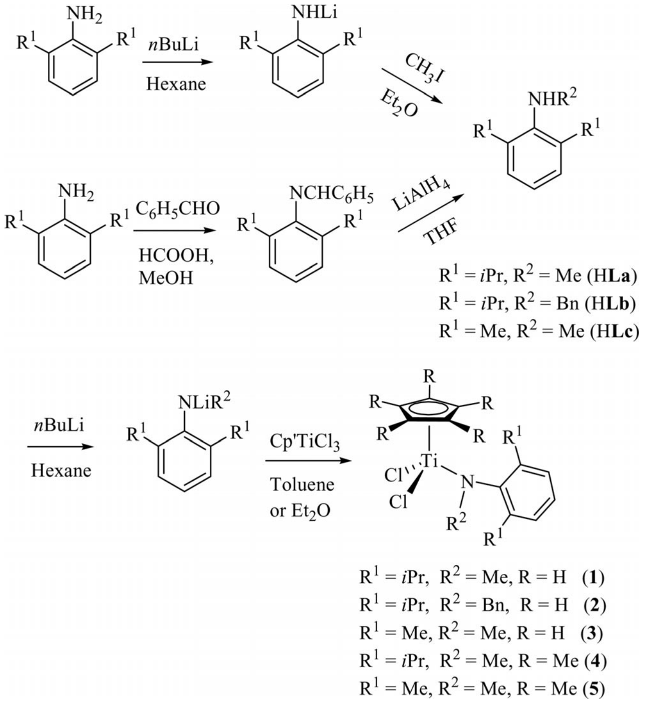
lymerization. We have recently synthesized a number of new titanium(IV) complexes of the type [Cp′TiCl$_2${N(2,6-R^1$_2$C$_6$H$_3$)R^2}] [R^1 = *i*Pr (**1**, **2**, **4**), Me (**3**, **5**); R^2 = Me (**1**, **3**, **4**, **5**), Bn (**2**); Cp′ = Cp (**1**, **2**, **3**), Cp* (**4**, **5**)] and found that they show good catalytic activity in ethylene/1-hexene copolymerization and produce high-molecular-weight poly(ethylene-*co*-1-hexene)s with high co-monomer incorporation. In this paper we report the synthesis and characterization of these complexes and their catalytic performance in ethylene polymerization and ethylene/1-hexene copolymerization.

Results and Discussion

Synthesis and Characterization of the New Complexes

The free ligands HN(2,6-R^1$_2$C$_6$H$_3$)Me [R^1 = *i*Pr (H**La**), Me (H**Lc**)] were synthesized in high yields (>85%) from the reaction of CH$_3$I with the corresponding lithium 2,6-R^1$_2$-anilide following a modified literature procedure[21] reported for the preparation of *N*,*N*′-disilyl-*o*-phenylenediamine. The lithium 2,6-R^1$_2$-anilide salts were obtained from the reaction of the corresponding 2,6-R^1$_2$-aniline with *n*BuLi. The free ligand HN(2,6-*i*Pr$_2$C$_6$H$_3$)Bn (H**Lb**) was synthesized in about 80% yield by a two-step procedure, a condensation reaction of benzaldehyde with 2,6-diisopropylaniline followed by reduction of the Schiff base formed with LiAlH$_4$. Complexes **1**–**5** were synthesized from the reactions of LiN(2,6-R^1$_2$C$_6$H$_3$)R^2 [R^1 = *i*Pr, R^2 = Me (Li**La**), Bn (Li**Lb**); R^1 = Me, R^2 = Me (Li**Lc**)] with [Cp′TiCl$_3$] (Cp′ = Cp, Cp*) in moderate yields (45–61%; Scheme 1). With the exception of complex [CpTiCl$_2${N(2,6-Me$_2$C$_6$H$_3$)Me}] (**3**), all the other complexes were synthesized in toluene at 50 °C. It was found that both higher and lower reaction temperatures led to lower yields. Complexes [CpTiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)Me}] (**1**) and [CpTiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)Bn}] (**2**) with a Cp ligand can be obtained in higher yields than complexes [Cp*TiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)-Me}] (**4**) and [Cp*TiCl$_2${N(2,6-Me$_2$C$_6$H$_3$)Me}] (**5**) with a Cp* ligand. To obtain complexes **4** and **5** in good yields, it was necessary to perform the reaction of [Cp*TiCl$_3$] with 1.3 equiv. of Li**La** or Li**Lc** in toluene at 50 °C for about 20 h. A longer reaction time led to a decrease in the reaction yield probably due to a gradual decomposition of these complexes under the reaction conditions. It was difficult to obtain complex **3** in reasonable yield in toluene. Fortunately, the reaction of [CpTiCl$_3$] with 1 equiv. of Li**Lc** in diethyl ether at room temperature gave complex **3** in a relatively good yield. In addition, attempts to synthesize complex [Cp*TiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)Bn}] by the reaction of [Cp*TiCl$_3$] with Li**Lb** in both toluene and diethyl ether were unsuccessful. It was found that the reaction does not proceed at low temperatures whereas an unidentifiable polymeric product was formed at high temperatures.



Scheme 1. Synthesis of complexes **1**–**5**.

The new titanium complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy along with elemental analyses. The ^{1}H NMR spectra of complexes **1**, **2**, and **4** show two sets of doublets for the methyl protons of the *i*Pr group in ligand **La** or **Lb** and the ^{13}C NMR spectra of these complexes show two signals for the two methyl groups of the *i*Pr group, which indicates that the rotation of the 2,6-*i*Pr$_2$C$_6$H$_3$ group about the N–C bond is restricted in these complexes,[22,23] in contrast to similar aryl oxide complexes [Cp′TiCl$_2$(O-2,6-*i*Pr$_2$C$_6$H$_3$)]; it has been reported that only one doublet for the methyl protons of the *i*Pr group is observed in the ^{1}H NMR spectra of the aryl oxide complexes.[18a,24] In comparison with the corresponding signals of the free ligand H**La**, the signals observed for the methine protons of the *i*Pr group in complexes **1** and **4** are shifted upfield from 3.33 to 2.83–2.89 ppm, whereas the signals of the NCH$_3$ protons in both complexes are significantly shifted downfield from 2.79 to 3.95–4.18 ppm. Similar phenomena were also observed for the corresponding signals in complexes **2**, **3**, and **5**. The resonance of the methylene protons of the NCH_2Ph group in complex **2** is even shifted 2 ppm downfield from 4.10 to 6.10 ppm. The ^{1}H and ^{13}C NMR spectroscopic analyses of these complexes confirm that the anilide ligand is attached to the titanium metal center of these complexes.

Crystal Structures of Complexes 1, 4, and 5

The molecular structures of complexes **1**, **4**, and **5** were determined by single-crystal X-ray diffraction analysis. The ORTEP drawings of their molecular structures together with data of selected bond lengths and angles are given in Figures 1, 2, and 3, respectively. Complex **4** crystallizes with four independent molecules in the unit cell. Because there are slight differences in these molecules, only one molecular

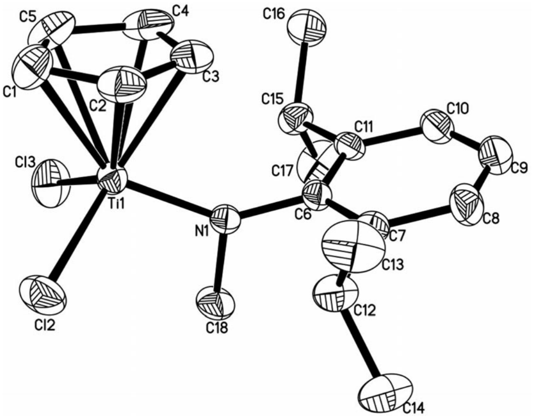


Figure 1. Molecular structure of complex **1**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.867(3), Ti(1)–Cp(cent) 2.020, Ti(1)–Cl(1) 2.2754(12), Ti(1)–Cl(2) 2.2751(12), Cl(1)–Ti(1)–Cl(2) 105.22(5), N(1)–Ti(1)–Cl(1) 103.21(8), N(1)–Ti(1)–Cl(2) 104.26(8), C(6)–N(1)–Ti(1) 141.4(2), Cp(cent)–Ti(1)–Cl(1) 115.7, Cp(cent)–Ti(1)–Cl(2) 113.8, Cp(cent)–Ti(1)–N(1) 113.4.

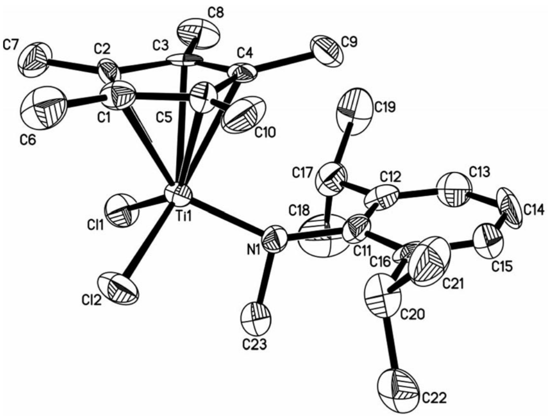


Figure 2. Molecular structure of complex **4**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.874(8), Ti(1)–Cp(cent) 2.047, Ti(1)–Cl(1) 2.285(3), Ti(1)–Cl(2) 2.286(3), Cl(1)–Ti(1)–Cl(2) 104.91(12), N(1)–Ti(1)–Cl(1) 102.5(3), N(1)–Ti(1)–Cl(2) 101.9(3), C(11)–N(1)–Ti(1) 147.1(7), Cp(cent)–Ti(1)–Cl(1) 113.1, Cp(cent)–Ti(1)–Cl(2) 113.2, Cp(cent)–Ti(1)–N(1) 119.5.

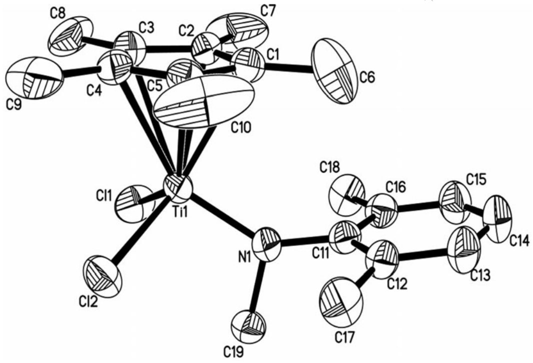


Figure 3. Molecular structure of complex **5**. Thermal ellipsoids are shown at the 30% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ti(1)–N(1) 1.878(6), Ti(1)–Cp(cent) 2.053, Ti(1)–Cl(1) 2.284(3), Ti(1)–Cl(2) 2.278(2), Cl(1)–Ti(1)–Cl(2) 102.74(10), N(1)–Ti(1)–Cl(1) 101.99(19), N(1)–Ti(1)–Cl(2) 102.21(18), C(11)–N(1)–Ti(1) 142.4(4), Cp(cent)–Ti(1)–Cl(1) 113.8, Cp(cent)–Ti(1)–Cl(2) 114.8, Cp(cent)–Ti(1)–N(1) 119.3.

structure is chosen for discussion. The structural analyses reveal that complexes **1**, **4**, and **5** all have a pseudo-octahedral coordination environment in their solid-state structures and adopt a three-legged piano stool geometry with the anilide N atom and the two Cl atoms being the three legs and the Cp or Cp* ring being the seat. The aryl ring in the anilide ligand in these complexes is almost parallel to the Cp or Cp* ring with the N–Me group directed away from the cyclopentadienyl ring. A symmetry plane consisting of the Ti atom and the N and C atoms of the N–Me unit is nearly perpendicular to the plane of the cyclopentadienyl ring. The Ti–N distances of complexes **1** (1.867 Å), **4** (1.874 Å), and **5** (1.878 Å) are shorter than that reported for $[(1,3\text{-}Me_2C_5H_3)\{N(2,6\text{-}Me_2C_6H_3)(SiMe_3)\}TiCl_2]$ (1.898 Å).[20] The Ti–N distances in these complexes are all shorter than the estimated value (2.02 Å) for a Ti–N single bond according to Pauling's covalent radii,[25] which demonstrates that they have Ti=N double-bond character. The average Ti–Cl distances in complexes **1** (2.275 Å), **4** (2.285 Å), and **5** (2.281 Å) are similar to those reported for $[(1,3\text{-}Me_2C_5H_3)\{N(2,6\text{-}Me_2C_6H_3)(SiMe_3)\}TiCl_2]$ (2.266–2.277 Å).[20] The Cp′(cent)–Ti distance in complex **1** (2.020 Å) is shorter than the corresponding values in complexes **4** (2.047 Å) and **5** (2.053 Å), which can be related to the steric effect of the Cp′ ring. For the same reason, the Cp(cent)–Ti–N angle in complex **1** (113.4°) is significantly smaller than those in complexes **4** (119.5°) and **5** (119.3°). The Cl(1)–Ti–Cl(2) angle in complex **5** (102.74°) is smaller than those in complexes **1** (105.22°) and **4** (104.91°). It is clear that the larger Cl(1)–Ti–Cl(2) angles in complexes **1** and **4** should be mainly caused by the bulky $Me(2,6\text{-}i\text{Pr}_2C_6H_3)N$ ligand. The average value of the Cl–Ti–N angles in complex **1** (103.73°) is slightly larger than those in complexes **4** (102.20°) and **5** (102.10°). Owing to the relatively large mutual repulsion between the Cp* and $Me(2,6\text{-}i\text{Pr}_2C_6H_3)N$ ligands, the Ti–N–C(phenyl) angle in complex **4** (147.1°) is significantly larger than those in complexes **1** (141.4°) and **5** (142.4°). The Ti–N–C(phenyl) angles in these complexes are much larger than the reported value for $[(1,3\text{-}Me_2C_5H_3)\{N(2,6\text{-}Me_2C_6H_3)(SiMe_3)\}TiCl_2]$ (111.6°).[20] As mentioned above, the aryl ring in the anilide ligand in these complexes is nearly parallel to the Cp′ ring with the angle between the Cp′ and aryl rings being 13.2, 4.0, and 9.8° for complexes **1**, **4**, and **5**, respectively.

Ethylene Polymerization

Ethylene polymerizations using complexes **1**–**5** as precatalysts under different conditions were examined and the results are summarized in Table 1. When activated with

Table 1. Data for the ethylene polymerizations catalyzed by the **1**–**6**/Al*i*Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ and **4**,**5**/MAO systems.[a]

Run	Catalyst	Temperature [°C]	Al/Ti mol ratio	Yield [g]	Activity[b]	$M_\eta \times 10^{-4}$[c]	T_m[d] [°C]
1	**1**[e]	20	200	0.316	316	371.5	137.9
2	**1**[e]	35	200	0.330	330	105.5	136.5
3	**2**[e]	20	200	0.340	340	383.5	137.7
4	**2**[e]	35	200	0.354	354	138.8	136.9
5	**3**[e]	20	200	0.220	220	325.4	136.8
6	**3**[e]	35	200	0.231	231	103.3	136.4
7	**4**	20	200	0.926	1852	94.1	138.9
8	**4**	35	200	0.987	1974	70.6	138.1
9	**4**	50	200	0.635	1270	55.9	139.0
10	**4**	35	300	0.846	1692	83.5	139.5
11	**4**	35	400	0.797	1594	68.3	140.1
12	**5**	20	200	0.903	1806	96.8	139.3
13	**5**	35	200	0.962	1924	82.1	139.0
14	**5**	35	300	0.928	1856	58.4	137.9
15	**6**	35	200	0.805	1610	50.6	137.8
16[f]	**4**	35	2000	0.370	740	60.4	137.2
17[f]	**4**	35	4000	0.424	848	57.6	137.4
18[f]	**5**	35	2000	0.307	614	49.3	136.8
19[f]	**5**	35	4000	0.344	688	45.4	137.1

[a] Polymerization conditions: 70 mL toluene, 2×10^{-6} mol catalyst, 1.5 B/Ti molar ratio, 15 min, 5 bar ethylene pressure. [b] Activity in kg PE (mol Ti)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}. The data from the second scans have been used. [e] 4×10^{-6} mol. [f] MAO was used instead of Al*i*Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ as co-catalyst.

MAO, complexes **4** and **5** showed relatively low catalytic activity, which is in agreement with the results reported previously for similar complexes.[24,26] However, upon activation with Al*i*Bu$_3$ and Ph$_3$CB(C$_6$F$_5$)$_4$, complexes **1**–**5** all exhibited moderate catalytic activity in the ethylene polymerization reaction. Under similar conditions, the catalytic activity decreased in the order **4** > **5** >> **2** > **1** > **3**, which indicates that the catalytic activities of these complexes are significantly influenced by the nature of the substituents on both the Cp′ and anilide ligands. As is known for group 4 metallocene catalysts, electron-donating substituents on the ligands stabilize the catalytically active cationic species during the polymerization and improve the catalytic activity of the catalyst,[24] which explains the above experimental results well. On the other hand, bulky Cp′ and anilide ligands would weaken the interaction between the catalytically active cationic species and the anionic co-catalyst[27] and therefore could increase the catalytic activity of the complex too, which is in agreement with the observed experimental results. The fact that the catalytic activity of complex **2** with a bulkier but less electron-donating **Lb** ligand is higher than the catalytic activity of complex **1** with a less bulky but more electron-donating **La** ligand further demonstrates the steric effects of the ligands. As observed in other olefin polymerization catalyst systems, the catalytic activities of these titanium catalyst systems are dependent on the Al/Ti molar ratio. Maximal catalytic activities were obtained at Al/Ti molar ratios of about 200. The catalytic activities of these catalyst systems were also examined at different polymerization temperatures with the maximal values being observed at around 35 °C. These observations are similar to those reported previously for related [Cp′TiCl$_2$(NR^{1}R^2)] catalyst systems.[19] The molecular weight of the resultant polyethylene was found to be remarkably dependent on the structure of the catalyst. It is interesting that the molecular weights of the polyethylenes produced by the Cp-based catalysts **1**–**3** are much higher than those obtained with the bulky Cp*-based complexes **4** and **5**. Usually, high-molecular-weight polyethylenes are produced by catalysts with bulky ligands due to the relatively large steric hindrance of the ligands in the chain-transfer reaction.[28] The reason why the Cp-based catalysts **1**–**3** produce ultra-high-molecule-weight polyethylene (up to 380×10^4 g mol^{-1}) is not very clear. It is possible that the relatively strong interaction between the cationic catalyst and the anionic co-catalyst in these Cp-based catalyst systems means that the catalyst possesses a bulky environment around the metal center and thus decelerates the chain-transfer reaction. Similar results have also been reported for other half-sandwich titanium(IV) catalyst systems.[26] The influence of the Al/Ti molar ratio and the polymerization temperature on the polymer molecular weight was also investigated. As expected, the molecular weight of the polyethylene obtained decreases with an increase in Al/Ti molar ratio and a rise in polymerization temperature due to acceleration of both the chain-transfer reaction to alkylaluminium and the β-hydride elimination reaction. In addition, the melting temperature of the resultant polyethylene (136–141 °C) is in the normal range for linear polyethylene.

Copolymerization of Ethylene with 1-Hexene

The copolymerization reactions of ethylene with 1-hexene using complexes **1**–**5** as catalysts activated with Al*i*Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ or MAO (for complexes **4** and **5**) were explored and the copolymerization results are summarized in Table 2. As reported previously for similar complexes,[19,24,26] when activated with MAO, complexes **4** and **5** both showed relatively low catalytic activity and co-

Table 2. Data for the ethylene/1-hexene copolymerization reactions catalyzed by the **1**–**6**/Al*i*Bu_3/$Ph_3CB(C_6F_5)_4$ and **4**,**5**/MAO systems.[a]

Run	Catalyst	1-Hexene [$mol\,L^{-1}$]	Yield [g]	Activity[b]	1-Hexene content[c] [mol-%]	$M_w \times 10^{-4}$[d]	M_w/M_n[d]
20	**1**[e]	0.5	0.135	135	6.0	16.09	3.61
21	**1**[e]	1.0	0.163	163	7.8	15.37	3.35
22	**1**[e]	1.5	0.142	142	9.7	15.72	3.41
23	**2**[e]	0.5	0.145	145	6.4	16.25	3.68
24	**2**[e]	1.0	0.174	174	8.4	12.22	3.75
25	**2**[e]	1.5	0.152	152	10.0	10.42	3.62
26	**3**[e]	0.5	0.092	92	5.4	13.51	3.57
27	**3**[e]	1.0	0.110	110	7.0	11.52	3.46
28	**3**[e]	1.5	0.072	72	8.7	10.04	3.53
29	**4**	0.5	1.682	3364	18.4	26.33	2.42
30	**4**	1.0	2.331	4662	25.4	20.00	2.20
31	**4**	1.5	1.804	3608	31.8	20.14	2.55
32	**5**	0.5	0.778	1556	19.0	22.50	3.36
33	**5**	1.0	1.358	2716	28.4	20.45	3.33
34	**5**	1.5	0.805	1610	35.9	17.45	3.31
35	**6**	1.0	1.046	2092	47.9	10.10	4.63
36[f]	**4**	1.0	trace	–	–	–	–
37[g]	**4**	1.0	0.271	542	8.9	0.61	1.49
38[f]	**5**	1.0	trace	–	–	–	–
39[g]	**5**	1.0	0.225	450	9.4	0.59	1.62

[a] Polymerization conditions: total 70 mL of toluene + 1-hexene, 2×10^{-6} mol catalyst, 200 Al/Ti molar ratio, 1.5 B/Ti molar ratio, 15 min, 35 °C, 5 bar ethylene pressure. [b] Activity in kg polymer (mol Ti)$^{-1}$ h^{-1}. [c] Calculated based on ^{13}C NMR spectra. [d] Measured by GPC analysis. [e] 4×10^{-6} mol. [f] MAO was used as co-catalyst, 2000 Al/Ti molar ratio. [g] MAO was used as co-catalyst, 4000 Al/Ti molar ratio.

monomer incorporation ability. However, upon activation with Al*i*Bu_3/$Ph_3CB(C_6F_5)_4$ co-catalyst, complexes **1**–**5** all exhibited high catalytic activity and comonomer incorporation ability for the copolymerization reaction. In addition, the MAO-activated systems produced copolymers with low molecular weights and narrow molecular weight distributions. The reason for the poor catalytic performances of the MAO-activated systems is not clear. The above-mentioned feature of producing copolymers with low co-monomer incorporation, low molecular weights, and narrow molecular weight distributions seems to indicate that the coordination environment around the metal center in the catalyst cation/co-catalyst anion pair formed in the MAO-activated systems is too bulky to catalyze the copolymerization reaction efficiently. In the Al*i*Bu_3/$Ph_3CB(C_6F_5)_4$-activated systems, the catalytic activities of these complexes in the ethylene/1-hexene copolymerization under similar conditions changes in the same order as observed in the ethylene homopolymerization reaction: **4** > **5** >> **2** > **1** > **3**. Note that the catalytic activities of complexes **4** and **5** in the copolymerization reaction are significantly higher than those in the homopolymerization reaction whereas complexes **1**–**3** showed slightly lower catalytic activity in the copolymerization than in the homopolymerization reaction. Except for the electronic effects discussed above for the ethylene homopolymerization, it seems that the steric effect of the ligands in these complexes on their catalytic activity in the copolymerization reaction is clearly important. The relatively weak interaction between the cationic catalyst and the anionic co-catalyst[27] in the Cp*-based catalyst systems would favor the coordination and insertion of the olefins, whereas the strong interaction between the cationic catalyst and the anionic co-catalyst in the Cp-based catalyst systems would slow down the coordination and insertion of the olefins, especially the bulky 1-hexene. Similar results have previously been observed in the ethylene/1-hexene copolymerization reaction with other half-sandwich titanium(IV) catalyst systems.[29] In addition, a co-monomer effect was clearly observed for the catalyst systems **4** and **5**. As can be seen from Table 2, the catalytic activities of complexes **4** and **5** in the copolymerization reaction increase with an increase in the 1-hexene feed concentration and reach the maximal value with a 1-hexene feed concentration of about 1.0 mol L^{-1}.

The poly(ethylene-*co*-1-hexene)s obtained were analyzed by ^{13}C NMR and GPC. The ^{13}C NMR spectra of typical copolymer samples are shown in Figure 4. Based on the ^{13}C NMR analysis,[30] the co-monomer contents of the poly(ethylene-*co*-1-hexene)s were calculated and the data are presented in Table 2. It can be seen from the data that the Cp*-based complexes **4** and **5** show remarkably higher co-monomer incorporation ability than the Cp-based complexes **1**–**3** under the same conditions. A similar high co-monomer incorporation ability of the Cp*-based complexes has also been observed for the nonbridged (cyclopentadienyl)(aryloxy)titanium catalyst systems.[29a] In contrast to the high co-monomer incorporation ability of complexes **4** and **5**, the similar complex $[Cp^*TiCl_2\{N(2,6\text{-}Me_2C_6H_3)(SiMe_3)\}]$ (**6**) has been reported to show very low co-monomer incorporation ability in the ethylene/1-hexene copolymerization when activated with MAO.[19a,20] To compare the catalytic properties of these complexes under similar conditions, the known complex **6** was synthesized according to a literature procedure[20] and the ethylene/1-hexene copolymerization catalyzed with **6**/Al*i*Bu_3/$Ph_3CB(C_6F_5)_4$ catalyst system was investigated. The copolymerization results show that the co-monomer incorporation ability of complex **6** is very good (see Figure 5) and even higher than that of complexes **4** and **5** under the same conditions, although its cata-

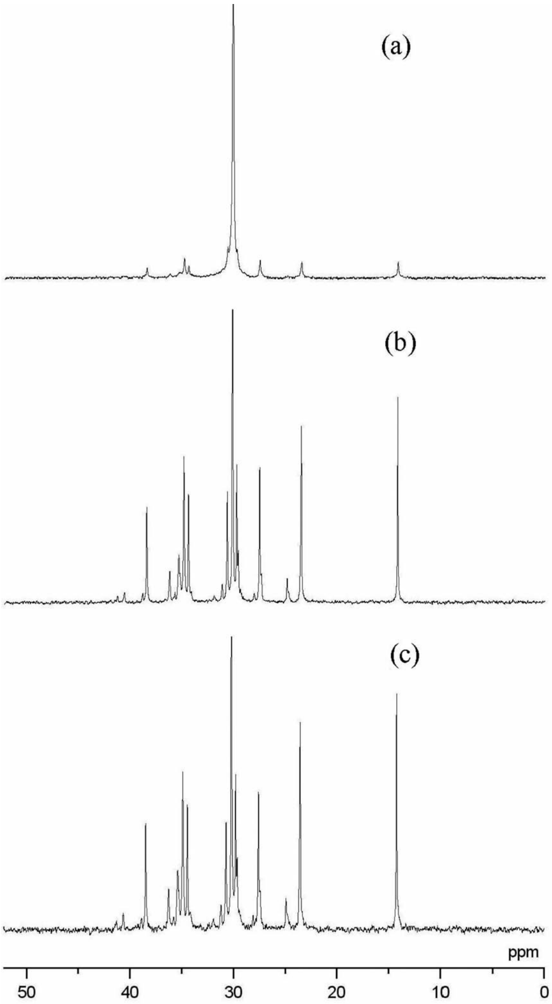


Figure 4. ^{13}C NMR spectra of poly(ethylene-*co*-1-hexene)s obtained with (a) complex **2** (run 25); (b) complex **4** (run 31), and (c) complex **5** (run 34) under similar polymerization conditions.

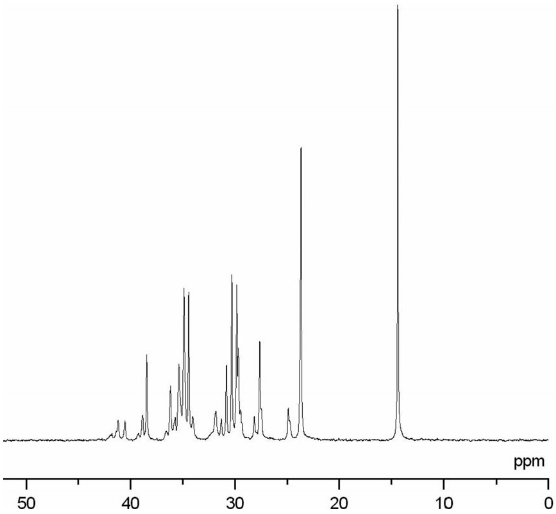


Figure 5. ^{13}C NMR spectrum of a poly(ethylene-*co*-1-hexene) sample obtained with complex **6** (run 35).

lytic activity is somewhat lower than those of **4** and **5**. The clearly higher co-monomer incorporation ability of the **6**/Al*i*Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system in comparison with that of the **5**/Al*i*Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ catalyst system indicates that the co-monomer incorporation ability of these catalysts could be further improved by changing the R^2 group on the anilide N atom. Table 3 summarizes the monomer sequence distribution and the r_Er_H values for typical poly(ethylene-*co*-1-hexene) samples estimated on the basis of ^{13}C NMR spectroscopy.[30] The calculated r_Er_H values of 0.39–0.55 are similar to those obtained in the nonbridged (cyclopentadienyl)(aryloxy)titanium catalyst systems,[18b] which indicates that 1-hexene incorporation in the present system does not proceed in a random manner as observed in the constrained geometry catalyst systems.[31] GPC analysis revealed that the poly(ethylene-*co*-1-hexene)s produced by these catalysts possess relatively high molecular weights (M_w = 10–26 × 10^4 g mol^{-1}). As reported previously for the nonbridged (cyclopentadienyl)(aryloxy)titanium catalyst systems,[18,32] the molecular weights of the copolymers are clearly dependent on the structure of the catalyst and the co-monomer content. The molecular weight distributions are basically unimodal and narrow, a characteristic of metallocene polyolefins.

Conclusions

A number of half-sandwich titanium(IV) complexes bearing an anilide ligand of general formula [Cp′TiCl$_2${N(2,6-R$^1_2$C$_6$H$_3$)R^2}] have been synthesized in moderate yields from the reaction of [Cp′TiCl$_3$] with the corresponding lithium anilide (Cp′ = cyclopentadienyl and

Table 3. Monomer sequence distributions for poly(ethylene-co-1-hexene)s obtained with the **1**–**6**/Al*i*Bu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ systems.[a]

Run	Cat.	1-Hexene content [mol-%][b]	Triads[c] [%]						Dyads[d] [%]			r_Er_H[e]
			EEE	EEH + HEE	HEH	EHE	EHH + HHE	HHH	EE	EH + HE	HH	
22	**1**	9.7	76.3	8.5	0.8	14.4	trace	trace	80.6	19.4	trace	–
25	**2**	10.0	76.4	8.5	trace	14.0	1.1	trace	80.6	18.8	0.6	0.547
28	**3**	8.7	79.3	6.6	trace	14.1	trace	trace	82.6	17.4	trace	–
29	**4**	18.4	61.0	8.4	1.4	26.8	0.8	1.6	65.2	32.8	2.0	0.485
31	**4**	31.8	31.3	22.5	6.2	30.1	7.7	2.3	42.5	51.4	6.1	0.393
34	**5**	35.9	26.6	20.7	3.0	35.9	10.2	3.6	37.0	54.3	8.7	0.437
35	**6**	47.9	10.3	18.5	3.7	41.5	21.0	5.0	19.6	65.0	15.5	0.288

[a] Polymerization conditions: see Table 2. [b] 1-Hexene content in mol-% estimated on the basis of the ^{13}C NMR spectra. [c] Calculated by analysis of the ^{13}C NMR spectra. [d] [EE] = [EEE] + ½[EEH + HEE], [EH + HE] = [HEH] + [EHE] + ½([EEH + HEE] + [HHE + EHH]), [HH] = [HHH] + ½[HHE + EHH]. [e] r_Er_H = 4[EE][HH]/[EH + HE]^2.

pentamethylcyclopentadienyl). These titanium complexes were all characterized by ^1H and ^{13}C NMR spectroscopy, as well as by elemental analyses. The molecular structures of complexes **1**, **4**, and **5** were confirmed by X-ray crystallography. Upon activation with Al*i*Bu$_3$/$Ph_3CB(C_6F_5)_4$, complexes **1**–**5** exhibited moderate catalytic activity in ethylene polymerization, producing high- or ultra-high-molecular-weight polyethylene. Complexes **1**–**5** also showed good catalytic activity in ethylene/1-hexene copolymerization in the presence of Al*i*Bu$_3$/$Ph_3CB(C_6F_5)_4$, producing high-molecular-weight poly(ethylene-*co*-1-hexene)s with moderate-to-high co-monomer incorporation. The catalytic activities of complexes **1**–**5** in both ethylene polymerization and ethylene/1-hexene copolymerization under similar conditions decrease in the order **4** > **5** >> **2** > **1** > **3**. Complexes **4** and **5** with a pentamethylcyclopentadienyl ligand exhibit markedly higher catalytic activity and co-monomer incorporation ability than complexes **1**–**3** with a less bulky cyclopentadienyl ligand.

Experimental Section

General: All manipulations involving air- and/or moisture-sensitive compounds were carried out under nitrogen (ultra-high purity) using either standard Schlenk or glove-box techniques. Toluene, diethyl ether, THF, and *n*-hexane were distilled under nitrogen in the presence of sodium and benzophenone. CH_2Cl_2 and 1-hexene were purified by distilling over calcium hydride before use. [CpTiCl$_3$], [Cp*TiCl$_3$],[33] and $Ph_3CB(C_6F_5)_4$[34] were prepared according to literature procedures. Polymerization-grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. Al*i*Bu$_3$, *n*BuLi, MAO, and $TiCl_4$ were purchased from Aldrich or Acros. ^1H and ^{13}C NMR spectra were recorded by using a Varian Mercury-300 NMR spectrometer. ^{13}C NMR spectra of the copolymers were recorded with a Varian Unity-400 NMR spectrometer at 125 °C with *o*-$C_6D_4Cl_2$ as the solvent. The molecular weights of the polyethylenes were measured in decahydronaphthalene at 135 °C by using a Ubbelohde viscometer according to the equation $[\eta] = 6.77 \times 10^{-4} M_\eta^{0.67}$. The molecular weights and molecular-weight distributions of the copolymer samples were measured with a PL-GPC 220 instrument at 140 °C with 1,2,4-trichlorobenzene as the solvent. The melting points of the polymers were measured by differential scanning calorimetry (DSC) with a NETZSCH DSC 204 instrument at a heating/cooling rate of 10 °C min^{-1} from 35 to 180 °C and the data from the second heating scans were used.

HN(2,6-*i*Pr$_2$C$_6$H$_3$)Me (HLa): A solution of *n*BuLi (18.0 mL, 1.60 M in *n*-hexane, 28.8 mmol) was added to a solution of 2,6-diisopropylaniline (5.00 mL, 26.5 mmol) in *n*-hexane (40 mL) at –20 °C. The reaction mixture was warmed to room temperature and stirred for 3 h. The precipitate was collected on a frit and washed with cold *n*-hexane. The obtained white lithium salt (4.62 g, 25.2 mmol) was dissolved in diethyl ether (40 mL) and added to a solution of CH_3I (1.73 mL, 27.7 mmol) in diethyl ether (20 mL) at –20 °C. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was then quenched with H_2O (40 mL). The organic phase was separated, dried with anhydrous $MgSO_4$, filtered, and concentrated by distillation under reduced pressure to give the product (4.34 g, 23.2 mmol, 88%) as a yellowish oil. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.06–7.18 (m, 3 H, Ar*H*), 3.33 [sept., $^3J_{H,H}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 3.00 (s, 1 H, N*H*), 2.79 (s, 3 H, NHC*H*$_3$), 1.30 [d, $^3J_{H,H}$ = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$] ppm.

HN(2,6-*i*Pr$_2$C$_6$H$_3$)Bn (HLb): 2,6-Diisopropylaniline (5.00 mL, 26.5 mmol) and benzaldehyde (2.70 mL, 26.5 mmol) were dissolved in methanol (20 mL). A catalytic amount of formic acid was added to the mixture. Then the reaction mixture was stirred and heated at reflux for 8 h. The mixture was then cooled to 0 °C to precipitate the Schiff base product as a yellow powder, which was collected on a frit, washed with cold methanol, and dried under vacuum to obtain the pure product (6.31 g, 23.9 mmol, 90%). The Schiff base was then dissolved in THF (50 mL). $LiAlH_4$ (0.91 g, 24.0 mmol) was slowly added to the solution at 0 °C. The mixture was warmed to room temperature and stirred overnight. The reaction was quenched with water (20 mL) and the insoluble solids were filtered off. Further H_2O (40 mL) was added to the filtrate and the product was extracted with diethyl ether (50 mL). The organic phase was separated, dried with anhydrous $MgSO_4$, filtered, and concentrated by distillation under reduced pressure to give the final product (5.65 g, 21.3 mmol, 89%) as a white powder. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.30–7.46 (m, 5 H, Ph*H*), 7.10–7.18 (m, 3 H, Ar*H*), 4.10 (s, 2 H, PhC*H*$_2$), 3.33 [sept., $^3J_{H,H}$ = 4.2 Hz, 2 H, C*H*(CH$_3$)$_2$], 1.25 [d, $^3J_{H,H}$ = 4.2 Hz, 12 H, CH(C*H*$_3$)] ppm.

HN(2,6-Me$_2$C$_6$H$_3$)Me (HLc): HN(2,6-Me$_2$C$_6$H$_3$)Me was synthesized by using a procedure identical to that used for the synthesis of HN(2,6-*i*Pr$_2$C$_6$H$_3$)Me with 2,6-dimethylaniline as the starting material. The pure product was obtained as a yellowish oil in a yield of 85%. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.02 (d, $^3J_{H,H}$ = 7.5 Hz, 2 H, Ar*H*), 6.85 (t, $^3J_{H,H}$ = 7.5 Hz, 1 H, Ar*H*), 3.03 (s, 1 H, N*H*), 2.81 (s, 3 H, NC*H*$_3$), 2.32 (s, 6 H, PhC*H*$_3$) ppm.

LiN(2,6-R$^1{}_2$C$_6$H$_3$)R^2: The lithium salts of the anilide ligands, LiN(2,6-R$^1{}_2$C$_6$H$_3$)R^2, were prepared according to the following typical procedure. A solution of *n*BuLi (1.60 M in *n*-hexane, 14.2 mL, 22.7 mmol) was slowly added to a solution of HN(2,6-*i*Pr$_2$C$_6$H$_3$)Me (4.34 g, 22.7 mmol) in *n*-hexane (15 mL) at –20 °C. A large amount of a white precipitate formed during the addition. The reaction mixture was warmed to room temperature and stirred for 4 h. The resultant precipitate was collected on a frit, washed with cold *n*-hexane (2 × 10 mL) and dried under vacuum to give the pure product (3.09 g, 15.7 mmol, 69%).

[CpTiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)Me}] (1): LiN(2,6-*i*Pr$_2$C$_6$H$_3$)Me (538 mg, 2.73 mmol) and [CpTiCl$_3$] (598 mg, 2.73 mmol) were mixed in toluene (40 mL) at –78 °C. The reaction mixture was warmed to room temperature first, then placed in an oil bath at 50 °C and stirred for 15 h. The precipitate was filtered off and the filtrate was concentrated to leave a reddish residue. Recrystallization from CH_2Cl_2/*n*-hexane gave pure **1** as orange crystals (622 mg, 1.66 mmol, 61%); m.p. 123.8–126.0 °C. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.18–7.32 (m, 3 H, Ar*H*), 6.46 (s, 5 H, Cp*H*), 4.18 (s, 3 H, NC*H*$_3$), 2.83 [sept., $^3J_{H,H}$ = 6.9 Hz, 2 H, C*H*(CH$_3$)$_2$], 1.36 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.15 [d, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ = 140.5, 127.4, 125.5, 124.3, 119.6, 48.2, 27.2, 26.5, 23.6 ppm. $C_{18}H_{25}Cl_2NTi$ (374.19): calcd. C 57.78, H 6.73, N 3.74; found C 57.56, H 6.69, N 3.72.

[CpTiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)Bn}] (2): Complex **2** was synthesized by using a procedure identical to that used for the synthesis of complex **1** with LiN(2,6-*i*Pr$_2$C$_6$H$_3$)Bn (740 mg, 2.71 mmol) and [CpTiCl$_3$] (594 mg, 2.71 mmol) as starting materials. Pure **2** (710 mg, 1.58 mmol, 58%) was obtained as orange crystals by recrystallization from CH_2Cl_2/*n*-hexane; m.p. 116.9–120.0 °C. ^1H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.20–7.52 (m, 8 H, Ar*H*), 6.70 (s, 5 H, Cp*H*), 6.10 (s, 2 H, PhCH_2), 2.82 [sept., $^3J_{H,H}$ = 6.6 Hz, 2 H, C*H*(CH_3)$_2$], 1.42 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH(CH_3)$_2$], 0.71 [d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ = 141.7, 136.9, 131.2, 128.2, 128.1, 127.4, 124.4, 122.2, 120.2, 59.2, 27.4, 25.2, 24.6 ppm. $C_{24}H_{29}Cl_2NTi$ (450.29): calcd. C 64.02, H 6.49, N 3.11; found C 64.34, H 6.54, N 3.06.

[CpTiCl$_2${N(2,6-Me$_2$C$_6$H$_3$)Me}] (3): LiN(2,6-Me$_2$C$_6$H$_3$)Me (385 mg, 2.73 mmol) and [CpTiCl$_3$] (598 mg, 2.73 mmol) were mixed in diethyl ether (40 mL) at –78 °C. The reaction mixture was warmed to room temperature and stirred overnight. The solvent was removed under reduced pressure and the residue was extracted with toluene (20 mL). The extraction was concentrated to leave a reddish residue. Recrystallization from CH_2Cl_2/*n*-hexane gave pure **3** as orange crystals (523 mg, 1.64 mmol, 60%); m.p. 100.5–103.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.06–7.20 (m, 3 H, Ar*H*), 6.39 (s, 5 H, Cp*H*), 4.09 (s, 3 H, NCH_3), 2.10 (s, 6 H, PhCH_3) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ = 130.0, 129.5, 128.8, 126.5, 119.7, 46.0, 17.6 ppm. $C_{14}H_{17}Cl_2NTi$ (318.09): calcd. C 52.87, H 5.39, N 4.40; found C 52.68, H 5.41, N 4.38.

[Cp*TiCl$_2${N(2,6-*i*Pr$_2$C$_6$H$_3$)Me}] (4): Complex **4** was synthesized by using a procedure identical to that used for the synthesis of complex **1** with LiN(2,6-*i*Pr$_2$C$_6$H$_3$)Me (513 mg, 2.60 mmol) and [Cp*TiCl$_3$] (579 mg, 2.00 mmol) as starting materials. Pure **4** (435 mg, 0.98 mmol, 49%) was obtained as orange crystals by recrystallization from CH_2Cl_2/*n*-hexane; m.p. 204.0–207.0 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.10–7.24 (m, 3 H, Ar*H*), 3.95 (s, 3 H, NCH_3), 2.89 [sept., $^3J_{H,H}$ = 6.5 Hz, 2 H, C*H*(CH_3)$_2$], 2.01 (s, 15 H, Cp*Me*$_5$), 1.34 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH(CH_3)$_2$], 1.10 [d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH(CH_3)$_2$] ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ = 153.3, 142.6, 130.4, 126.7, 123.8, 46.7, 27.1, 27.0, 23.9, 13.1 ppm. $C_{23}H_{35}Cl_2NTi$ (444.32): calcd. C 62.18, H 7.94, N 3.15; found C 62.46, H 7.98, N 3.13.

[Cp*TiCl$_2${N(2,6-Me$_2$C$_6$H$_3$)Me}] (5): Complex **5** was synthesized by using a procedure identical to that used for the synthesis of complex **1** with LiN(2,6-Me$_2$C$_6$H$_3$)Me (371 mg, 2.63 mmol) and [Cp*TiCl$_3$] (584 mg, 2.02 mmol) as starting materials. Pure **5** (388 mg, 0.91 mmol, 45%) was obtained as orange crystals by recrystallization from CH_2Cl_2/*n*-hexane; m.p. 140.2–143.2 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.00–7.18 (m, 3 H, Ar*H*), 3.83 (s, 3 H, NCH_3), 2.07 (s, 6 H, PhCH_3), 1.95 (s, 15 H, Cp*Me*$_5$) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz, 298 K): δ = 155.1, 131.3, 130.3, 128.2, 125.9, 44.7, 17.5, 12.8 ppm. $C_{19}H_{27}Cl_2NTi$ (388.22): calcd. C 58.79, H 7.01, N 3.61; found C 58.96, H 7.04, N 3.63.

X-ray Structural Analysis of Complexes 1, 4, and 5: All measurements were made with a Rigaku RAXIS-RAPID diffractometer with Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved by direct methods[35] and refined by full-matrix least-squares on F^2. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included in idealized positions. The pentamethylcyclopentadienyl group of complex **5** was refined with occupancies of 0.582:0.418 due to rotational disorder. All calculations were performed by using the SHELXTL crystallographic software packages.[36] Details of the crystallographic parameters, data collections, and structure refinements are summarized in Table 4.

CCDC-788037 (for **1**), -788038 (for **4**), and -788039 (for **5**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Polymerization Reactions: The ethylene polymerization experiments were carried out as follows. A dry 250 mL steel autoclave with a magnetic stirrer was charged with toluene (60 mL), thermostatted at the desired temperature, and saturated with ethylene (1.0 atm). The polymerization reaction was started by the simultaneous addition of a mixture of catalyst and Al*i*Bu$_3$ in toluene (5 mL) and a solution of $Ph_3CB(C_6F_5)_4$ in toluene (5 mL). The vessel was pressurized to 5 atm with ethylene immediately and the pressure was maintained by the continuous feeding of ethylene. The reaction

Table 4. Crystallographic parameters, data collection, and structure refinements for complexes **1**, **4**, and **5**.

	1	4	5
Formula	$C_{18}H_{25}Cl_2NTi$	$C_{23}H_{35}Cl_2NTi$	$C_{19}H_{27}Cl_2NTi$
M_r	374.19	444.32	388.22
Wavelength [Å]	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$C2/c$	$P2(1)$	$P2_1/n$
a [Å]	25.007(5)	8.5063(10)	8.1796(16)
b [Å]	10.881(2)	33.296(4)	27.742(6)
c [Å]	16.723(4)	16.570(2)	9.850(2)
α [°]	90	90	90
β [°]	122.172(3)	91.411(2)	113.31(3)
γ [°]	90	90	90
V [Å^3]	3851.7(14)	4691.6(10)	2052.7(7)
Z	8	8	4
F(000)	1568	1888	816
D_c [g cm^{-3}]	1.291	1.258	1.256
Absorption coefficient [mm^{-1}]	0.718	0.601	0.676
Crystal size [mm]	0.11 × 0.09 × 0.08	0.24 × 0.16 × 0.12	0.23 × 0.19 × 0.15
θ range [°]	1.92–26.02	1.37–25.08	3.08–25.00
Reflections	10549	24507	13092
Independent reflections	3791	15398	3260
R_{int}	0.0534	0.0894	0.0603
Data/restraints/parameters	3791/0/204	15398/19/1013	3260/295/284
GOF	0.991	0.993	1.059
R_1, Rw [$I > 2\sigma(I)$]	0.0556, 0.1016	0.0846, 0.1237	0.0872, 0.2511
R_1, Rw (all data)	0.1074, 0.1220	0.1724, 0.1546	0.1308, 0.2886
Max., min. diff. peaks [e Å^{-3}]	0.333, –0.210	0.579, –0.419	0.719, –0.661

mixture was stirred at the desired temperature for 15 min. The polymerization was then quenched by injecting ethanol acidified with HCl (3 M). The polymer was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum. For the ethylene/1-hexene copolymerization experiments, appropriate amounts of 1-hexene were added in toluene.

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