{[2-(Dimethylamino)ethyl]cyclopentadienyl}titanium Complexes. Influence of the Dimethylamino Group in Ziegler−Natta Polymerization Catalysis

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ABSTRACT: [2-(Dimethylamino)ethyl]-substituted cyclopentadienyltitanium complexes (**3**−**6**) have been synthesized and characterized. Structural data indicates intramolecular coordination of the dimethylamino group to titanium. The catalytic activities and selectivities for styrene, ethylene, and propylene polymerization with **3**−**6** have been compared with the reference compounds $CpTiCl_3$ (**1**), Cp^*TiCl_3 (**2**), and Cp_2TiCl_2 (**7**), and are consistent with Ti−N Lewis acid−base interaction.

Introduction

The discovery of the first homogeneous Ziegler−Natta (ZN) catalyst for ethylene polymerization (Cp_2TiCl_2/AlR_2Cl; Cp = η^5-cyclopentadienyl; R = alkyl)[1] opened the way to study well-defined model systems and elucidate the mechanisms of ZN catalysis. The finding of a 10^5 increase of ethylene polymerization activity for Cp_2ZrCl_2 by using methylaluminoxane (MAO) in place of AlR_2Cl as the catalyst[2] and the production of highly isotactic polypropylene by group 4 chiral *ansa*-metallocene/MAO systems[3] stimulated renewed world-wide R&D activities concerning ZN catalysts. Some of the significant advances include the synthesis of new tailored catalysts producing the syndiospecific polymerization of propylene,[4] as well as other new materials[5] such as syndiotactic polystyrene,[6] which has been selected as a firm candidate to be commercially produced in the near future.[7] The isolation of metallocenium species (Cp_2M^+R)[8] by reacting alkylmetallocenes with a strongly acidic salt of a noncoordinating anion (i.e. $[Ph_3C]^+[B(C_6F_5)_4]^-$) and their applications in the polymerization of ethylene, propylene,[9] and styrene[10] have helped in the understanding of the ZN-catalysis mechanism. It is now generally accepted that the role of MAO with the group 4 metallocene dichloride is the generation of a catalytically active metallocenium-type species, (Cp_2M^+R).[8,11] The extension of this idea to the action of MAO on half-sandwich metallocene trichlorides (formation of $CpM^+R_xCl_{2-x}$ species) is fairly appealing, but this point has not been firmly demonstrated.[10,12]

With only a few exceptions,[13] group 4 metallocenes have dominated ZN olefin polymerizations,[1−5,8,9,14] whereas group 4 monocyclopentadienyl complexes [i.e. $CpTiCl_3$ (**1**) and Cp^*TiCl_3 (**2**)] are better known as precursors for styrene polymerization catalysis.[6,10,12]

There is a growing interest in the study of substituted cyclopentadienyl-metal compounds containing a terminal donor group in the side chain.[15] Due to the strong Lewis acidity of the metal in the postulated active species in polymerization catalysis, coordination of the "pendant" Lewis base to the transition metal center might be anticipated. In fact, Wang et al.[16] have reported intramolecular coordination of the amino group of the [2-(dimethylamino)ethyl]cyclopentadienyl ligand in manganese and molybdenum complexes. Similar structures were observed by Jutzi et al.[17] for calcium, samarium, iron, aluminum, and cobalt complexes with the [1-(2-dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl ligand. Okuda et al.[18] have shown the terminal double bond of the 1-(3-butenyl)-2,3,4,5-tetramethylcyclopentadienyl ligand to be intramolecularly coordinated in cobalt compounds as well. Yanlong et al.[19] have determined the chelation of the [2-(methoxy)-ethyl]cyclopentadienyl ligand in ($C_5H_4CH_2CH_2OMe$)-$TiCl_3$, with a Ti−O bond length of 2.214 Å. The above type of intramolecular coordination is also expected to affect both the activity and the selectivity of a ZN catalyst.

We have recently reported the synthesis of Cp^NTiCl_3 (**3**) ($Cp^N = C_5H_4CH_2CH_2NMe_2$) and, in view of its structural data, proposed the intramolecular coordination of the nitrogen atom to titanium.[20] This Lewis acid−base interaction involves the lone pair electrons on nitrogen and the e degenerate LUMO that lies parallel to the cyclopentadienyl ring in $CpTiCl_3$ (**1**).[21] Compared with **1**, compound **3** was found to behave differently in polymerization reactions with styrene (S), ethylene (E), and propylene (P), which can be only attributed to the presence of the "pendant" ligand. Recently, Herrmann et al.[22a] have reported the pyrrolidine (*N*) and piperidine (*N*) analogs of **3**, confirming for the former (i.e., $[C_5H_4CH_2CH_2N(CH_2)_4]TiCl_3$) the Ti−N intramolecular coordination by X-ray diffraction studies. During the course of the present study, Jutzi et al.[22b] have reported the synthesis of several mono- and bis-cyclopentadienyl Ti and Zr compounds containing the Cp^N ligand and also proposed the chelation of this ligand in some of them [e.g., ($C_5H_4CH_2CH_2$-NMe_2)$ZrCl_3$·THF].

We report here an extension of the Cp^NTiCl_3 study[20] for the preparation of $Cp^{*N}TiCl_3$ (**4**) ($Cp^{*N} = C_5Me_4CH_2$-CH_2NMe_2), the titanocene $Cp^NCpTiCl_2$ (**5**), and the hydrolysis product of the latter $(Cp^{N\cdot HCl}CpTiCl)_2(\mu\text{-}O)$ (**6**) ($Cp^{N\cdot HCl} = C_5H_4CH_2CH_2NMe_2\cdot HCl$). The characterization of these compounds, their olefin polymerization behaviors, and a comparison of these new catalysts with **1**, **2**, and Cp_2TiCl_2 (**7**) are described in this paper.

Results and Discussion

Synthesis. Synthetic procedures have been previously described for $CpTiCl_3$ (**1**),[23a] Cp^*TiCl_3 (**2**) ($Cp^* = C_5Me_5$),[23b] and Cp^NTiCl_3 (**3**).[20] $Cp^{*N}TiCl_3$ (**4**) ($Cp^{*N} = C_5Me_4CH_2CH_2NMe_2$) was similarly prepared by reacting $Cp^{*N}SiMe_3$[24b] with $TiCl_4$ in CH_2Cl_2 or toluene (Scheme

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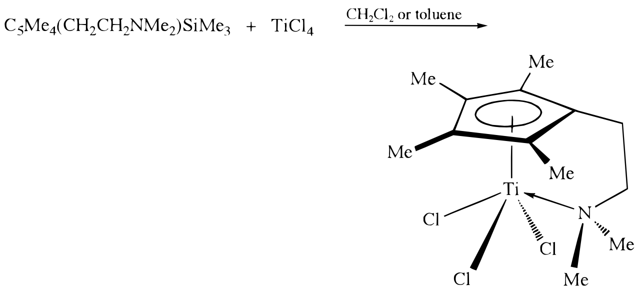
Table 1. Comparison of ^{1}H-NMR ($CDCl_3$) Data for $Cp^{*N}TiCl_3$ (4)

	δ (ppm)			
(ppm)	$Cp^{*N}H$	$Cp^{*N}SiMe_3$	**4**	$\Delta\delta$ (ppm)
δ NMe_2	2.24	2.21	2.36	0.12−0.15
δ CH_2N	2.29	2.43	2.96	0.54−0.67

Scheme 1



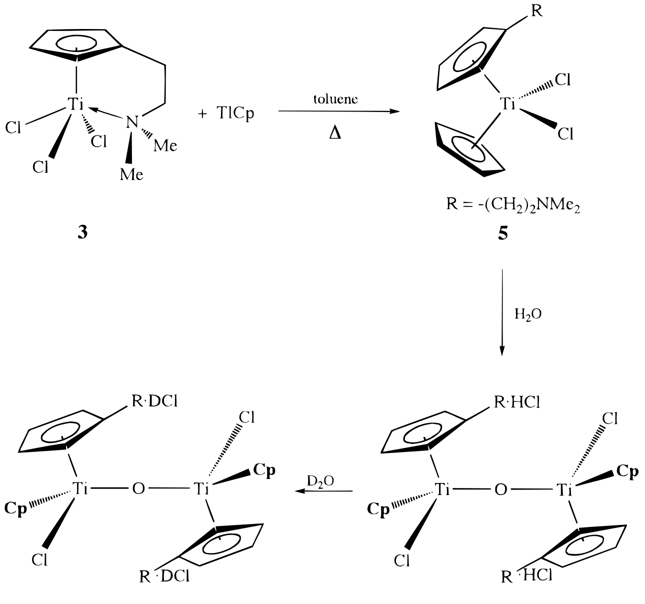
4

1). In either solvent and under a range of reaction conditions, the yield of **4** was always 14% or lower. Compound **4** was isolated as a red-orange microcrystalline solid from toluene. Detailed ^{1}H-NMR and analytical data for **4**−**6** are given in the Experimental Section. The ^{1}H-NMR spectrum of **4** shows a relatively broad singlet (6 Hz) for the four methyl groups on the five-membered ring, a singlet for the $N(CH_3)_2$ protons, and an A_2B_2 splitting pattern for the CH_2CH_2 protons of the ligand backbone. In the case of compound **3**, the chemical shifts of the $N(CH_3)_2$ and the CH_2N protons were observed to be shifted by 0.43 and 0.74 ppm, respectively, downfield from the corresponding resonances for $C_5H_5(CH_2CH_2NMe_2)$ and $C_5H_4(CH_2CH_2NMe_2)SiMe_3$.[20] These chemical shifts were attributed to the intramolecular coordination of the dimethylamino group to titanium. Table 1 summarizes the ^{1}H-NMR data for the same analysis in **4**. The comparisons here are made with $C_5Me_4H(CH_2CH_2NMe_2)$ and $C_5Me_4(CH_2CH_2NMe_2)SiMe_3$[24] in order to avoid any anisotropic effect due to the presence of a different cyclopentadienyl ring. The $\Delta\delta_{(NMe_2)}$ and $\Delta\delta_{(CH_2N)}$ values are significantly smaller than those found for **3**. This result is in agreement with the finding that methyl substitution on a cyclopentadienyl ring in an organometallic compound increases the electron density of the complexed metal.[25] Permethylation of the ring in compound **3** (i.e. **4**) must lower the Lewis acidity of the titanium center, weakening the Ti−NMe_2 interaction. Therefore, the change in the electronic environment of the nitrogen in **4** is much smaller than that in **3**. This weaker interaction has an observable impact on the polymerization behavior of **4** (*vide infra*).

For the synthesis of the mixed-ring titanocene dichloride **5**, we used the metathesis reaction of the corresponding monocyclopentadienyltitanium trichloride with CpTl.[26] Thus, reaction of **3** with CpTl in boiling toluene overnight gave a dark red solution, from which crude $CpCp^NTiCl_2$ (**5**) was obtained by filtration of TlCl and evaporation of the volatiles (Scheme 2). Recrystallization from CH_2Cl_2 afforded **5** as a garnet-red microcrystalline solid.

The ^{1}H-NMR spectrum of **5** in $CDCl_3$ is fairly similar to the one observed for **3**, with the addition of an intense singlet for the nonsubstituted ring. It also shows an AA′BB′ pattern for the protons of the C_5H_4-ring, a singlet for the $N(CH_3)_2$ group, and an A_2B_2 pattern for the ethylenic side chain.

Scheme 2



3 **5** **6(D)** **6**

Compound **5** was exceedingly moisture sensitive in contrast with the stability of Cp_2TiCl_2 (**7**). The former has high solubility in water to form the hydrolysis product **6** (Scheme 2). Compound **6** was also readily prepared by controlled hydrolysis of **5** in CH_2Cl_2. After evaporation of the solvent, **6** was obtained as a bright-red crystalline solid in quantitative yield. Together with the signals for the cyclopentadienyl ring, the ^{1}H-NMR spectrum of **6** in $CDCl_3$ shows the protons of the ammonium groups as a broad resonance at very low field, the dimethylamino group as a doublet ($J_{(HN\text{-}CH)}$ = 4.9 Hz) by coupling with the ammonium proton, and the ethylene side chain as two close singlets. The most interesting feature of the ^{1}H NMR spectrum of **6** in D_2O is the absence of a resonance for N−H protons and the singlet observed for the dimethylamino groups, indicating the displacement of N−H for N−D bonds in deuterated water [**6**(**D**) in Scheme 2]. The sensitivity of **5** to hydrolysis is related to the moisture sensitivity of **3**. It is understandable for both cases because the presence of the amino groups acts as a driving force to facilitate their hydrolysis by removing the HCl byproduct.[27] In fact, compound **6** was completely stable in aqueous solution and it could be recrystallized from H_2O as the solvent. Once compound **5** is hydrolyzed to **6**, the amine substituent is already consumed and no further reaction with water occurs.

Polymerization

Styrene. The production of syndiotactic polystyrene (*s*-PS) with **1** or **2** and methylaluminoxane (MAO) was first reported by Ishihara et al.[6a] Both precursors showed similar catalytic activity. In this paper, *A*(S), *A*(E), and *A*(P) will be used to denote activity for styrene, ethylene, and propylene polymerization, respectively. The *A*(S) for both **1** or **2** are much superior to that of the titanocene compounds (i.e. **7**). We have reported **3**/MAO to have a relatively low *A*(S) (2.7×10^5 g of PS/(mol_{Ti}·mol of S·h); conditions as in run 3, Table 2).[20] Compound **4** activated with MAO is also found to be poorly active for styrene polymerization (Table 2), with *A*(S) on the same order of magnitude as observed for **3**.

Table 2. Styrene Polymerization Catalyzed by $Cp^{*N}TiCl_3$ (4)/MAO[a]

run no.	Al/Ti	T_p (°C)	yield (mg)	activity[b] $\times 10^{-5}$	% *s*-PS[c]
1	2000	25	26	1.60	77
2	4000	25	31	1.90	81
3	4000	50	59	3.62	73

[a] Polymerization conditions: volume, 50 mL toluene + 5 mL styrene; [Ti] = 50 μM; t_p = 1.5 h. [b] g of polymer/($mol_{Ti}\cdot mol_{styrene}\cdot h$). [c] % *s*-PS = (g of 2-butanone insoluble polymer/g of bulk polymer) × 100.

In contrast, **1**/MAO[6d] or **2**/MAO[10d] have *A*(S) on the order of 10^7 g of PS/($mol_{Ti}\cdot$mol of S·h) under similar conditions. Zambelli et al.[12b] have proposed a monocyclopentadienyltitanium active site structure that comprises the coordination of styrene to Ti by both the vinylic double bond and the aromatic ring. This structure is supported by recent reports relating group 4 monocyclopentadienyl cationic complexes with arene or benzylic interactions with the metal center,[10c,28] and we have very recently found the phenyl group in $[C_5Me_4(CH_2CH_2Ph)TiMe_2]^+[B(C_6F_5)_4]^-$ to be intramolecularly coordinated.[10f] Multi-hapto-coordination of styrene would be hindered for the additional Cp substituent in a metallocene such as **5** or **7**, and/or be destabilized by the interaction of the dimethylamino group in **3** and **4**. The low *A*(S) of these precursors in styrene polymerizations can thus be explained. The slightly higher activity for **4** compared with **3**[20] can be attributed to the weaker Ti–N interaction (*vide supra*).

Despite their sluggish *A*(S), precursors **3** and **4** afforded syndiospecific active species, as indicated by the high yields of syndiotactic polystyrene, *s*-PS, which were 88% and 73%, respectively. These values lie in between those for **1** (~70%)[6d] and for **2** (~95%).[10d]

Ethylene. Catalytic polymerization reactions of ethylene involving **3**–**6** were carried out at various [Ti] and cocatalyst/Ti ratios. The active species were generated by using MAO as cocatalyst or by *in situ* alkylation with TIBA (triisobutylaluminum) and subsequent reaction with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**8**).[9] Ethylene polymerization results are summarized in Table 3 and represent a selection of results under the same polymerization conditions, at which most of the organotitanium precursors vs the two cocatalysts showed maximum performance. In this table has also been included comparative data for the reference compounds **1**, **2**, and **6**.

There is a different trend in *A*(E) between monocyclopentadienyl (mono-Cp) and biscyclopentadienyl (bis-Cp) compounds. In general, the latter complexes are more active than the former (runs 4–7 and 11–14 vs runs 8–10 and 15–17), but the difference in reactivity is considerably reduced in compounds containing the [2-(dimethylamino)ethyl]cyclopentadienyl ring[10] group (runs 4 vs 6 and 8, or runs 11 and 17 vs 13 and 15). With either cocatalyst the trend in *A*(E) is **3** > **2** > **4** > **1** for mono-Cp's (runs 4–7 and 11–14) and **7** > **5** ≥ **6** for bis-Cp's (runs 8–10 and 15–17). It is noteworthy that **5** and **6** have almost the same *A*(E)'s with MAO as cocatalyst (runs 7 and 8), but differ by three-fold when the cocatalyst is **8**/TIBA (runs 15 and 16).

Considering the active species to be $CpTi^+R'R_nCl_{1-n}$ (R′ = R or Cp or Cl; *n* = 0 or 1) for either mono- or bis-Cp compounds, the reactivity of the cations derived from **1**–**4** might be expected to be higher than the corresponding cations from the titanocenes **5**–**7** for both steric and electronic reasons. However, such a higher reactivity may compromise the stability of the mono-Cp cation, resulting in its decomposition to a different species. In fact, EPR studies have shown the facile formation of Ti(III) complexes in 80–98% yield by reacting mono-Cp titanium compounds with MAO.[12c] This decomposition seems to be prevented by the multicoordination of styrene (*vide supra*), a second cyclopentadienyl ring, or by the presence of a better stabilizer ring such as pentamethylcyclopentadienyl or those with the "pendant" donor dimethylamino group. Counterion association with the metal center might be important in terms of *A*(E) for these catalysts. The fact that all of them increase *A*(E) with the **8**/TIBA catalyst in place of MAO, where in the former the counterion is inert and noncoordinative, is consistent with a contribution of ion-pair coupling. Nevertheless, this contribution does not seem to be responsible for the differences in *A*(E) for **1**–**4** with a particular cocatalyst. Assuming that an increased ion-pair interaction with the metal center in **1** vs **3** causes the lowering in *A*(E) for the former, it might be expected that **4** would be more active than **2** for the same reason, and that is not the case. Therefore, we propose that the stability of the cationic species could be responsible for the different performance of mono- and bis-Cp titanium complexes for ethylene and propylene (*vide infra*) polymerization. The trend in *A*(E) **3** > **2** > **4** > **1** is consistent with this idea since the coordination of the nitrogen to titanium confers more metallocene-like character to **3** and **4** (Figure 1), and the active site promoted from **2** must be more stable than the corresponding site from **1**. The lower *A*(E) for

Table 3. Ethylene Polymerization Catalyzed by 1–7 Precursors[a]

run no.	catalyst	cocatalyst[b]	t_p (min)	yield (g)	activity[c] $\times 10^{-6}$	T_m (°C)	M_w $\times 10^{-5}$
4	$CpTiCl_3$ (**1**)	MAO	150	0.143	0.06	123.7	0.49
5	Cp^*TiCl_3 (**2**)	MAO	60	0.544	0.58	128.6	0.43
6	Cp^NTiCl_3 (**3**)	MAO	10	0.767	4.96	138.5	2.14
7	$Cp^{*N}TiCl_3$ (**4**)	MAO	60	0.185	0.20	138.1	1.00
8	$CpCp^NTiCl_2$ (**5**)	MAO	3	0.662	14.30	142.8	2.19
9	$[CpCp^{N\cdot HCl}TiCl]_2(O)$ (**6**)	MAO	3	0.592	12.80	139.6	2.65
10	Cp_2TiCl_2 (**7**)	MAO	3	0.809	17.40	141.0	1.40
11	**1**	**8**/TIBA	120	0.735	0.40	139.7	2.96
12	**2**	**8**/TIBA	10	0.884	5.72	134.7	4.25
13	**3**	**8**/TIBA	3	0.572	12.33	136.5	*d*
14	**4**	**8**/TIBA	10	0.152	0.98	135.0	*d*
15	**5**	**8**/TIBA	5	0.487	6.30	141.7	2.02
16	**6**	**8**/TIBA	5	0.151	1.90	139.6	1.99
17	**7**	**8**/TIBA	4	0.929	15.00	142.1	1.07

[a] Polymerization conditions: volume, 50 mL toluene; [Ti] = 50 μM; T_p = 20 °C; $P_{C_2H_4}$ = 15 psig ($[C_2H_4]$ = 0.37 M). [b] MAO: Al/Ti = 4000; TIBA = triisobutylaluminum (Al/Ti = 20); **8** = $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**8**/Ti = 1). [c] g of polymer/$mol_{Ti}\cdot[C_2H_4]\cdot h$). [d] Polymers gave an unhomogeneous (gluey) solutions after 2 days in decaline at 135 °C.

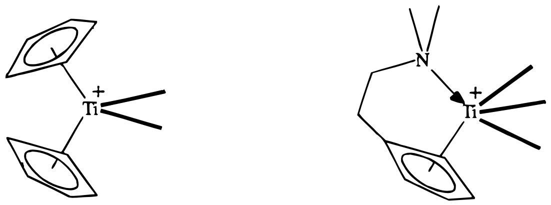


Figure 1. Generalized structure for titanocene active species compared to that proposed for **3**. Solid bars represent coordination positions.

4 relative to **3** and **2** can be attributed to the steric bulk of the ancillary ligand[9d] in **4**.

The order of *A*(E) among the titanocenes (**7** > **5** ≥ **6**) is in agreement with earlier findings, where steric factors were thought to be dominant.[29] In the present study, however, this trend may also be due to Ti−N interactions in **5** and **6** during the catalytic process, which could hinder the coordination of the monomer [lower *A*(E)].

The different *A*(E) values observed for **5** and **6** with **8**/TIBA contrasts with the nearly identical values when MAO is the cocatalyst. The reaction of $AlEt_2Cl$ with μ-oxo titanium compounds has been found to be an efficient procedure to remove the oxygen atom from titanium, chlorinating the latter as well.[30] Furthermore, the reaction of TMA (trimethylaluminum) with $[Cp_2ZrCl]_2$ (μ-O) is a useful method for the synthesis of $Cp_2Zr(Cl)Me$.[31] Since MAO has been found to be a mixture of several aluminum formula compounds (TMA among them)[32] and is employed in this study at an Al/Ti ratio of 4000, it is likely taht **6**/MAO and **5**/MAO produce the same catalytic species. On the other hand, when **6** is activated with **8**/TIBA, the different nature of the aluminum cocatalyst, which also has to react with the HCl coordinated on the nitrogens, as well as the small Al/Ti ratio (20), may produce the active species in lower yield.

The polyethylenes (PE's) produced by **1**−**7** exhibit single DSC endotherms consistent with a single active species for each catalyst. The T_m (melting temperature) of a PE depends both upon its molecular weight and linearity. It is known that metallocene catalysts yield very linear PE's. This can be observed in Table 3. T_m is is above 140 °C for almost all of the bis-Cp compounds, whereas T_m is lower for all of the mono-Cp derivatives. An example of low T_m as a result of low molecular weight is represented by run 4.

Another interesting feature in the morphology of these PE's is the higher M_w found in compounds containing the dimethylamino group (compare runs 4−7, 8−10, or 15−17).

Propylene. Table 4 summarizes a selection of the results obtained with **1**−**7** in the catalytic polymerization of propylene.

In general, the *A* of a given catalyst is lower for propylene than for ethylene polymerization reactions, as shown by comparing Tables III and IV. The larger size of both the monomer and the nearest units of the growing polymer chain to the metal center probably require a higher activation energy for the *cis*-insertion and propagation. The higher stability of the π-complex of propylene also would contribute to a slowing of the polymerization rate of propylene. However, steric factors are most likely dominant.

The lowering in *A*(P) relative to *A*(E) is drastic for the titanocenes **5**−**7** using either cocatalyst. For precursor **1**, *A*(P) = 0 with either cocatalyst, and for **2** it is also 0 when activated with MAO or very low when activated with **8**/TIBA (run 26). However, the mono-Cp precursors with pendant amino coordination (**3** and **4**) both activated with MAO have *A*(P) not much smaller than *A*(E). This is also true for **3** activated with **8**/TIBA. Thus, compound **3** is the most active propylene polymerization catalyst among the mono- and bis-Cp titanium complexes reported in Table 4. A possible explanation is that the highly reactive cation is prevented from decomposition by the coordination of the nitrogen, which can support part of the positive charge by resonance. As a result, the active species has a pseudo-titanocene structure (see Figure 1) that makes it active of polymerizing ethylene, but unfavorable for styrene polymerization since the stronger coordination of the NMe_2 group destabilizes the multi-hapto-complexation of styrene. Finally, the less hindered environment of this species as compared to the titanocenes and the availability of an extra coordination position relieve the steric congestion that may occur with propylene and facilitates its polymerization.

The polypropylenes produced by the active catalysts in Table 4 are all atactic in nature, as indicated by the absence of melting transitions. It is also remarkable that the polypropylene MW observed for **3** with either cocatalyst is very high as was the one observed for **2** activated with **8**/TIBA.

Experimental Section

Synthesis. All operations were performed under an argon atmosphere using Schlenk or glovebox techniques. Argon was deoxygenated with activated BTS catalyst and dried with

Table 4. Propylene Polymerization Catalyzed by 1−7 Precursors[a]

run no	catalyst	cocatalyst[b]	t_p (min)	yield (g)	activity[c] $\times 10^{-6}$	M_w $\times 10^{-5}$
18	$CpTiCl_3$ (**1**)	MAO	120	0	0	
19	Cp^*TiCl_3 (**2**)	MAO	150	0	0	
20	Cp^NTiCl_3 (**3**)	MAO	30	1.851	1.90	4.52
21	$Cp^{*N}TiCl_3$ (**4**)	MAO	150	0.711	0.15	0.49
22	$CpCp^NTiCl_2$ (**5**)	MAO	30	0.125	0.13	1.75
23	$[CpCp^{N\cdot HCl}TiCl]_2(O)$ (**6**)	MAO	30	0.070	0.07	0.66
24	Cp_2TiCl_2 (**7**)	MAO	120	0.051	0.03	1.01
25[d]	**1**	**8**/TIBA	120	0	0	
26[d]	**2**	**8**/TIBA	150	0.372	0.04	4.78
27[d]	**3**	**8**/TIBA	7	2.192	4.82	4.52
28[d]	**4**	**8**/TIBA	150	0	0	
29[d]	**5**	**8**/TIBA	60	0	0	
30[d]	**6**	**8**/TIBA	60	0	0	
31[d]	**7**	**8**/TIBA	60	0.584	0.16	0.01

[a] Polymerization conditions: volume, 50 mL toluene; [Ti] = 50 μM; T_p = 20 °C; $P_{C_3H_6}$ = 20 psig ($[C_3H_6]$ = 0.78 M). [b] MAO:Al/Ti = 4000; TIBA = triisobutylaluminum (Al/Ti = 20); **8** = $[Ph_3C]^+[B(C_6F_5)_4]^-$ (**8**/Ti = 1). [c] g of polymer/($mol_{Ti}\cdot[C_2H_4]\cdot h$). [d] [Ti] = 100 μM.

molecular sieves and P_2O_5. Solvents were purified as described elsewhere.[33] MAO was purchased from Akzo, and other chemicals were from Aldrich. $CpTiCl_3$,[23a] $[(C_5H_4CH_2CH_2NMe_2)TiCl_3]$,[20] $C_5Me_4(CH_2CH_2NMe_2)H$,[24a] $C_5Me_4(CH_2CH_2NMe_2)SiMe_3$,[24b] CpTl,[34] and $[Ph_3C]^+[B(C_6F_5)_4]^-$ [9b] were prepared by literature procedures. ^{1}H-NMR spectra were recorded on a Varian XL200 FT spectrometer. Chemical shifts (δ) are reported referenced to TMS. Elemental analyses were performed by the University of Massachusetts Microanalytical Laboratory.

{1-[2-(Dimethylamino)ethyl]-2,3,4,5-tetramethylcyclopentadienyl}trichlorotitanium (**4**) was synthesized as follows. $C_5Me_4(CH_2CH_2NMe_2)SiMe_3$ (5.00 g, 18.8 mmol) was added dropwise to a stirred solution of $TiCl_4$ (3.57 g, 18.3 mmol) in 50 mL of CH_2Cl_2 at −78 °C. The dark-red reaction mixture was allowed to warm to room temperature and stirred for 3 h. After removal of the solvent the residue was treated with toluene (2 × 50 mL), and the extracts were filtered from a large amount of insoluble material. Concentration of the toluene solution and cooling overnight afforded **4** as a red-orange microcrystalline solid. Yield: 0.92 g (14%). ^{1}H-NMR spectra ($CDCl_3$): δ 2.96 (t, 2H, $J = 6.8$ Hz, CH_2N); 2.66 (t, 2H, $J = 6.8$ Hz, CH_2); 2.44 (br s, $J = 6$ Hz, 12H, C_5Me_4); 2.36 (s, 6H, NMe_2). Anal. Calcd for $C_{13}H_{22}NCl_3Ti$: C, 45.05; H, 6.40; N, 4.04. Found: C, 44.96; H, 6.88; N, 3.78. If the above synthesis was performed using toluene instead of CH_2Cl_2 as reaction solvent, the final yield of **4** was almost identical. Attempts to grow a single crystal of **4** were unsuccessful.

{[2(Dimethylamino)ethyl]cyclopentadienyl}(cyclopentadienyl)dichlorotitanium (**5**) was prepared as follows. $[(C_5H_4CH_2CH_2NMe_2)TiCl_3]$ (3.39 g, 11.7 mmol) and freshly sublimed TlCp (3.15 g, 11.7 mmol) were weighed in a glovebox and transferred to a Schlenk tube. The mixture was refluxed overnight in 80 mL of toluene, followed by cooling to room temperature, addition of 60 mL of CH_2Cl_2, and filtration of the TlCl byproduct. The solvents were removed under vacuum, and the residue was recrystallized from CH_2Cl_2. Compound **5** was isolated as a garnet-red microcrystalline solid, and both ^{1}H-NMR and elemental analysis indicated that it crystallized with 1 equiv of CH_2Cl_2 in its crystal lattice. Yield: 2.88 g (61%). ^{1}H-NMR spectra ($CDCl_3$): δ 6.58 (s, 5H, C_5H_5); 6.44 (t, 2H, C_5H_4); 6.37 (t, 2H, C_5H_4); 5.30 (s, 2H, CH_2Cl_2); 3.16 (t, 2H, $J = 7.2$ Hz, CH_2N); 2.95 (t, 2H, $J = 7.2$ Hz, CH_2); 2.53 (s, 6H, NMe_2). Anal. Calcd for $C_{14}H_{19}NCl_2Ti{\cdot}CH_2Cl_2$: C, 44.48; H, 5.22; N, 3.46. Found: C, 44.90; H, 5.35; N, 3.37.

The synthesis of bis-[{[2-(dimethylamino)ethyl hydrochloride]cyclopentadienyl}(cyclopentadienyl)chlorotitanium](μ-oxo) (**6**) was carried out as follows. Compound **5** (1.13 g, 2.8 mmol) in 40 mL of CH_2Cl_2 at −78 °C was treated with H_2O (25 μL, 1.4 mmol). The reaction mixture was allowed to warm to room temperature and stirred overnight. The cloudy reaction mixture was filtered and the solvent was removed under vacuum. The μ-oxo compound (**6**) was collected pure as a bright red microcrystalline solid in quantitative yield. Again, ^{1}H-NMR and elemental analysis indicated the presence of CH_2Cl_2 in the crystal lattice of **6**, in this case 1.5 equiv per μ-oxo molecule. This composition was unchanged upon recrystallization from CH_2Cl_2 and/or keeping the solid under high vacuum overnight. Yield: 1.09 g (100%). ^{1}H-NMR spectra ($CDCl_3$): δ 12.68 (br s, ~40 Hz, 2H, N−H); 6.60 (s, 10H, C_5H_5); 6.43 (t, 4H, C_5H_4); 6.29 (t, 4H, C_5H_4); 5.29 (s, 3H, CH_2Cl_2); 3.48 and 3.47 (2s, 8H, CH_2CH_2N); 2.85 (d, 12H, $J_{HN-CH} = 4.9$ Hz, NMe_2). ^{1}H-NMR spectra (D_2O): δ 6.49 (t, 4H, C_5H_4); 6.48 (s, 10H, C_5H_5); 6.33 (t, 4H, C_5H_4); 5.30 (s, 3H, CH_2Cl_2); 3.17 (t, 4H, $J = 7.7$ Hz, CH_2N); 2.76 (t, 4H, $J = 7.7$ Hz, CH_2); 2.74 (s, 12H, NMe_2). Anal. Calcd for $C_{28}H_{40}N_2Ti_2C_{14}O{\cdot}{}^3/_2CH_2Cl_2$: C, 45.10; H, 5.52; N, 3.56. Found: C, 45.35; H, 5.65; N, 3.72.

Polymerization Studies. Styrene was purified by distillation from calcium hydride under reduced pressure and stored at −25 °C under argon in darkness. Polymerization grade ethylene and propylene were dried and purified by passage through Matheson gas purifiers (Model 6436). All olefin polymerization reactions were carried out in toluene in 250-mL crown-capped glass pressure reactors equipped with magnetic stirring and thermostated to the desired temperature. The reproducibility of the amount of total polymer obtained, activity, and MW is estimated at ±7%. The procedures used to polymerize styrene[6d,e] and ethylene or propylene[5,9c] have previously been given in detail. A Perkin-Elmer DSC-4 thermoanalytic instrument was used to obtain DSC melting endotherms. Molecular weight determinations were made by viscosity measurements in decalin at 135 °C.

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