

Ethylene and Propylene Polymerization by a Series of Highly Electrophilic, Chiral Monocyclopentadienyltitanium Catalysts

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The compounds $\text{Cp}^*\text{TiMe}_2\text{C}_6\text{F}_5$, $\text{Cp}^*\text{TiMe}_2\text{OC}_6\text{F}_5$, and $\text{Cp}^*\text{TiMe}_2\text{Cl}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) react with the borane $\text{B}(\text{C}_6\text{F}_5)_3$ to form the thermally unstable, chiral complexes $\text{Cp}^*\text{TiMe}(\text{C}_6\text{F}_5)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Cp}^*\text{TiMe}(\text{OC}_6\text{F}_5)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$, and $\text{Cp}^*\text{TiMeCl}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$, respectively, which are similar to the known $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$. All four $\mu\text{-Me}$ compounds behave as sources of the highly electrophilic species $[\text{Cp}^*\text{TiMeE}]^+$ ($E = \text{Me}, \text{Cl}, \text{C}_6\text{F}_5, \text{OC}_6\text{F}_5$) when treated with the borane, the last three being chiral, and all four systems exhibit catalytic activities for the polymerization of ethylene to high-molecular-weight polyethylene. Despite the chirality at titanium of three of the compounds, polymerization of propylene by all of them results in the formation of atactic, elastomeric polypropylene. NMR analyses of the propylene polymers formed show that initiation involves 1,2-insertion into a Ti–Me bond, and while propagation involves primarily head-to-tail 1,2-insertions, an unusually high (by metallocene standards) proportion of the insertions also involves 2,1-misinsertions but essentially no 1,3-enchainment. The major olefinic end groups are vinylidene ($\text{CH}_2=\text{CMe}-$), resulting from β -hydrogen transfer following a 1,2-insertion, and vinyl ($\text{CH}_2=\text{CH}-$), resulting from β -hydrogen transfer from the methyl group following a 2,1-insertion or, more likely, β -methyl transfer following a 1,2-insertion. Small amounts of internal olefins are also formed via β -hydrogen transfer following a 2,1-insertion. An EPR study of the $\text{Cp}^*\text{TiMe}_2/\text{B}(\text{C}_6\text{F}_5)_3$ system in toluene indicates that <0.01% of the titanium is occasionally present during polymerization as a complex of titanium(III), suggesting that a contribution to catalysis by titanium(III) species is unlikely.

Recent research into the formation of highly stereoregular polypropylene (PP) has highlighted group 4 metallocene catalysts of the type $\text{Cp}'_2\text{ZrCl}_2/\text{MAO}$ ($\text{Cp}' = \eta^5$ -functionalized cyclopentadienyl, MAO = methylaluminoxane) as potentially viable alternatives to existing commercial catalysts.^{1,2} The active species are generally accepted as being 14-electron cations of the type $[\text{Cp}'_2\text{MMe}]^+$, which can be tailored to produce iso- or syndiotactic PP via appropriate functionalization of the cyclopentadienyl rings.¹ The crystal structures of non-MAO complexes $\text{Cp}'_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ have also been reported;^{3a–c} these dissociate the borate anion $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$ to generate the catalytically active species $[\text{Cp}'_2\text{ZrMe}]^+$,³ thus confirming the role of this type

of cationic complex as the active species in $\text{Cp}'_2\text{ZrCl}_2/\text{MAO}$ systems.

A growing interest in the related half-sandwich complexes of the type $\text{Cp}'\text{ML}_3^4$ has led our group and others to the formation of rather similar cationic species by the general method of alkyl ligand abstraction using

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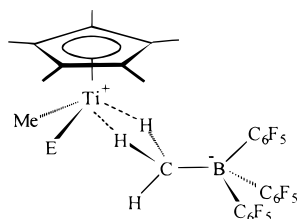
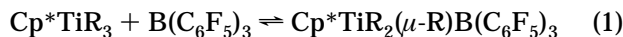


Figure 1. Proposed structure of $\text{Cp}^*\text{TiMeE}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ (**A–D**).

the strongly Lewis acidic borane $\text{B}(\text{C}_6\text{F}_5)_3$ and formation of alkyl-bridged complexes of the type $\text{Cp}^*\text{TiR}_2(\mu\text{-R})\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (eq 1).^{4j,r,u,v,5}



We have proposed that the methyl-bridged bonding mode in $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ (**A**, Figure 1, $\text{E} = \text{Me}$; CD_2Cl_2 , -50°C)⁵ is similar to that found in $\text{Cp}'_2\text{ZrMe}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ in solution and in the solid state^{3a–c} and have demonstrated the versatility of **A** as an active polymerization initiator for a number of olefins.⁶ In addition, polymerization of ethylene and propylene has been achieved using CpTiCl_3 and Cp^*TiCl_3 activated with large excesses of MAO, and Pellecchia has reported the polymerization of ethylene using the related MAO-free catalysts $\text{Cp}^*\text{MR}_2(\mu\text{-R})\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{M} = \text{Zr}$, $\text{R} = \text{CH}_2\text{-Ph}$; $\text{M} = \text{Ti}$, $\text{R} = \text{CH}_2\text{Ph}$, Me), although propylene was polymerized only with the benzyl complexes.^{4j}

During the initiation step for Ziegler–Natta catalysis, insertion of the monomer into an alkyl–metal bond is required. The active species in half-sandwich compounds $[\text{Cp}^*\text{MR}_2]^+$ contains a redundant R ligand during the polymerization, and thus replacement of one of the R groups with other coordinated anions provides scope for altering the steric and electronic properties of the metal, and possibly for altering the catalyst activity. Since cationic complexes generally form more active polymerization catalysts than do neutral species,¹ we have hypothesized that substitution of one of the methyl groups of $[\text{Cp}^*\text{TiMe}_2]^+$ with a more electron withdrawing ligand could result in the formation of more active initiators.^{7a} This expectation is contrary to current conventional wisdom for metallocene systems,⁸ since, for instance, incorporation of electron-withdrawing groups on the Cp' rings of metallocenes of the type $(\eta^5\text{-5,6-X}_2\text{C}_9\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$ (Figure 2, **E**) has been found to result in both decreased activity and reduced polymer

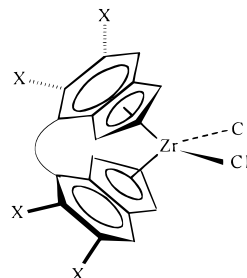


Figure 2. Structure of metallocenes of the type $(\eta^5\text{-5,6-X}_2\text{C}_9\text{H}_5)_2\text{ZrCl}_2/\text{MAO}$ (**E**).

molecular weights.^{8c} However, the relative rates of initiation, propagation, termination, and chain transfer are all affected unpredictably by ligand substitution, and the reasons for the observed deactivation were not assessed in detail,^{8c} although it has been shown elsewhere that enhanced Lewis acidity of the metal can result in stronger binding of the counteranion.³ The latter phenomenon could result in both inhibition of monomer coordination and more facile termination of polymer growth via olefin ligand displacement. Utilization of a counteranion which, for steric or electronic reasons, could not coordinate strongly would obviate the latter modes of deactivation, and thus the effects of increased metal ion Lewis acid strength on catalytic activity arguably remain open for discussion.

Here we describe the production of high-molecular-weight polyethylene (PE) and high-molecular-weight regio- and stereoirregular PP using the catalytic systems $\text{Cp}^*\text{TiMeE}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$, in which E varies in electron-withdrawing capability ($\text{E} = \text{Me}$ (**A**), Cl (**B**), OC_6F_5 (**C**), C_6F_5 (**D**)). The syntheses^{7a} and solution dynamics^{5c,7} of compounds **A**, **C**, and **D** have been previously reported, and while similar studies of **B** have been thwarted by as yet unidentified side reactions during the reaction of $\text{Cp}^*\text{TiMe}_2\text{Cl}$ with $\text{B}(\text{C}_6\text{F}_5)_3$, the similarities in the catalytic properties of **B** to those of **A**, **C**, and **D** justify its inclusion. The catalysts studied here are of interest not only because they offer a potential test of the effects of electron-withdrawing groups on polymerization processes but also because catalysts **B–D** are the first *chiral*, monocyclopentadienyl systems to be studied in this way. Stereoregular propylene polymerization by metallocene systems generally requires significant steric crowding at the catalytic site, ensured by appropriate elaboration of the cyclopentadienyl rings,^{1,2} and it is important to ascertain the effects on propylene polymerization of a chiral environment right at the active site, the metal ion.

Results and Discussion

Polymerization Processes. Abstraction of a methyl ligand from $\text{Cp}^*\text{TiMe}_2\text{E}$ using 1 equiv of $\text{B}(\text{C}_6\text{F}_5)_3$ in methylene chloride provides a general route to a number of active olefin coordination catalysts of the type $\text{Cp}^*\text{TiMeE}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ (**A–D**) (Figure 1). For typical polymerization runs, toluene or methylene chloride solutions of the catalyst precursors $\text{Cp}^*\text{TiMe}_2\text{E}$ were saturated with monomer before addition of $\text{B}(\text{C}_6\text{F}_5)_3$, which resulted in rapid formation of polymer in reactions completed within 5–20 min. The results of ethylene and propylene polymerization runs initiated at -78 ,

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Table 1. Polymerization of Ethylene (25 °C)

sample run no. ^a	catalyst precursor	yield (g)	A* (kg of PE/(mol of Ti) h atm)
1	Cp*TiMe ₃ (A)	0.23	46
2	Cp*TiMe ₂ Cl (B)	0.16	32
3	Cp*TiMe ₂ C ₆ F ₅ (D)	0.08	16
4	Cp*TiMe ₂ OC ₆ F ₅ (C)	0.22	44

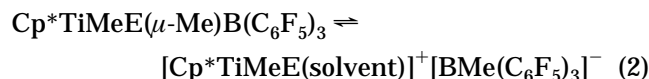
^a Run time 5 min.

0, and 25 °C are reported in Tables 1–4, although it should be noted that the polymerizations initiated at 25 °C were not thermostated effectively and quickly became quite hot. For PE, catalytic activities (16–46 kg of PE/(mol of Ti h atm)) were somewhat lower than for CpTiCl₃/MAO (62 kg PE/(mol of Ti h atm)) (Table 1), although, of course, conditions were not identical.^{4s} The PE materials formed were insoluble in 1,2,4-trichlorobenzene (145 °C), and molecular weights are therefore conservatively estimated to be >300 000. The PE formed is generally linear, as indicated by single resonances at δ 1.39 in the ¹H NMR spectra of soluble fractions (1,1,2,2-C₂D₂Cl₄ at 135 °C).

In a previous paper, we reported that Cp*TiMe₂(μ -Me)B(C₆F₅)₃ (A) exhibits low activity for polymerization of propylene in toluene,^{6a} but we have since found that propylene polymerization is in fact possible with all of the catalysts A–D under rigorously dry conditions. The reasons for the earlier failures are not clear but were probably a result of insufficiently anhydrous conditions. Results of the propylene polymerizations are completely reproducible and are reported in Tables 2 and 4.

Polymerization runs at –78 °C in toluene resulted in the formation of PP with increased M_w (3×10^5 – 2×10^6) when the more electron-withdrawing ligands were used (D \approx C > B > A). These results are in contrast to what has been reported for some metallocene systems, where an increase in the electron-withdrawing ability of ligand substituents was found to reduce both catalytic activity and the molecular weights of the polymers formed.⁸ For example, compounds of the type (η^5 -5,6-X₂C₉H₅)₂ZrCl₂/MAO (Figure 2, E) were examined for the polymerization of ethylene,^{8c} with the result that smaller amounts of lower molecular weight PE were obtained when X was more electron-withdrawing. Unfortunately, no assessment could be made between the relative rates of polymerization and chain transfer, nor were the relative affinities of the cationic metal centers for monomer as opposed to counteranion assessed.

Previous low-temperature NMR evidence has shown that A and C but not D dissociate into separate ion pairs to some extent in CD₂Cl₂, as in eq 2.⁷ The counterion



must be displaced by an incoming monomer for polymerization to occur, and thus the relative polymerization activities in toluene (A > C > D; Table 2) generally correlate with the ease of the borate displacement of eq 2. The trend is certainly significant for the polymerizations at –78 °C, where unimodal, nearly monodisperse polymers were reproducibly obtained. On the other hand, these conclusions are clouded by the fact that the complex cation [Cp*TiMe₂]⁺ forms the arene complex [Cp*TiMe₂(η^6 -toluene)]⁺ in toluene^{5b} while [Cp*TiMeE]⁺

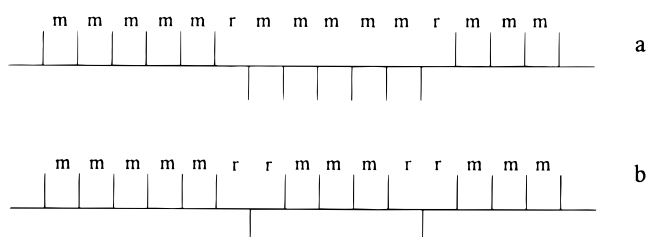


Figure 3. Representation for isotactic PP containing stereoregularities caused by (a) chain-end control and (b) enantiomorphic site control.

species (E = C₆F₅, OC₆F₅) do not, presumably for steric reasons.^{7c} Solvent effects on the propylene polymerizations are discussed below.

Stereoregularity. The relative stereochemistries of consecutive propylene units in the PP polymer chain are best described as sequences of isotactic meso (m) dyads and/or syndiotactic racemic (r) dyads.⁹ Polymer microstructure analysis by ¹³C{¹H} NMR provides valuable information on the mechanism of monomer insertion,¹⁰ the methylene, methine, and methyl resonances being observed at δ 45–47, 28–29 and 19–23, respectively. Integration of the nine observable methyl pentad resonances provides information on the relative distribution of the dyads, with m:r ratios being 1:0, 0:1, and 1:1 for ideal cases of iso-, syndio-, and atactic polymers, respectively.^{9,10} For polymerizations operating under stereocontrol, isolated stereoregularities provide information on whether the regulating mechanism is chain-end control (regulated by the last inserted monomer) or enantiomorphic site control (regulated by the ligand arrangement at the metal).^{10b,c} In the former, a stereoregularity is propagated until the next defect corrects the error (Figure 3a), while in the latter the error is corrected immediately (Figure 3b). Statistical evidence for the chain-end control mechanism results from analyses of the stereoregularities of isolated r dyads exhibiting a characteristic mmmr:mmrm pentad ratio of 1:1. In contrast, the evidence for enantiomorphic site control results from analyses of the stereoregularities of isolated rr triads, with the population of the mmmr:mmrm:rrmm pentads in a 2:2:1 ratio.¹⁰

The four catalyst systems (A–D) produce very similar atactic PP products in toluene at a given polymerization temperature, and representative ¹³C{¹H} NMR spectra (50.38 MHz) of PP samples produced in reactions initiated at 25, 0, and –78 °C are respectively shown in parts a–c of Figure 4. In all three cases, the spectra exhibit prominent methylene, methine, and methyl resonances, as anticipated. Interestingly, however, while the NMR spectrum of the polymer prepared at –78 °C exhibits no other resonances, spectra of the samples prepared at 0 and 25 °C, especially the latter, exhibit multiple resonances in the regions δ 12–16 and 30–40. The methyl and methylene resonances of the higher temperature materials are also relatively complex, and it is clear that the polymerization processes

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Table 2. Polymerization of Propylene (in Toluene)

run no. ^d	catalyst precursor	temp (°C)	10 ⁻⁵ M _w	M _w /M _n	% m dyads ^b	% 2, 1	yield (g)	A (kg of PE/ (mol of Ti) h atm)
4	Cp*TiMe ₃	-78	3.4	1.3	54.7	<1	0.86	43
5	Cp*TiMe ₂ Cl	-78	5.6	1.9	57.7	<1	0.86	43
6	Cp*TiMe ₂ C ₆ F ₅	-78	23.0	1.7	67.1	nd	0.43	22
7	Cp*TiMe ₂ OC ₆ F ₅	-78	20.0	1.7	69.8	nd	0.65	33
8	Cp*TiMe ₃	0	3.0	5.3	49.7	4	4.20	214
9	Cp*TiMe ₂ Cl	0	c	c	50.0	6	2.36	119
10	Cp*TiMe ₂ C ₆ F ₅	0	4.0	3.7	44.3	5	3.09	156
11	Cp*TiMe ₂ OC ₆ F ₅	0	2.8	3.3	44.1	11	3.06	155
12	Cp*TiMe ₃	25	2.6	5.2	48.5	12	2.40	122
13	Cp*TiMe ₂ Cl	25	1.6	5.4	49.8		1.56	79
14	Cp*TiMe ₂ C ₆ F ₅	25	2.7	3.9	42.4	12	1.45	74
15	Cp*TiMe ₂ OC ₆ F ₅	25	1.7	4.9	43.8	12	1.84	94

^a Calibrated using polystyrene standards. ^b m = mm + 1/2 mr. ^c Bimodel. ^d Run time 5 min.

Table 3. End Group Analysis Results for PP Produced at 70 °C in Toluene

sample run no.	catalyst precursor	10 ⁻⁴ M _w	amt of vinyl (%) ^a	amt of vinylidene (%) ^a	amt of 2-butenyl (%) ^a
16	Cp*TiMe ₃	4.1	40	53	7
17	Cp*TiMe ₂ Cl	2.8	39	53	8
18	Cp*TiMe ₂ C ₆ F ₅	3.8	40	52	8
19	Cp*TiMe ₂ OC ₆ F ₅	3.7	32	59	9

^a From ¹H NMR spectra.

at higher temperatures are rather more complicated than might be anticipated (see below).

The methyl pentad resonances are clearly resolved in each spectrum and, for the sample prepared at -78 °C, the pentad distributions deviate from ideally atactic (70% m dyads). An increase in the intensity of the mmmm pentad (δ 21.7) is clearly apparent (Figure 4c), indicating the presence of isotactic segments caused by an only moderately effective stereoregulating mechanism. Although the cationic catalysts formed from **C** and **D** are chiral, careful inspection of the methyl mmmr (δ 21.8) and mrrm (δ 20.7) pentads reveals that this slight stereoregulation is caused by chain-end control (mmmr:mrrm ≈ 1:1).^{10,11} Interestingly, however, as the polymerization temperature is raised (Figure 4a,b), the PP products show slight tendencies toward syndiotacticity (50–58% r dyads). Similar changes from isotacticity with increasing temperature have been attributed in other systems to the thermodynamic aspects of the transition state during the 1,2-insertion of an incoming monomer unit^{4g,w,12} and are probably not a result of ligand influence at the metal center. Further analyses of the pentad structures, as reported elsewhere,^{10d} also showed the absence of stereoblocks; the atactic PP prepared is in all cases completely random.

Regioregularity. Most Ziegler–Natta propylene polymerizations proceed via 1,2 (primary)-incorporation of monomer into the polymer–metal bond such that the methylene carbon (CH₂) of an inserting propylene becomes bound to the metal; the resulting polymer contains an isobutyl end group, although subsequent β-hydrogen elimination chain transfer processes (see below) result in most of the eventually isolated polymer containing *n*-propyl end groups arising from 1,2-inser-

tion of monomer into titanium–hydrogen bonds. The alternative 2,1 (secondary), insertion, resulting in the methine (CH) carbon being bound to the metal, results in regioerrors when 1,2-incorporation is the dominant process and can be detected as head-to-head or tail-to-tail enchainments (Figure 5). In general, 2,1-defects may be corrected immediately to give isolated errors (Figure 5b), or a number of 2,1-misinsertions may occur prior to reversion to the major 1,2-mechanism (Figure 5a).

As mentioned above, the ¹³C{¹H} NMR spectra of PP prepared at 0 °C and above exhibit resonances in the regions δ 38.2–42.4, 32.2–34.7, and 12.4–15.6 (Figure 4b,c). As has been shown elsewhere,^{13,14a} these groups of resonances correspond to the methylene, methine, and methyl resonances of 2,1-enchainments, respectively, and it is clear that the samples prepared at 0 °C and above are highly regioirregular. Indeed, the ¹³C{¹H} spectra of the elastomeric polymers produced here resemble those of the elastomeric PP prepared using soluble vanadium catalysts of the type VCl₄/AlEt₂X (X = halogen).^{13a} Integration of the total methine region of the NMR spectrum of PP formed at 25 °C indicates that >10% of the monomer units are oriented in a tail-to-tail manner, stereoirregularities in the neighboring units causing broadening of the resonances.^{13b,c} Particularly characteristic is the strong methine resonance at δ 30.4, attributed to the methine carbons of tail-to-tail units which are followed by blocks of 2,1-insertions.^{13b,c} Since a head-to-head unit must occur before primary 1,2-insertions are reestablished, 10% is therefore a lower limit for the number of 2,1-insertions in these polymers. There were, however, no resonances at δ 37.2, 30.8, and 27.5, which would be indicative of 1,3-enchainments.^{14a,b}

Such a high degree of regioerror incorporation is unprecedented with metallocene catalysts, which normally produce PP containing ~1% of *isolated* 2,1-errors,^{14a,b} although somewhat similar behavior has been observed for supported CpTiCl₃ and Cp*TiCl₃ systems.^{14c,d} Indeed, incorporation of 2,1-misinserted units reduces the activity of some metallocene catalysts

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(14) Cheng, H. N.; Ewen, J. A. *Makromol. Chem.* **1989**, *190*, 1931. (b) Guerra, G.; Longo, P.; Corradini, P.; Resconi, L. *J. Am. Chem. Soc.* **1997**, *119*, 4394. (c) Park, J. R.; Shiono, T.; Soga, K. *Macromolecules* **1992**, *25*, 521. (d) Uozumi, T.; Toneri, T.; Soga, K.; Shiono, T. *Macromol. Rapid Commun.* **1997**, *18*, 9.

(11) Note that the mrrm pentad needs to be corrected because of overlap with the rrrm pentad. Since the rrrm signal is equal in intensity to the mrrr signal, then mrrm = (mrrm + rrrm) - mrrr.

(12) Erker, G.; Fritze, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 199.

Table 4. Polymerization of Propylene in CH₂Cl₂

sample run no. ^a	catalyst precursor	temp (°C)	10 ⁻⁵ M _w ^c	M _w /M _n ^b	yield (g)	A (kg of PP/ (mol of Ti) h atm)
20	Cp*TiMe ₃	25	3.0	10.8	0.86	172
21	Cp*TiMe ₂ Cl	25	3.2	9.9	0.60	120
22	Cp*TiMe ₂ C ₆ F ₅	25	3.5	5.9	0.51	102
23	Cp*TiMe ₂ OC ₆ F ₅	25	2.5	7.9	1.06	212
24	Cp*TiMe ₃	-78	11.5 ^c	2.0	0.52	26
25	Cp*TiMe ₂ Cl	-78	21.3 ^c	1.7	0.31	16
26	Cp*TiMe ₂ C ₆ F ₅	-78	11.1 ^c	1.8	0.04	2
27	Cp*TiMe ₂ OC ₆ F ₅	-78	10.2 ^c	1.9	0.04	2

^a Polymerization time 5 min. ^b All GPC curves are multimodal. ^c Values from GPC curve with highest M_w.

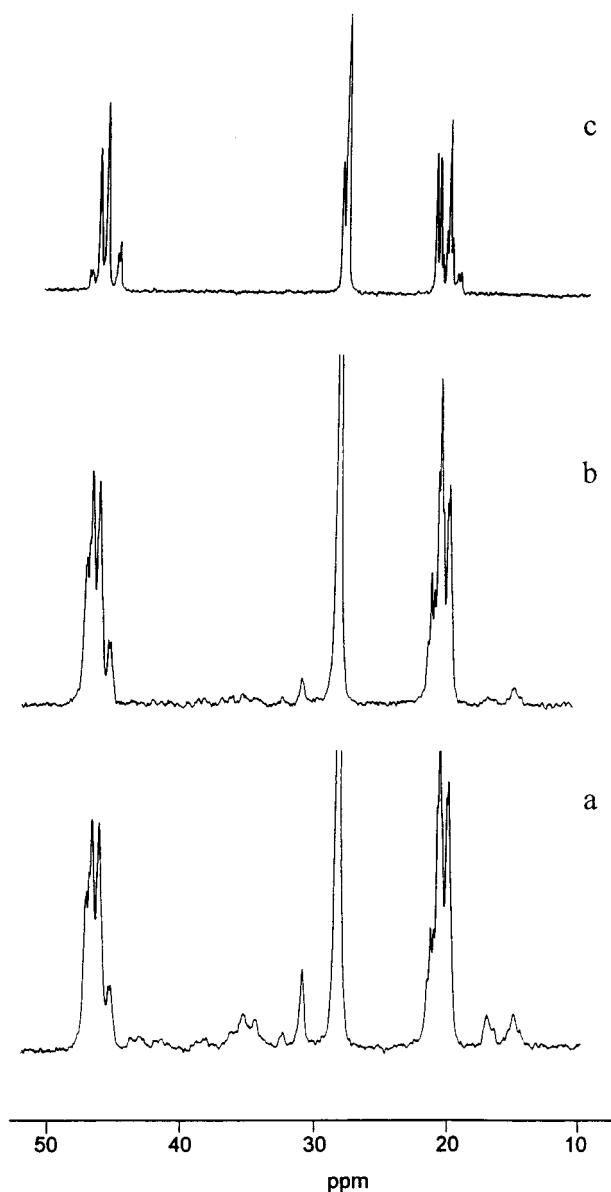


Figure 4. ¹³C{¹H} NMR spectra of polypropylene made using **D** in toluene at initiation temperatures of (a) 25 °C, (b) 0 °C, and (c) -78 °C.

considerably, since insertion of propylene after a 2,1-insertion occurs at a rate 100 times slower than that after a 1,2-insertion,¹⁵ resulting in lower activities in these systems. In addition, it has been shown that 2,1-insertion is often followed by β-H elimination to give 2-butenyl groups (see below);^{16,17} since 2,1-regioerrors within polymer chains are rarely found, it has thus been inferred that chain termination normally occurs

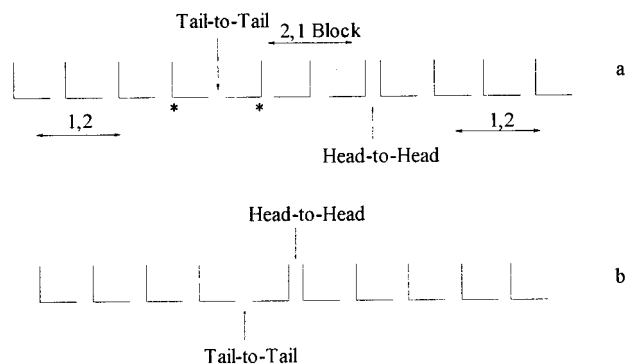


Figure 5. Block (a) and isolated (b) 2,1-insertions. Asterisks denote the methine signals observed at δ 30.4 in Figure 4a,b.

immediately after a 2,1-insertion.^{16,17} Considering the fact that the molecular weights and activities reported here are relatively high for PP formed at 25 °C (M_w ≈ 3 × 10⁵, A ≈ (2–4) × 10⁵), the restrictions on 1,2-insertions after a 2,1-regioerror must be considerably lower for these half-sandwich complexes than in metallocene systems. It seems likely that the relatively high propensity toward 2,1-insertion observed here arises from the less crowded nature of the half-sandwich complexes relative to metallocenes, thus permitting sterically more demanding secondary insertions to occur more readily.

The fact that the ¹³C NMR spectra of PP samples prepared at -78 °C exhibit no resonances in the regions δ 38.2–42.4, 32.2–34.7, and 12.4–15.6 (Figure 4c) implies that 2,1-misinsertions do not occur at this temperature. The reasons for this behavior are not clear, but it seems likely that steric factors result in a sufficiently high energy of activation for 2,1-insertion that this process occurs at a relatively low rate at -78 °C. The systems described here thus differ from the above-mentioned vanadium systems, which also give regioirregular PP, but at all temperatures studied.^{13b}

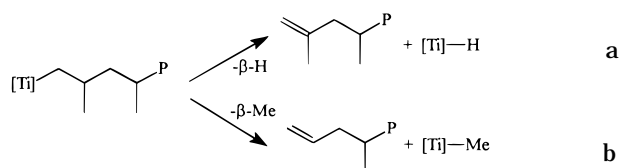
High-molecular-weight atactic PP is currently of interest because of its elastomeric properties,¹⁸ and different types of elastomeric PP (eIPP) have been discovered recently. For instance, the C_{2v} symmetric catalyst Me₂Si(9-Flu)₂ZrX₂ (of type **E**) with MAO pro-

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(16) Jüngling, S.; Mülhaupt, R.; Stehling, U.; Brintzinger, H.-H.; Fischer, D.; Langhauser, F. *J. Polym. Sci., Part A* **1995**, *33*, 1305. (b) Tsutsui, T.; Kashiwa, N.; Mizuno, A. *Makromol. Chem. Rapid Commun.* **1990**, *11*, 565.

(17) Resconi, L.; Piemontesi, F.; Camurati, I.; Balboni, D.; Sironi, A.; Moret, M.; Rychlicki, H.; Zeigler, R. *Organometallics* **1996**, *15*, 5046.

Following a 1,2 insertion:



Following a 2,1 misinsertion:

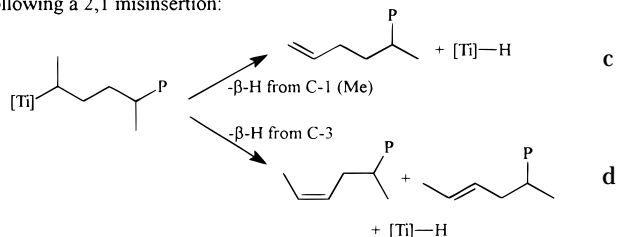


Figure 6. Chain termination mechanisms involving a 1,2-insertion followed by (a) β -H elimination from C-2, (b) β -Me elimination from C-2, and 2,1-insertion followed by (c) β -H elimination from C-1 (Me) and (d) β -H elimination from C-3 (two modes).

duces atactic ePP with molecular weights of $>200\,000$ ^{18d} and random incorporation of isotactic blocks.^{18b,c} In contrast, the elastomeric PP produced by the Coates-Waymouth C_2/C_2 symmetric "oscillating" catalyst contains isotactic blocks.^{18a} In all of these cases, the degree of regioerror incorporation is at the most 1%.

Chain Transfer Mechanisms. Identification of the chain transfer processes involved in the termination of polymer chain growth is an important aspect in the control of molecular weights and polydispersities and may in principle be effected by NMR analysis of the unsaturated chain end groups. For polypropylene, the main chain transfer mechanisms during group 4 metallocene/MAO polymerizations involve β -hydrogen transfer to the metal or to a coordinated monomer unit, resulting in a vinylidene end group (Figure 6a),¹⁸ chain transfer to the Al cocatalyst, resulting in saturated end groups following hydrolysis,¹⁹ and β -methyl elimination, giving vinyl end groups (Figure 6b).²⁰ Following 2,1-insertions, β -hydride transfer may result in the formation of both vinyl (Figure 6c) and 2-butenyl end groups (Figure 6d).^{17,18}

Unfortunately, the molecular weights of the PP samples discussed above were too high and the materials were too insoluble for the weak end group resonances to be identifiable by NMR spectroscopy. Samples of PP of relatively low molecular weight ($M_w \approx 4 \times 10^4$, $M_w/M_n \approx 5$) and hence also of greater solubility were therefore prepared at 70 °C, utilizing all four catalysts A–D. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were obtained at 400.14 (Figure 7) and 100.6 (Figure 8) MHz, respectively, higher frequencies than was the case for the ^{13}C -

$\{^1\text{H}\}$ spectra discussed above, and analyses of the olefinic end groups were now possible, although the molecular weights were still much higher than those of PP samples, for which accurate end group analyses have been achieved elsewhere utilizing $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy.

The olefinic region of the ^1H NMR spectrum is shown in Figure 7, where there are observed quite complex resonances attributable to vinyl (δ 5.78, m; δ 4.99, m) and vinylidene (δ 4.74, s; δ 4.67, s) end groups in approximately equal amounts, as well as weaker internal olefin resonances at $\sim\delta$ 5.35. The resonances at $\sim\delta$ 5.35, attributed to 2-butenyl end groups^{17a,18} arising from β -hydride elimination after a 2,1-insertion, are weak, suggesting that the β -hydrogen elimination process of Figure 6d does not occur to a significant extent. Proportions of the three types of olefinic functionalities, based on integrations of the ^1H chemical shift data, are listed in Table 3, and as can be seen, catalysts A–D all produce very similar materials. While the vinylidene resonances clearly provide firm evidence for the expected β -hydrogen elimination process of Figure 6a, it is interesting to note the presence of relatively strong resonances attributable to vinyl end groups. The latter may arise either via the β -methyl elimination process of Figure 6b or, following 2,1 insertion, via β -hydride elimination from the methyl group (Figure 6c). The formation of low-molecular-weight polypropylene using highly substituted metallocenes has been attributed to facile β -methyl elimination,^{19c,21} but no β -methyl elimination was evident using the less encumbered mixed cyclopentadienyl system $\text{Cp}^*\text{CpZrCl}_2/\text{MAO}$, possibly for steric reasons.¹⁰ No such steric argument can be applied to the mono- Cp^* systems investigated here, however, since the number of vinyl end groups present in PP samples prepared using both $\text{Cp}^*\text{TiMe}_2\text{Cl}/\text{B}(\text{C}_6\text{F}_5)_3$ and the more sterically demanding $\text{Cp}^*\text{TiMe}_2\text{C}_6\text{F}_5/\text{B}(\text{C}_6\text{F}_5)_3$ are the same ($\sim 40\%$) within experimental error. Thus, it is of interest to ascertain whether β -methyl elimination is a factor in these systems.

The 100.6 MHz $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum in the region δ 10–50 is shown in Figure 8, where the effects of greater chemical shift dispersion are obvious. Although only pentad resonances of the higher molecular weight materials could be resolved at 50.38 MHz, even at 120 °C, in this case hexad resolution of the methyl region was easily achieved in spectra run at room temperature. Of interest here, analysis of the spectrum revealed weak resonances at $\delta \sim 22.5$, ~ 23.5 , and ~ 25.2 , which are reasonably attributed to the methyl and methine resonances of isobutyl end groups. These resonances were clearly much more intense than those of the olefinic end groups, which were not observed at all, and thus it would seem that β -methyl elimination processes may well occur to a significant extent. However, the unusually high complexity of the vinyl and vinylidene ^1H resonances suggest that the corresponding ^{13}C resonances would be complex multiplets and that individual signals could be indistinguishable from baseline noise.

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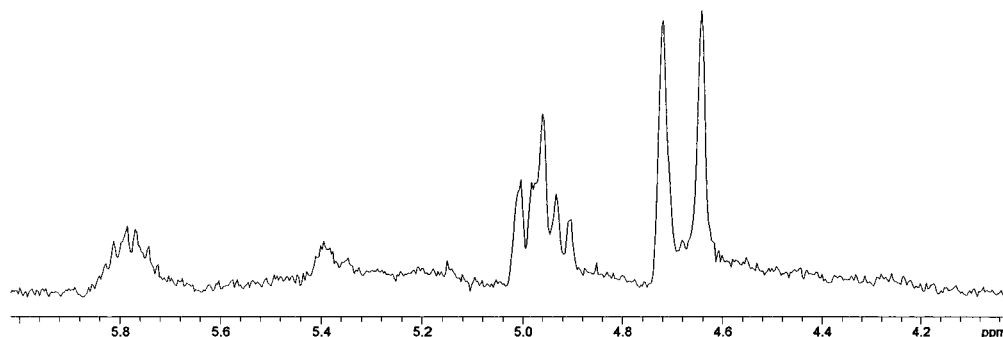


Figure 7. ^1H NMR spectrum (400 MHz) in the olefinic region of low-molecular-weight PP prepared at 70 °C.

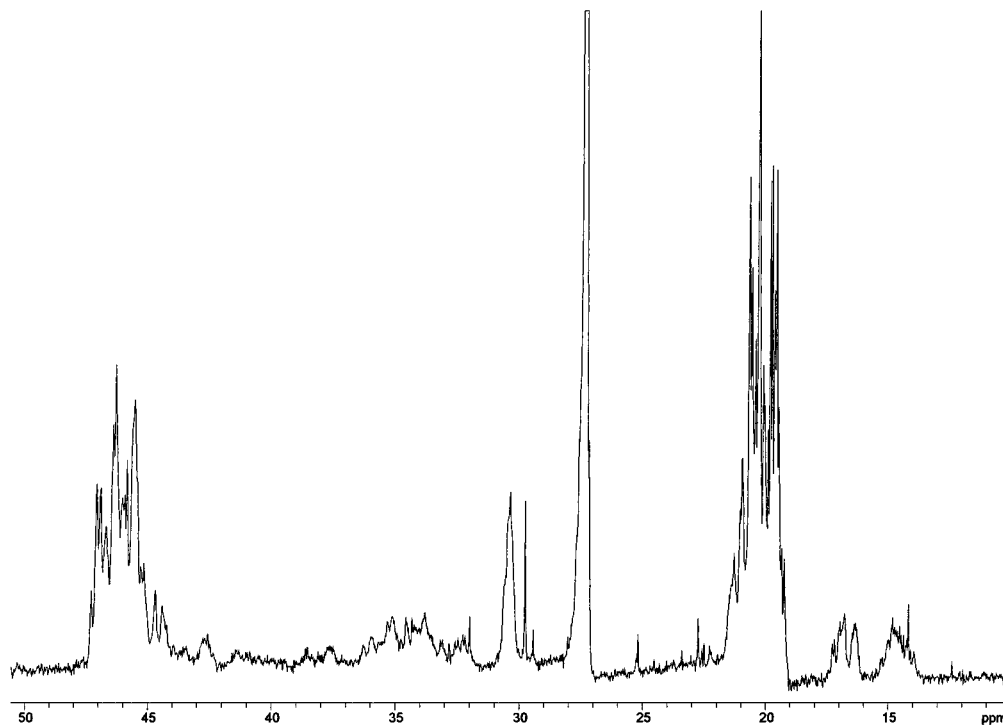


Figure 8. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum (100.6 MHz) of a low-molecular-weight PP prepared at 70 °C.

Thus, the question concerning β -methyl elimination processes perhaps remains moot.

As pointed out above, predominant β -hydrogen elimination would result in PP containing mostly *n*-propyl end groups. Although a sharp singlet at δ 14.2 is reasonably attributable to the *n*-propyl methyl resonance, the ^{13}C resonances of this group are largely obscured by the main backbone methylene resonance and the above-mentioned, broad resonances which result from regioirregularities. Significant β -methyl elimination would, however, result in chain transfer processes involving 1,2-insertion of monomer into newly formed Ti–Me bonds to give isobutyl end groups, as are obtained in the initiation step (see above), with $^{13}\text{C}\{^1\text{H}\}$ resonances at $\sim\delta$ 23 (Me) and $\sim\delta$ 25.5 (methine). If the initiation step were the only process leading to isobutyl end group formation, relatively few polymer chains should contain isobutyl groups and the isobutyl $^{13}\text{C}\{^1\text{H}\}$ resonances should be much weaker than those of the olefinic end groups, which occur in all polymer chains. If, however, all chain transfer processes involved β -methyl elimination, then the isobutyl and olefinic groups should be present in comparable amounts, although some of the former would also result from chain

termination induced by hydrolysis of Ti–CH₂CHMe~P linkages.

It must be made clear that the conclusions reached for PP prepared at 70 °C do not necessarily apply to materials prepared at lower temperatures. Although we can reasonably presume the identity of catalysts of the type $[\text{Cp}^*\text{TiMeE}]^+$ at –78 °C, which produce PP exhibiting ^1H NMR spectra that contain just methylene, methine, and methyl resonances (Figure 4c), the polymerization chemistry at 0 °C and above is clearly much more complicated, as attested to by Figure 4a,b and the broadened, albeit unimodal, molecular weight distributions (Table 2). Unfortunately, the very high molecular weights and low solubilities of the polymeric materials obtained at the lower temperatures prevented their thorough characterization by NMR spectroscopy.

Solvent Effects on the Polymerization Process.

There is compelling evidence that counterion interactions can play a vital role in the activity of metallocene catalysts, quite significant increases in activities of metallocene systems being observed when, for instance, $[\text{MeB}(\text{C}_6\text{F}_5)_3]^-$ is replaced by the more weakly coordi-

nating anion $[\text{B}(\text{C}_6\text{F}_5)_4]^-$.²² Catalysts incorporating *para*-substituted fluoroarylborate counteranions exhibit intermediate activities,^{3d} and it is now clear that displacement of counterion by olefin from the inner coordination sphere of the metal cation can be non-trivial.

There is, however, conflicting evidence concerning the effects of solvent polarity on catalyst activity.²³ Although a solvent of higher dielectric constant (CH_2Cl_2 , $\epsilon = 9.08$) is expected to promote separation of ion pairs (eq 2), shifting the equilibrium to the right to a greater extent than in toluene ($\epsilon = 2.38$) and thus increasing the catalyst activity, Chien et al. have reported negligible solvent effects on the activities of the *rac*-Et-(ind)₂ZrCl₂/MAO system^{23c} and Oliva et al. have noted a 100-fold increase in the activity of Cp₂TiCl₂ when activated with AlMe₃/AlMe₂F^{23a} on going from toluene to CH₂Cl₂, while Fink et al. have found a 15-fold increase in activity of a related zirconocene/MAO system.^{23b}

We have therefore repeated the propylene polymerizations in CH₂Cl₂ under the same conditions used for polymerizations in toluene, in part because we have spectroscopically characterized the catalysts **A–D** at -50°C in CD₂Cl₂, and polymerization in the same solvent would provide strong evidence that the cationic species $[\text{Cp}^*\text{TiMeE}]^+$ do indeed bind and activate monomers during polymerization. Indeed, for both solvents at -78°C , we find that the amount of polymer produced generally decreases as E becomes more electron-withdrawing, *i.e.* as the strength of the Ti⁺–MeB(C₆F₅)₃[–] interaction increases.⁷ However, the amount of polymer obtained in toluene is actually higher than that obtained in CH₂Cl₂, in which ion-pair dissociation is presumably more facile. While we have previously shown that $[\text{CpTiMe}_2]^+$ coordinates toluene in an η^6 -fashion,^{5a,b} possibly contributing to disruption of the interaction between the metal center and the counterion and thus resulting in a greater activity than one would otherwise expect, toluene coordination could also be expected to result in lowered polymerization activity because of competition for coordination sites by solvent. Another factor, difficult to assess, is the probability that those systems exhibiting broad molecular weight distributions involve multiple catalytic sites, possibly of varying lifetimes.

Possible evidence for mechanistic similarities in the two solvents, however, is that the NMR spectra of the PP (¹³C{¹H} NMR) formed at 25°C in CH₂Cl₂ are very similar to those of the PP produced in toluene. However, while polymerizations are complete within 5 min in CH₂Cl₂ under the same conditions which require 20 min in toluene, the activities of the catalysts **A–D** in CH₂Cl₂ are actually less than in toluene after correcting for the increased solubility of propylene in CH₂Cl₂ compared to toluene. Therefore, there does not appear to be an increase in the activities of the catalysts **A–D** in the more polar solvent, and the role of toluene in

these polymerizations may be more complex than was first anticipated.

Nature of the Active Catalytic Species. The compounds Cp*TiMeE(μ -Me)B(C₆F₅)₃ (E = Me, C₆F₅, OC₆F₅) are all precursors of the cationic species $[\text{Cp}^*\text{TiMeE}]^+$ which, on the basis of a very extensive literature,^{1,3–6} are reasonably believed to be the initiators of polymer chain growth. However, organotitanium(IV) compounds are susceptible to reduction, and there is now extensive evidence for the formation of titanium(III) species, detected utilizing EPR spectroscopy, in many olefin polymerization systems involving monocyclopentadienyltitanium compounds. Thus, not surprisingly, treatment of many monocyclopentadienyltitanium(IV) compounds with alkylaluminum compounds results in at least partial reduction to EPR-active species.^{4k,24} However, treatment of compounds of the type Cp*TiR₃ with B(C₆F₅)₃, expected to give only $[\text{Cp}^*\text{TiR}_2]^+$, has also been reported to yield EPR-active titanium(III) species, some of which are found to behave as olefin polymerization catalysts.^{4u,x} In addition, constrained-geometry compounds of the type (η^5 -C₅H₄SiR₂-NR')TiMe (R, R' = alkyl, aryl), in which η^5 coordination of the η^5 -C₅H₄SiR₂NR' ligand is reinforced by simultaneous coordination of the amide nitrogen atom to the titanium(III), are also good catalysts for the polymerization of ethylene and 1-octene,²⁵ and we have therefore utilized EPR spectroscopy to assess the possibility that titanium(III) species are involved in the catalytic system discussed here.

Our EPR investigation has involved treatment of Cp*TiMe₃ with B(C₆F₅)₃ in the solvents chlorobenzene and toluene, in the absence and in the presence of propylene under normal polymerization conditions. In contrast to results reported elsewhere,^{4u} we find that the EPR spectrum of a reaction mixture containing equimolar amounts of Cp*TiMe₃ and B(C₆F₅)₃ in chlorobenzene exhibited only a very weak doublet at $g = 1.994$ ($A = 8.4$ G). The magnitude of the hyperfine splitting implies that the resonance may reasonably be attributed to the type of titanium(III) hydride reported from the reaction of CpTi(OBu)₃ with MAO,^{4k} although on the basis of the integrated intensity, the titanium(III) species amounted to much less than 0.01% of the total titanium in solution. Repetition of this experiment in a toluene solution saturated with propylene resulted in the formation of copious amounts of polymer, as described above, and the EPR spectrum now exhibited either *no* titanium(III) resonance or a weak singlet at $g = 1.981$. Although the absence of hyperfine coupling to a hydride ligand may well be a result of olefin insertion,^{4k} it seems unlikely that major proportions of the polymers formed by the catalyst systems described here result from titanium(III) catalysis since, in at least one case, an active polymerizing mixture was EPR silent. However, in view of the somewhat broad molecular weight distributions in some cases, we cannot rule out the possibility that some of the polymers formed are generated by titanium(III).

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To our surprise, we observe no evidence in toluene for the species at $g = 1.979(3)$ and $g = 1.977(3)$ reported elsewhere as arising from reaction of Cp^*TiMe_3 with $\text{B}(\text{C}_6\text{F}_5)_3$ in chlorobenzene.^{4u} Further experiments will hopefully shed light on this apparent anomaly.

Conclusions

The compound $\text{Cp}^*\text{TiMe}_2(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ and the chiral compounds $\text{Cp}^*\text{TiMe}(\text{C}_6\text{F}_5)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Cp}^*\text{TiMe}(\text{OC}_6\text{F}_5)(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$, and $\text{Cp}^*\text{TiMeCl}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ all polymerize ethylene to high-molecular-weight polyethylene and propylene to atactic, elastomeric polypropylene (PP). In all cases, the catalytically active species are believed to be titanium(IV) complexes of the type $[\text{Cp}^*\text{TiMeE}]^+$ ($\text{E} = \text{Me}, \text{Cl}, \text{C}_6\text{F}_5, \text{OC}_6\text{F}_5$), but minor contributions from related titanium(III) complexes cannot be ruled out since very low concentrations of titanium(III) species are sometimes detected via EPR spectroscopy. Although the compounds $\text{Cp}^*\text{TiMeE}(\mu\text{-Me})\text{B}(\text{C}_6\text{F}_5)_3$ ($\text{E} = \text{C}_6\text{F}_5, \text{OC}_6\text{F}_5$), containing the more electron-withdrawing ligands, were expected to be the better catalysts, the anticipated results were only partially achieved. While PP molecular weights are higher with these catalysts, the activities are actually lower because the greater Lewis acidity of the cationic species $[\text{Cp}^*\text{TiMeE}]^+$ results in stronger coordination of the $[\text{BMe}(\text{C}_6\text{F}_5)_3]^-$ anion. Although comparisons of activities with data for similar systems are difficult because of differences in experimental procedures, the compounds investigated here are definitely more active than is $\text{CpTiCl}_3\text{-MAO}$ and probably comparable with $\text{Cp}^*\text{TiCl}_3\text{-MAO}$ and a series of MAO-activated [(2-(dimethylamino)ethyl)cyclopentadienyl]titanium compounds containing a substituted cyclopentadienyl group incorporating a donor group in a side chain.^{4v}

NMR analyses of the PP formed show that initiation involves 1,2-insertion into a Ti-Me bond, while propagation involves primarily head-to-tail 1,2-insertions. An unusually high proportion of the propagation steps involve 2,1-misinsertions but essentially no 1,3-enchainment. The major olefinic end groups are vinylidene ($\text{CH}_2=\text{CMe}-$), resulting from β -hydrogen transfer following a 1,2-insertion, and vinyl ($\text{CH}_2=\text{CH}-$), resulting from β -hydrogen transfer from the methyl group following a 2,1-insertion or, more likely, β -methyl transfer following a 1,2-insertion. Small amounts of internal olefins are also formed via β -hydrogen transfer following a 2,1-insertion. The indiscriminate nature of the propylene polymerization relative to catalysis by metallocenes appears to be a result of the relatively uncrowded nature of the inner coordination sphere of the mono- Cp^* catalysts. The sterically rather demanding transition state for 2,1-insertion can be achieved much more readily than is the case for metallocene systems, where sterically less demanding 1,2-insertion steps predominate.

Experimental Section

All experiments were carried out under nitrogen (prepurified grade) using standard Schlenk line techniques, a Vacuum

Atmospheres glovebox and dried, thoroughly deoxygenated solvents. Polymer samples for high-temperature NMR studies were prepared by dissolving ca. 200 mg of polymer in 2 mL of *o*-dichlorobenzene in a 10 mm o.d. NMR tube. The $^{13}\text{C}\{^1\text{H}\}$ spectra were referenced with respect to external TMS using the residual carbons of internal diglyme (5 mm o.d. coaxial tube placed within the sample) and were run at 120 °C on a Bruker CXP-200 NMR spectrometer operating at 50.38 MHz; 5 000–10 000 transients were collected for each spectrum. For end group analyses of the PP prepared at 70 °C, ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra were run at room temperature in CDCl_3 on a Bruker AM-400 spectrometer operating at 400.14 and 100.6 MHz, respectively. The NMR samples were prepared by dissolving ca. 100 mg of polymer in a 5 mm NMR tube in 0.7 mL of CDCl_3 and were referenced to external TMS using the residual protons or carbons of the solvent. Assignments were based on both the literature precedents cited and on model compounds.²⁶ EPR experiments involving equimolar amounts of Cp^*TiMe_3 and $\text{B}(\text{C}_6\text{F}_5)_3$ (0.01–0.06 mmol of each in 10 mL solution) were run on a Bruker R-B70 EPR spectrometer at ~ 9.7 GHz with the field centered at ~ 3400 G; the magnetic field was calibrated with DPPH ($g = 2.0037$), and standard solutions of TEMPO (1×10^{-3} – 1×10^{-5} M) were used for quantitative estimates of the concentrations of titanium(III) species present. Gel permeation chromatograms (GPC) of the polymers were obtained at 145 °C in 1,2,4-trichlorobenzene using a Waters Model 150-C GPC or in THF at room temperature using a Waters Model 440 liquid chromatograph; data were analyzed using polystyrene calibration curves. The compounds Cp^*TiMe_3 ,²⁷ $\text{Cp}^*\text{TiMe}_2\text{Cl}$,²⁷ $\text{Cp}^*\text{TiMe}_2\text{OC}_6\text{F}_5$,⁷ $\text{Cp}^*\text{TiMe}_2\text{C}_6\text{F}_5$ ⁷ and $\text{B}(\text{C}_6\text{F}_5)_3$ ²⁸ were prepared according to literature procedures.

Polymerization of Propylene and Ethylene. In a typical procedure, 0.06 mmol of catalyst precursor ($\text{Cp}^*\text{TiMe}_2\text{E}$, $\text{E} = \text{Me}, \text{Cl}, \text{C}_6\text{F}_5, \text{OC}_6\text{F}_5$) was dissolved in 5 mL of solvent which was saturated with monomer. The solution was then treated with $\text{B}(\text{C}_6\text{F}_5)_3$ (0.06 mmol, 31 mg) in 5 mL of solvent. Bubbling of monomer through the catalyst solution was continued throughout the polymerization for a further 5–20 min before quenching with an excess of methanol. The polymer samples were washed with methanol and dried under reduced pressure for 16 h. In experiments performed at -78 °C, 2 mL of propylene was cannulated into the solution of catalyst precursor, and the cocatalyst was added in 4 mL of solvent.

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