Organometallics **1996,** *15,* 693−703

Ethylene, Styrene, and α-Methylstyrene Polymerization by Mono(pentamethylcyclopentadienyl) (Cp*) Complexes of Titanium, Zirconium, and Hafnium: Roles of Cationic Complexes of the Type $[Cp^*MR_2]^+$ (R = Alkyl) as both Coordination Polymerization Catalysts and Carbocationic Polymerization Initiators

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Received March 14, 1995[⊗]

A variety of monocyclopentadienyl and mono(pentamethylcyclopentadienyl) complexes of titanium, zirconium, and hafnium are assessed for abilities to initiate polymerization of ethylene, styrene, and, in part, α-methylstyrene. In general, little or no activity was found for either neutral species of the types $CpMMe_3$ and $CpMMe_2OR$ or for cationic 12- and 14-electron species of the types $[CpMR_2L]^+$ and $[CpMR_2L_2]^+$, respectively (Cp = η^5-cyclopentadienyl; R = alkyl; L = amine, phosphine ligands). In contrast, much better olefin polymerization initiators result from abstraction of a methyl carbanion from Cp^*MMe_3 (Cp* = η^5-pentamethylcyclopentadienyl) by $B(C_6F_5)_3$, a reaction which gives cationic, 10-electron species of the type "$[Cp^*MMe_2][BMe(C_6F_5)_3]$". Of these, the complex $[Cp^*TiMe_2][BMe(C_6F_5)_3]$ (**A**) is an excellent initiator or initiator precursor for the polymerization of ethylene and styrene, resulting in high yields respectively of high molecular weight polyethylene and atactic (a-PS) and/or syndiotactic polystyrene (s-PS), depending on conditions; the tacticity of purified s-PS, as judged by $^{13}C\{^1H\}$ NMR spectroscopy, approaches 100%. While the polymerization of ethylene probably involves a classical Ziegler−Natta process, polymerization of styrene to s-PS and a-PS apparently involves respectively a Ziegler−Natta process and carbocationic initiation. High yields of essentially syndiotactic poly(α-methylstyrene) are obtained by utilizing the same initiator system, also apparently via a carbocationic process.

Introduction

There has in recent years been extensive research into the utilization of titanocene, zirconocene, and hafnocene derivatives as homogeneous catalysts for olefin polymerization,[1] and it is now realized that the best catalysts incorporate the following structural features: the presence of a coordinated alkyl ligand, of a vacant site, and of a positive charge. For instance, 16-electron complexes of the type $[Cp'_2MR(L)]^+$ (M = Ti, Zr, Hf; Cp′ = substituted η^5-cyclopentadienyl group; R = alkyl group; L = labile ligand) form probably the most extensively studied class of homogeneous catalysts for the polymerization of olefins.

In contrast, although it might be anticipated that electronically less saturated, sterically less hindered monocyclopentadienyl complexes of the general stoichiometries $[Cp'MRL_2]^{2+}$ or $[Cp'MR_2L]^+$ might behave as even more reactive catalysts, in fact until recently relatively few publications have described the utilization of monocyclopentadienyl compounds of titanium, zirconium, and hafnium as olefin polymerization initiators.[2]

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[⊗] Abstract published in *Advance ACS Abstracts*, December 1, 1995.

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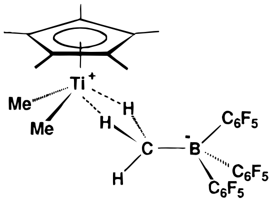
0276-7333/96/2315-0693$12.00/0

Interestingly, while very few reports concerning polymerization of styrene by metallocene systems have appeared, a majority of the reports[2b,c,j,l−r] describing monocyclopentadienylmetal catalysts, as well as a number of patents,[3] are concerned largely with polymerization of styrene to *syndiotactic* polystyrene (s-PS), a material which is currently receiving considerable attention[4] because of its high melting point and low solubility in organic solvents.[4f]

We have previously demonstrated that treatment of the compounds Cp*MMe$_3$ (M = Ti, Zr, Hf; Cp* = η^5-pentamethylcyclopentadienyl) with B(C$_6$F$_5$)$_3$ results in methyl carbanion abstraction and formation of the complexes [Cp*MMe$_2$][MeB(C$_6$F$_5$)$_3$], as shown in eq 1 for M = Ti.[5a]

$$Cp^*TiMe_3 + B(C_6F_5)_3 \rightarrow [Cp^*TiMe_2][MeB(C_6F_5)_3] \tag{1}$$

Similar results have been reported by others.[2j] When M = Ti, at least, the product appears to exist in methylene chloride solution as the labile, methyl-bridged species Cp*MMe$_2$(μ-Me)B(C$_6$F$_5$)$_3$ (**A**), in equilibrium probably with the solvent-separated, ionic complex [Cp*MMe$_2$(CH$_2$Cl$_2$)][MeB(C$_6$F$_5$)$_3$].[5a] Analogous metallocene compounds, with methyl groups linking this same borate anion to transition metal ions in a similar fashion, have been reported.[6]



A

In aromatic solvents, on the other hand, arene complexes of the type [Cp*MMe$_2$(η^6-arene)][MeB(C$_6$F$_5$)$_3$] are formed.[5a] Since the MeB(C$_6$F$_5$)$_3^-$, CH$_2$Cl$_2$, and arene ligands are readily displaced, these complexes all behave in solution as sources of the cationic, 10-electron species [Cp*MMe$_2$]$^+$, which might be expected to behave as excellent homogeneous olefin polymerization catalysts. We now describe our findings on the use of [Cp*MMe$_2$]$^+$ and related species as catalysts/initiators for the polymerization of ethylene, styrene, and α-methylstyrene, and we provide evidence that this family of complexes can operate as *carbocationic polymerization initiators* as well as precursors of conventional Ziegler−Natta polymerization catalysts. In particular, we show that compound **A** is an excellent initiator or initiator precursor for the polymerization of ethylene and styrene, resulting in high yields respectively of high molecular weight polyethylene and atactic (a-PS) and/or highly stereoregular syndiotactic polystyrene (s-PS), depending on conditions. While the polymerizatio of ethylene probably involves a classical Ziegler−Natta process, polymerization of styrene to s-PS and a-PS apparently involves respectively a Ziegler−Natta process and carbocationic initiation.

To our knowledge, **A** is the first soluble, metallocene-like compound which can initiate polymerization of an olefin via two fundamentally different mechanisms, all others being considered (albeit not always demonstrated) to behave only as single-site initiator species. Aspects of this work have appeared previously as a communication,[5b] but we now retract the earlier conclusion[5b] that s-PS is formed via a carbocationic process.

Experimental Section

All experiments were carried out under nitrogen using standard Schlenk line techniques, a Vacuum Atmospheres glovebox and dried, thoroughly deoxygenated solvents. ^{1}H, ^{13}C{^{1}H}, and ^{19}F NMR spectra were run using a Bruker AM 400 spectrometer operating at 400.14, 100.6, and 376.5 MHz, respectively; ^{1}H and ^{13}C{^{1}H} spectra are referenced with respect to internal TMS using residual proton resonances or carbon resonances, respectively, of the solvents, and ^{19}F spectra to external CFCl$_3$. Spectra of polymers at high temperatures were also run in 1,1,2,2-tetrachloroethane-d_2 on a Bruker CXP-200 NMR spectrometer. Differential scanning calorimetric (DSC) measurements were recorded using a Mettler TA 3000 system or a DuPont Instruments Model 912 differential scanning calorimeter. 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 DuPont Instruments Model 850 or a Waters Model 440 liquid chromatograph; data were analyzed using polystyrene calibration curves. Elemental analyses were performed by Canadian Microanalytical Services or at E. I. DuPont de Nemours, Central Research and Development, Wilmington, DE.

The following compounds were prepared as described previously: Cp*MMe$_3$ (M = Ti,[7a] Zr,[7b] Hf[7c]), CpTiMe$_3$,[7d] Cp*ZrPh$_3$,[7b] B(C$_6$F$_5$)$_3$,[7e] Cp*Ti(CH$_2$Ph)$_3$,[7a] [(C$_5$H$_4$Me)$_2$Fe][BPh$_4$],[7g] [Cp*ZrMe$_2$(THF)$_2$][BPh$_4$].[7h]

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$[HNEt_3][B(C_6F_5)_4]$. A solution of 0.35 g of triethylammonium chloride (2.50 mmol) in distilled water was added to a stirred solution of 1.62 g of $Li[B(C_6F_5)_4]$[7e] (2.36 mmol) in water at 0 °C. The reaction mixture was stirred for 1 h at room temperature, and then the white precipitate was collected by filtration, washed with water, and dried in vacuo for 20 h. Yield: 1.57 g (85%). ^1H NMR (CD_2Cl_2): δ 4.93 (br t, 1H, J_{NH} 52.8 Hz, NH), 3.27 (dq, 6H, J 2.28, 7.32 Hz, CH_2), 1.36 (t, 9H, Me). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 148.7 (d, J_{CF} 245.3 Hz), 138.8 (d, J_{CF} 249.4 Hz), 136.9 (d, J_{CF} 247.6 Hz), 128.2 (br, *ipso* C), 48.6 (CH_2), 9.2 (Me). ^{19}F NMR (CD_2Cl_2): δ −133 (d, *o*-F), −165 (t, *m*-F), −168 (t, *p*-F).

$[Ph_3C][MeB(C_6F_5)_3]$. This compound was synthesized by utilizing a procedure provided by Bochmann.[7j] To a solution of 0.75 g of $Li[MeB(C_6F_5)_3]$ (1.5 mmol), prepared by reacting equimolar amounts of MeLi and $B(C_6F_5)_3$, in 20 mL of CH_2Cl_2 was added 0.45 g of Ph_3CCl (1.5 mmol) in 10 mL of CH_2Cl_2. After the mixture was stirred overnight at room temperature, the resulting orange precipitate was collected by filtration, washed with hexane, and dried *in vacuo*.

$CpTiMe_2(OPr^i)$. $CpTiCl_3$ (1.12 g, 5.11 mmol) in 100 m L of ethyl ether was treated dropwise with 2-propanol (0.39 mL; 5.11 mmol) and triethylamine (0.71 mL; 5.11 mmol) in 25 mL of ethyl ether. The reaction mixture was stirred for 12 h, after which the resulting yellow suspension was filtered off. The solvent was then removed from the filtrate, and the resulting product, $CpTiCl_2(OPr^i)$, was purified by sublimation. Yield: 1.03 g (83%). ^1H NMR (toluene-d_8): δ 6.07 (s, 5H, Cp), 4.32 (septet, J_{HH} 6.2, 1H, CH), 0.96 (d, 6H, Me).[7f] A solution of $CpTiCl_2(OPr^i)$ (0.83 g, 3.42 mmol) in 25 mL of ethyl ether, cooled to 0 °C, was treated with 6.84 mmol of MeMgBr (2.30 mL of 3.0 M solution). The reaction mixture was filtered through Celite, and the filtrate was taken to dryness. Anal. Calcd for $C_{10}H_{18}OTi$: C, 59.42; H, 8.97. Found: C, 59.57; H, 9.04. ^1H NMR (benzene-d_6): δ 5.92 (s, 5H, Cp), 4.51 (septet, J_{HH} 6.1, 1H, CH), 1.17 (d, 6H, CMe), 0.64 (s, 6H, TiMe).

$CpTiMe_2(OBu^t)$. $CpTi(OBu^t)_3$ was formed by treating a solution of $CpTiCl_3$ (0.915 g, 4.17 mmol) in 150 mL of ethyl ether with *tert*-butanol (0.93 g, 12.5 mmol) and triethylamine (1.74 mL, 12.5 mmol). The reaction mixture was stirred for 16 h and filtered through Celite, and the solvent was removed from the filtrate to give a lemon-yellow oil. The latter was sublimed at 35 °C onto a cold finger at −78 °C to give $CpTi(OBu^t)_3$ as a colorless oil. Yield: 0.54 g (39%). ^1H NMR (toluene-d_8): δ 6.18 (s, 5H, Cp), 1.22 (s, 27H, Me). Reaction of $CpTiCl_3$ (0.172 g, 0.78 mmol) with $CpTi(OBu^t)_3$ (0.13 g, 0.39 mmol) in 100 mL of ethyl ether for 16 h, followed by solvent removal, yielded a yellow-green solid which, on sublimation, gave $CpTi(OBu^t)Cl_2$ as a bright yellow, crystalline solid. Yield: 0.18 g (88%). ^1H NMR (benzene-d_6): δ 6.14 (s, 5H, Cp), 1.09 (s, 9H, Me). A solution of $CpTi(OBu^t)Cl_2$ (0.11 g, 0.43 mmol) in 25 mL of ethyl ether at 0 °C was treated with 0.86 mmol of MeMgBr (0.29 mL of 3.0 M ethyl ether solution). The reaction mixture was stirred for 3 h and filtered through Celite, after which the solvent was removed from the filtrate to give $CpTiMe_2(OBu^t)$ as a lime green oil. Yield: 0.051 g (55%). Anal. Calcd for $C_{11}H_{20}OTi$: C, 61.12; H, 9.32. Found: C, 61.03; H, 9.19. ^1H NMR (benzene-d_6): δ 5.91 (s, 5H, Cp), 1.14 (s, 9H, CMe), 0.63 (s, 6H, TiMe).

$CpTiMe(OBu^t)_2$. $CpTi(OBu^t)_2Cl$ was prepared by treating a solution of $CpTiCl_3$ (2.58 g, 11.8 mmol) in 150 mL of ethyl ether with *tert*-butanol (1.74 g, 23.6 mmol) and triethylamine (2.38 mL, 23.6 mmol). The reaction mixture was stirred for 16 h and filtered through Celite, and the solvent was removed from the filtrate to give a dark yellow oil. The latter was sublimed at 45 °C onto a cold finger at −78 °C to give $CpTi(OBu^t)_2Cl$ as a yellow, crystalline solid. Yield: 2.71 g (78%). ^1H NMR (benzene-d_6): δ 6.21 (s, 5H, Cp), 1.18 (s, 18H, Me). A solution of $CpTi(OBu^t)_2Cl$ (0.78 g, 2.65 mmol) in 25 mL of ethyl ether was treated with 2.65 mmol of MeMgBr (0.88 mL of 3.0 M ethyl ether solution) at 0 °C. The reaction mixture was stirred for 3 h and filtered through Celite, and the solvent was then removed from the filtrate to give $CpTi(OBu^t)_2Me$ as a dark green oil. Yield: 0.30 g (41%). Anal. Calcd for $C_{14}H_{26}O_2Ti$: C, 61.31; H, 9.55. Found: C, 61.58; H, 9.66. ^1H NMR (benzene-d_6): δ 6.01 (s, 5H, Cp), 1.20 (s, 18H, CMe), 0.72 (s, 3H, TiMe).

$Cp^*TiMe_2(OCPh_3)$. A solution of Cp^*TiMe_3 (0.114 g, 0.50 mmol) in 50 mL of pentanes was treated dropwise with Ph_3COH (0.13 g, 0.50 mmol in 25 mL of 10:1 pentanes/toluene) at −78 °C. The reaction mixture was allowed to warm to room temperature over 2 h, and the solvent was removed under reduced pressure to give a solid residue which was dissolved in 5 mL of warm pentanes. On cooling of the solution to −15 °C for 16 h, $Cp^*TiMe_2(OCPh_3)$ was obtained as light yellow crystals. Yield: 0.17 g (70%). Anal. Calcd for $C_{31}H_{36}OTi$: C, 78.80; H, 7.68. Found: C, 79.16; H, 7.75. ^1H NMR (CD_2Cl_2): δ 7.0−7.5 (m, 15H, Ph), 1.76 (s, 15H, CMe), 0.25 (s, 6H, TiMe).

$Cp^*ZrMe_2(OCPh_3)$. A solution of Cp^*ZrMe_3 (0.272 g, 1.00 mmol) in 50 mL of pentanes was treated dropwise with Ph_3COH (0.26 g, 1.00 mmol in 25 mL of 10:1 pentanes/toluene) at −78 °C. The reaction mixture was allowed to warm to room temperature over 4 h, and the solvent was removed under reduced pressure to give a solid residue which was dissolved in 5 mL of warm pentanes. On cooling of the solution to −15 °C for 16 h, $Cp^*ZrMe_2(OCPh_3)$ was obtained as off-white crystals. Yield: 0.45 g (88%). Anal. Calcd for $C_{31}H_{36}OZr$: C, 72.18; H, 7.03. Found: C, 72.36; H, 7.13. ^1H NMR (toluene-d_8): δ 7.0−7.5 (m, 15H, Ph), 1.74 (s, 15H, CMe), 0.14 (s, 6H, ZrMe).

$Cp^*ZrMe_2(OCMePh_2)$. A solution of Cp^*ZrMe_3 (0.272 g, 1.00 mmol) in 50 mL of hexanes was treated dropwise with Ph_2CO (0.182 g, 1.00 mmol in 25 mL of hexanes) at −78 °C. The reaction mixture was allowed to warm to room temperature over 3 h, and the solvent was removed under reduced pressure to give a solid residue which was dissolved in 10 mL of hexanes. On cooling of the solution to −15 °C for 16 h, $Cp^*ZrMe_2(OCMePh_2)$ was obtained as white crystals. Yield: 0.41 g (91%). Anal. Calcd for $C_{26}H_{34}OZr$: C, 68.82; H, 7.55. Found: C, 68.96; H, 7.53. ^1H NMR (benzene-d_6): δ 7.0−7.5 (m, 10H, Ph), 1.91 (s, 3H, OCMe), 1.72 (s, 15H, CMe), 0.23 (s, 6H, ZrMe).

$Cp^*ZrMe(OCMePh_2)_2$. A solution of Cp^*ZrMe_3 (0.272 g, 1.00 mmol) in 50 mL of hexanes was treated dropwise with Ph_2CO (0.364 g, 2.00 mmol in 25 mL of hexanes) at −78 °C. The reaction mixture was allowed to warm to room temperature over 3 h, and the solvent was removed under reduced pressure to give a solid residue which was dissolved in 10 mL hexanes. On cooling of the solution to −15 °C for 16 h, $Cp^*ZrMe(OCMePh_2)_2$ was obtained as white crystals. Yield: 0.59 g (93%). Anal. Calcd for $C_{39}H_{44}O_2Zr$: C, 73.66; H, 6.97. Found: C, 73.35; H, 6.78. ^1H NMR (benzene-d_6): δ 7.0−7.4 (m, 20H, Ph), 1.89 (s, 6H, OCMe), 1.69 (s, 15H, Cp*), 0.58 (s, 3H, ZrMe).

$[Cp^*ZrMe_2(PMe_3)_2][MeB(C_6F_5)_3]$. A stirred solution of 0.272 g of Cp^*ZrMe_3 (1.00 mmol) in 10 mL of toluene at −78 °C was treated first with a solution of 0.511 g of $B(C_6F_5)_3$ (1.00 mmol) in CH_2Cl_2 cooled to −78 °C and then with a solution of 0.38 g of PMe_3 (5.0 mmol; added dropwise over 45 min) in 200

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mL of hexanes, also cooled to −78 °C. The resulting yellow precipitate was stirred at −78 °C for 30 min, and the product was collected by filtration, washed with hexanes, and dried in vacuo. Yield: 0.73 g (78%). Anal. Calcd for $C_{37}H_{42}BF_{15}P_2Zr$: C, 47.49; H, 4.52. Found: C, 47.94; H, 4.56. ^{1}H NMR (CD_2Cl_2 at 0 °C): δ 2.02 (s, 15H, Cp*), 1.38 (deceptively simple triplet, 18H, PMe), 0.41 (br s, 3H, BMe), 0.07 (t, *J* 5.4 Hz, 6H, ZrMe). $^{13}C\{^1H\}$ NMR (CD_2Cl_2 at 0 °C): δ 123.9 (Cp* ring C), 54.5 (t, J_{PC} 10.4 Hz, ZrMe), 12.6 (d, J_{PC} 10.2 Hz, PMe), 11.9 (br, BMe), 11.2 (Cp*Me).

[Cp*ZrMe$_2$(NEt$_3$)][MeB(C$_6$F$_5$)$_3$]. This compound was prepared as was the trimethylphosphine analogue but decomposed at room temperature. It was therefore generated by treating the previously described[5a] arene complex [Cp*ZrMe$_2$(η^6-toluene)$_2$][MeB(C$_6$F$_5$)$_3$] with triethylamine at low temperature and characterized spectroscopically. ^{1}H NMR (CD_2Cl_2 at −50 °C): δ 3.06 (q, J_{HH} 7.2 Hz, 6H, CH$_2$), 2.03 (s, 15H, Cp*), 1.04 (t, 9H, amine Me), 0.61 (s, 6H, ZrMe), 0.38 (br s, 3H, BMe).

[Cp*TiMe$_2$(NEt$_3$)][MeB(C$_6$F$_5$)$_3$]. This compound was formed by treating [Cp*TiMe$_2$][MeB(C$_6$F$_5$)$_3$] with triethylamine in CD_2Cl_2 at −50 °C, but it also could not be isolated. ^{1}H NMR (CD_2Cl_2 at 0 °C): δ 3.32 (q, J_{HH} 7.3 Hz, 6H, CH$_2$), δ 2.01 (s, 15H, Cp*), 1.35 (t, 9H, amine Me), 0.98 (s, 6H, TiMe), 0.45 (br s, 3H, BMe).

[Cp*TiMe$_2$(dmpe)][MeB(C$_6$F$_5$)$_3$]. A stirred solution of 0.114 g of Cp*TiMe$_3$ (0.50 mmol) in 20 mL of CH_2Cl_2 at −78 °C was treated first with a solution of 0.256 g of B(C$_6$F$_5$)$_3$ (0.50 mmol) in 15 mL of CH_2Cl_2 cooled to −78 °C and then with 0.15 g of dmpe (1.0 mmol). The resulting yellow solution was stirred at −78 °C for 30 min, and the product was precipitated with 200 mL of hexanes cooled to −78 °C, collected by filtration, washed with hexanes, and dried in vacuo. Yield: 0.39 g (88%). Anal. Calcd for $C_{37}H_{40}BF_{15}P_2Ti$: C, 49.91; H, 4.52. Found: C, 50.03; H, 4.58. ^{1}H NMR (CD_2Cl_2 at 0 °C): δ 1.97 (s, 15H, Cp*), 1.58 (deceptively simple triplet, 6H, PMe), 1.40 (deceptively simple triplet, 6H, PMe), 0.96 (br s, 4 H, CH$_2$) 0.72 (*t*, J_{PH} 10.4 Hz, 6H, PMe), 0.38 (br s, 3H, BMe).

Polymerization of Ethylene. In a typical procedure, 0.10 mmol of Cp*TiMe$_3$ was dissolved in 50 mL of solvent which was saturated with and blanketed by 1 atm of monomer. The solution was then treated with 0.10 mmol of B(C$_6$F$_5$)$_3$ in 10 mL of solvent, and the reaction mixture was stirred for 30 min under 1 atm of monomer. The polymerization was then quenched by adding 150 mL of methanol, and the precipitated polymer was collected by filtration, washed with methanol, and dried under reduced pressure at 50 °C for 16 h.

In an experiment involving efficient mixing, to 0.007 g of Cp*TiMe$_3$ (0.03 mmol) in 190 mL of vigorously stirred toluene under nitrogen was added 0.015 g of B(C$_6$F$_5$)$_3$ (0.03 mmol) in 10 mL of toluene at 35 °C. The solution initially turned bright yellow and then dark; the reaction vessel was pressurized with 3 atm of ethylene and maintained at 35 °C. The reaction was quenched, as above, after 1 h to give 280 g of polyethylene. In a separate experiment, polymerization was observed to continue at least 10 h.

Polymerization of Styrene. Styrene (typically 2 mL, purified of inhibitor by passage through an Aldrich inhibitor removal column) and Cp*TiMe$_3$ (0.03 mmol) were introduced into a flask, either at room temperature or thermostated at some other temperature. Polymerization was initiated by the rapid addition of B(C$_6$F$_5$)$_3$ (0.03 mmol) dissolved in 2 mL of solvent (which may be styrene), at which point the temperature increased rapidly unless held constant. Reactions in CH_2Cl_2 were stirred for 0.5 h (20 °C) or 1.5 h (0 °C, −78 °C), and polymerizations were then terminated by the addition of 1% HCl in methanol; the resulting polymer was washed with methanol and dried to constant weight at 100 °C.

Polymerizations in aromatic solvents at temperatures ≥0 °C were generally terminated in a similar manner within a few minutes, although some samples solidified within seconds (see below). In the latter cases, purification of the solids to remove unreacted monomer and entrained catalyst was accomplished by dissolving them in 1,2,4-trichlorobenzene at 130 °C followed by precipitation in 1% HCl in methanol. The precipitates were then washed three times with 50 mL aliquots of methanol, dried *in vacuo* at 100 °C, and then extracted with methyl ethyl ketone in a Soxhlet extractor to obtain a-PS (soluble) and s-PS fractions. Reactions in toluene at −15, −47, and −78 °C did not result in precipitation of polymer and were treated as were reactions in CH_2Cl_2.

Polymerization of Styrene in the Presence of Ethylene. Ethylene was bubbled through a solution of 40 mg of Cp*TiMe$_3$ (0.175 mmol) and 9.09 g of styrene (87.3 mmol) in 40 mL CH_2Cl_2 at 20 °C for 10 min. At this point, 90 mg of B(C$_6$F$_5$)$_3$ (0.175 mmol) dissolved in 10 mL of CH_2Cl_2 was added. Bubbling of ethylene was continued for 1 h, the reaction turning dark brown and a precipitate appearing. The reaction was quenched with 100 mL of methanol, and the solid polymer was filtered off, washed with methanol, and dried at room temperature *in vacuo.* Yield: 9.1 g, The ^{1}H NMR spectrum indicated the presence of a-PS and polyethylene. The material was only partially soluble in toluene, THF, and CH_2Cl_2 and was extracted overnight in a Soxhlet extractor with CH_2Cl_2. Only about 100 mg remained unextracted; this was identified (NMR) as polyethylene rather than as a copolymer.

A reaction run similarly but at −30 °C turned orange and became viscous within 1 h, but no precipitate formed. The polymeric product precipitated as above with methanol was pure a-PS. Yield: 4.8 g.

Polymerization of α-Methylstyrene. The monomer was passed through an inhibitor remover column, stirred overnight over CaH$_2$, and then filtered, degassed, and distilled under reduced pressure. Polymerization was initiated by the rapid addition of 15 mg of B(C$_6$F$_5$)$_3$ (0.03 mmol) dissolved in 2 mL of a solvent (toluene or dichloromethane) to 7 mg of Cp*TiMe$_3$ (0.03 mmol) dissolved in α-methylstyrene monomer (15 mmol). Polymerizations were carried out at room temperature and −78 °C, reaction mixtures turning orange. After a few minutes, the polymerization solution was quenched in methanol (1% HCl). The precipitated polymer was then washed with methanol and dried in *vacuo* at room temperature.

In a separate experiment, a solution of 30 mg of B(C$_6$F$_5$)$_3$ (0.06 mmol) dissolved in 1.5 mL of toluene was added to a solution of 14 mg (0.06 mmol) of Cp*TiMe$_3$ dissolved in 1.5 mL of toluene and maintained at −78 °C. A solution of 2 mL of α-methylstyrene in 8 mL of toluene was then added slowly in three aliquots (3, 3, 4 mL) such that the ratio of α-methylstyrene:titanium after the three additions was 77:1. 154:1, and 256:1, respectively. After each addition, a small aliquot of the reaction mixture was withdrawn and treated as above, and the resulting poly(α-methylstyrene) was characterized by GPC.

Synthesis of a Random Copolymer of Ethyl Vinyl Ether and Styrene. To 14 mg (0.06 mmol) of Cp*TiMe$_3$ dissolved in 1.5 mL of CH_2Cl_2 at −78 °C were added 30 mg (0.06 mmol) of B(C$_6$F$_5$)$_3$ dissolved in 1.5 mL of CH_2Cl_2. The solution turned orange, and a solution containing 1.5 mL (15 mmol) of ethyl vinyl ether and 3.5 mL (30 mmol) of styrene in 4 mL of CH_2Cl was added slowly. After 5 min, the reaction was terminated by the addition of methanol to give a suspended solid, which was concentrated by centrifugation, separated from the liquid phase, and dried in vacuum. The solvent of the supernatant was removed under reduced pressure to give a yellow, sticky material. Both materials were characterized by NMR spectroscopy and GPC.

***In Situ* NMR Investigations.** A mixture of Cp*Ti(^{13}CH$_3$)$_3$[5f] (10 mg, 0.042 mmol) and B(C$_6$F$_5$)$_3$ (23 mg 0.042 mmol) was placed in an NMR tube sealed with a septum. The sample was cooled to −78 °C, and 0.4 mL of CD_2Cl_2 was added to dissolve the solids. The solution turned orange immediately as **A** formed. A solution containing 0.10 mL of styrene-d_8 (1.26 mmol) in 0.32 mL of CH_2Cl was added slowly with good mixing, and the NMR tube was placed in the probe of an AM400 NMR spectrometer at −50 °C; ^{1}H and $^{13}C\{^1H\}$ NMR spectra were obtained over 30−60 min. The temperature was then raised to −25 and 0 °C, at each of which temperatures the reaction mixture was held for 15 min before ^1H and ^{13}C-{^1H} NMR spectra were obtained.

Results and Discussion

Syntheses of Potential Polymerization Initiators. The new compounds $CpTiMe_2(OR)$ ($R = Pr^i$, Bu^t, CPh_3) $CpTiMe(OBu^t)_2$, $Cp^*ZrMe_2(OR)$ ($R = CPh_3$, $CMePh_2$), and $Cp^*ZrMe(OCMePh_2)_2$ were synthesized in order to test these types of species as either polymerization initiators or as precursors to possible polymerization initiators. The compounds were prepared in several ways, by treating the corresponding chloro compounds with MeMgBr or by treating Cp^*MMe_3 (M = Ti, Zr) with 1 equiv of either an alcohol or a ketone. The latter two processes involve protonation of a methyl group and insertion of a ketone into a methyl−metal bond, respectively, and are quite general.[7i]

The compounds $[Cp^*ZrMe_2(THF)_2][BPh_4]$, $[Cp^*ZrMe_2(PMe_3)_2][MeB(C_6F_5)_3]$, $[Cp^*ZrMe_2(NEt_3)][MeB(C_6F_5)_3]$, and $[Cp^*TiMe_2(dmpe)][MeB(C_6F_5)_3]$ were prepared as representatives of a type of complex similar to the established polymerization initiators $[Cp^*MMe_2][MeB(C_6F_5)_3]$ (M = Ti, Zr, Hf)[5a] but with coordination sites at least partially occupied by ligands which should not be readily displaced by olefins. A variety of such compounds may be synthesized, but many are unstable and we report here only a few which are relevant to the theme of this paper.

The ^1H NMR spectrum of $[Cp^*TiMe_2(dmpe)][MeB(C_6F_5)_3]$ exhibits *inter alia* two distinct PMe environments and a BMe resonance at a chemical shift characteristic of the free borate anion[5a] but little temperature dependence. Therefore the dmpe does not dissociate significantly or take part in any intramolecular exchange process; indeed, unlike $[Cp^*TiMe_2][MeB(C_6F_5)_3]$ (**A**),[5a] $[Cp^*TiMe_2(dmpe)][MeB(C_6F_5)_3]$ behaves in solution as a single, solvent-separated, 14-electron species. The ^1H NMR spectrum of $[Cp^*ZrMe_2(PMe_3)_2][MeB(C_6F_5)_3]$ also exhibits little variation with temperature or on addition of free PMe_3 to the solution between −50 and 0 °C. Interestingly, however, spin saturation transfer experiments at both temperatures indicated that exchange between free and coordinated PMe_3 does occur. Similar results were obtained with $[Cp^*ZrMe_2(NEt_3)][MeB(C_6F_5)_3]$; addition of free NEt_3 has no affect on the ^1H NMR spectrum, but spin saturation transfer experiments demonstrate that exchange between free and coordinated ligands does occur. The analogous titanium complex $[Cp^*TiMe_2(NEt_3)][MeB(C_6F_5)_3]$ could be formed by treating **A** with triethylamine in CD_2Cl_2 at −50 °C and exhibited similar exchange properties but could not be isolated. The ^1H NMR spectra of all of these complexes exhibit methyl resonances attributable to the free borate anion, as expected.

Polymerization Investigations. Neutral Compounds. No appreciable activity for ethylene or styrene polymerization was observed for Cp^*MMe_3 (M = Ti, Zr, Hf), $CpTiMe_2(OPr^i)$, $CpTiMe_2(OBu^t)$, $CpTiMe(OBu^t)_2$, $Cp^*TiMe_2(OCPh_3)$, $Cp^*ZrMe_2(OCPh_3)$, $Cp^*ZrMe_2(OCMePh_2)$, or $Cp^*ZrMe(OCMePh_2)_2$.

Cationic Compounds. Ethylene Polymerization. We have earlier shown that $[Cp^*TiMe_2][MeB(C_6F_5)_3]$, generated by treating Cp^*TiMe_3 with an equimolar amount of $B(C_6F_5)_3$ at −20 °C in CD_2Cl_2, exhibits spectroscopic properties consistent with the structure shown as **A**.[5a] The formation of **A** clearly involves initial abstraction of a methyl carbanion from the titanium by the strong Lewis acid $B(C_6F_5)_3$, followed by binding of the resulting borate anion to the electrophilic metal center via the somewhat hydridic methyl hydrogen atoms.[6] The borate anion, as anticipated, is readily displaced by a variety of ligands, and thus **A** provides a source of the 10-electron, cationic species $[Cp^*TiMe_2]^+$, which should be an excellent catalyst for olefin polymerization.[1]

A number of monocyclopentadienylmetal systems have been shown to polymerize ethylene,[2e,g,h,j,r,s] and we find that bubbling ethylene through solutions of **A**, formed by combining equimolar amounts of Cp^*TiMe_3 and $B(C_6F_5)_3$ in methylene chloride, 1,2-dichloroethane, or toluene at room temperature, results in significant heating and almost immediate polyethylene (PE) gel formation. Treatment, after 30 min, of the reaction mixtures with acidic methanol followed by drying at 80 °C results in white, low-solubility polymers with T_m varying from ∼127 to ∼141 °C and measured $M_w = (4.1-22.3) \times 10^4$; in other cases, the PE was insufficiently soluble for molecular weights to be made (see below), and we estimate that $M_w \geq 300\,000$ for these samples. The PE appears largely to be linear, since ^1H NMR spectra of soluble samples exhibit only a singlet at δ 1.39 (135 °C in 1,1,2,2-$C_2D_2Cl_4$).

While slow monomer diffusion results in low total conversion to PE under these conditions, that the catalyst is highly active is attested to by the observation that dissolution of Cp^*TiMe_3 and $B(C_6F_5)_3$ in liquid ethylene, at −197 °C, also results in PE formation; the polymerization process continues at the boiling point of ethylene (−104 °C). Indeed, in an experiment carried out with vigorous stirring and careful control of temperature, a much higher yield of PE was obtained. Exposure of a toluene solution of $[Cp^*TiMe_2(\eta^6\text{-toluene})][BMe(C_6F_5)_3]$ to 3 atm of ethylene at 35 °C, with a controlled monomer feed in order to prevent runaway conditions, resulted in polymerization which continued for at least 10 h and which produced 280 g of PE within 1 h. The latter corresponds to unoptimized production of 9.3×10^6 g of polymer/mol of Ti/h. The PE would not dissolve in either 1,2,4-trichlorobenzene or α-chloronaphthalene (6 days at 150 °C), could not be forced through a melt indexer (ASTM method D-1238, procedure 8, condition E), and melted at 141 °C (DSC remelt). Thus the material presumably has a very high weight average molecular weight.

The borane, $B(C_6F_5)_3$, is a very poor catalyst for ethylene polymerization, while no cationic catalysts for ethylene polymerization could be obtained by treating Cp^*TiMe_3 with $B(n\text{-}Bu)_3$ or BPh_3; methyl abstraction does not occur in these cases. The cationic complex $[Cp^*TiMe_2(NEt_3)][BMe(C_6F_5)_3]$, formed by treating Cp^*TiMe_3 with the proton source $[HNEt_3][B(C_6F_5)_4]$, was also much less active for ethylene polymerization, presumably because ethylene coordination was severely hindered by the presence of the amine or the counterion; anion effects have also been reported for metallocene systems.[1h] The dmpe complex, $[Cp^*TiMe_2(dmpe)][BMe(C_6F_5)_3]$, also exhibited very low activity, presumably for the same reason.

Catalysts of the type $[Cp^*MMe_2][BMe(C_6F_5)_3]$ (M = Zr, Hf) were found to be good but not excellent ethylene polymerization initiators in toluene, in which they exist as the arene complexes $[Cp^*MMe_2(\eta^6\text{-toluene})][BMe(C_6F_5)_3]$,[5a] yielding PE with $T_m > 140$ °C. However, coordination of good ligands, as in $[Cp^*ZrMe_2(PMe_3)_2][MeB(C_6F_5)_3]$, $[Cp^*ZrMe_2(THF)_2][MeB(C_6F_5)_3]$, and $[Cp^*ZrMe_2(NEt_3)][MeB(C_6F_5)_3]$, resulted in very poor catalyst systems. The complex $[Cp^*ZrMe_2][BPh_4]$, formed by treating Cp^*ZrMe_3 with $[(C_5H_4Me)_2Fe][BPh_4]$, was also a relatively poor catalyst, suggesting that the nature of the counteranion is important.[1h]

The yields and weight average molecular weights of the PE produced by initiator systems based on **A** are comparable with those produced with many metallocene catalysts,[1] a finding consistent with the hypothesis, proposed above, that 10-electron systems of the type $[Cp'MR_2]^+$ or 12-electron complexes of the types $[Cp'MRL_2]^{2+}$ or $[Cp'MR_2L]^+$ might, for both steric and electronic reasons, behave as more reactive catalysts than their metallocene analogues. Our results are also rather different from those reported earlier[2i] for the same initiator system, the PE melting points reported here being higher. The reasons for the discrepancy are not clear, but we find that rigorous exclusion of moisture is necessary for rapid and reproducible polymerization to high molecular weight product to occur.

Styrene and α-Methylstyrene Polymerization. Treating solutions of styrene in CH_2Cl_2 with Cp^*TiMe_3 and $B(C_6F_5)_3$ (1:1 molar ratio) at 20, 0, and −78 °C, followed by addition of 1% HCl in methanol after 0.5−1.5 h, yielded a-PS in yields of 97%, 99%, and 55%, respectively. The values of M_w increased from 9.1×10^3 to 5.7×10^4 as the temperature decreased in this range, but the polydispersities varied little (2.5 ± 0.3). Addition of solutions of $B(C_6F_5)_3$ in toluene to solutions of Cp^*TiMe_3 (1:1 molar ratio) in styrene at −15, −47, and −78 °C resulted in darkening of the solutions and increasing of the viscosities; frozen styrene monomer (mp −31 °C) precipitated from the reaction mixture at −78 °C. Addition of methanol after about 2 h resulted in the precipitation of a-PS (yields 72 and 66% at −15 and −47 °C, respectively) which exhibited weight average molecular weights $\sim 10^4$ and polydispersities ~2.8 ± 0.3. The a-PS formed at −78 °C exhibited a lower weight average molecular weight, $\sim 5.3 \times 10^3$, presumably because of the freezing out of the monomer before polymerization was complete, but a significantly narrower molecular weight distribution, 2.1. The a-PS samples were readily soluble in many organic solvents, including methyl ethyl ketone, and were identified by ^1H NMR spectroscopy.[4a] No s-PS was formed in any of the toluene polymerizations carried out at temperatures <0 °C.[5c]

In vivid contrast to the reactions which result in the formation of a-PS, addition of solutions of $B(C_6F_5)_3$ in toluene to solutions of Cp^*TiMe_3 (1:1 molar ratio) in styrene under strictly anhydrous conditions in the temperature range 0−70 °C resulted in significant heating and darkening and in almost immediate formation of *solid* blocks of material that were predominantly s-PS. Since $B(C_6F_5)_3$ itself slowly polymerizes styrene to a-PS, addition of more than 1 equiv of the borane to the titanium complex resulted in an increase in the proportion of a-PS formed. The crude, solid materials normally contained relatively small amounts of a-PS, but as much as 15−20% by weight entrapped monomer (by TGA), consistent with the general tendency of the s-PS helices to trap aromatic molecules.[8] The monomer is only partially removed by heating *in vacuo* at 80 °C for 24 h but is almost completely removed by heating *in vacuo* at 80 °C for 48 h. Since we did not initially appreciate the tenacity with which monomer is retained by the solid, crude polymer, the yields claimed originally are high by ~15%.[5b]

The crude s-PS was generally purified by dissolution in 1,2,4-trichlorobenzene at 150 °C, followed by precipitation with acidified methanol to give white s-PS. The tacticities were in all cases assessed by $^{13}C\{^1H\}$ NMR spectroscopy on solutions in 1,1,2,2-tetrachloroethane-d_2 at 120 °C, the resonances of the *ipso*-carbon atoms being well-resolved singlets at δ 145.36, characteristic of the rrrr pentad of s-PS.[4a,d,e] In general, values of M_w increased from $\sim 1 \times 10^5$ at 70 °C to $\sim 2 \times 10^6$ at 0 °C, while M_w/M_n was essentially constant at ~2.3. Glass transition temperatures and melting points were generally ~104 and ~272 °C, respectively, comparable with data from the literature,[3,4] but the yields obtained here and our observations of rapid solidification of the product are not reported previously for this and similar initiators.[2b,c,i,k−o,3] However, we find that rigorous exclusion of moisture is necessary for rapid and reproducible polymerization to solid s-PS to occur. The overall percentage conversion of styrene to s-PS appears to be significantly higher than those reported elsewhere for this and similar initiators.[2,3]

Good yields of and selectivities to s-PS are obtained in *n*-hexanes, neat styrene, and some other aromatic solvents such as mesitylene and *m*- and *p*-xylene, but reactions run in benzene and anisole give lower yields. While a number of the above-mentioned cationic complexes which initiate ethylene polymerization also initiate styrene polymerization at room temperature, only low yields of a-PS are formed. Interestingly, we find that the cationic complex $[Cp^*Ti(CH_2Ph)_2][B(CH_2Ph)(C_6F_5)_3]$, formed by treating $Cp^*Ti(CH_2Ph)_3$ with $B(C_6F_5)_3$ in toluene, does initiate the formation of s-PS, and we note recent reports that apparently analogous indenyl and other variously substituted cyclopentadienyl systems are also effective *in toluene*.[2l,n] Indeed, toluene seems generally to be the solvent of choice in almost all cases for the polymerization of styrene to s-PS by monocyclopentadienyltitanium systems,[2b,c,k−m,p] although electron-withdrawing substituents on the aromatic solvent ring can enhance s-PS yields.[2p]

Polymerizations of purified α-methylstyrene were carried out in toluene and methylene chloride at room temperature and at −78 °C; in most cases, the resulting orange solutions were quenched in methanol (1% HCl) to give white, polymeric materials which are soluble in organic solvents (CH_2Cl_2, $CHCl_3$, THF, and toluene). Conversion of the monomer is almost 100% at −78 °C, but only 20−40% at room temperture. Poly(α-methylstyrene) formed at room temperature in toluene was of relatively low molecular weight ($M_w < 10^3$) and T_g (44 °C), but polymer formed at −78 °C in toluene exhibited $M_w = 9 \times 10^4$, $M_w/M_n = 2.7$, and $T_g = 158$ °C. $^{13}C\{^1H\}$

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[8] (a) Roels, T.; Deberdt, F.; Berghmans, J. *Macromolecules* **1994**, *27*, 6216. (b) A suggestion[4h] that the sample contained residual acetone from the extraction procedure seems quite unlikely in view of the conditions under which the material was dried.

NMR spectroscopy indicated that the polymer formed is predominantly syndiotactic in nature (84% rr triads).[9a−c] Polymer formed in methylene chloride was of lower molecular weight and higher polydispersity, but the M_w values, the tacticity, and the glass transition temperature reported here for material prepared in toluene at −78 °C are comparable with those of poly(α-methylstyrene) prepared elsewhere using a variety of initiators.[9d−h]

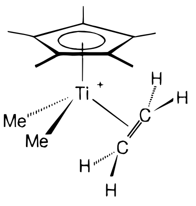
Interestingly, the growing poly(α-methylstyrene) appears to be partially living.[10] Incremental additions of monomer to a cooled (−78 °C) solution of initiator in methylene chloride such that the monomer:initiator ratios were ~77:1, ~154:1, and 256:1 resulted in the formation of poly(α-methylstyrene) samples exhibiting $M_n = 1.4 \times 10^4$ ($M_w/M_n = 8.1$), 3.0×10^4 ($M_w/M_n = 4.1$), and 3.9×10^4 ($M_w/M_n = 2.9$), respectively. The close correlation between number average molecular weights and amount of monomer added is consistent with the existence of a living carbocationic polymer chain in this system (see below).[9f,10]

Mechanisms of Olefin Polymerizations by $[Cp^*TiMe_2][MeB(C_6F_5)_3]$. The enormous contrast in catalytic activity between neutral compounds of the types Cp^*MMe_3, $CpMMe_2(OR)$, $CpMMe(OR)_2$ (M = Ti, Zr, Hf), and the various cationic derivatives described above is consistent with the similar trends reported previously for neutral and cationic metallocene catalyst systems[1] and recently rationalized theoretically for Ziegler−Natta processes in general.[1f,g] The same types of factors presumably affect catalytic activity, namely the presence of both a positive charge to facilitate olefin coordination and an alkyl group to initiate olefin insertion.[1d,e] Consistent with this hypothesis, treatment of Cp^*TiMe_3 with $[Ph_3C][MeB(C_6F_5)_3]$ in toluene at room temperature has also been found by us and others[2q] to result in the formation of an excellent system for polymerization of styrene to s-PS. This reaction is expected to proceed as in eq 2 and, thus, should result simply in the formation of the now well-characterized **A**.

$$Cp^*TiMe_3 + [Ph_3C][MeB(C_6F_5)_3] \rightarrow [Cp^*TiMe_2][MeB(C_6F_5)_3]\ (\mathbf{A}) + MeCPh_3 \quad (2)$$

The olefin polymerization initiator system described here is complicated since, while **A** can confidently be identified by its characteristic ^1H NMR spectrum in CD_2Cl_2 in the temperature range 0 to −78 °C,[5a] warming a solution to room temperature results in the appearance of many new resonances in the methyl region of the ^1H NMR spectrum. While a similar experiment cannot be carried out in toluene because the titanium complex forms an insoluble oil, comparable results were obtained in an NMR experiment involving **A** and carried out in chlorobenzene-d_5, in which **A** is stable for a few minutes, at least, at room temperature.[5e] Interestingly, we also find a remarkable cut-off point somewhat below 0 °C for the formation of s-PS in toluene, such that only a-PS is formed at lower temperatures.[5c] This observation strongly suggests that at least two different types of polymerization initiators, and hence titanium species, are present at 0 °C and above in this solvent also.

We previously observed that ethylene and styrene are seemingly polymerized by **A** faster in toluene at room temperature than is propylene, and noted that these relative rates appeared qualitatively to be inconsistent with a generally applicable coordination polymerization (Ziegler−Natta) mechanism.[5b] Although ethylene would be expected to coordinate to the $Cp^*TiMe_2^+$ ion, as in **B**, more readily than propylene[11] and hence might well polymerize faster, the much more sterically demending olefins styrene and α-methylstyrene should coordinate much less strongly than propylene and, in spite of their higher solubilities, might therefore be expected to undergo relatively slow Ziegler−Natta polymerization. Since styrene and especially α-methylstyrene also undergo very effective carbocationic polymerization,[10] however, we suggested[5b] tht the strongly electrophilic $[Cp^*TiMe_2]^+$ may behave not only as a Ziegler−Natta polymerization catalyst but as a carbocationic polymerization initiator[10] with these monomers under some conditions.



B

Indeed, consistent with a carbocationic mechanism[10] for styrene polymerization in CH_2Cl_2 and at low temperatures in toluene, we found that generally higher molecular weights are obtained at lower temperatures and with high monomer:initiator ratios. We also found, for α-methylstyrene, that incremental addition of monomer to a polymerization reaction in toluene at −78 °C results in the formation of partially living poly(α-methylstyrene), with increases of M_n correlating well with the amounts of α-methylstyrene added. Similar results have been reported using other carbocationic initiators.[9f]

The interpretations drawn from these considerations, apparently supported by complementary analyses of the end groups formed when low-temperature polymerizations were quenched with alcohols, resulted in an erroneous but ultimately serendipitous conclusion concerning the applicability of a carbocationic mechanism for the formation of s-PS.[5b] In brief, carbocationic initiation of olefin polymerization by **A** would occur as in Scheme 1. Here the olefin coordinates in **C** in a nonclassical η^1-fashion, the metal−olefin interaction being stabilized by a complementary borate−olefin

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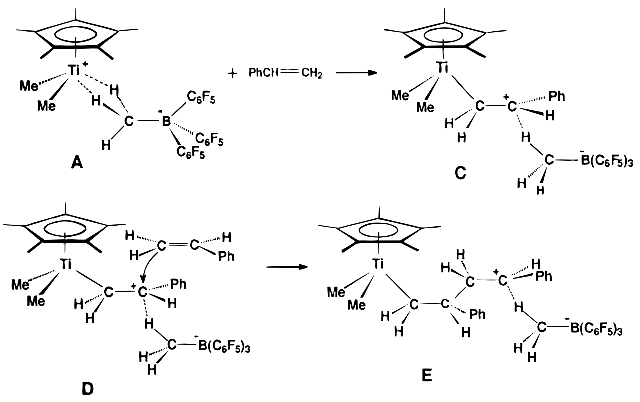
Scheme 1



interaction. The structure of **C** resembles the structures of several vinyl alcohol, vinyl ethyl ether, vinyl amine, and methyleneimidazoline complexes of electrophilic metals[12] and also the probable transition state involved in nucleophilic attack on olefins activated by coordination to electrophilic metals.[13] The next step in the polymerization process would involve the carbocationic center of the metal ion-activated olefin molecule being attacked by a second olefin monomer (**D**), in a manner normally postulated for carbocationic polymerization processes,[10] followed by chain growth as in **E**.

In the case of a Ziegler–Natta catalyst system,[11] alcoholysis of a growing polymer should result in protonation of the titanium–carbon bond and formation of a saturated hydrocarbon polymer backbone containing no alkoxy group. In contrast, alcoholysis of the growing chain of Scheme 1 could involve nucleophilic attack on the carbenium ion of **E** accompanied by protonation of the titanium–carbon bond, resulting in the formation of a polymer with methyl and alkoxy end groups. Analysis by ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy of a sample of s-PS formed in toluene at 0 °C and obtained after quenching with *tert*-butanol and drying overnight at 80 °C initially gave seemingly promising results, as indicated previously.[5b] However, although the spectra exhibited *tert*-butoxy resonances with chemical shifts slightly different than those of the free alcohol, we eventually found that drying samples *in vacuo* at 110 °C for 8 h results in complete removal of the alkoxy resonances. Thus our original findings are now shown to be in error, arising possibly because of the tenacity with which molecules are trapped in the helical structure of s-PS.[8a,b]

A more definitive study of Pellecchia *et al.*[4h] has presented strong evidence that polymerization of styrene by **A** to s-PS proceeds via a Ziegler–Natta process which involves initial secondary insertion of monomer into a Ti–Me bond. Utilizing a mixture of $Cp^{*}TiMe_3$ and ^{13}C-labeled $AlMe_3$, in which there occurs rapid methyl ligand exchange between titanium and aluminum, they obtained purified s-PS which exhibited in its $^{13}C\{^{1}H\}$ NMR spectrum a sharp resonance at 9.8 ppm relative to hexamethyldisiloxane (in 1,1,2,2-$C_2D_2Cl_4$ at 120 °C). This resonance was attributed to the ^{13}C-enriched $-CHPhCH_2{}^{13}CH_3$ end groups which would result from the secondary insertion process of eq 3.

$$[Cp^{*}Ti(^{13}CH_3)_2]^{+} + PhCH{=}CH_2 \rightarrow [Cp^{*}Ti(^{13}CH_3)(CHPhCH_2{}^{13}CH_3)]^{+} \quad (3)$$

Since a carbocationic process would not result in the observed ^{13}C-enriched end group, Pellecchia *et al.* interpreted their results as providing unambiguous evidence that only a Ziegler–Natta insertion process applies in the formation of s-PS.

We have carried out a similar synthesis of s-PS by utilizing purified $Cp^{*}Ti(^{13}CH_3)_3$, prepared via the reaction of $Cp^{*}TiCl_3$ with $Li(^{13}CH_3)$.[5f] The $^{13}C\{^{1}H\}$ NMR spectrum of the resulting s-PS, prepared in toluene as above, exhibited a sharp resonance at 11.70 ppm relative to TMS (1,1,2,2-$C_2D_2Cl_4$ at 80 °C); assuming a chemical shift of 1.5–2.0 ppm for hexamethyldisiloxane relative to TMS,[14a,b] this result confirms that of Pellecchia *et al.* and indicates that their result was not unduly influenced by the presence in solution of trimethylaluminum. We have, for other reasons, independently come to the conclusion that the formation of s-PS does not involve a carbocationic process (see below).

We have in the meantime, however, carried out a series of experiments which strongly implicate a carbocationic mechanism for the polymerization of styrene by **A** to *a-PS* in CH_2Cl_2. These experiments have involved (a) NMR monitoring of polymerization reactions of styrene-d_0 and styrene-d_8 by solutions of $Cp^{*}Ti(^{13}CH_3)_3$ and $B(C_6F_5)_3$ (1:1) in CD_2Cl_2 at −50, −30, and 0 °C and (b) characterization by NMR spectroscopy of the products of polymerization of styrene-d_0 by solutions of $Cp^{*}Ti(^{13}CH_3)_3$ and $B(C_6F_5)_3$ (1:1) in CH_2Cl_2 at room temperature and −30 °C.

The ^{1}H NMR spectrum of $[Cp^{*}Ti(^{13}CH_3)_2][(^{13}CH_3)B(C_6F_5)_3]$ in CD_2Cl_2 in the temperature range −30 to −60 °C exhibits resonances at δ 1.98 (s, 15H, Cp* methyl), 1.53 (d, J 125 Hz, 6H, Ti–Me), and 1.19 (br d, J 114 Hz, 3H, B–Me). Spectra also usually contain an extremely weak resonance at δ 0.16 (d, J 126 Hz), possibly attributable to partially hydrolyzed material.[5g] The $^{13}C\{^{1}H\}$ NMR spectrum of $[Cp^{*}Ti(^{13}CH_3)_2][(^{13}CH_3)B(C_6F_5)_3]$ in CD_2Cl_2 in the temperature range −30 to −60 °C exhibits resonances at δ 131.1 (w, Cp* ring C), 80.1 (vs, Ti–Me), ~44.3 (br, m, B–Me), and 12.6 (w, Cp* methyl). Addition of styrene-d_8 to solutions of **A** (30:1 ratio) in CD_2Cl_2 at −78 °C, followed by warming in a spectrometer probe to −50 °C, resulted initially in the rapid disappearance of the ^{1}H (residual) and ^{13}C resonances of the monomer and in the appearance of broad resonances attributable to deuterated a-PS in the

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^1H and $^{13}C\{^1H\}$ spectra.[14f] There were slight (~0.06 ppm), apparently media-induced, changes in chemical shifts of the ^1H and $^{13}C\{^1H\}$ resonances of the titanium species in solution and slight darkening of the color of the solution on the addition of styrene. Although very weak Ti−Me ^{13}C resonances appeared at δ 94.2 and 102.6, *there were no new resonances attributable to ^{13}C-enriched methyl end groups of any kind in either the ^1H or the $^{13}C\{H\}$ NMR spectra*. Thus we observed no resonances in the $^{13}C\{^1H\}$ NMR spectrum at δ ~11.70 or ~22, which could be attributed to $-CD(C_6D_5)CD_2(^{13}CH_3)$ or $-CD_2CD(C_6D_5)(^{13}CH_3)$ end groups, respectively,[4b,h,14c,d] or in the region δ 0.5−1.5 in the ^1H spectrum, where resonances of $^{13}CH_3$ end groups would appear.[14e] This experiment was found to be readily reproducible.

Although warming the reaction mixture to −25 °C resulted in little discernible change in the ^1H spectrum, warming to 0 °C resulted in diminishing of the resonances of the $[Cp^*Ti(^{13}CH_3)_2][^{13}CH_3)B(C_6F_5)_3]$ accompanied by the appearance of new Cp* methyl (δ 2−2.5) and Ti−Me resonances (δ 0.217−0.16), of varying relative intensities, in the ^1H spectrum. The $^{13}C\{^1H\}$ spectrum exhibited very weak Cp* methyl resonances, as well as the weak Ti−Me resonances noted above. The new species have not been identified but may be products of hydrolysis arising from traces of water desorbing from the walls of the NMR tubes[5g] and/or, more likely, products of thermal decomposition (the relative intensities of these resonances increased with time). On standing at 0 °C and above, this and similar solutions darkened and became quite viscous. The resonances noted above in the ^1H spectrum shifted little but became significantly weaker and broader; no new methyl resonances of significant intensity appeared.

Complementary experiments, with lower styrene-d_8:Ti ratios, exhibited similar NMR spectra at −50 °C. However, different experiments with somewhat different rates of warming resulted in the appearance of C−Me resonances, of varying relative intensities, in the regions δ ~11.8−13.8 (Cp* Me region) and 15.8−16.2 (C−Me region) and Ti−Me resonances at δ ~64.3, 94.2, and 102.6 in the $^{13}C\{^1H\}$ spectra. In one case where the polystyrene produced was precipitated with methanol, twice dissolved in CH_2Cl_2 and reprecipitated with methanol, and then dried, the $^{13}C\{^1H\}$ NMR spectrum exhibited no enriched methyl end groups although the spectrum of the reaction mixture had clearly exhibited a resonance at δ 16.2.

Our interpretation of these observations is that the deuterated polystyrene induced in the low-temperature reaction by **A** is formed via other than a Ziegler−Natta polymerization process. Since free radical initiated processes seem under the circumstances quite unlikely, carbocationic initiation seems indicated although no species of type **E** could be detected. Apparently only a small proportion of the total titanium in solution is present as a very highly reactive **E** rather than as **A**. Interestingly, although Cp^*TiMe_3 readily transfers a methyl ligand to the tritylcarbenium ion (eq 2), the results discussed here indicate that methyl transfer from alkyltitanium species of type **E** to the carbenium ion centers of the growing polymer chain does not occur.

In larger scale reactions, aliquots of styrene-d_0 (0.5 mL in 2 mL of CH_2Cl_2) were polymerized in solutions of $[Cp^*Ti(^{13}CH_3)_2][(^{13}CH_3)B(C_6F_5)_3]$ in CH_2Cl_2; the reactions were initiated at −30 °C and at room temperature, but both may have became warmer because of the exothermicity of the reactions. The lower temperature reaction mixture quickly turned dark brown, and the reaction was quenched with methanol after 15 min. The polymer was purified as above, and the $^{13}C\{^1H\}$ NMR spectrum was found to exhibit a methyl end group resonance at δ 12.9 (br) and a weaker resonance at δ 11.8 (br). The similar experiment carried out at room temperature quickly turned dark blue, and the $^{13}C\{^1H\}$ NMR spectrum of the purified a-PS exhibited the same resonances at δ 12.9 and 11.8 as well as weaker methyl resonances to slightlyl lower field.

In these cases, the onset of dark coloration, especially blue in the room-temperature reaction, seems to imply the presence of the type of Ti(III) species implicated below for the formation of s-PS. If so, the onset of Ziegler−Natta processes is possible, and although the resonance at δ 11.8 suggests the presence of a $-CHPhCH_2{}^{13}CH_3$ end group, that at δ 12.9 cannot be assigned with confidence. It does not correspond to the any of the end group resonances reported elsewhere for a-PS.[14c] The increases in viscosity in the NMR experiments where the styrene$_8$:Ti ratio was 30:1 may also be indicative of reduced titanium species. The viscosity increases could not be a result of increased monomer incorporation, since no monomer was left, and instead it seems likely that thermal decomposition of **A** involved formation of methyl radicals, which in turn induced crosslinking of the already formed polymer.

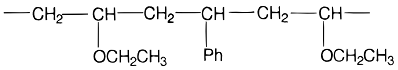
Desiring further evidence for the apparent carbocationic mechanism for the formation of a-PS at low temperatures, we treated ethylene-saturated solutions of styrene in CH_2Cl_2, at 20 and −30 °C, with first Cp^*TiMe_3 and then $B(C_6F_5)_3$. Interestingly, the reaction carried out at −30 °C produced *only* a-PS ($M_w = 8.3 \times 10^4$, $M_w/M_n = 1.7$), no polyethylene being found. This result, obtained under conditions where **A** is thermally stable and where the individual homopolymers are readily formed, provides very strong evidence that the active sites for the formation of polyethylene and polystyrene are quite different. Indeed, if styrene were polymerized to a-PS via intermediate η^2-styrene complexes analogous to **B**, then ethylene should compete very effectively for metal coordination sites and at least some polyethylene should be formed. On the other hand, if polystyrene initiation and growth occur as in Scheme 1, then the titanium complexes would become neutral trialkyltitanium species, similar to Cp^*TiMe_3, which is inactive as an ethylene polymerization initiator. Although some titanium centers may in principle coordinate ethylene initially, exchange with styrene would remove these sites irreversibly from the polyethylene catalytic cycle.

In contrast, the reaction carried out at 20 °C turned dark brown rather than orange and became warm; precipitation of some polyethylene was observed within 1 min. The polymeric product isolated after 1 h at 20 °C contained a-PS ($M_w = 1.8 \times 10^4$, $M_w/M_n = 3.9$) and a small amount of polyethylene, identified by ^1H NMR spectroscopy. Clearly the thermal decomposition of **A** above ~0 °C, noted above, results in a degree, at least, of Ziegler−Natta polymerization, perhaps by Ti(III) species (see below).

We have obtained further support for the relevance of Scheme 1 in the formation of a-PS by successfully synthesizing random copolymers of styrene with ethyl vinyl ether (EVE). Since EVE is polymerized via carbocationic rather than Ziegler–Natta processes,[10,15] it follows that any EVE–styrene copolymer formed under the same conditions as is styrene hompolymer would involve the styrene being able to participate in a carbocationic polymerization process induced by the titanium initiator under consideration here. In a typical experiment, a 2:1 molar mixture of styrene and EVE in CH_2Cl_2 was added slowly (30 min) to an orange solution of **A**[5a] in CH_2Cl_2 at −78 °C. On completion of the addition, methanol was added to the reaction mixture to give a small amount of a fine, white suspension which was concentrated by centrifugation, separated from the supernatant solution, washed with methanol, and dried at room temperature *in vacuo* for 2 h. This material was quite different in appearance from a-PS prepared in the same way but in the absence of EVE, which precipitates cleanly to give a white solid and a clear supernatant. Removal of solvent from the supernatant resulted in a sticky, yellow oil which could be purified of residual monomers by elution of a solution in $CDCl_3$ through a Celite column prior to NMR analysis.

Two symmetric bands were observed in the GPC of the solid suspension, with $M_w = 4.5 \times 10^5$ (minor fraction) and 2.9×10^4 (major fraction). These are both significantly higher than the value of M_w found for poly(EVE) (3.3×10^3), formed under the same conditions. A single symmetric peak was observed in the GPC of the oil, with $M_w = 1.9 \times 10^4$.

The ^1H NMR spectra ($CDCl_3$) of both materials exhibited resonances of the two incorporated monomers and are readily assigned on the basis of comparisons with spectra of poly(EVE) and a-PS[14f] prepared under the same conditions; there were essentially no differences in chemical shifts between spectra of the homopolymers and of the copolymers.[14f] Integrations of the resonances of the solid copolymer suggested that the ratio of incorporated styrene:EVE is ~1.8:1, although the possibility that the material contains some a-PS homopolymer cannot be ruled out on the basis of the chemical shifts. However, since any poly(EVE) formed would be very soluble in methanol, the material which precipitated clearly is not solely a mixture of homopolymers but contains a significant amount of (presumably) random copolymer, as in **F**. Integrations of the spectrum of the oil suggested that the ratio of EVE:a-PS in this material was ~5.5:1, and while the possibility that this fraction contains some EVE homopolymer cannot be ruled out, a-PS is insoluble in methanol and it is clear that the material must also contain a copolymer, also incorporating both monomers as in **F**. The oil may be lower melting and/or of greater solubility because of its lower weight average molecular weight or, more likely, because of a higher proportion of EVE.



$$-CH_2-\underset{\displaystyle OCH_2CH_3}{CH}-CH_2-\underset{\displaystyle Ph}{CH}-CH_2-\underset{\displaystyle OCH_2CH_3}{CH}-$$

F

The $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of the oil is distinctly different from spectra of both the individual homopolymers[14f] and of mixtures of homopolymers. In particular, the CH_2 ^{13}C multiplet resonance of a-PS at $\sim\delta$ 43 is absent, apparently because it has shifted in the spectrum of the copolymer and is obscured by the near-lying, overlapping EVE CH_2 and a-PS CH ^{13}C multiplet resonances in the region δ 39–42. The change in chemical shift presumably occurs because of a change in environment on going from a-PS to a random copolymer in which most of the styrene CH_2 groups are bound to an EVE OCH group, as in **F**.

Attempts to confirm that the oil contained styrene bonded to EVE by obtaining a COSY spectrum[16] of the oil in $CDCl_3$ at room temperature were of limited success. The CH and CH_2 ^1H resonances of the individual atactic hompolymers are all closely spaced, largely unresolved multiplets because of the variety of microstructures possible,[17] and the styrene CH and CH_2 resonances of the copolymer are largely obscured by the stronger EVE CCH_2 resonance. However, a weak cross-peak between the very broad OCH resonance(s) of the EVE and a CH_2 resonance of the styrene at δ ~1.4 (shoulder, $CDCl_3$) was observed, as anticipated for **F**.

Addition of alcohols to polystyrene reaction mixtures in CH_2Cl_2 at low temperatures does not result in the formation of alkoxy end groups, but this finding does not in fact provide evidence against a carbocationic mechanism. It has been found that even known, living styrene polymers do not add a methoxy end group on treatment with methanol.[18]

Returning to s-PS, the process producing this material in toluene presumably involves coordination polymerization,[2b,c,k−m,3,4a−g] but the nature of the catalytic species is not at all clear since the originally formed **A** is unstable above about 0 °C (see above). While a high-temperature carbocationic process initiated by a cationic thermal decomposition product of **A** might seem feasible and was earlier advocated by us on the basis of arguments outlined above,[5b] the carbenium ion end groups of the growing polymer chain would be stabilized as in Scheme 1 and a-PS should still be formed. We had not yet investigated in detail the reactions in CH_2Cl_2 at the time of our preliminary communication[5b] and did not realize that a-PS is formed via the type of carbocationic process under consideration. However, s-PS initiating systems based on $CpTi(OBu)_3$/MAO[2k] and $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$[4i] exhibit ESR spectra attributable to Ti(III) species, and it has been sugested that the Ziegler–Natta catalyst for s-PS in these cases are methyltitanium(III) compounds.[2k,4i] We have observed similar ESR resonances on treatment of solutions of Cp^*TiMe_3 in toluene and chlorobenzene with equimolar amounts of $B(C_6F_5)_3$ under the conditions utilized in ref 4i, and again a Ti(III) species seems possible although other workers have failed to observe an ESR resonance using Cp^*TiMe_3 activated with either $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$.[2q]

In complementary experiments, we found that initiating the polymerization process in toluene at room temperature in the presence of excess trimethylalumi-

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num (TMA) resulted in the formation of s-PS with M_w only ~2.6×10^4. Since the probable role of TMA would be to transfer methyl groups to titanium, it would seem that the catalytically most active titanium species in solution does indeed contain methyl groups, but possibly fewer than three, the presumed maximum possible in the presence of TMA.

In contrast, initiating the polymerization process in toluene and at room temperature under 1 atm of hydrogen resulted in very little change in the molecular weight distribution of the product s-PS; $M_w = 5 \times 10^5$. Hydrogen is well-known for its ability to cleave alkyl−titanium bonds and may be used to control the molecular weights of polymers formed via Ziegler−Natta processes.[19] While we find that Cp^*TiMe_3 and **A** are relatively inert to hydrogen gas (1 atm) at low temperatures, we have no way of knowing how a Ti(III) species might behave. In any case, however, the major reason for the lack of effect of hydrogen during polymerization to s-PS may be that polymerization is too fast for effective diffusion of hydrogen to the Ti−polymer bonds to occur. This suggestion is quite reasonable given the low solubility of hydrogen in toluene under these conditions and the rapidity with which the reaction mixtures solidify.

Finally, we note that free radical initiation of styrene polymerization, which might be expected to be induced by homolysis of titanium−methyl bonds at the relatively high temperatures at which s-PS is most readily formed, cannot be a factor in the formation of s-PS. While radical-generating homolysis processes would be accentuated at higher temperatures, free radical styrene polymerization would produce a-PS.[20] The fact that relatively little a-PS is formed at higher temperatures by **A** thus argues very effectively against free radical initiation of polymerization being a significant factor.

Summary

Treatment of Cp^*TiMe_3 with the highly electrophilic borane $B(C_6F_5)_3$ results in the formation of the methyl-bridged complex $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ (**A**), which is a good source in solution of the cationic species $[Cp^*TiMe_2]^+$. The latter is a very effective carbocationic initiator for polymerization of styrene to atactic polystyrene and α-methylstyrene to largely syndiotactic polymer at low temperatures and is an excellent catalyst or catalyst precursor for the Ziegler−Natta polymerization of ethylene and, in aromatic media at temperatures ≥0 °C, of styrene to syndiotactic polystyrene.

Acknowledgment. We are indebted to the Natural Sciences and Engineering Research Council of Canada for financial support of this research (Research, Collaborative Research and Development, and Strategic Grants to M.C.B., Graduate Fellowship to D.J.G.), to the Government of Ontario for a graduate fellowship to D.J.G., and to DuPont Canada Inc. for both generous and financial support and for a leave of absence to D.J.G. We also thank A. L. Natansohn, K. E. Russell, and M. Bochmann for helpful discussions and T. M. Liu for helpful discussions and TGA and DSC measurements.

OM9501945

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[19] Reference 11, section 1.1.2.

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