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Cationic Titanocene Catalysts for Syndiospecific Polymerization of Styrene

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ABSTRACT: The reaction of pentamethylcyclopentadienyltris((trimethylsilyl)methyl)titanium ($Cp^{*}Ti(CH_2SiMe_3)_3$) with 1 equiv of $B(C_6F_5)_3$ was almost quantitative to give the "cationic" compound $[Cp^{*}Ti(CH_2SiMe_3)_2]^+[B(CH_2SiMe_3)(C_6F_5)_3]^-$ (**1**), which was readily identified spectroscopically. The complex **1**, prepared in situ by reacting the precursor with $B(C_6F_5)_3$, has also been found to be active for the syndiospecific polymerization of styrene, producing over 95% syndiotactic PS at an activity of 0.86×10^7 g of PS/(mol of Ti·mol of styrene·h). Both activity and syndiospecificity significantly increased when triisobutylaluminum (TIBA) was used to scavenge the polymerization system. The maximum polymerization activities for the cationic complex were found at $T_p = 70$ °C. The electron-withdrawing substituents on the aromatic solvent ring could increase the activity and s-PS yields, although toluene is the polymerization medium of best choice in the styrene polymerization. Through the comparison of various Lewis acids as cocatalysts by virtue of their difference in both Lewis acidity and ion-pair interactions, the role of the key titanocene−cocatalyst interaction was unambiguously demonstrated, suggesting that the nature of Lewis acids and the structure of their corresponding counteranions were important.

Introduction

Half-sandwich organotitanium compounds containing η^5-C_5H_5, η^5-C_5Me_5, η^5-C_5Me_4H, and η^5-C_9H_7 ligands were found to be the favored precursors to catalyze syndiospecific polymerization of styrene at ambient temperature.[1] To form active catalysts, the titanocenes must be activated by methylaluminoxane (MAO) cocatalyst. Although many of its constitutional features remain unclear, MAO is currently so far the most effective metallocene cocatalyst, and the role of MAO is now generally thought to act as a Lewis acid that abstracts a methide (alkide) or hydride anion and by doing so facilitates the formation of electron-deficient/coordinatively unsaturated "cationic" titanocene alkyl species $[CpTiR_2]^+$, which may be active species for catalysis (Cp = cyclopentadienyl-type ligand), although other proposed species $[CpTiR]^+$ cannot be ruled out.[1c,d,2] Direct syntheses of this type of active species by the action of a Lewis acidic cocatalyst on half-sandwich titanocenes have led to the acceptance of a catalytically active titanocenium species $[CpTiR_2]^+$ or $[CpTiR]^+$. However, without exception, the titanocene cation is too thermally unstable to isolate analytically pure, and the cationic titanocene catalysts have therefore not been the most widely studied. Up to now, two appealing Lewis acidic cocatalysts, $B(C_6F_5)_3$ and $Ph_3CB(C_6F_5)_4$, have been developed, and several "cationic" complexes of the types $[CpMR_2]^+$ and $[CpMR_2L]^+$ or even $[CpTiR]^+$, based on group 4 monocyclopentadienyltitanium compound precursors such as $Cp^{*}TiMe_3$, $Cp^{*}Ti(CH_2Ph)_3$, and $(C_5Me_4CH_2CH_2Ph)TiMe_3$ (Cp* = η-pentamethylcyclopentadienyl), have been reported.[2,3] Some of the complexes were successfully used for the syndiospecific polymerization of styrene.[2d,3f,g,4] In this paper, we report that a new cationic titanocene complex, obtained by the reaction of $Cp^{*}Ti(CH_2SiMe_3)_3$ with Lewis acidic $B(C_6F_5)_3$, is a highly active catalyst for the syndiospecific polymerization of styrene. At the same time we have also investigated the relationship between the structures of cocatalysts and their cocatalytic behavior by virtue of their differences in both Lewis acidity and ion-pair interactions in order to probe the possibility of devising other potent Lewis acids as effective cocatalysts.

Experimental Section

Materials. All operations were performed using Schlenk tube and/or glovebox techniques under a nitrogen atmosphere. Toluene was refluxed 48 h over sodium−benzophenone and distilled before use. Monomer grade styrene was treated over Al(i-Bu)$_3$ and CaH_2, respectively, and then distilled under reduced presure. $Cp^{*}Ti(CH_2SiMe_3)_3$,[5] $B(C_6F_5)_3$,[6] $Ph_3CB(C_6F_5)_4$,[2a,7] $Ph_3CMeB(C_6F_5)_3$,[3f] $Ph_3CB(C_6H_5)_4$,[8] $Bu_3NHB(C_6H_5)_4$,[9] $Et_3NHB(C_6H_5)_4$,[3f] and $(CH_3)_2N(C_6H_5)HB(C_6H_5)_4$[10] were prepared according to literature procedures. BPh_3, $SnPh_4$, BF_3, BCl_3, PF_5, SbF_5, Me_3SnCl, and Ph_3CBF_4 were purchased from Aldrich and Fluka. $Ph_3CB(CH_2SiMe_3)(C_6F_5)_3$ was prepared by mixing $LiB(CH_2SiMe_3)(C_6F_5)_3$ (1.125 g, 2.25 mmol), obtained by in situ reacting $B(C_6F_5)_3$ with equimolar amounts of $LiCH_2SiMe_3$, and triphenylmethyl chloride (0.675 g, 2.25 mmol) in 100 mL of dry hexane and refluxing overnight. The yellow solid was dissolved in CH_2Cl_2 and LiCl removed by filtration. Recrystallization of the product from CH_2Cl_2/hexane afforded orange crystals (65% yield): ^{1}H NMR (CD_2Cl_2): δ 8.32 (t, 3H), 7.91 (t, 6H), 7.72 (t, 6H), 0.23 (s, 9H, $SiMe_3$), 0.90 (br, s, 2H, BCH_2SiMe_3). Anal. Found: C, 58.40; H, 2.99. Calcd: C, 58.46; H, 3.09.

Polymerization Procedure. In the glovebox, a 150 mL glass reactor equipped with a magnetic stirring bar was charged with a prescribed amount of $Cp^{*}Ti(CH_2SiMe_3)_3$ and cocatalyst, and the reactor was then reattached to the high-vacuum line. A measured amount of toluene was next condensed onto the solids by a syringe, and the mixture was warmed to 10 °C with stirring for 10 min to preactivate the catalyst. The pale yellow to dark solution was then equilibrated at the desired reaction temperature using an external constant temperature bath. A measured amount of styrene was quickly introduced by a syringe with rapid stirring under a nitrogen atmosphere, and the reaction mixture was stirred and polymerization started at the desired temperature. After a measured time interval (1 h), the polymerization was terminated by the addition of 150 mL of 10% HCl in methanol. The polymer was collected by filtration and washed liberally with methanol. Due to the general tendency of the s-PS helixes to trap aromatic molecules, crude materials contained

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Table 1. Syndiospecific Polymerization of Styrene Catalyzed by Cp*Ti(CH_2SiMe_3)$_3$/B(C_6F_5)$_3$ Catalyst[a]

run no.	[Ti] (mM)	cocatalyst compd	cocatalyst concn (mM)	Al/Ti (mol/mol)	activity[b] ($\times 10^{-7}$)	% s-PS[c]	T_m (°C)	$10^{-5}M_w$	M_w/M_n
1	0	$B(C_6F_5)_3$	0.35	0	0.24[d]	atactic		10.8	4.3
2	0	$Ph_3CB(CH_2SiMe_3)(C_6F_5)_3$	0.35	0	0.20[d]	atactic			
3	0.25	$B(C_6F_5)_3$	0.25	0	0				
4	0.35	$B(C_6F_5)_3$	0.35	0	0.73	95.0	270	3.0	2.2
5	0.50	$B(C_6F_5)_3$	0.50	0	0.86	95.2	270	2.9	2.1
6	0.35	$B(C_6F_5)_3$	0.50	0	0.53	87.4			
7	0.35	$B(C_6F_5)_3$	1.00	0	0.21	atactic			
8	0.25	$B(C_6F_5)_3$/TIBA	0.25	300	1.04	94.8	270	3.2	2.3
9	0.35	$B(C_6F_5)_3$/TIBA	0.35	50	0.88	96.0	270	3.2	2.2
10	0.35	$B(C_6F_5)_3$/TIBA	0.35	100	1.16	96.5	271	3.5	2.3
11	0.35	$B(C_6F_5)_3$/TIBA	0.35	300	1.37	97.2	270	3.8	2.0
12	0.35	$B(C_6F_5)_3$/TIBA	0.35	500	1.28	97.0	268	2.3	3.8

[a] Polymerization conditions: T_p, 70 °C; t_p, 1 h; total volume, 10 mL of styrene + 10 mL of toluene; aging time of the catalysts prepared in situ by mixing of Cp*Ti(CH_2SiMe_3)$_3$ with B(C_6F_5)$_3$, 10 min. [b] Activity in units of grams of bulk polymer/(mole of Ti·mole of styrene·h). [c] % s-PS = (grams of 2-butanone insoluble polymer/grams of bulk polymer) × 100. [d] Activity in units of grams of bulk polymer/(mole of cocatalyst·mole of styrene·h).

at least 15 wt % entrapped monomer.[11] So the polymer was then dried in vacuo at 80 °C for 48 h to remove solvent and monomer entrapped in crude materials. The obtained polymer was next extracted with boiling 2-butanone to give syndiotactic (insoluble) and atactic (soluble) polystyrene.

Analytical Procedures. NMR spectra were recorded on a JEOL FX-100 spectrometer. Chemical shifts for ^1H and ^{13}C spectra were referenced using internal solvent resonances and are reported related to tetramethylsilane. Elemental analyses were performed on a PE-2400 spectrometer. The melting temperature was determined with a Perkin-Elmer DSC-7 system at 10 °C/min. Gel-permeation chromatography (GPC) of the polymers was conducted on a Waters 150C using standard PS as the reference and 1,2,4-trichlorobenzene as the eluent at 135 °C. The molecular weights were determined by a universal calibration technique.

Results and Discussion

Formation of the Cationic Titanocene Complex in the Cp*Ti(CH_2SiMe_3)$_3$/B(C_6F_5)$_3$ Catalytic System. Treatment of a solution of Cp*Ti(CH_2SiMe_3)$_3$ in toluene/hexanes with equimolar amounts of B(C_6F_5)$_3$ at −30 °C results in the almost quantitative formation of a yellow precipitate of new cationic complex [Cp*Ti(CH_2SiMe_3)$_2$]$^+$[B(CH_2SiMe_3)(C_6F_5)$_3$]$^-$ (**1**)(eq 1).

$$\mathrm{Cp^*Ti(CH_2SiMe_3)_3 + B(C_6F_5)_3 \rightarrow} \\ \underset{\mathbf{1}}{\mathrm{[Cp^*Ti(CH_2SiMe_3)_2]^+[B(CH_2SiMe_3)(C_6F_5)_3]^-}} \quad (1)$$

Like other titanocene alkyl cations reported,[3,4] the present cationic complex was not isolable due to thermal lability at room temperature. The complex was also exceedingly air- and moisture-sensitive and required high-vacuum line/glovebox techniques for efficient handling. However, this compound was thermally stable below 10 °C and could be purified. After being thoroughly washed and extracted with hexane, and then dried in vacuo at 10 °C, the complex was readily identified by elemental analyses[12] and characterized spectroscopically. [Cp*Ti(CH_2SiMe_3)$_2$][B(CH_2SiMe_3)(C_6F_5)$_3$]: ^1H NMR (CD_2Cl_2, 0 °C) δ 1.93 (s, 15H, Cp*), 1.35 (s, 4H, TiCH_2SiMe_3), 0.23−0.28 (m, 27H, $SiMe_3$), 1.65 (br, s, 2H, BCH_2SiMe_3);$^{13}C\{^1H\}$ NMR δ131.0 (Cp* ring C), 84.5 (TiCH_2SiMe_3), 2.98 ($SiMe_3$), 12.4 (C_5Me_5), 35.5 (br, s, BCH_2SiMe_3). Anal. Calcd for $C_{40}H_{48}BF_{15}Si_3Ti$: C, 50.23; H, 5.02. Found: C, 51.05; H, 5.10. In addition to Cp* (δ1.93) and the Ti(CH_2SiMe_3) methylene proton (δ1.35) resonances, the ^1H NMR spectrum exhibits a broadened singlet at δ1.65, very different from the above-mentioned resonance of free borate anion in the Experimental Section (the free [B(CH_2SiMe_3)(C_6F_5)$_3$]$^-$ ion exhibits a relatively broad ^1H NMR resonance at δ 0.9) and assigned to the bridging methylene group, which appears to coordinate to the titanium.

As anticipated, the ^{19}F NMR spectra of the complex at 0 °C in CD_2Cl_2 exhibited well-resolved, single resonances for each of the ortho (δ −133), meta (δ −165), and para (δ −169) fluorine sites, consistent with the proposed ionic formation.

Syndiospecific Polymerization of Styrene Catalyzed by Cationic Complex 1. Table 1 summarizes the results obtained by cationic complex **1,** prepared in situ by reacting Cp*Ti(CH_2SiMe_3)$_3$ with 1 equiv of B(C_6F_5)$_3$, for the syndiospecific polymerization of styrene. The Cp*Ti(CH_2SiMe_3)$_3$/B(C_6F_5)$_3$ catalytic system was found to be highly active and syndiospecific for styrene polymerization, producing over 95% syndiotactic PS at an activity of 0.86 × 10^7 g of PS/mol of Ti·mol of styrene·h). In the absence of organotitanium Cp*Ti(CH_2SiMe_3)$_3$, both B(C_6F_5)$_3$ and Ph_3CB(CH_2SiMe_3)(C_6F_5)$_3$ only give small amounts of atactic PS, suggesting that [Cp*Ti(CH_2SiMe_3)$_2$]$^+$ should be an active species for the syndiospecific polymerization of styrene. Since B(C_6F_5)$_3$ itself slowly polymerizes styrene to a-PS, the addition of more than 1 equiv of the borane to the titanium complex resulted in an increase in the proportion of a-PS formed, together with a significant decrease of catalytic activity.

As compared with MAO-cocatalyzed styrene polymerization,[1] the application of reaction 1 to catalyze polymerization was found to require higher threshold amounts of Cp*Ti(CH_2SiMe_3)$_3$, some of which is probably consumed to scavenge impurities. Chien and coworkers have shown that for stoichiometric borate-cocatalyzed olefin polymerization in the zirconocene catalytic system, as much as 96% of the active catalyst is sacrificed to the aforementioned impurities if scrupulous purification procedures are not employed.[13] It is noteworthy that the activity and syndiospecificity of this catalytic system significantly increased when triisobutylaluminum (TIBA) was used to scavenge monomer or solvent impurities. The activity of the catalyst increased with increasing the additional amount of TIBA. For instance, when Al/Ti molar ratio approached 300, the activity of the catalyst was even enhanced to be 1.37 × 10^7 g of PS/mol of Ti·mol of styrene·h). In

Table 2. Effect of Polymerization Temperature (T_p) on the Syndiospecific Polymerization with Cp*Ti(CH_2SiMe_3)$_3$/B(C_6F_5)$_3$ Catalyst[a]

run no.	T_p (°C)	cocatalyst	Al/Ti (mol/mol)	activity[b] (× 10^{-7})	% s-PS[c]	$10^{-5}M_w$	M_w/M_n
13	0	B(C_6F_5)$_3$	0	0			
14	0	B(C_6F_5)$_3$/TIBA	100	0			
15	10	B(C_6F_5)$_3$	0	0.07	96.0	8.0	2.0
16	10	B(C_6F_5)$_3$/TIBA	100	0.15	96.8	8.5	2.1
17	30	B(C_6F_5)$_3$	0	0.41	95.4	6.4	2.3
18	30	B(C_6F_5)$_3$/TIBA	100	0.80	96.5		
19	50	B(C_6F_5)$_3$	0	0.62	95.0		
20	70	B(C_6F_5)$_3$	0	0.73	95.2	3.0	2.2
21	70	B(C_6F_5)$_3$/TIBA	100	1.16	96.5	3.5	2.3
22	90	B(C_6F_5)$_3$	0	0.32	80.0		

[a] Polymerization conditions: Cp*Ti(CH_2SiMe_3)$_3$, 0.35 mM; ratio B(C_6F_5)$_3$/Ti = 1; other conditions, see Table 1. [b] Activity in units, see note *b* of Table 1. [c] % s-PS, see note *c* of Table 1.

addition, additional TIBA could reduce the threshold amounts of Cp*Ti(CH_2SiMe_3)$_3$ but increase the catalytic activity (runs 3, 5, and 8). Even at different polymerization temperatures, the similar effect of additional TIBA on the catalysis was also observed (vide infra). Therefore, the use of additional TIBA is necessary for highly catalytic activity, and for rapid and reproducible polymerization if rigorous exclusion of air, moisture, and other impurities in the solvent and monomer feed is not maintained. The additional TIBA also contributes to enhancing the molecular weight of s-PS, possibly relative to the improved life span of the active species of a growing chain when TIBA was used to scavenge monomer or solvent impurities that could poison a catalytically active species. TIBA is not only a stronge alkylating agent but also a good chain transfer agent. Therefore, excess additional TIBA (for instance, Al/Ti = 500) in polymerization system significantly results in the reduction of molecular weight of the polymers.

As shown in Table 2, it was found that the addition of styrene to cationic complex solutions in toluene, generated in situ by mixing Cp*Ti(CH_2SiMe_3)$_3$ with B(C_6F_5)$_3$ (1:1 molar ratio), under strictly anhydrous conditions in the temperature range 10−90 °C resulted in obvious heating and darkening and in almost immediate formation of solid blocks of predominant s-PS. The activity of catalyst increased with increasing polymerization temperature. The values of M_w, however, decreased from 8.0×10^5 at 10 °C to $\sim 3.0 \times 10^5$ at 70 °C. The maximum polymerization activities were found at T_p = 70 °C, which decreased with either higher or lower temperature. Both catalytic activity and the yield of sPS are lower at 90 °C, which could be due to decomposition of the titanium complex.

The effect of polymerization medium has been tested by substituting o-dichlorobenzene ($\epsilon = 9.93$), *m*-dichlorobenzene ($\epsilon = 5.04$), chlorobenzene ($\epsilon = 5.62$), and benzene ($\epsilon = 2.28$) for toluene ($\epsilon = 2.38$) (Table 3). Indeed, the electron-withdrawing substituents on the aromatic solvent ring can increase the activity of the cationic complex and enhance sPS yields, although toluene is the solvent of best choice in almost all cases for the polymerization of styrene to sPS by monocyclopentadienyltitanium systems.[1b−d,3f,14] Due to the B(CH_2SiMe_3)(C_6F_5)$_3^-$ counterion being coordinative, the catalytic activity of the system with this counterion was elevated by using a medium of high dielectric constant in which dissociation of the ion couple may be facilitated. That is to say, a weak bonding interaction between the titanium and methylene group of the counterion in the cationic complex examined may be significantly weakened in a polar medium, thus forming more bare cation Cp*Ti(CH_2SiMe_3)$_2^+$ to promote the styrene polymerization.

Table 3. Effect of Polymerization Medium on Syndiospecific Polymerization with Cp*Ti(CH_2SiMe_3)$_3$/B(C_6F_5)$_3$ Catalyst[a]

run no.	polymerization medium	dielectric constant (ϵ)	yield (g)	activity[b] (×10^{-7})	% s-PS[c]
23	*o*-dichlorobenzene	9.93	6.5	1.06	96.0
24	*m*-dichlorobenzene	5.04	5.4	0.88	95.9
25	chlorobenzene	5.62	5.8	0.95	95.8
26	toluene	2.38	4.5	0.73	95.2
27	benzene	2.28	1.2	0.20	92.7

[a] Polymerization conditions: Cp*Ti(CH_2SiMe_3)$_3$, 0.35 mM; ratio B(C_6F_5)$_3$/Ti = 1; total volume, 20 mL (10 mL styrene); other conditions, see Table 1. [b] Activity in units, see note *b* of Table 1. [c] % s-PS, see note *c* of Table 1.

It is noted that the polymerization reactions run in benzene give a lower yield of s-PS, even though the dielectric constant of benzene ($\epsilon = 2.28$) is close to that of toluene ($\epsilon = 2.38$). Similar findings were also observed in Cp*TiMe$_3$/B(C_6F_5)$_3$ catalyst for styrene polymerization.[3f] We have found that the interactional defference of the cationic complex **1** in these two solvents is largely responsible for the observed discrepancies in catalytic activity. It was found that addition of toluene to a CD_2Cl_2 solution of [Cp*Ti(CH_2SiMe_3)$_2$][B(CH_2SiMe_3)(C_6F_5)$_3$] resulted in partial conversion of the latter to [Cp*Ti(CH_2SiMe_3)$_2$ (η^6-toluene)][B(CH_2SiMe_3)(C_6F_5)$_3$].[15] The ^{1}H NMR spectrum exhibited a resonance at $\delta \sim 0.9$ attributable to free borate, the Cp* and B(CH_2SiMe_3) resonances of the complex **1,** and new resonances attributable to the species [Cp*Ti(CH_2SiMe_3)$_2$ (η^6-toluene)]$^+$. Thus an equilibrium is established between the neutral borate complex **1** and the cationic arene complex **2**, which can actually promote the styrene polymerization (eq 2). But no reaction was observed

$$\underset{\mathbf{1}}{[\mathrm{Cp^*Ti(CH_2SiMe_3)_2}][\mathrm{B(CH_2SiMe_3)(C_6F_5)_3}]} + \mathrm{toluene} \rightleftharpoons \underset{\mathbf{2}}{[\mathrm{Cp^*Ti(CH_2SiMe_3)_2}\,(\eta^6\text{-toluene})]^+} + [\mathrm{B(CH_2SiMe_3)(C_6F_5)_3}]^- \quad (2)$$

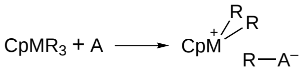
with benzene at the same conditions. Only the resonances of the free arene and [Cp*Ti(CH_2SiMe_3)$_2$][B(CH_2SiMe_3)(C_6F_5)$_3$] were present. Baird and co-workers have also observed the similar findings in the Cp*TiMe$_3$/B(C_6F_5)$_3$ catalytic system.[3h] The lack of coordination of benzene was thought to be attributable to the lowered electron density on the ring of this ligand in comparison to toluene.

Table 4. Comparison of Various Lewis Acids as Cocatalysts for the Syndiospecific Polymerization of Styrene[a]

run no.	cocatalysts	activity[b] ($\times 10^{-7}$)	% s-PS[c]	T_m (°C)	$10^{-5}M_w$
28	$SnPh_4$	0			
29	BPh_3	0			
30	BCl_3	0			
31	BF_3	0			
32	PF_5	0			
33	SbF_5	0			
34	Me_3SnCl	0			
35	$[Ph_3C]^+[BPh_4]^-$	0			
36	$[Ph_3C]^+[BF_4]^-$	0			
37	$B(C_6F_5)_3$	0.73	95.0	270	3.0
38	$[Ph_3C]^+[B(C_6F_5)_4]^-$	1.16	97.2	270	4.9
39[d]	$[Ph_3C]^+[B(C_6F_5)_4]^-$/TIBA	1.38	98.1	270	5.3
40	$[Ph_3C]^+[MeB(C_6F_5)_3]^-$	0.88	95.3	270	2.8
41[d]	$[Ph_3C]^+[MeB(C_6F_5)_3]^-$/TIBA	1.18	96.8	270	3.8
42	$[Bu_3NH]^+[B(C_6F_5)_4]^-$	0.07	atactic		
43[d]	$[Bu_3NH]^+[B(C_6F_5)_4]^-$/TIBA	0.06	atactic		
44	$[Et_3NH]^+[B(C_6F_5)_4]^-$	0.06	atactic		
45	$[(Ph)(Me_2)NH]^+[B(C_6F_5)_4]^-$	0.04	atactic		

[a] Polymerization conditions: $Cp^*Ti(CH_2SiMe_3)_3$, 0.35 mM; ratio cocatalysts/Ti = 1; other conditions, see Table 1. [b] Activity in units, see note *b* of Table 1. [c] % s-PS, see note *c* of Table 1. [d] Ratio additional TIBA/Ti, 100.

Role of Lewis Acid Cocatalysts and the Effect of Counterion Structure on Titanocenium Catalysis of Styrene Polymerization. The results of this study argue that in $Cp^*Ti(CH_2SiMe_3)_3/B(C_6F_5)_3$-catalyzed styrene polymerization the active centers are cationic $[Cp^*Ti(CH_2SiMe_3)_2]^+$ species. This indicates that the role of cocatalyst is to act as a Lewis acid, which creates and maintains the coordinative unsaturation and electron deficiency at the metal center necessary for substrate activation (eq 3). We have compared a series of potent Lewis acids as cocatalysts, which activate $Cp^*Ti(CH_2SiMe_3)_3$ to form active species, and investigated the relationship between the structure and properties of cocatalysts and their cocatalytic behavor for the styrene polymerization (Table 4). It is obvious that the high Lewis acidity of an effective cocatalyst (A) is a necessary requirement because if the cocatalyst is not more acidic (electrophilic) than the resulting cationic complex **3,** which is itself a very strong Lewis acid, then the equilibrium of eq 3 will lie far to the left. This requirement alone excludes a lot of simple Lewis acids from being effective cocatalysts. For instance, BPh_3 and $SnPh_4$ do not abstract a (trimethylsilyl)methyl group from $Cp^*Ti(CH_2SiMe_3)_3$ to form an identifiable cation. The reaction with $Cp^*Ti(CH_2SiMe_3)_3$ only results in the formation of unidentified, noncationic species. However, high acidity alone also cannot guarantee that a Lewis acid is an effective cocatalyst, as shown in Table 4. Although BCl_3, BF_3, PF_5, SbF_5, Me_3SnCl, Me_3SiCl, and Ph_3CBF_4 reagents have comparable or even greater Lewis acidities than $B(C_6F_5)_3$, they are not suitable candidates at all, because the halide atoms can either strongly coordinate to, or irreversibly transfer to, the titanocene cations. Similar findings have been observed in other group 4 metallocene systems.[16] Catalysis by $Cp^*Ti(CH_2SiMe_3)_3$ with $Ph_3CB(C_6H_5)_4$ as cocatalyst produced no polystyrene, possibly attributable to the interaction of alkyltitanocenium ions with a phenyl ring of $B(C_6H_5)_4^-$ to form a coordination complex without catalytic activity. This interaction has also been demonstrated for other titanocene or zirconocene systems.[3g,17]



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(3)

On the other hand, $Cp^*Ti(CH_2SiMe_3)_3$ can be converted to a catalytically active species by the reaction with other boron cocatalysts besides $B(C_6F_5)_3$ (run 37–39). In analogy to the other reaction to produce metallocene "cation",[3,16] the reaction of these cocatalysts with $Cp^*Ti(CH_2SiMe_3)_3$ produces "cationic" species by alkide abstraction (eqs 4 and 5),[18] which are highly

$$Cp^*Ti(CH_2SiMe_3)_3 + Ph_3C^+B(C_6F_5)_4^- \rightarrow \underset{\mathbf{4}}{[Cp^*Ti(CH_2SiMe_3)_2]^+[B(C_6F_5)_4]^-} + Ph_3CCH_2SiMe_3 \quad (4)$$

$$Cp^*Ti(CH_2SiMe_3)_3 + Ph_3C^+MeB(C_6F_5)_3^- \rightarrow \underset{\mathbf{5}}{[Cp^*Ti(CH_2SiMe_3)_2]^+[MeB(C_6F_5)_3]^-} + Ph_3CCH_2SiMe_3 \quad (5)$$

active and syndioselective for the styrene polymerization. However, $Ph_3CB(CH_2SiMe_3)(C_6F_5)_3$ does not react with $Cp^*Ti(CH_2SiMe_3)_3$ to form an unidentified cation. The reaction only leads to the formation of an unidentified, noncationic species that is insoluble oil in toluene. According to eqs 1 and eq 4 or 5, the intermediates **1**, **4**, and **5** have the same cation but dissimilar counterions. Not only is there counterion influence on product molecular weight but also there is a marked anion influence on both stereospecificity and catalyst activity. The difference of counterions should be largely responsible for the observed discrepancies in the polymerization. For instance, the cationic catalyst **4** has a higher activity and syndiotacticity ($A = 1.16 \times 10^7$ g of PS/mol of Ti·mol of styrene·h, syndiotacticity = 96.5%) than the cationic catalyst **1** ($A = 0.73 \times 10^7$ g of PS/mol of Ti·mol styrene·h, syndiotacticity = 95.0%), relative to the fact that the former produces the noncoordinating $B(C_6F_5)_4^-$ counterion. That is to say, this difference can be explained by the better accessibility or coordination and insertion of styrene into the Ti–C bond cationic center when the counterion is noncoordinating $B(C_6F_5)_4^-$ rather than weakly coordinating $MeB(C_6F_5)_3^-$ and $(CH_2SiMe_3)B(C_6F_5)_3^-$. It was found that the use of additional TIBA, which scavenges monomer or solvent impurities, in the catalytic systems with different counteranions was also necessary for highly catalytic activity and reproducible polymerization (runs 21, 39, and 41).

The molecular weight of the polymer increases from $\sim 3 \times 10^5$ for the catalyst **1** or **5** to $\sim 5 \times 10^5$ for the catalyst **4.** ^{13}C NMR spectra of the polymers indicate that β-hydride elimination is the only significant chain transfer pathway, consistent with the findings reported by Zambelli and Haddleton.[19] Therefore, the molecular weight of the polymer is controlled by the relative rates of two competing processes, β-hydride elimination and styrene insertion. This means that the effect of the present counterions in "cations" **1, 4,** or **5** on molecular weight (M_w) reasonably reflects disparities in both $K_{insertion}$ and $K_{\beta\text{-hydride}}$ elimination.

Without exception, the present cationic titanocene catalysts of **1**, **4**, and **5** were not isolable due to thermal lability in solution over room temperature. Aged catalyst solutions (24–25 °C) exhibit no polymerization activity. If any, the aged catalyst solutions show little polymerization activity to give a small amount of atactic PS. The possible decomposition pathways of these catalyst solutions are unclear.

The cocatalyst $R_3NHB(C_6F_5)_4$ (R = −Bu, −Et, $-(CH_3)_2(C_6H_5)$) was also used to prepared "cationic" species **6** by protonolysis (eq 6). However, in situ generation of

$$\mathrm{Cp^*Ti(CH_2SiMe_3)_3 + R_3NH^+B(C_6F_5)_4^- \rightarrow \underset{\mathbf{6}}{[Cp^*Ti(CH_2SiMe_3)_2]^+[B(C_6F_5)_4]^-} + SiMe_4 + R_3N} \quad (6)$$

$$(\mathrm{R} = -\mathrm{Bu}, -\mathrm{Et}, -(\mathrm{CH_3})_2(\mathrm{C_6H_5}))$$

$$\mathrm{[Cp^*Ti(CH_2SiMe_3)_2]^+[B(C_6F_5)_4]^- + R_3N \rightarrow \underset{\mathbf{7}}{[Cp^*Ti(CH_2SiMe_3)_2(R_3N)][B(C_6F_5)_4]}} \quad (7)$$

the "cationic" species incurs the coordination of trialkylamine to the titanocene cation to form a new compound **7** (eq 7), as identified by ^1H NMR,[20] thus inhibiting catalytically active species or severely increasing the hindrance of monomer coordination by the presence of the amine or the counterion for styrene polymerization. As a result, catalysis by $Cp^*Ti(CH_2SiMe_3)_3$ with $R_3NHB(C_6H_5)_4$ as cocatalyst only produced a small amount of atactic polystyrene.

Conclusion

The reaction of $B(C_6F_5)_3$ with $Cp^*Ti(CH_2SiMe_3)_3$ in hydrocarbon solvents affords a "cationic" complex $[Cp^*Ti(CH_2SiMe_3)_2]^+[B(CH_2SiMe_3)(C_6F_5)_3]^-$ in quantitative yields, which is active for the syndiospecific polymerization of styrene. As to the authentic structure of the catalyst, we have previously found that,[21] by combined NMR and ESR spectra, the active site in polymerization did have a different oxidation state or structure than the cation found prior to addition of styrene in the $Cp^*Ti(CH_2SiMe_3)_3/B(C_6F_5)_3$ system. The initially formed $[Cp^*Ti(CH_2SiMe_3)_2]^+[B(CH_2SiMe_3)(C_6F_5)_3]^-$ ionic complex decomposes to a Ti(III) species, possibly the $[Cp^*Ti(CH_2SiMe_3)]^+$ cationic complex, after the addition of styrene. The Ti(III)species concentration monitored with NMR and ESR spectra greatly increases not only by the addition of styrene but also by the enhanced polymerization temperature in the presence of styrene. Therefore, it is believed that the $[Cp^*Ti(CH_2SiMe_3)]^+$ cationic complex is actually active.[21] This finding also provides further experimental evidence that a cationic Ti(III) complex $[Cp^*TiR]^+$ could be the catalytically active species for the syndiospecific polymerization of styrene.[1c−d,2] More importantly, through the comparison of various Lewis acids as cocatalysts, we unambiguously demonstrated the role of the key titanocene−cocatalyst interaction and the effect of counterion structure on catalysis, suggesting that the nature of the counteranion is much more important. From the abovementioned findings it occurs to us that it might be possible to devise other potent Lewis acids as cocatalyst as long as they possess all of the following properties: (a) high Lewis acidity, (b) good solubility in nonpolar, noncoordinating solvents, (c) lower substituent nucleophilicity in either Lewis acids themselves or the corresponding counterion of cationic complexes, (d) high thermal and chemical stability, and (e) lower nucleophilicity (or chemical intertia) of byproducts, which produces in the formation of cation, metallocene cationic species.

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(15) $[Cp^*Ti(CH_2SiMe_3)_2\ (\eta^6\text{-toluene})][B(CH_2SiMe_3)(C_6F_5)_3]$: ^1H NMR (CD_2Cl_2 at 0 °C) δ 7.75 (2H, d, o-H), 7.30 (t, m-H), 6.80 (t, 1H, p-H), 2.76 (s, 3H, PhMe), 1.93 (s, 15H, Cp*), 0.65 (br, s, 2H, BCH_2SiMe_3), 0.84 (s, 4H, $TiCH_2SiMe_3$), 0.27 (s, 27H, $SiMe_3$).

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