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Ethylene and propylene polymerization by cationic monocyclopentadienyl titanium catalysts containing the weakly coordinating anion $[B(C_6F_5)_4]^-$

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Abstract

The compounds Cp^*TiMe_2E ($Cp^* = \eta^5$-C_5Me_5; E = Me, C_6F_5, OC_6F_5, Cl) react with trityl tetrakis(perfluorophenyl)borate, $[Ph_3C][B(C_6F_5)_4]$, to form the thermally unstable dititanium complexes $[(Cp^*TiMeE)_2(\mu\text{-}Me)][B(C_6F_5)_4]$, all of which behave as sources of the highly electrophilic species $[Cp^*TiMeE]^+$. An investigation of the activities of these $[B(C_6F_5)_4]^-$ salts as ethylene and propylene polymerization catalysts shows that they are more active than the analogous compounds $Cp^*TiMeE(\mu\text{-}Me)B(C_6F_5)_3$, as anticipated since $[B(C_6F_5)_4]^-$ is a poorer ligand than is $[BMe(C_6F_5)_3]^-$. However, contrary to current perceived wisdom, substitution of a methyl ligand of $[Cp^*TiMe_2]^+$ by the more electron withdrawing C_6F_5, OC_6F_5 and Cl ligands in these monocyclopentadienyl systems does not generally result in catalysts exhibiting lower activities and producing lower molecular weight polymers. An EPR study of the $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$ system in chlorobenzene at room temperature indicates that $< 0.01\%$ of the titanium is present occasionally during polymerization as a complex of titanium(III), suggesting that a contribution to the catalytic processes by titanium(III) species is unlikely. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ziegler–Natta catalysis; Polyolefins; Titanium

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1. Introduction

There have in recent years been numerous investigations into the use of Group 4 organometallic complexes as homogenous catalysts for the polymerization of olefins [1]. The most studied and successful of the precursor compounds have been metallocenes of the type Cp'_2MR_2 (M = Ti, Zr, Hf; R = alkyl; Cp' = substituted cyclopentadienyl), which undergo alkyl abstraction on reaction with Lewis acid co-catalysts, such as the borane $B(C_6F_5)_3$ (Eq. (1)) to give the formally 14-electron, cationic species $[Cp'_2MR]^+$ [2], which are believed to be the actual catalysts.

$$Cp'_2MR_2 + B(C_6F_5)_3 \rightarrow [Cp'_2MR]^+ + [BR(C_6F_5)_3]^- \quad (1)$$

Similar species are apparently formed on treating for example metallocene dihalides with the oligomeric methylalumoxane (MAO), and commercially viable processes are based on use of this co-catalyst, although research with $B(C_6F_5)_3$ has perhaps provided greater insight into polymerization mechanisms.

Relatively recent work has also focused on the related monocyclopentadienyl precursors $Cp'TiR_3$ [3], which may be readily converted to the active, 10-electron species $[Cp'TiR_2]^+$. These monocyclopentadienyl catalysts are electronically less saturated and sterically less hindered than their metallocene counterparts, and have been used to polymerize a wide variety of olefins with substantial success. We have previously shown that the precursor Cp^*TiMe_3, when reacted in a 1:1 ratio with the strong Lewis acid $B(C_6F_5)_3$, forms exclusively the methyl bridged species $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (**1**; Eq. (2)) [4].

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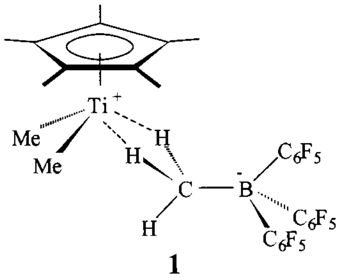

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$$Cp^{*}TiMe_3 + B(C_6F_5)_3 \rightarrow Cp^{*}TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$$

(**1**) (2)

The latter behaves as a source of the active species $[Cp'TiMe_2]^+$ [4], which has been utilized as an initiator for both Ziegler–Natta and carbocationic polymerizations of a variety of olefins [5].

Since cationic complexes of both the mono- and the dicyclopentadienyl series generally form more active polymerization catalysts than do neutral species [1,5d], we have earlier hypothesized that substitution of one of the methyl groups of $[Cp^{*}TiMe_2]^+$ by more electron withdrawing ligands could result in the formation of more active initiators [6]. This expectation is apparently contrary to at least some findings for metallocene systems [7], since, for instance, incorporation of electron-withdrawing groups X on the indenyl rings of metallocenes of the type $(\eta^5\text{-}5,6\text{-}X_2C_9H_5)_2ZrCl_2$ (**2**) have been found to result in both decreased activity and reduced polymer molecular weights [7c]. While these results seem to imply that electron-withdrawing ring substituents increase the rates of termination and/or chain transfer relative to the rates of initiation and chain propagation, in fact the reactions are expected to be affected unpredictably by ligand substitution, and the reasons for the observed deactivation were not assessed in detail [7c]. Indeed, it has been shown that enhanced Lewis acidity of the metal can result in stronger binding of the counter anion [2], which could result in both inhibition of monomer coordination and more facile termination of polymer growth via olefin ligand displacement. Thus, the effects of increased metal ion Lewis acid strength on catalytic activity arguably remain unclear.

In order to test the hypothesis concerning the effects of replacing a methyl group of $Cp^{*}TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ by more electronegative ligands, we have previously synthesized the chiral compounds $Cp^{*}TiMeE(\mu\text{-}Me)B(C_6F_5)_3$ (**3**; $E = C_6F_5$, OC_6F_5, Cl), for which the electron-withdrawing powers of the ligands E in the precursor compounds appear to decrease in the order C_6F_5, Cl > OC_6F_5 > Me [6b,c]. All of these compounds polymerize ethylene to high molecular weight polyethylene and propylene to atactic, elastomeric polypropylene, the major catalytically active species in all cases being titanium(IV) complexes of the type $[Cp^{*}TiMeE]^+$ ($E = Cl$, C_6F_5, OC_6F_5), similar to the above-mentioned $[Cp^{*}TiMe_2]^+$. However, although the compounds $Cp^{*}TiMeE(\mu\text{-}Me)B(C_6F_5)_3$ containing the more electron-withdrawing ligands E were expected to be the better catalysts, the anticipated results were only partially achieved. Although higher molecular weight polypropylenes of low polydispersities (M_w/M_n 1.3–1.9) were formed at −78°C when $E = Cl$, C_6F_5, OC_6F_5 than when E = Me, the amounts of polymers formed were actually comparable or lower, apparently because the greater Lewis acidity of the cationic species $[Cp^{*}TiMeE]^+$ resulted in stronger coordination of the $[BMe(C_6F_5)_3]^-$ anion. It was in fact possible to show that the compounds containing the more electron withdrawing ligands coordinate the methyl borate anion much more strongly, and thus the anion competes with the monomer for the vacant site, reducing the catalytic activity of the resulting system [6]. Rather similar ion pairing effects have been found for metallocene systems [2a], and much new research currently focuses on the design of new co-catalysts that can provide a more poorly coordinating counterion for more active catalytic systems [2].

With these developments in mind, we have endeavored to synthesize a series of new compounds $[Cp^{*}TiMeE]X$ ($E = Cl$, C_6F_5, OC_6F_5; $X = B(C_6F_5)_4$), in which the counteranion $B(C_6F_5)_4^-$, for steric or electronic reasons, cannot coordinate strongly and thus induce deactivation. In this publication we describe the use of the trityl borate co-catalyst $[Ph_3C][B(C_6F_5)_4]$, which normally readily abstracts methyl anions to form cationic complexes containing the relatively poorly coordinating counteranion $[B(C_6F_5)_4]^-$ [2a]. The four systems $Cp^{*}TiMe_2E/[Ph_3C][B(C_6F_5)_4]$ all behave as good olefin polymerization catalysts with ethylene and propylene, the polymerization activities correlating with the nature of E as indicated in part by complementary solution dynamics study of these systems. We also describe unsuccessful attempts to synthesize similar catalysts utilizing the very bulky borane tris(2,2′,2″-perfluorobiphenyl)borane, $B(C_{12}F_9)_3$, which is expected to react with $Cp^{*}TiMe_2E$ to form the poorly coordinating anion $[BMe(C_{12}F_9)_3]^-$ [2i].

2. Results and discussion

The reaction of $Cp^{*}TiMe_3$ with one molar equivalent of $[Ph_3C][B(C_6F_5)_4]$ occurred cleanly at −50°C in CD_2Cl_2 on an NMR scale to form only the thermally unstable, dititanium compound $[(Cp^{*}TiMe_2)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**4a**). The reaction involves abstraction of a methyl ligand from half of the available $Cp^{*}TiMe_3$ by trityl cation, followed by preferential coordination of the remaining $Cp^{*}TiMe_3$ at the vacant site produced (Eq. (3)).

$$2Cp^*TiMe_3 + 2[Ph_3C][B(C_6F_5)_4] \rightarrow [(Cp^*TiMe_2)_2(\mu\text{-}Me)][B(C_6F_5)_4]\ (\mathbf{4a}) + [Ph_3C][B(C_6F_5)_4] + Ph_3CMe \tag{3}$$

As indicated by Eq. (3), only one half of the $[Ph_3C][B(C_6F_5)_4]$ reacts, leaving a half equivalent remaining in solution and thus resonances of both the trityl cation and 1,1,1-triphenylethane were observed in the ^{1}H-NMR spectrum of the reaction mixture. No further reaction ensues, although our polymerization results imply that $[(Cp^*TiMe_2)_2(\mu\text{-}Me)]^+$ reacts further with $[Ph_3C][B(C_6F_5)_4]$ in the presence of olefin (see below).

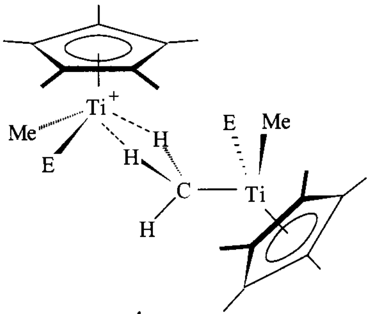
Although the dititanium product **4a** is thermally too labile to isolate, a compound containing the same cationic complex has been previously synthesized via the reaction of Cp^*TiMe_3 and the borane $B(C_6F_5)_3$ in a 2:1 ratio (Eq. (4)) [4c].

$$2Cp^*TiMe_3 + B(C_6F_5)_3 \rightarrow [(Cp^*TiMe_2)_2(\mu\text{-}Me)][BMe(C_6F_5)_3] \tag{4}$$

As before, the unstable cation is readily identified on the basis of its ^{1}H-NMR spectrum which exhibits resonances attributable to the three methyl proton environments, at δ 2.06 (Cp*), 1.46 (Ti–Me) and 0.15 (μ-Me). Interestingly, as with $[(Cp^*TiMe_2)_2(\mu\text{-}Me)][BMe(C_6F_5)_3]$ [4c], spin saturation transfer experiments showed that irradiation of the terminal methyl resonance of **4a** at δ 1.46 results in the appearance of an otherwise vanishingly weak resonance at δ 0.61, assigned to the Ti–Me group of free Cp^*TiMe_3, and suggesting the equilibrium shown in Eq. (5). A complementary experiment showed that the Cp* resonances of **4a** (δ 2.06) and Cp^*TiMe_3 (δ 1.88) also undergo exchange.

$$[(Cp^*TiMe_2)_2(\mu\text{-}Me)]^+ \rightleftharpoons Cp^*TiMe_3 + [Cp^*TiMe_2]^+ \tag{5}$$

Metallocene complexes containing methyl groups bridging two Group 4 metals have been reported previously [2d,8] and provide precedents for the structure (**4**) proposed.



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The equilibrium shown in Eq. (5) is vital to the process of olefin polymerization since the cationic complex $[Cp^*TiMe_2]^+$ is believed to be the active species that coordinates monomer and thus initiates the polymerization process. The equilibrium of Eq. (5) must lie well to the left, however, as the neutral Cp^*TiMe_3 is not available in the absence of monomer to react with the remaining $[Ph_3C][B(C_6F_5)_4]$, even upon warming to 0°C. Compound **4a** can also be synthesized by the reaction of Cp^*TiMe_3 with a half equivalent of $[Ph_3C][B(C_6F_5)_4]$, yielding **4a** alone with no $[Ph_3C][B(C_6F_5)_4]$ remaining in solution. Interestingly, as will be shown below, the full equivalent of co-catalyst is needed to obtain optimal polymerization results.

Our observation that the trityl cation of $[Ph_3C][B(C_6F_5)_4]$ is apparently less effective at removing a methyl carbanion from Cp^*TiMe_3 than is the neutral borane $B(C_6F_5)_3$ seems counterintuitive [2j]. However, a factor increasing the spontaneity of the chemistry of Eq. (1) is the ability of the methylborate counteranion, $[BMe(C_6F_5)_3]^-$, to coordinate to the titanium in **1**. Although the type of non-classical bonding involved might be expected to be weak, in fact the $[BMe(C_6F_5)_3]^-$ has also been shown to be a better ligand in metallocene systems [2] than is $[B(C_6F_5)_4]^-$ and as is shown below, the same is true for the type of compounds under consideration here. Thus, the driving force for the methyl transfer reaction of Cp^*TiMe_3 with $[Ph_3C][B(C_6F_5)_4]$ is lowered in large measure by the inability of the $[B(C_6F_5)_4]^-$ to compete with Cp^*TiMe_3 for the inner coordination sphere of the $[Cp^*TiMe_2]^+$ ion.

Our observation that the reaction of Cp^*TiMe_3 with $[Ph_3C][B(C_6F_5)_4]$ yields solely the dititanium species **4a** is of some interest in that it shows that previous assumptions [3k] concerning the chemistry of Eq. (3) may not apply. While attempting to rationalize the appearance of complex EPR resonances in reaction mixtures containing equimolar amounts of Cp^*TiMe_3 and $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene, Grassi et al. [3k] presumed that $[Cp^*TiMe_2]^+$ was the dominant species formed and that this cationic complex subsequently undergoes reduction to an EPR-active but otherwise uncharacterized titanium(III) species. In fact, as we have now demonstrated, the major species present in methylene chloride is $[(Cp^*TiMe_2)_2(\mu\text{-}Me)][B(C_6F_5)_4]$, which is quite stable with respect to reduction. Indeed, on monitoring the reaction of Cp^*TiMe_3 with $[Ph_3C][B(C_6F_5)_4]$ under the same conditions as previously [3k], i.e. at room temperature in chlorobenzene by EPR spectroscopy, we observe only a weak doublet at $g = 1.992$, exhibiting a hyperfine coupling constant of 8.2 G. This finding is similar to both the type of titanium(III) hydride reported from the reaction of $CpTi(OBu)_3$ with MAO [3c] and the very weak doublet we have previously observed in reaction mixtures containing equimolar amounts of Cp^*TiMe_3 and $B(C_6F_5)_3$ in chlorobenzene ($g = 1.994$, $A = 8.4$ G) [6c].

Integration using standard TEMPO solutions showed that the titanium(III) species being observed amounted to only ca. 0.01% of the total titanium in solution, and thus we cannot confirm the previous report that this same system in chlorobenzene contains relatively high proportions of Ti(III)-containing species [3k]. Working under scrupulously anhydrous and anaerobic conditions, we observe neither the stronger (by ca. 10^2) trityl and titanium-centered resonances nor the resonances attributed to putative alkoxytitanium(III) byproduct species that have been previously reported [3k]. In view of the highly reproducible and definitive NMR and EPR spectroscopic evidence presented herein, however, we feel that we have defined well the reaction between Cp^*TiMe_3 and $[Ph_3C][B(C_6F_5)_4]$.

$Cp^*TiMe_2OC_6F_5$ reacts with $[Ph_3C][B(C_6F_5)_4]$ in a manner similar to Cp^*TiMe_3 at −50°C, forming the interesting chiral complex $[(Cp^*TiMeOC_6F_5)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**4b**), which has also previously been synthesized via the reaction of $Cp^*TiMe_2OC_6F_5$ with a half equivalent of $B(C_6F_5)_3$ [6b]. Like **4a**, complex **4b** is thermally unstable and has been characterized by NMR spectroscopy (^1H, $^{13}C\{^1H\}$, ^{19}F). Unlike **4a**, however, **4b** contains two chiral titanium centers and the ^1H- and $^{13}C\{^1H\}$-NMR spectra are characterized by doubling of many of the resonances because of the presence of diastereomers in approximately equal amounts. Thus, the ^1H-NMR spectrum of **4b** exhibits two TiMe resonances (δ 1.50, 1.47), while the $^{13}C\{^1H\}$-NMR spectrum exhibits doubling of each of the C_5Me_5 (δ 132.0, 131.9), $C_5\mathit{Me}_5$ (δ 12.3, 12.2) and TiMe (79.7, 79.3) resonances. Spin saturation experiments have, interestingly, shown **4b** to be in equilibrium with $Cp^*TiMe_2OC_6F_5$ and $[Cp^*TiMeOC_6F_5][B(C_6F_5)_4]$ in much the same manner as described for **4a** in Eq. (5). Irradiation of the Cp* peak in **4b** at δ 2.01 gives rise to a new peak at δ 1.86, attributed to a very low concentration of $Cp^*TiMe_2OC_6F_5$.

The products of the reactions of $Cp^*TiMe_2C_6F_5$ and Cp^*TiMe_2Cl with $[Ph_3C][B(C_6F_5)_4]$ have proven to be much more difficult to identify because they form only at temperatures at which decomposition also occurs. The Cl and C_6F_5 groups are more electron withdrawing than the Me or OC_6F_5 groups [6b], apparently resulting in more electron deficient titanium centers that hold the anionic methyl ligands more tightly and thus inhibit removal of a methyl carbanion. In any case, no reactions occur between $Cp^*TiMe_2C_6F_5$ or Cp^*TiMe_2Cl and $[Ph_3C][B(C_6F_5)_4]$ at −50°C, a result in contrast with the facile methyl abstraction reactions of $Cp^*TiMe_2C_6F_5$ and Cp^*TiMe_2Cl with $B(C_6F_5)_3$, which occur readily at −50°C [6b]. Again, the neutral $B(C_6F_5)_3$ acts as a much more effective methyl abstractor than does the trityl cation. To our knowledge, these precursors represent the only titanium methyl compounds that exhibit such reluctance to react with the trityl cation.

Reactions of $Cp^*TiMe_2C_6F_5$ and Cp^*TiMe_2Cl with $[Ph_3C][B(C_6F_5)_4]$ do occur on warming to ca. 10°C, however, and appear to form the dititanium species $[(Cp^*TiMeC_6F_5)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**4c**) and $[(Cp^*TiMeCl)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**4d**), respectively. Unfortunately, unambiguous identification of the products is difficult as the release of methane (δ 0.2) and the appearance of new resonances in the spectra show that thermal decomposition occurs at these elevated temperatures. Evidence that species **4c** and **4d** are formed, however, is that only a half equivalent of the $[Ph_3C][B(C_6F_5)_4]$ reacts, analogous to the formation of **4a** and **4b**, and that the ^1H- and $^{13}C\{^1H\}$-NMR spectra of **4d** exhibit pairs of Ti–Me resonances, consistent with the formation of chiral, diasteromeric products although in this case they appear to formed in a ca. 3:2 ratio. Double irradiation experiments performed on **4d** gave no evidence of resonances attributable to $Cp^*TiMe_2C_6F_5$ or $[Cp^*TiMeC_6F_5]^+$, suggesting there was no observable equilibration between **4d** and its precursors, as is the case for **4a** and **4b**. This is perhaps not a surprising result as we have previously shown that $Cp^*TiMeC_6F_5(\mu\text{-}Me)B(C_6F_5)_3$ does not dissociate to detectable amounts of $Cp^*TiMeC_6F_5^+$ and $MeB(C_6F_5)_3^-$, contrary to the behavior of the analogous $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ and $Cp^*TiMeOC_6F_5(\mu\text{-}Me)B(C_6F_5)_3$ [6b]. The more electron deficient titanium center in $Cp^*TiMeC_6F_5^+$ acts to hold its neutral counterpart much more strongly, not allowing dissociation to occur. The variable temperature ^{19}F spectra of **4d** is also of interest as the broadness of the *ortho* and *meta* resonances changes with temperature, sharpening as the temperature increases and suggesting hindered rotation of the C_6F_5 ring, as was reported for $Cp^*TiMeC_6F_5(\mu\text{-}Me)B(C_6F_5)_3$ [6b].

2.1. Polymerization results

All four precursors Cp^*TiMe_3, $Cp^*TiMe_2OC_6F_5$, Cp^*TiMe_2Cl and $Cp^*TiMe_2C_6F_5$ have previously been shown to be highly effective catalysts for the polymerization of ethylene and propylene when activated by $B(C_6F_5)_3$ co-catalyst (as in Eq. (1)) [6b]. As outlined above, it was anticipated that the more electron deficient catalysts derived from $Cp^*TiMe_2C_6F_5$ and Cp^*TiMe_2Cl would be more active because of their greater propensities to coordinate an olefin, the first step in the polymerization mechanism. However, experimental results showed that this was not the case as these catalysts produced comparable amounts or less of polymer, depending on the nature of E and the polymerization temperature.

Interestingly, however, the polypropylene formed at −78°C in toluene by $Cp^*TiMeC_6F_5(\mu\text{-}Me)B(C_6F_5)_3$ exhibited a significantly higher value of M_w (2.3×10^6; M_w/M_n 1.7) than that formed under the same condi-

Table 1
Data for ethylene polymerization

Precursor	Activities[a]	
	Using $B(C_6F_5)_3$	Using $[Ph_3C][B(C_6F_5)_4]$
Cp^*TiMe_3	23	30
$Cp^*TiMe_2OC_6F_5$	22	23
$Cp^*TiMe_2C_6F_5$	8	24
Cp^*TiMe_2Cl	16	24

[a] kg of polymer per (mol Ti atm h).

tions by $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$ (3.4×10^5; M_w/M_n 1.3) [6c]. Clearly the rate of chain propagation was not decreased relative to those of chain termination/transfer by the presence of the electron-withdrawing C_6F_5 group. Since the decreased activity was suspected to be a result of stronger coordination of the $[MeB(C_6F_5)_3]^-$ anion to the titanium center competing with the incoming monomer for the active coordination site, we have now investigated the use of $[Ph_3C][B(C_6F_5)_4]$ rather than the borane because the trityl salt would incorporate a more poorly coordinating counteranion, $[B(C_6F_5)_4]^-$, into the catalyst. Unfortunately, as is shown above, the free active species $[Cp^*TiMeE]^+$ ($E = C_6F_5$, Cl) are not formed in solution with $[Ph_3C][B(C_6F_5)_4]$ at −78 °C, at which temperature high molecular weight polypropylenes of narrow molecular weight distributions are formed by clearly single site catalysts, such as $Cp^*TiMeC_6F_5(\mu\text{-}Me)B(C_6F_5)_3$. The neutral precursors Cp^*TiMe_2E compete extremely effectively for the active site of the cation of $[Cp^*TiMeE]^+[B(C_6F_5)_4]^-$, no polymer was formed, and the desired comparisons are impossible.

Polymerizations of ethylene and propylene by the $Cp^*TiMe_2E/[Ph_3C][B(C_6F_5)_4]$ systems were therefore of necessity carried out at 25°C, at which temperature some decomposition is apparent in both the $B(C_6F_5)_3$ and the $[Ph_3C][B(C_6F_5)_4]$ systems. Indeed, at this temperature the $B(C_6F_5)_3$ initiated catalysts give relatively low molecular weight polypropylene (ca. 2×10^5) of relatively high polydispersities (M_w/M_n ca. 5), consistent with the presence of more than one catalytically active species in solution [6c]. The activities obtained with the $[Ph_3C][B(C_6F_5)_4]$ co-catalyst are compared with those obtained when using the same four precursors with the borane cocatalyst in Tables 1 and 2, where it should be noted that the activities for the ethylene polymerizations with the $[Ph_3C][B(C_6F_5)_4]$ activated systems are in all cases lower limits. The polymerizations were hindered by extremely viscous solutions that formed, preventing effective monomer diffusion through the solution. In addition, the insolubility of the polyethylene in 1,2,4-trichlorobenzene at 140°C implies that this material was both linear and of high molecular weight.

Interestingly, the molecular weights and polydispersities of the polypropylene obtained were in all cases essentially identical to those prepared utilizing the borane as co-catalyst [6c], indicating that ion pairing has little effect on the polypropylene molecular weights. As with the polypropylene formed utilizing the borane as co-catalyst [6c], the materials produced here were primarily atactic (52–58% r dyads), and contained as much as 18% 2,1 inserted regioerrors, as indicated by a resonance at δ 28.2 in the $^{13}C\{^1H\}$-NMR spectra [6c]. These regioerrors are comparable with those observed with soluble vanadium catalysts [9a] and heterogenized monocyclopentadienyl titanium complexes [9b]. However, by using $[Ph_3C][B(C_6F_5)_4]$ as a cocatalyst in lieu of $B(C_6F_5)_3$, we appear to have increased the polymerization activities most notably for the two precursors, $Cp^*TiMe_2C_6F_5$ and Cp^*TiMe_2Cl, with the strongly electron withdrawing ligands. Although strict comparisons arguably should not be made in view of the differing exotherms for the different reactions, it is probably significant that polymerizations by the $Cp^*TiMe_2C_6F_5/[Ph_3C][B(C_6F_5)_4]$ system quickly became much hotter than the others, consistent with lower activities for the latter.

We are still left with the problem of trying to understand how the neutral species remaining in solution affect the polymerization activities. Upon initiation of polymerization, the dititanium complexes **4a–d** must dissociate to allow monomer to coordinate. The neutral precursors remaining in solution can then either react with the excess $[Ph_3C][B(C_6F_5)_4]$, also in solution, or compete with the incoming olefins for the active site. In order to study this further, we carried out some polymerization runs with only a half molar equivalent of

Table 2
Data for propylene polymerization

Precursor	Activities[a] using $B(C_6F_5)_3$	M_w (M_w/M_n) using $B(C_6F_5)_3$	Activities[a] using $[Ph_3C][B(C_6F_5)_4]$	M_w (M_w/M_n) using $[Ph_3C][B(C_6F_5)_4]$	Activities[a] using $\frac{1}{2}[Ph_3C][B(C_6F_5)_4]$
Cp^*TiMe_3	77	2.6×10^5 (5.2)	225	2.2×10^5 (4.5)	133
$Cp^*TiMe_2OC_6F_5$	160	1.7×10^5 (4.9)	174	1.4×10^5 (3.7)	0
$Cp^*TiMe_2C_6F_5$	78	2.7×10^5 (3.9)	222	2.6×10^5 (3.9)	0
Cp^*TiMe_2Cl	29	Bimodal	246	Bimodal	0

[a] kg of polymer per (mol Ti atm h).

$[Ph_3C][B(C_6F_5)_4]$ for each precursor, conditions under which NMR experiments demonstrate the formation of the dititanium complexes **4a**–**d** in the absence of unreacted $[Ph_3C][B(C_6F_5)_4]$. In all cases but Cp^*TiMe_3, propylene polymerizations were quenched completely. Some activity was observed with Cp^*TiMe_3, but less than with a full equivalent of co-catalyst; this is probably due to the equilibrium between the bridged dititanium species and the active species $[Cp^*TiMe_2]^+$ for this system. These results show clearly that the compounds Cp^*TiMe_2E in solution compete very effectively with propylene for the vacant sites of $[Cp^*TiMeE]^+$. Furthermore, the decreased activities observed when only a half equivalent of $[Ph_3C][B(C_6F_5)_4]$ is reacted with Cp^*TiMe_2E demonstrate clearly that the excess $[Ph_3C][B(C_6F_5)_4]$, which was originally remaining in solution at the beginning of a polymerization run, does eventually react with the neutral species obtained from initiator dissociation, preventing it from recoordinating to the active site. Therefore, we can conclude that after initial induction periods, all of the precursors are converted into the active species Cp^*TiMeE^+. It is also interesting to note that for polymerization runs involving $Cp^*TiMe_2C_6F_5$ and Cp^*TiMe_2Cl, the induction periods appear to be much longer, ca. 1 min, than for polymerization runs involving Cp^*TiMe_3 and $Cp^*TiMe_2OC_6F_5$ (ca. 10 s), measured by the time it takes for the reaction to begin to evolve heat. This longer induction period is possibly a result of the lower dissociation rate of compounds **4c** and **4d**, as indicated by the double resonance experiments as well as the lower rates of reaction between their neutral precursors and the $[Ph_3C][B(C_6F_5)_4]$ co-catalyst, as seen by variable temperature NMR experiments.

Attempts to react Cp^*TiMe_3 with the sterically hindered $B(C_{12}F_9)_3$ failed at low temperatures, presumably because of steric hindrance, and gave decomposition products that were poor propylene polymerization catalysts at room temperature. The compound $Cp^*TiMe_2C_6F_5$ failed to react with $B(C_{12}F_9)_3$ even at 30°C, and work with this borane, which does activate metallocenes and some other monocyclopentadienyl compounds [2i], was terminated.

3. Experimental

All experiments were carried out using standard Schlenk line techniques or a Vacuum Atmospheres glovebox, dry, prepurified nitrogen atmosphere and dried, thoroughly deoxygenated solvents. ^1H-, $^{13}C\{^1H\}$- and ^{19}F-NMR spectra were run using a Bruker AM 400 spectrometer operating at 400.14, 100.6 and 376.5 MHz, respectively; ^1H- and $^{13}C\{^1H\}$-NMR spectra are referenced with respect to internal TMS using residual proton or carbon resonances from the solvents, ^{19}F spectra with respect to internal C_6F_6. GPC data were obtained on a Waters Model 150-C in 1,2,4-trichlorobenzene solvent running at 145°C. EPR experiments involving equimolar amounts of Cp^*TiMe_3 and $[Ph_3C][B(C_6F_5)_4]$ (0.01–0.06 mmol of each in 10 ml solution) were run at 22°C on a Bruker R-B70 EPR spectrometer at ca. 9.7 GHz with the field centered at ca. 3400 G; the magnetic field was calibrated with DPPH ($g = 2.0037$), and standard solutions of TEMPO (1×10^{-3}–1×10^{-5} M) were used for quantitative estimates of the concentrations of titanium(III) species present. The compounds Cp^*TiMe_3 [10a], Cp^*TiMe_2Cl [10b], $Cp^*TiMe_2OC_6F_5$ [6], $Cp^*TiMe_2C_6F_5$ [6], $B(C_6F_5)_3$ [11a,b], $B(C_{12}F_9)_3$ [2i] and $[Ph_3C][B(C_6F_5)_4]$ [11c] were prepared by literature methods.

3.1. Polymerization experiments

In a typical polymerization run, a solution of 14 mg (0.06 mmol) of titanium precursor in 25 ml toluene saturated with monomer at 25°C was treated with a solution of 56 mg (0.06 mmol) of $[Ph_3C][B(C_6F_5)_4]$ in 10 ml toluene. Monomer was constantly bubbled through the solution, which warmed somewhat for 15 min before cooling to nearly room temperature after 20 min. For ethylene polymerizations, solutions became thick and viscous as polyethylene precipitated. Polymerization was continued for 20 min, and then 10 ml of methanol were added to terminate polymerization. The resulting polymers were collected by filtration, washed with methanol to remove residual catalyst and dried in vacuo.

3.2. *In situ NMR studies of the reactions of Cp^*TiMe_2E with $[Ph_3C][B(C_6F_5)_4]$ to form $[(Cp^*TiMeE)_2(\mu\text{-}Me)][B(C_6F_5)_4]$*

As the same basic procedure was followed in all cases, we describe here only our investigation of $[(Cp^*TiMe_2)_2(\mu\text{-}Me)][B(C_6F_5)_4]$ (**4a**). In an NMR experiment, 14 mg (0.06 mmol) of Cp^*TiMe_3 and 56 mg (0.06 mmol) of $[Ph_3C][B(C_6F_5)_4]$ were placed in an NMR tube and dissolved in 0.5 ml CD_2Cl_2 at −78°C. The resulting deep-red solution was then placed in the NMR spectrometer probe at −50°C. ^1H-NMR (CD_2Cl_2) of **4a**: δ 2.06 (30H, C_5Me_5), 1.46 (12H, TiMe), 0.15 (3H, μ-Me). $^{13}C\{^1H\}$-NMR of **4a**: δ 129.1 (C_5Me$_5$), 12.7 (C$_5$*Me*$_5$), 79.1 (TiMe). ^{19}F-NMR of **4a**: δ −133.3 (m, 6F, *ortho*), −163.9 (m, 3F, *para*), −167.7 (m, 6F, *meta*). The ^1H-NMR spectrum also exhibited resonances attributable to the trityl cation at δ 8.23 (br m, 3H, *para*), 7.84 (br m, 6H, *meta*) and 7.65 (br m, 6H, *ortho*), and to 1,1,1-triphenylethane at δ 7.27 (m, 9H, *para*, *meta*), 7.04 (m, 6H, *ortho*) and 2.14 (s, 3H, Me).

^{1}H-NMR (CD_2Cl_2) of [(Cp*TiMeOC_6F_5)$_2$(μ-Me)][B$(C_6F_5)_4$] (**4b**): δ 2.01 (30H, C_5Me_5), 1.50, 1.47 (6H, TiMe), −0.31 (3H, μ-Me). ^{13}C{^{1}H}-NMR of **4b**: δ 132.0, 131.9 (*C*$_5$Me$_5$), 12.3, 12.2 (C$_5$*Me*$_5$), 79.7, 79.3 (TiMe). ^{19}F-NMR of **4b**: δ −133.3 (m, 6F, *o*-F of BC_6F_5), −159.4, −159.6 (m, 4F, *o*-F of $TiOC_6F_5$), −163.9 (m, 3F, *p*-F of BC_6F_5), −163.6, −164.1 (m, 4F, *m*-F of $TiOC_6F_5$), −165.0 (m, 2F, *p*-F of $TiOC_6F_5$), −167.7 (m, 6F, *m*-F of B–C_6F_5). The ^{1}H-NMR spectrum also exhibited resonances attributable to the trityl cation at δ 8.23 (br m, 3H, *para*), 7.84 (br m, 6H, *meta*) and 7.65 (br m, 6H, *ortho*), and to 1,1,1-triphenylethane at δ 7.27 (m, 9H, *para*, *meta*), 7.04 (m, 6H, *ortho*) and 2.14 (s, 3H, Me).

In similar attempts to synthesize [(Cp*TiMeC_6F_5)$_2$(μ-Me)][B$(C_6F_5)_4$] (**4c**) and [(Cp*Ti–MeCl)$_2$(μ-Me)][B$(C_6F_5)_4$] (**4d**), only resonances attributable to the starting materials were observed at −78°C. The solutions were therefore warmed to 10°C to give deep red colors, but the ^{1}H- and ^{13}C{^{1}H}-NMR spectra were very complicated, indicating extensive decomposition. Only partial assignments of the NMR spectra of **4c** are possible. ^{1}H-NMR (CD_2Cl_2) of [(Cp*TiMeC_6F_5)$_2$(μ-Me)][B $(C_6F_5)_4$] (**4c**): δ 2.16 (30H, C_5Me_5), 2.34, 2.35 (6H, TiMe). ^{13}C{^{1}H}-NMR of **4c**: δ 139.2, 139.7 (*C*$_5$Me$_5$), 14.6 (C$_5$*Me*$_5$), 79.7, 79.3 (TiMe). Resonances attributed the trityl cation and 1,1,1-triphenylethane (see above) were observed in a 1:1 ratio in the ^{1}H-NMR spectra of **4c** and **4d**, as was a resonance attributed to methane (δ 0.2).

3.3. In situ NMR studies of the reactions of Cp*TiMe$_2$E with B$(C_{12}F_9)_3$

In NMR experiments similar to the above, addition of an equimolar amount of B$(C_{12}F_9)_3$ to solutions of the compounds Cp*TiMe$_3$ and Cp*TiMe$_2C_6F_5$ in CD_2Cl_2 at −50°C was shown to result in no reaction. In the case of Cp*TiMe$_3$, warming to 10°C did result in apparent methyl abstraction, but extensive decomposition of the product also occurred as the resulting NMR spectrum was very complicated and indicated the evolution of methane. An attempted propylene polymerization experiment using this system in toluene at 30°C yielded only a very small amount of polypropylene.

There was no reaction between Cp*TiMe$_2C_6F_5$ and B$(C_{12}F_9)_3$ even at 30°C, and this system failed to polymerize propylene at 50°C in toluene.

4. Summary

The compounds Cp*TiMe$_2$E (E = Me, C_6F_5, OC_6F_5, Cl) react with trityl tetrakis(perfluorophenyl)borate, [Ph$_3$C][B$(C_6F_5)_4$], to form the thermally unstable dititanium complexes [(Cp*TiMeE)$_2$(μ-Me)][B$(C_6F_5)_4$]. The latter function as sources of the highly electrophilic species [Cp*TiMeE]$^+$, and behave as more active olefin polymerization catalysts than do the analogous compounds Cp*TiMeE(μ-Me)B$(C_6F_5)_3$ since [B$(C_6F_5)_4$]$^-$ is a poorer ligand than is [BMe$(C_6F_5)_3$]$^-$. Interestingly, substitution of a methyl ligand of [Cp*TiMe$_2$]$^+$ by the more electron withdrawing C_6F_5, OC_6F_5 and Cl ligands does not generally result in catalysts exhibiting lower activities and producing lower molecular weight polymers. Indeed, it seems that more electron withdrawing ligands on the titanium result in better catalysis.

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References

[1] For recent reviews see (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. Waymouth, Angew. Chem. Int. Ed. Engl. 34 (1995) 1143. (b) M. Bochmann, J. Chem. Soc. Dalton Trans. (1996) 255. (c) W. Kaminsky, M. Arndt, Adv. Polym. Sci. 127 (1997) 143. (d) P.C. Möhring, N.J. Coville, J. Organomet. Chem. 479 (1994) 1.

[2] (a) L. Jia, X. Yang, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 842. (b) Y. Kim, B.H. Koo, Y. Do, J. Organomet. Chem. 527 (1997) 155. (c) C. Sishta, R.M. Hathorn, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 1112. (d) M.A. Giardello, M.S. Eisen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 12 114. (e) X. Yang, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 116 (1994) 10 015. (f) P.A. Deck, T.J. Marks, J. Am. Chem. Soc. 117 (1995) 6128. (g) A.R. Siedle, R.A. Newmark, J. Organomet. Chem. 497 (1995) 119. (h) Y.-X. Chen, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 119 (1997) 2582. (i) Y.-X. Chen, C.L. Stern, S. Yang, T.J. Marks, J. Am. Chem. Soc. 119 (1997) 12 451. (j) P.A. Deck, C.L. Beswick, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 1772. (k) Y.-X. Chen, M.V. Metz, L. Liting, C.L. Stern, T.J. Marks, J. Am. Chem. Soc. 120 (1998) 6287.

[3] For recent studies, see (a) C. Pellecchia, P. Longo, A. Proto, A. Zambelli, Makromol. Chem. Rapid Commun. 13 (1992) 265. (b) C. Pellecchia, P. Longo, A. Proto, A. Zambelli, Makromol. Chem. Rapid Commun. 13 (1992) 277. (c) J.C.W. Chien, Z. Salajka, S. Dong, Macromolecules 25 (1992) 3199. (d) A. Kucht, H. Kucht, S. Barry, J.C.W. Chien, M.D. Rausch, Organometallics 12 (1993) 3075. (e) T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, Macromolecules 26 (1993) 5822. (f) A. Zambelli, C. Pellecchia, L. Oliva, P. Longo, A. Grassi, A. Makromol. Chem. 192 (1991) 223. (g) H. Kucht, A. Kucht, J.C.W. Chien, M.D. Rausch, Appl. Organomet. Chem. 8 (1994) 393. (h) C. Pellecchia, A. Immirzi, A. Grassi, A. Zambelli, Organometallics 12 (1993) 4473. (i) J.C. Flores, J.C.W. Chien, M.D. Rausch, Organometallics 13 (1994) 4140. (j) J.C. Flores, J.S. Wood, J.C.W. Chien, M.D. Rausch, Organometallics 15 (1996) 4944. (k) A. Grassi, A. Zambelli, F. Laschi, Organometallics 15 (1996)

480. (l) J. Sassmannshausen, M. Bochmann, J. Organomet. Chem. 548 (1997) 23. (m) C. Pellecchia, D. Pappalardo, L. Oliva, A. Zambelli, J. Am. Chem. Soc. 117 (1995) 6593. (n) Y.-X. Chen, P.-F. Fu, C.L. Stern, T.J. Marks, Organometallics 16 (1997) 5958.

[4] (a) D.J. Gillis, M.-J. Tudoret, M.C. Baird, J. Am. Chem. Soc. 115 (1993) 2543. (b) D.J. Gillis, R. Quyoum, M.-J. Tudoret, Q. Wang, D. Jeremic, A.W. Roszak, M.C. Baird, Organometallics 15 (1996) 3600. (c) Q. Wang, R. Quyoum, D.J. Gillis, D. Jeremic, M.C. Baird, J. Organomet. Chem. 527 (1997) 7.

[5] (a) F. Barsan, M.C. Baird, J. Chem. Soc. Chem. Commun. (1995) 1065. (b) D. Jeremic, Q. Wang, R. Quyoum, M.C. Baird, J. Organomet. Chem. 497 (1995) 143. (c) Q. Wang, M.C. Baird, Macromolecules 28 (1995) 8021. (d) Q. Wang, R. Quyoum, D.J. Gillis, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, Organometallics 15 (1996) 693. (e) M.C. Murray, M.C. Baird, J. Mol. Cat. 128 (1998) 1.

[6] (a) T.L. Tremblay, S.W. Ewart, M.J. Sarsfield, M.C. Baird, J. Chem. Soc. Chem. Comm. (1997) 831. (b) M.J. Sarsfield, S.W. Ewart, T.L. Tremblay, A.W. Roszak, M.C. Baird, J. Chem. Soc. Dalton Trans. (1997) 3097. (c) S.W. Ewart, M.J. Sarsfield, D. Jeremic, T.L. Tremblay, E.F. Williams, M.C. Baird, Organometallics 17 (1998) 1502. (d) S.W. Ewart, M.J. Sarsfield, M.C. Baird, unpublished results. The reaction of Cp*$TiMe_2Cl$ with $B(C_6F_5)_3$ gives a mixture of compounds since two strong and several weak Cp* methyl resonances are observed. Although both methyl and chloro abstraction may be occurring, the polymerization activity of the mixture requires that there be present some Cp*TiMeCl(μ-Me)$B(C_6F_5)_3$, the Ti–Me resonance of which is obscured by the Cp* resonances.

[7] (a) A.-L. Mogstad, R.M. Waymouth, Macromolecules 25 (1992) 2282. (b) N. Piccolrovazzi, P. Pino, G. Consiglio, A. Sironi, M. Moret, Organometallics 9 (1990) 3098. (c) I.-M. Lee, W.J. Gauthier, J.M. Ball, B. Iyengar, S. Collins, Organometallics 11 (1992) 2115.

[8] M. Bochmann, S.J. Lancaster, Angew. Chem. Int. Ed. Eng. 33 (1994) 1634.

[9] (a) Y. Doi, Macromolecules 12 (1979) 248. (b) K. Soga, D.H. Lee, Makromol. Chem. 193 (1992) 1687.

[10] (a) M. Mena, P. Royo, R. Serrano, M.A. Pellinghelli, A. Tiripicchio, Organometallics 8 (1989) 476. (b) A. Martín, M. Mena, M.A. Pellinghelli, P. Royo, R. Serrano, A. Tiripicchio, J. Chem. Soc. Dalton Trans. (1993) 2117.

[11] (a) A.G. Massey, A.J. Park, J. Organomet. Chem. 2 (1964) 245. (b) R. Uson, A. Laguna, Inorg. Synth. 21 (1982) 72. (c) J.C.W. Chien, W.-M. Tsai, M.D. Rausch, J. Am. Chem. Soc. 113 (1991) 8570.