Reactivity of the [(η^5-C_5Me_5)$TiCH_3$][$RB(C_6F_5)_3$] Complexes Identified as Active Species in Syndiospecific Styrene Polymerization

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ABSTRACT: The reactivity of the alkyl complexes [Cp*Ti(III)(CH_3)][$RB(C_6F_5)_3$] (Cp* = η^5-C_5Me_5; R = CH_3, $-C_6F_5$) with α-^{13}C-enriched *p*-chlorostyrene has been investigated by means of ESR spectroscopy in order to gain insight into the chemical structure of the active species in syndiospecific polymerization of styrene and substituted styrenes promoted by "half-titanocene"-based catalysts. Secondary (2,1) polyinsertion of *p*-chlorostyrene into a Ti(III)−alkyl bond has been observed under polymerization conditions. The role of Cp*Ti^{III}R$^+$ complexes in syndiospecific styrene polymerization has conclusively been confirmed. Furthermore, the reaction of the ^{13}C-enriched complex [Cp*Ti($^{13}CH_3$)][$RB(C_6F_5)_3$] with PMe_3 and Al($^{13}CH_3$)$_3$ has also been investigated by ESR spectroscopy. PMe_3 displaces the methylborate anion from the coordination sphere of the Cp*Ti$^{13}CH_3$(μ-$^{13}CH_3$)$B(C_6F_5)_3$ ion pair and produces the corresponding phosphine adduct Cp*Ti(CH_3)(PMe_3)$_2^+$. In the same manner, the reaction of [Cp*Ti($^{13}CH_3$)][$B(C_6F_5)_4$] with Al($^{13}CH_3$)$_3$ affords the [Cp*Ti(μ-$^{13}CH_3$)$_3$Al($^{13}CH_3$)]$^+$ adduct. The increase of the intensity of the Ti(III) signals observed in the ESR spectra of these catalytic systems after addition of the monomer has been explained on the basis of the ESR results reported above.

Introduction

Cationic alkyl complexes of the general type Cp*TiR$^+$ (Cp* = η^5-C_5Me_5; R = CH_3, CH_2Ph) are currently believed to be the active species in homogeneous catalyzed styrene[1] and conjugated diene[2] polymerization. These species are elusive because of their high chemical reactivity and/or thermal instability and have never been isolated.

Cp*TiR$^+$ complexes, stabilized by the proper counterion, have been obtained as byproducts in the reaction of Cp*TiR$_3$ with equimolar amounts of such strong ionizing agents as $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$.[1d,e]

Treatment of Cp*Ti(CH_3)$_3$ with 1 equiv of $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$ in chlorobenzene at room temperature produces ESR-active solutions[1e] whose spectra exhibit one sharp single signal at $g_{iso} = 1.977$ ($\Delta H_{iso} = 15$ G) without any observable hyperfine structure. This signal has been previously attributed to the Cp*Ti(CH_3)$^+$ cation produced by reduction of the initially formed Cp*Ti(CH_3)$_2^+$ species through a mechanism unknown at present. The ESR spectrum of a chlorobenzene solution of the ^{13}C-enriched complex Cp*Ti($^{13}CH_3$)$_3$ contacted with an equimolar amount of $Ph_3CB(C_6F_5)_4$ displays a doublet ($a(^{13}C) = 6.0$ G) centered at $g_{iso} = 1.977$. A doublet and a triplet with the same *g* value and with the same $a(^{13}C)$ coupling constant were observed in the ESR spectrum of the Cp*Ti($^{13}CH_3$)$_3$/$B(C_6F_5)_3$ system under the same conditions. We assumed that the doublet results from the coupling of the Ti(III) d^1 electron with one ^{13}C-enriched methyl, as expected for the Cp*Ti($^{13}CH_3$)$^+$ species (**1**), and the triplet would then be due to the coupling of the same d^1 electron with two ^{13}C-enriched methyls, as expected for the Cp*Ti$^{13}CH_3$(μ-$^{13}CH_3$)$B(C_6F_5)_3$ associated ion pair (**2**). Thus, for the Cp*Ti($^{13}CH_3$)$_3$/$B(C_6F_5)_3$ system, the associated and separated ion pairs are in equilibrium at room temperature.[1e]

Either **1** or both **1** and **2** react with styrene. Addition of p-chlorostyrene (PCS) to the chlorobenzene solution of Cp*Ti($^{13}CH_3$)$_3$/$B(C_6F_5)_3$ and Cp*Ti($^{13}CH_3$)$_3$/$Ph_3CB(C_6F_5)_4$ systems produces the disappearance of the ESR signals at g_{iso}= 1.977 and the appearance of an anisotropic signal displaying the parallel ($g_{\|}$) and perpendicular ($g_{\perp}$) components at 1.968 and 1.973 (g_{ave} = 1.971), respectively. It is noteworthy that this new signal does not display any coupling with ^{13}C nuclei, indicating that the ^{13}C-enriched methyl is not bound anymore to the Ti(III) probably because of styrene insertion into the reactive Ti−methyl bond.

We previously reported that syndiospecific styrene polymerization proceeds through 2,1-insertion (secondary) of the monomer into the Ti−alkyl bond.[3] To finally assess the role played by Cp*TiR$^+$ species in styrene polymerization herein, we report on the reactivity of these complexes with α-^{13}C-enriched *p*-chlorostyrene (α-^{13}C−PCS).

Furthermore, the relevance of ionic interaction between Cp*TiR$^+$ complexes and the borate anions was investigated with the aim of providing an explanation for the polymerization activities and the average molecular weights of the polymer products obtained with these catalysts.[4]

Results and Discussion

Reactivity of Cp*TiR$^+$ Complexes with (α-^{13}C)-PCS Monomer. A chlorobenzene solution of Cp*Ti(CH_3)$_3$ and $B(C_6F_5)_3$ ([Ti] = 0.01 M; B/Ti molar ratio = 1) was treated with a chlorobenzene solution of PCS (200 mg; [PCS] = 1.5 M) and Al(*i*-Bu)$_3$ (40 mg, Al/Ti molar ratio = 20) in a vial at ambient temperature. Soon after the mixing, the resulting dark solution was quickly

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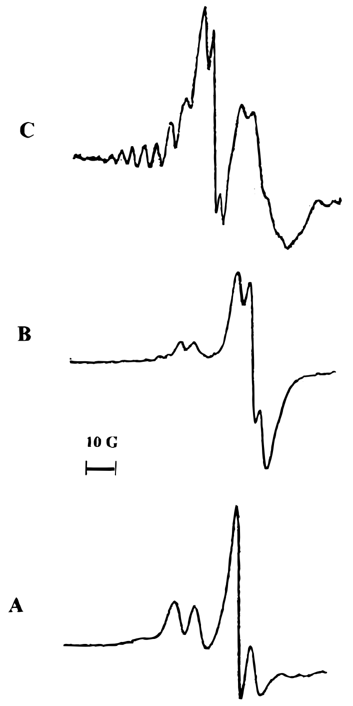


Figure 1. ESR spectra (chlorobenzene, 298 K, [Ti] = 0.01 M) of the following catalytic systems: (A) $Cp^*Ti(CH_3)_3$/MAO system after the addition of PCS (Al/Ti molar ratio = 100). This ESR spectrum is similar to that observed for the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$/PCS system under the same conditions (see ref 1e). (B) $Cp^*Ti(CH_3)_3$/MAO /α-^{13}C−PCS system. (C) $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$/PCS system after the addition of α-^{13}C−PCS.

transferred into the ESR tube by syringe. The ESR spectrum exhibits the broad signal at $g_{ave} = 1.971$ assigned to the active species in the polymerization conditions. After 5 min α-^{13}C−PCS was introduced into the ESR tube, and the reaction was monitored for about 1 h at ambient temperature. After a few minutes two intense signals were detected in the spectrum: one at $g_{iso} = 1.982$ (triplet, $a(^{13}C) = 3.0$ G) and the other one, with minor hyperfine resolution, replacing the broad signal at $g_{ave} = 1.971$ (see Figure 1C). Both ESR Ti(III) signals clearly show coupling with ^{13}C-enriched nuclei. Typically, the ESR signal observed at low field, in the range $g = 1.980-1.990$, is due to impurities introduced in the ESR tube through the experimental procedure we used. To have a better understanding of the ^{13}C-coupled signal observed at $g_{ave} = 1.971$, we tried to obtain cleaner spectra by using a $Cp^*Ti(CH_3)_3$/methylaluminoxane (MAO) catalyst where the high concentration of the alkylaluminum compound scavenges impurities from the reactor.

Actually, the ESR spectrum of a chlorobenzene solution recorded soon after the addition of $Cp^*Ti(CH_3)_3$ to a solution of α-^{13}C−PCS and MAO (Ti = 0.01 M; Al /Ti molar ratio = 100; [α-^{13}C−PCS] = 0.36 M) clearly contains only the anisotropic signal centered at $g_{ave} = 1.971$ (see Figure 1B). Computer simulation[5] of this anisotropic signal shows that it can be interpreted as the Ti(III) species in very slow-motion conditions observed in Figure 1A with both the perpendicular and parallel components coupled with ^{13}C nuclei ($a(^{13}C) = 4.7$ G; $a(^{13}C) = 1.7$ G). The corresponding isotropic $a(^{13}C)$ value is 2.7 G, a value smaller than that observed for the $Ti-^{13}CH_3$ bond (6.0 G). Considering that the Ti−polymer bond in the active species exhibits a Ti−benzyl character as a consequence of the secondary styrene insertion (see Scheme 1), the weaker coupling of the d^1 electron with the ^{13}C nuclei suggests a delocalization of this electron on the aromatic ring of the last inserted monomer unit.

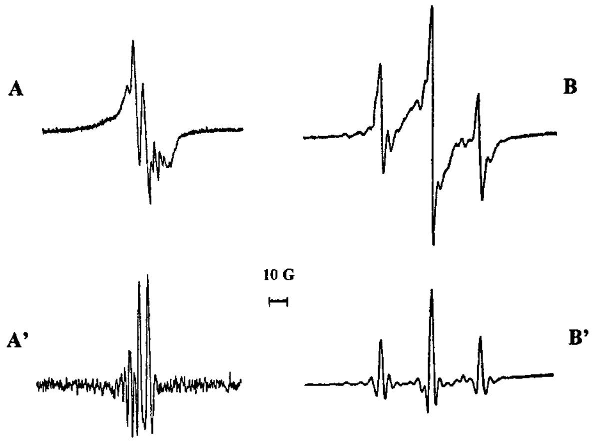
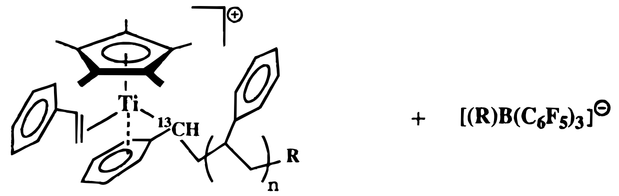


Figure 2. First derivative (A) and second derivative (A′) ESR spectra of the $Cp^*Ti(^{13}CH_3)_3/Ph_3CB(C_6F_5)_4$ catalytic system (chlorobenzene, 240 K, [Ti] = 0.01 M; B/Ti molar ratio = 1). First derivative (B) and second derivative (B′) ESR spectra of the phosphine adduct (**3**) obtained by in situ addition of PMe_3 to this system (P/Ti molar ratio = 20).

Scheme 1



In previous papers we proposed[1a,6] that the last inserted styrene unit of the growing polymer chain is η^n-coordinated to the metal center of the active species (with $n \geq 3$).[7] The present ESR investigation of the chemical structure of the active species confirms our previous suggestions.

The above-reported results seem to show conclusively that the cationic monoalkyltitanium(III) complexes, Cp^*TiR^+, actually are the active species promoting syndiospecific styrene polymerization with monocyclopentadienyltitanium precursors.

Reactivity of Cp^*TiR^+ Complexes with $Al(^{13}CH_3)_3$ and $P(CH_3)_3$. The ESR spectrum of a chlorobenzene solution containing equimolar amounts of $Cp^*Ti(^{13}CH_3)_3$ and $Ph_3CB(C_6F_5)_4$ ([Ti] = 0.01 M; Ti/B molar ratio = 1) prepared at room temperature and analyzed soon after (minutes) at 253 K exhibits a doublet ($g_{iso} = 1.977$; $a(^{13}C) = 6.0$ G) (see Figure 2).[8]

Treatment of this solution with an excess of PMe_3 (P/Ti molar ratio = 10) produces the phosphine adduct $Cp^*Ti(^{13}CH_3)(PMe_3)_2^+$ (**3**) identified in the ESR spectrum as a triplet at the same g value ($g_{iso} = 1.977$; $a(^{31}P) = 30$ G) (Figure 2). The coupling with the ^{13}C nuclei is not detected anymore and/or could be lost in the spectral line width ($\Delta H_{iso} = 3.0$ G). Addition of the phosphine in the ESR tube produces a large increase of the ESR signal, qualitatively recognized by the large increase of the signal-to-noise ratio of the spectral lines. The $a(^{31}P)$ coupling is slightly greater than that observed in a neutral titanocenes−phosphine adduct, namely, $Cp'_2TiMe(PR_3)$ ($Cp' = \eta^5$-cyclopentadienyl, η^5-indenyl; R = Me, Ph) ($a(^{31}P) = 18-25$ G),[9,10] indicating a stronger

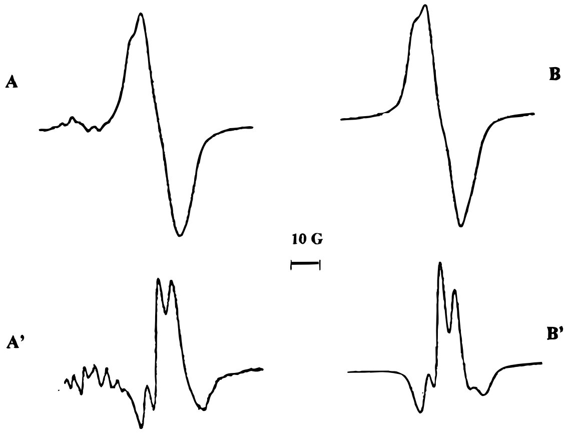
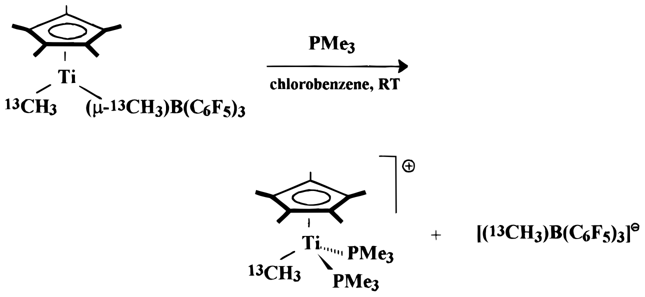


Figure 3. Comparison of the experimental and simulated ESR spectra of the $Cp^*Ti(^{13}CH_3)_3/Ph_3CB(C_6F_5)_4/Al(^{13}CH_3)_3$ system (chlorobenzene, 240 K, [Ti] = 0.01M; B/Ti molar ratio = 1; Al/Ti molar ratio = 3). (A and A′) First and second derivative experimental spectra, respectively. (B and B′) First and second derivative computer-simulated spectra obtained with $a(^{13}C) = 4.7$ G, respectively.

Scheme 2



interaction between the cationic Ti(III) complex and the phosphine ligands. The phosphine adduct (**3**) is thermally stable in a chlorobenzene solution for several hours. As a matter of fact, the intensity of the corresponding ESR signal did not change when the ESR solution was monitored versus time.

The addition of PMe_3 to a chlorobenzene solution of mixtures of $Cp^*Ti(^{13}CH_3)_3$ and $B(C_6F_5)_3$ (253 K, [Ti] = 0.01 M, B/Ti molar ratio = 1; P/Ti molar ratio = 20) produces the same ESR signal (triplet, $g_{iso} = 1.977$; $a(^{31}P) = 30$ G) observed in the previous experiment, indicating that the phosphine is a stronger ligand than the methylborate anion toward the cationic $Cp^*Ti(^{13}CH_3)^+$ complex under the reported experimental conditions (see Scheme 2).

However, when the phosphine adduct (**3**) is treated with a large excess of MAO, the resulting species is still able to polymerize styrene to syndiotactic polymer.

Addition of $Al(^{13}CH_3)_3$ to a chlorobenzene solution of $Cp^*Ti(^{13}CH_3)_3$ and $Ph_3CB(C_6F_5)_4$ (Ti/B molar ratio = 1; [Ti] = 0.01 M; Al/Ti molar ratio = 3; $T = 240$ K) produces an intense ESR signal at $g_{iso} = 1.977$, which can be interpreted, by means of spectral simulation, as a quadruplet (1:3:3:1) with $a(^{13}C) = 4.7$ G (Figure 3). When the temperature was raised to 298 K, broadening of the signal ($\Delta H_{iso} = 25$ G) and disappearance of the hyperfine structure have been detected. Similar results were obtained in the reaction of $Cp^*Ti(^{13}CH_3)_3$ and $B(C_6F_5)_3$ with $Al(^{13}CH_3)_3$ under the same experimental conditions.

Lappert et al. reported that reaction of $[(\eta^5\text{-}C_5H_5)_2TiCl]_2$ with $LiAl(CH_3)_4$ affords the $(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}CH_3)_2Al(CH_3)_2$ adduct, whose ESR spectrum exhibits a broad line (toluene, 233 K) at $g_{iso} = 1.977$ without resolved fine structure.[11] The quadruplet that we observed at the same g most likely arises from the coupling of the Ti(III) d^1 electron with three equivalent ^{13}C-enriched nuclei. If ^{13}C-enriched trimethylaluminum coordinates the highly unsaturated cationic $Cp^*Ti(^{13}CH_3)^+$ species, the $[Cp^*Ti(\mu\text{-}^{13}CH_3)_3Al(^{13}CH_3)]^+$ adduct (**4**) could be formed with the Ti(III) d^1 electron coupled with three equivalent ^{13}C-enriched methyls. The increase of the temperature promotes a fast ligand exchange, resulting in the loss of the hyperfine coupling of the signal. The formation of the adduct **4** in the polymerization condition could explain why catalytic systems containing very large amounts of TMA are poorly active in syndiospecific styrene polymerization.

Preliminary attempts to crystallize the adducts **3** and **4** adducts were unsuccessful. Only oily products were obtained from the respective chlorobenzene solutions, precluding any further characterization.

ESR quantitative analysis of the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ system showed that only 1% of the total titanium is reduced from Ti(IV) to Ti(III) species in the activation reaction[1e] but the addition of the monomer increases the Ti(III) content up to 10% of the total titanium in the polymerization conditions.

We evaluated the molar concentration of the active species in this system by kinetic methods and found that it roughly corresponds to the Ti(III) molar concentration determined by ESR spectroscopy.[4] On the basis of these results, one could suppose that the reaction of the monomer with the Ti(IV)−alkyl complexes promotes the reduction of Ti(IV) to Ti(III) species. However, the addition of TMA or PMe_3 to the catalytic system produces the same large increase of the Ti(III) signals observed after the addition of styrene monomers. The latter finding suggests that the molar concentration of Ti(III) species produced in the activation reaction could be larger than that initially measured by quantitative ESR analysis. Most of Ti(III) could be under the form of polynuclear, ESR-silent Ti(III) species. Ti(III)−Ti(III) short distances favored by alkyl bridges could produce ESR-inactive species because of active electron spin−electron spin interactions. The addition of the monomer or Lewis bases (L) could convert the polynuclear Ti(III) species into the monomeric cationic complexes $Cp^*Ti(III)R(L)^+$, which can actually be detected by ESR spectroscopy.

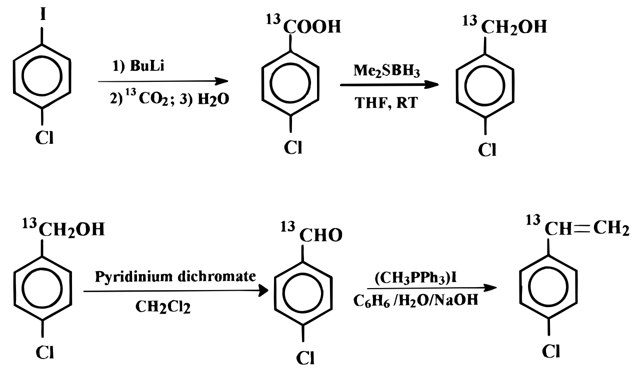
Experimental Section

General Procedures and Materials. All manipulations were performed under a nitrogen atmosphere using standard Schlenk type techniques or a MBraun drybox. Solvents were distilled, after refluxing (48 h), from the appropriate drying/deoxygenating agents and stored under nitrogen prior to use. Chlorobenzene was distilled from phosphorus pentoxide at reduced pressure. PMe_3 was used as received. $Al(^{13}CH_3)_3$,[12] $Cp^*Ti(^{13}CH_3)_3$,[13] $B(C_6F_5)_3$,[14] and $Ph_3CB(C_6F_5)_4$[15] were synthesized according to the procedures described in the literature. Styrene and *p*-chlorostyrene (Aldrich) were purified by distillation at reduced pressure from calcium hydride. α-^{13}C-enriched *p*-chlorostyrene was synthesized according to Scheme 3 including well-known organic reactions.

α-^{13}C-enriched *p*-chlorostyrene was obtained in 50% yields and was distilled over triisobutylaluminum before use.

$Al(i\text{-}Bu)_3$ (Aldrich) was checked for the purity by ^1H NMR before use. MAO was purchased from Witco as a 30% (w/w) toluene solution. In the ERS experiments we used solid MAO obtained by distillation of the solvent at 50 °C in high vacuum.

Scheme 3



Under this condition the "noncoordinated $AlMe_3$" co-distill with toluene, producing a white powder with low $AlMe_3$ content.

X-band electron spin resonance (ESR) spectra were recorded with a ER 200 D-SRC Bruker spectrometer operating a ν = 9.62 GHz using a HS Bruker rectangular cavity. The control of the operational frequency was obtained with a Hewlett-Packard ×5−32 B wavemeter, and the magnetic field was calibrated with a DPPH (diphenylpicrylhydrazyl) free radical as a suitable field marker. The control of the temperature was obtained with a Bruker ER 4111 VT device (±1 K). The g values are referred to DPPH ($g = 2.0036$) used as the external standard reference. The errors affecting the g, a, and ΔH values are $\pm 5 \times 10^{-3}$, $\pm 2 \times 10^{-1}$ G, and ±2 G, respectively.

ESR Samples. The samples were prepared according to the following general procedure. The proper amount of solid sample (titanium complex or activators) was weighed in a glass vial and sealed with a rubber septum in a drybox. Solvent was introduced into the vial by a syringe for dissolving the sample, and finally the solution of the organometallic precursor and the proper cocatalyst was mixed in a Schlenk tube in order to have a 0.01 M solution of the catalytic system. The solution was transferred into the ESR tube by a syringe and analyzed in the experimental condition described in the text.

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Supporting Information Available: Computer simulation of the ESR spectrum reported in Figure 1B (1 page) Ordering information is given on any current masthead page.

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(7) It is interesting to note that if the last styrene unit of the growing polymer chain is η^6-coordinated to the Ti(III) of the active species (see Scheme 1), the electronic count for the titanium in this complex is similar to that of the titanium in the Cp_2TiR^+ complexes promoting olefin polymerization.

(8) We previously reported the spectrum of this mixture in which additional spectral lines in the range $g = 1.980-1.990$ were detected. We attributed these signals to byproducts generated during the manipulation of these highly reactive species in the ESR tube. The monitoring of the same reaction at low temperature (254 K) permitted us to detect the doublet at $g = 1.973$ without any signal due to byproducts.

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