# Articles

## Oxidation State(s) of the Active Titanium Species during Polymerization of Styrene to Syndiotactic Polystyrene Catalyzed by $Cp^*TiMe_3/B(C_6F_5)_3$, $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$, and $Cp^*TiCl_{2,3}$/MAO

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ABSTRACT: A combined NMR/EPR investigation of the catalyst systems $Cp^*TiMe_3/B(C_6F_5)_3$, $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$, and $Cp^*TiCl_{2,3}$/MAO for the polymerization of styrene to syndiotactic polystyrene suggests that evidence for the involvement of EPR-active titanium(III) species as catalysts is ambiguous.

Since the initial report of its discovery in 1986,[1] syndiotactic polystyrene (s-PS) has been the subject of intense investigation because of useful properties which include a high melting point (270 °C), a high rate of crystallization, and a high modulus of elasticity.[2] This new material also exhibits a low specific gravity and dielectric constant, in addition to general resistance to water and organic solvents at ambient temperature.[2b] While relatively few compounds of transition metals other than titanium have been found to initiate the polymerization of styrene to s-PS,[2] it has been reported that titanium compounds of oxidation states I to IV, but especially III, can behave as initiators or initiator precursors.[2]

Indeed, there has appeared in recent years a number of reports specifically implicating compounds of titanium(III) as primary initiators, the evidence to a significant extent involving EPR studies of polymerization systems. For instance, EPR resonances attributed to $d^1$ titanium(III) species have been observed in a number of catalyst systems in which a titanium(IV) compound has been treated ("activated") with an alkyl aluminum compound, i.e., with a type of compound that might well be expected to reduce titanium(IV) to titanium(III).[3] Thus, quite strong EPR resonances have been reported for active catalyst systems based on the compounds $CpTiCl_3$, $CpTi(OR)_3$ (R = Me, Bu, Ph), and $Cp^*TiCl_3$, either in solution or supported on silica, after treatment with methylaluminoxane (MAO), the EPR-active compounds being attributed to a variety of types of species.[3] While none of these assignments have in fact been confirmed by isolation or further characterization of the putative catalytic species, the possible role of titanium(III) in s-PS formation has apparently also been demonstrated by the greater activity of $Cp^*Ti(OMe)_2$/MAO than of $Cp^*Ti(OMe)_3$/MAO[3d] and, in some cases, by correlations of catalyst activities with intensities of EPR signals.[3c]

Complementary to the above, Grassi et al. have reported EPR investigations of the chemistry involved during reactions of the catalyst precursors $Cp^*TiMe_3$ and $Cp^*Ti(CH_2Ph)_3$ with $B(C_6F_5)_3$ and $[Ph_3C][B(C_6F_5)_4]$.[4] These reactions are generally believed to result in alkyl carbanion abstraction and formation of the titanium(IV) complexes $[Cp^*TiR_2]^+$ (R = Me, $PhCH_2$),[2] which are excellent initiators or initiator precursors for Ziegler−Natta polymerization of ethylene, α-olefins, and styrene (to s-PS).[2] Interestingly, it was found that the titanium(IV) precursors were converted to significant extents (up to >75%) to EPR-active but MAO-free catalytic systems, results which were interpreted in terms of polymerization of styrene by titanium(III) rather than by titanium(IV).[4] The proportions of reduced species were generally somewhat lower than was the case with the MAO-activated systems discussed above, consistent with the fact that no obvious reducing agents were added although the proportions reduced tended to increase on the addition of styrene.

Largely on the basis of NMR and EPR studies of isotopically enriched species, the actual initiators of styrene polymerization to s-PS were suggested to be of the type $[Cp^*TiR]^+$ (R = Me, $PhCH_2$) although no such titanium(III) complexes have actually been characterized other than by in situ EPR studies. A kinetics investigation of s-PS formation induced by the compounds $Cp^*TiR_3$ (R = Me, $PhCH_2$) activated by MAO, $B(C_6F_5)_3$, and $[Ph_3C][B(C_6F_5)_4]$ suggested that the catalytic species were in all cases very similar and probably identical and that the concentrations of active species were similar to the concentrations of titanium(III) species derived from EPR data.[4c] Detailed EPR monitoring of the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ and $Cp^*TiMe_3/B(C_6F_5)_3$ styrene polymerization systems showed that a variety of titanium(III) species may form, depending on the extent of aging and the presence or absence of styrene. However, the major species in catalytically active solutions were believed to be of the type $[Cp^*TiR]^+$, amounting to 30% and 10% of the of the total titanium in the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ and $Cp^*TiMe_3/B(C_6F_5)_3$ systems, respectively. On the other hand, in many instances not all of the titanium(III) appeared to be catalytically active, as is the case with several of the

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MAO-based systems discussed above.[3]

In contrast to these results, Chien and Rausch et al. could detect no signals in EPR spectra of catalytically active solutions of either the $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$ or $Cp^*TiMe_3/B(C_6F_5)_3$ systems, although treatment of the same precursors with MAO did result in up to 28% reduction.[5a] More recently, Baird et al. have also reported exploratory EPR investigations of the $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$ and the $Cp^*TiMe_3/B(C_6F_5)_3$ systems, observing only very weak signals, different from those reported by Grassi et al. and representing <0.01% of the total titanium.[5b,c] Working with purified materials and under scrupulously anhydrous and anaerobic conditions, they also observed neither the trityl radical resonance nor the resonances attributed to impurity alkoxytitanium(III) species which had been previously reported.[4b] Following this, a very recent study by Chien and Rausch et al. of the activities of a series of substituted indenyl titanium−MAO catalyst systems has demonstrated that while titanium(III) species are generated, in fact it is the catalysts with the *lowest* proclivities to reduction which exhibit the *highest* activities for styrene polymerization to s-PS.[6] For these reasons, the role(s) of titanium(III) complexes in these catalytic processes would seem, despite the weight of much *circumstantial* evidence, as yet uncertain and ambiguous.

Curious about the discrepancies in the published literature concerning the possible role(s) of titanium(III) and cognizant of the facts that titanium compounds in three different oxidation states and containing a wide variety of ligands can induce the polymerization process, we have carried out a detailed investigation of the polymerization of styrene to s-PS by four different Cp* catalyst systems, including the very active[7] $Cp^*TiMe_3/B(C_6F_5)_3$ system. This study has involved careful spectroscopic ($^1H$ and $^{13}C\{^1H\}$ NMR, EPR) characterizations of the species in solution when $Cp^*TiMe_3$ and $B(C_6F_5)_3$ are combined in the presence and absence of styrene. We also describe EPR experiments involving the $Cp^*TiMe_3/[Ph_3C][B(C_6F_5)_4]$ system and comparisons (EPR, formation of s-PS) of the catalysts formed by treating $Cp^*TiCl_2$ and $Cp^*TiCl_3$ with MAO. As a result of these investigations, it is clear that relatively minor alterations of the catalyst composition can have major impact on catalyst activity, and the conclusion must be reached that case for involvement of titanium(III) in catalyzed s-PS formation remains undecided.

## Experimental Section

All experiments were carried out utilizing standard Schlenk line techniques or a Vacuum Atmospheres glovebox and dry, prepurified nitrogen and dried, thoroughly deoxygenated solvents. $^1H$ and $^{13}C\{^1H\}$ NMR spectra were normally run using a Bruker AM 400 spectrometer operating at 400.14 and 100.6 MHz, respectively, and are referenced with respect to internal TMS using residual proton or carbon resonances of the solvents. $^{13}C\{^1H\}$ NMR spectra of polymer samples were run on a Bruker CXP 200 NMR spectrometer at 135 °C in *o*-dichlorobenzene. GPC data were obtained on a Waters model 150-C in 1,2,4-trichlorobenzene solvent running at 145 °C and were calibrated using polystyrene standards. EPR experiments involving equimolar amounts of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ (0.01−0.06 mmol of each in 10 mL solution) were run at 22 °C on a Bruker B-R70 X-band EPR spectrometer at ∼9.72 GHz with the field centered at ∼3400 G; the magnetic field was calibrated with DPPH ($g = 2.0037$), and standard solutions of TEMPO ($1 \times 10^{-3}$−$1 \times 10^{-5}$ M) were used where appropriate for quantitative estimates[8] of the concentrations of titanium(III) species present. UV−visible spectra were run on a Hewlett-Packard model 8425A spectrometer on solutions in quartz cuvettes specially designed to accommodate air-sensitive samples. The compounds $Cp^*TiCl_3$,[9a] $Cp^*TiMe_3$,[9b] $Cp^*Ti(^{13}CH_3)_3$,[10a] $B(C_6F_5)_3$,[9c,d] and $[Ph_3C][B(C_6F_5)_4]$[9e] were prepared by literature methods, while MAO was purchased from Aldrich. The compounds $Cp^*TiCl_2$ and $Cp^*TiCl_2$(THF) were prepared via zinc reduction in THF,[11a] but the $ZnCl_2$ byproduct did not appear to be reliably and consistently removed and the compounds were therefore also prepared via reduction with manganese metal and characterized spectroscopically. The $MnCl_2$ byproduct is insoluble in THF and could readily be removed by filtration.

Polymerizations of styrene by various catalyst systems were generally carried out by treating solutions containing 2 mL of styrene and 0.06 mmol of catalyst ($Cp^*TiMe_3$, $Cp^*TiCl_2$, $Cp^*TiCl_3$) in 5 mL of toluene with 0.06 mmol of $B(C_6F_5)_3$ or $[Ph_3C][B(C_6F_5)_4]$ or either 20 or 40 mL of a 10 wt % solution of MAO in toluene (500:1, 1000:1 molar ratios), as appropriate. The reactions were terminated by the addition of methanol and the polymeric products were collected, washed with methanol, dried under vacuum at 80 °C, and extracted with boiling 2-butanone to remove any atactic PS.

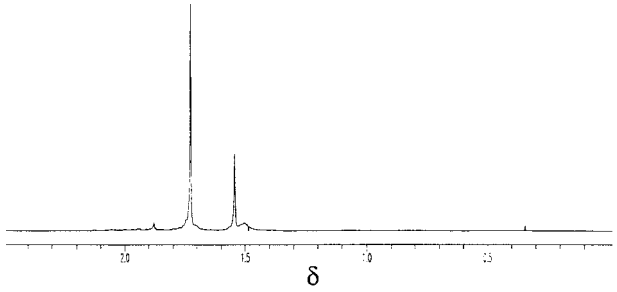


**Figure 1.** $^1H$ NMR spectra of the reaction of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ in $C_6D_5Cl$ at −30 °C.

## Results and Discussion

**NMR and EPR Monitoring of the Reaction of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ in Chlorobenzene-$d_5$.** The reaction of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ in $CD_2Cl_2$ and chlorobenzene-$d_5$ has been previously been studied by $^1H$ and $^{13}C\{^1H\}$ NMR spectroscopy, the initially formed product being the bridged methyl borate species $Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3$ (**A**, eq 1) which dissociates to the ionic species $[Cp^*TiMe_2]^+$ and $[BMe(C_6F_5)_3]^-$.[10]

$$Cp^*TiMe_3 + B(C_6F_5)_3 \rightarrow Cp^*TiMe_2(\mu\text{-Me})B(C_6F_5)_3 \quad (1)$$

Compound **A** was previously shown to decompose above about 0 °C, and although the nature of the decomposition processes was not ascertained, a number of new NMR resonances were observed.[10] Consistent with this earlier work, we find that the $^1H$ NMR spectrum of a 1:1 molar mixture of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ in chlorobenzene-$d_5$ at −30 °C exhibits resonances at $\delta$ 1.58 (Cp*), 1.42 (Ti−Me), and 1.37 (br, B−Me) (Figure 1), attributable to **A**. In a series of experiments, samples were prepared at −30 °C and warmed to 25 °C for various periods of time; in general, the original resonances weakened and were replaced by strong resonances in the region $\delta$ 1.7−2.2, probably Cp* methyl resonances, and several relatively weak resonances in the range $\delta$ 1.0−2.5, which may be Cp* or Ti−Me resonances. The spectra also exhibited a methane resonance at $\delta$ ∼0.3 in addition to a broadened resonance at ∼$\delta$ 1.7 which is not indicative of free $[BMe(C_6F_5)_3]^-$ but which may be attributed to a Me−B group on the

basis of its intensity and line width.[10] On further heating of one sample to 55 °C, the relative intensities of the new resonances were found to vary with time, implying the formation of a variety of intermediates/products. Ultimately the overall integrated intensity of the resonances in the methyl region had decreased by about half, the methane resonance contributing less than ∼20% of the total although many weak, sharp resonances remained after several hours at 55 °C. At no time during the experiment was there observed the total loss of intensity of narrow methyl resonances which might indicate complete conversion of diamagnetic titanium compounds to paramagnetic ($S = {}^1/_2$) titanium(III) species. As is shown below, however, the $^1$H NMR spectrum of Cp*$TiCl_2$ exhibits a Cp* methyl resonance at $\delta$ 2.30, and thus other dissolved Cp*Ti(III) complexes would also be expected to contribute to the overall integrated intensities in the methyl region. Addition of styrene *at the conclusion* of the NMR experiment resulted in the formation of no s-PS.

Several NMR experiments were then carried out in chlorobenzene-$d_5$ under various conditions and utilizing a 1:1 ratio of Cp*Ti($^{13}CH_3$)$_3$[10a] ($\delta$ Ti-$^{13}C$H$_3$ 58.8 (s), $\delta$ $C_5$Me$_5$ 119.8 (w), $\delta$ C$_5$*Me*$_5$ 9.8 (w) at −50 °C) and B($C_6F_5$)$_3$. All of the reactions were initiated at −25 °C and were monitored by $^1$H and$^{13}$C{$^1$H} NMR spectroscopy. In general, the $^1$H resonances of the Cp*Ti($^{13}CH_3$)$_3$ were replaced immediately by the $^1$H resonances of Cp*Ti($^{13}CH_3$)$_2$($\mu$-$^{13}CH_3$)B($C_6F_5$)$_3$ at $\delta$ 1.58 (Cp* C*H*$_3$) and 1.39 (Ti−$^{13}$C*H*$_3$, $J_{CH}$ 120 Hz), while in the $^{13}$C{$^1$H} NMR spectrum the intense Ti−$^{13}C$H$_3$ resonance at $\delta$ 58.8 ($\delta$ 61.3 in $CD_2Cl_2$[10a]) was replaced by the corresponding Ti−$^{13}C$H$_3$ and $\mu$-$^{13}C$H$_3$ resonances of Cp*Ti($^{13}CH_3$)$_2$($\mu$-$^{13}CH_3$)B($C_6F_5$)$_3$ at $\delta$ 81.1 and $\delta$ 45.6 (br), respectively ($\delta$ 80.1, 44.3 in $CD_2Cl_2$ at −50 °C[10a]). In an experiment designed to detect *all* species containing $^{13}$C-enriched products formed, the solution was warmed to 27 °C and held at that temperature for ∼18 h while $^{13}$C{$^1$H} NMR spectral data were acquired (>15 000 transients). The resonances at $\delta$ 80.7 and $\delta$ 44.9 were replaced by resonances at $\delta$ 147.9, 110.6, 69.0, 16.8, 10.6, and −4.0 (methane), but no other resonances were observed in the range $\delta$ −282 to 2202. In view of the time involved in accumulating the data, the signal:noise ratio was quite high, and we can anticipate that we have indeed observed all compounds, including transient species, formed from the thermal decomposition of the Cp*Ti($^{13}CH_3$)$_2$($\mu$-$^{13}CH_3$)B($C_6F_5$)$_3$ during the time of the experiment. Interestingly, although the formation of some insoluble material was apparent during the experiment, the sum of the total intensities of the new species was greater than the sum of the intensities of the original resonances at $\delta$ 81.1 and $\delta$ 45.6. Thus, some of the observed resonances are indeed reasonably attributed to transients.

In a separate experiment designed to obtain "snapshots" of the reaction at relatively short time intervals, a solution of Cp*Ti($^{13}CH_3$)$_2$($\mu$-$^{13}CH_3$)B($C_6F_5$)$_3$, freshly prepared at −25 °C, was warmed quickly to 25 °C. A $^1$H NMR spectrum was run, and then a $^{13}$C{$^1$H} NMR spectrum over ∼4 min (53 transients). Both spectra indicated that little change had occurred, although weak methane resonances in the $^1$H ($\delta$ 0.16, $J_{CH}$ 126 Hz) and $^{13}$C{$^1$H} ($\delta$ −4.0) spectra had appeared. Over approximately the next hour, a *J*-modulated spin echo$^{13}$C{$^1$H} spectrum was accumulated (512 transients, ∼40 min), and then a heteronuclear multiple quantum correlation (HMQC) experiment was carried out (∼30 min), both at 25 °C. As the methane resonance at $\delta$ −4.0 was found to have increased somewhat in intensity in the $^{13}$C{$^1$H} spectrum, thermal decomposition was clearly occurring during the experiments although the resonances of the starting Cp*Ti($^{13}CH_3$)$_2$($\mu$-$^{13}CH_3$)B($C_6F_5$)$_3$ were still dominant. New, weak $^{13}$C *methyl* resonances appeared in the *J*-modulated spin echo spectrum at $\delta$ 110.8, 77.2, 71.5 and 12.3, and these were also present in the HMQC experiment in addition to resonances at $\delta$ 68, 58, 56, 55, 31.5, and 16.5. In Table 1, we present the $^{13}$C−$^1$H chemical shift correlations and relative intensities of the resonances observed in the HMQC experiment. Although the broad $\mu$-$^{13}C$H$_3$ resonance of Cp*Ti($^{13}CH_3$)$_2$($\mu$-$^{13}CH_3$)B($C_6F_5$)$_3$ at $\delta$ 45.6 and a similarly broad $^{13}CH_3$ resonance at $\delta$ 11.5, possibly attributable to a small amount of [B($^{13}CH_3$)($C_6F_5$)$_3$]$^-$ displaced by the solvent, were observed in the $^{13}$C{$^1$H} spectrum run prior to the HMQC experiment, neither was apparent in the HMQC experiment. This is possibly a result of quadrupolar relaxation by the boron nuclei, since the anticipated shortening of the carbon $T_2$ values would render the HMQC experiment unrealizable for these carbons given the experimental parameters utilized. We also did not observe a cross-peak for the Cp* methyl resonance, presumably because of the relatively low concentration of $^{13}$C (natural abundance) at this position.

**Table 1. $^{13}$C and $^1$H NMR Spectral Correlations (HMQC)**

| $^{13}$C chemical shifts ($\delta$) | $^1$H chemical shifts ($\delta$) | $^{13}$C chemical shifts ($\delta$) | $^1$H chemical shifts ($\delta$) |
|---|---|---|---|
| 110.8 (s) | 2.40 (s) | 58 (vw) | 0.56 (vw) |
| 81.3 (vs) | 1.42 (vs) | 56 (vw) | 0.88 (vw) |
| 80.5 (sh, m) | 1.15 (s) | 55 (vw) | 0.81 (vw) |
| 77.0 (w) | 1.22 (w), 0.97 (w) | 31.5 (vw) | 0.9 (w) |
| 71 (vw) | ∼1.2 (obscured) | 16.5 (s) | 1.55 (m) |
| 68 (w) | 1.32 (w) | −4.0 (vw) | 0.14 (w) |

The $^1$H and $^{13}$C{$^1$H} (*J*-modulated spin echo, 512 transients) NMR spectra of the same sample were run again after it had been maintained at 25 °C for a further 14 h. The only observable $^{13}$C resonance arising now from positions containing $^{13}$C-enrichment was that previously observed at $\delta$ 110.8. The corresponding $^1$H resonance at $\delta$ 2.4 ($J_{CH}$ 126 Hz) was also observed, as were the $^1$H and $^{13}$C resonances of methane. The intensity of the resonance at $\delta$ 110.8 was significantly lower than that of the original starting material, in part at least because of the formation of both methane and a small amount of insoluble material. These types of NMR experiments could not be carried out in the presence of styrene because of the proclivity of s-PS to precipitate from solution.

The EPR spectrum of a freshly prepared solution containing equimolar amounts of Cp*$TiMe_3$ and B($C_6F_5$)$_3$ ([Ti] = 0.01 M) in chlorobenzene at room temperature exhibited a weak doublet centered at $g = 1.994$ with a hyperfine coupling constant $a = 8.4$ G (Figure 2a). The coupling constant and observed $g$ value lead to the reasonable assignment of this doublet to a titanium(III) hydride species similar to those reported previously for homogeneous Cp$TiCl_3$/MAO ($g = 1.989$, $a = 7.4$ G; $g = 1.995$, $a = 4.5$ G)[3a] and CpTi(OBu)$_3$/MAO ($g = 1.989$, $a = 7$ G)[3b] systems and a supported Cp$TiCl_3$/MAO ($g = 1.989$, $a \sim 7.5$ G)[3f] system. On the basis of comparisons with TEMPO standards, the concentration of EPR observable species present in the sample was found to be ≪0.01% of the initial titanium concentration in the sample. These results, which are very reproducible

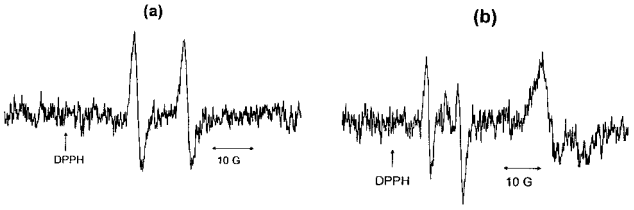


**Figure 2.** EPR spectra of the room-temperature reaction of $Cp^*TiMe_3$ with $B(C_6F_5)_3$ (a) in chlorobenzene and (b) the same with added styrene.

(three experiments), differ markedly with those reported for the same system elsewhere,[4b] i.e., a sharp singlet at $g = 1.977$ with intensity accounting for almost 1% of the initial titanium in the sample.

The addition of 0.1 mL of styrene to the EPR tube produced a spectrum exhibiting a doublet at $g = 1.994$ (Figure 2b); this eventually disappeared over ~5 min and was replaced by a broad singlet at $g = 1.978$. During this time, the initially bright orange reaction mixture turned very dark with some heating and within 2−3 min became a solid mass of s-PS. Again, contrary to the results previously reported,[4b] the concentration of EPR-active titanium(III) was not observed to increase upon addition of styrene and still remained ≪0.01% of the initial titanium present in the sample. The collapse of the initially observed doublet would be consistent with monomer insertion into a Ti−H bond, which would eliminate the apparent coupling to hydrogen.

Our inability to reproduce the EPR experiments reported in the literature for the $Cp^*TiMe_3/B(C_6F_5)_3$ system[4] led us to wonder whether small differences in sample preparation had led to the differing results. Since irradiation of many monocyclopentadienyl complexes and metal alkyl compounds by both UV and visible light has been shown to produce EPR observable paramagnetic species,[14a,b] it was thought that inadvertent exposure to bright sunlight[14c] might be the cause for the high titanium(III) concentrations reported by Grassi et al.[4] To investigate this possibility, solutions containing equimolar amounts of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ were irradiated with sunlight in an attempt to reproduce the literature results. Two experiments were carried out, with one solution being irradiated continuously for 1 h and another sample being irradiated five times for 1 min at a time. Upon EPR analysis of the irradiated samples, it was determined that these photolysis experiments were unsuccessful in increasing spectral intensity or in producing any of the species previously reported.[4]

The discrepancies between the extremely low concentration of titanium(III) species observed here and the much higher proportions reported elsewhere[4] led us to also consider the possibility that titanium(III) species were formed initially but had then taken part in secondary processes that would render them EPR-inactive. The $[CpTi(III)]^{2+}$ ion can coordinate up to five electron pair donor atoms,[15a] and dimerization of titanium(III) compounds via bridging ligands is known to result in many cases in spin-pairing of the $d^1$ ions to give EPR silent and even diamagnetic products.[11c,15b] Alternatively, spin exchange between titanium(III) centers in solution could result in severe EPR line broadening, and it thus seemed possible that either type of behavior might somehow account for the differences in our results and those reported elsewhere.[4] Certainly the EPR resonance of $Cp^*TiCl_2$ in THF solution is significantly broadened when at higher concentrations (see below).

To assess these possibilities, excess amounts of the potential ligands pyridine and $PPh_3$ were introduced into solutions containing equimolar amounts of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ in chlorobenzene at 25 °C. If the reaction solutions contained ligand bridged dimers that can dissociate and coordinate styrene, then coordination of better ligands should also occur and should produce monomeric titanium(III) species which should be EPR active and might even exhibit hyperfine couplings to $^{31}P$ and $^{14}N$. In the same way, coordination of bulky ligands would hinder intermolecular spin exchange interactions between titanium(III) complexes in solution, and rates of electron exchange would also be altered significantly. However, while the above-mentioned doublet disappeared on the addition of $PPh_3$, the spectrum exhibited no new EPR resonance. Furthermore, the addition of pyridine to a second sample resulted in neither significant changes in the spectral features nor a measurable increase in spectral intensity. We note a previous study in which $PMe_3$ was added to a solution containing equimolar amounts of $Cp^*TiMe_3$ and $B(C_6F_5)_3$ in chlorobenzene at −20 °C.[4d] A new EPR resonance was observed, superimposed on the resonance previously noted, but no mention was made of change in intensity.

While the differences in $g$ values discussed here are generally in the range of experimental errors (perhaps ±0.003), our spectra are all carefully calibrated with respect to internal DPPH and are quite reproducible. It is very important to note, moreover, that the multiplicities that we observe are different from those reported in the literature and that we *never* observe the high concentrations of EPR active species which are reported elsewhere. These results are important because they make it clear that s-PS can be formed by the $Cp^*TiMe_3/B(C_6F_5)_3$ system in the absence of the EPR active titanium(III) species reported elsewhere[4b] and, indeed, in the absence of significant amounts of any detectable titanium(III) species. For this reason, the necessity of titanium(III) for s-PS formation is clearly called into question.

**EPR Monitoring of the Reaction of $Cp^*TiMe_3$ and $[Ph_3C][B(C_6F_5)_4]$ in Chlorobenzene-$d_5$.** The reaction of $Cp^*TiMe_3$ and $[Ph_3C][B(C_6F_5)_4]$ in $CD_2Cl_2$ has been shown[5c] to proceed as in eq 2, producing the dititanium compound $[(Cp^*TiMe_2)_2(\mu\text{-Me})][B(C_6F_5)_4]$ (**B**) rather than the compound $[Cp^*TiMe_2][B(C_6F_5)_4]$ earlier presumed by Grassi et al.[4]

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

The dititanium compound is thermally labile at ambient temperatures, however, decomposing to give hitherto unidentified products exhibiting a number of resonances in the $^1H$ NMR spectrum.[5c] An EPR spectrum of a solution containing equimolar amounts of $Cp^*TiMe_3$ and $[Ph_3C][B(C_6F_5)_4]$ in chlorobenzene ([Ti] = 0.01 M) at 23 °C is shown in Figure 3a. Again a doublet, similar to that in Figure 2a, was observed ($g = 1.992$, $a = 8.2$ G) and is tentatively attributed to a titanium(III) hydride. The titanium(III) concentration was again apparently negligible, however, with <0.01% of the initial titanium present as EPR-active, paramagnetic species.


**Figure 3.** EPR spectra (a) of the room-temperature reaction of $Cp^*TiMe_3$ with $[Ph_3C]^+[B(C_6F_5)_4]^-$ in chlorobenzene and (b) the same with added styrene.

Addition of styrene resulted in very little change to the spectrum except for some broadening of the peaks (Figure 3b). No darkening or solidification of the mixture was noted, although a significant amount of heat was generated. Furthermore, much of the polymer recovered from the EPR sample was atactic polystyrene (a-PS), lower yields of s-PS being obtained than with the $Cp^*TiMe_3/B(C_6F_5)_3$ system. Formation of the a-PS may well have been initiated by the half molar equivalent of free trityl cation, which remains in solution as in eq 1 when $Cp^*TiMe_3$ and $[Ph_3C][B(C_6F_5)_4]$ are combined in a 1:1 ratio and which in the presence of traces of moisture is an effective carbocationic initiator for the polymerization of styrene.[12]

**EPR and Polymerization Study of the Reactions of Styrene with $Cp^*TiCl_{2,3}$/MAO.** Most of the research reported on monocyclopentadienyltitanium s-PS catalytic systems has been done utilizing titanium(IV) precursors even though much of the evidence has pointed to a reduced form of the initial compound acting as the active catalytic species. Direct, explicit comparisons of analogous titanium(III) and -(IV) catalysts are rare, apparently being limited to a comparison of the polymerization abilities of the compounds $Cp^*Ti(OMe)_2$ and $Cp^*Ti(OMe)_3$ activated with MAO.[3d] If titanium(III) species are indeed the primary catalytic species, one might anticipate that a catalytic system derived from a titanium(III) complex would be superior in some way (shorter induction periods, higher activities, and/or higher molecular weights) to one derived from a titanium(IV) analogue. This need not necessarily be so, of course, as similar precursors in both oxidation states may well form low, somewhat variable but comparable amounts of the same active species. As it happens, the $Cp^*Ti(OMe)_2$/MAO system was found to exhibit somewhat higher activities at lower MAO:Ti ratios than did the system based on $Cp^*Ti(OMe)_3$/MAO, but the differences were not large, the active species were not identified, and no mention was made of the concentrations of the various possible titanium species in solution.[3d]

To shed light on this issue, we have investigated the presumably similar catalyst systems formed on treating the compounds $Cp^*TiCl_2$[11a] and $Cp^*TiCl_3$ with MAO under identical conditions such that comparisons could be made of the EPR-active species, the catalytic activities, and the nature of the products. The compound $Cp^*TiCl_2$ is easily obtained as the blue-green THF adduct by reduction of $Cp^*TiCl_3$ with zinc metal, but we were concerned about apparent contamination by zinc chloride. The latter coprecipitated with the $Cp^*TiCl_2$-(THF) during workup, and since it might well react with MAO to form methylzinc compounds which might well affect Ziegler polymerization processes, we investigated alternative reducing agents. We eventually found that we could readily reduce $Cp^*TiCl_3$ with manganese metal, the byproduct now being $MnCl_2$ which is insoluble in THF and could be separated from the reaction

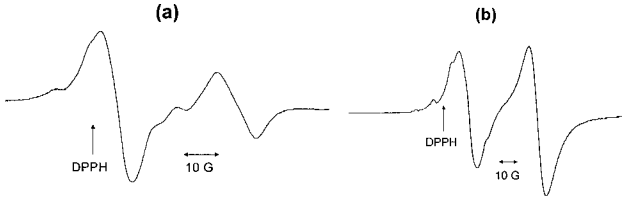


**Figure 4.** EPR spectra of (a) $Cp^*TiCl_2$/MAO (Al/Ti = 500:1) in toluene and (b) the same with added styrene.

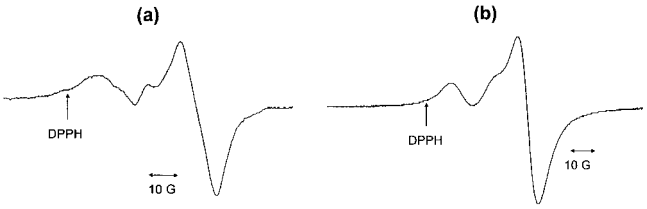


**Figure 5.** EPR spectra of (a) $Cp^*TiCl_3$/MAO (Al/Ti = 500:1) in toluene and (b) the same with added styrene.

solution by filtration. UV−vis spectra of the $Cp^*TiCl_2$-(THF) formed via the two routes showed that they were identical (absorptions at 238, 256, and 422 nm).

The THF may be reversibly removed from solid $Cp^*TiCl_2$(THF) to give the maroon solid $Cp^*TiCl_2$, the EPR spectrum of which exhibited a very broad resonance with $g = 1.971$. By way of comparison, crystalline $CpTiCl_2$ has been reported to be polymeric but magnetically dilute, with $g$ values of ∼1.976 depending on the medium.[11b−f] The compound $Cp^*TiCl_2$ readily redissolves in THF to give the blue-green solution of the THF adduct ($g = 1.975$, broad)[11g] and also dissolves somewhat in toluene to give a deep red-maroon solution ($g = 1.970$, broad). The $^1$H NMR spectra of $Cp^*TiCl_2$ in toluene-$d_8$ and chlorobenzene-$d_5$ exhibit broad Cp* methyl resonances at $\delta$ 2.10 and 2.30, respectively (widths at half-height 0.1−0.2 ppm).

Solutions of $Cp^*TiCl_2$ in toluene turn deep purple upon addition of toluene solutions of MAO and remain EPR-active. The EPR spectrum of a solution of $Cp^*TiCl_2$ activated with MAO ([Ti] = 0.003 M, 500:1 molar ratio) exhibited two major broad resonances at $g = 1.975$ and $g = 1.997$ (Figure 4a), while the spectrum of a similar solution of $Cp^*TiCl_3$/MAO exhibited similarly broad resonances at $g = 1.977$ and $g = 1.991$ (Figure 5a). No hyperfine splitting was observed, nor did we observe the variety of resonances observed over many hours by Chien et al. for the $Cp^*TiCl_3$/MAO system.[3a] The concentrations of EPR active titanium(III) species were found to be ∼5% for $Cp^*TiCl_2$ and ∼0.5% for $Cp^*TiCl_3$, apparently comparable with those observed by Chien et al. for the $Cp^*TiCl_3$/MAO system[3a] but much higher than those observed in this study (see above) for the $Cp^*TiMe_3/B(C_6F_5)_3$ system. It is not clear what the EPR-inactive species might be; if they are odd electron species, their resonances are presumably broadened by the effects of spin exchange processes.[11g]

The addition of styrene (0.1 mL) to each sample produced little change in the EPR spectrum of either (Figures 4b and 5b), although the intensity of the peak at $g = 1.974$ in the spectrum of $Cp^*TiCl_2$/MAO did increase noticeably. The downfield peaks in both spectra were essentially unchanged by the addition of styrene and most likely represent catalytically inactive species. However, the concentration of EPR observable species increased dramatically, up to almost 30% in the case of $Cp^*TiCl_2$ and over 20% in the case of $Cp^*TiCl_3$ for both

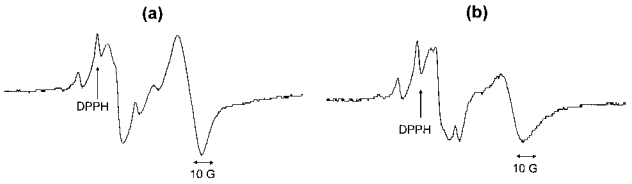


**Figure 6.** EPR spectra of (a) $Cp^*TiCl_2$/MAO (Al/Ti = 1000:1) in toluene and (b) the same with added styrene.

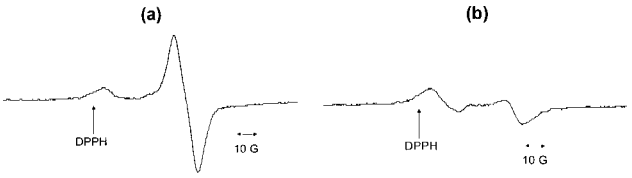


**Figure 7.** EPR spectra of (a) $Cp^*TiCl_3$/MAO (Al/Ti = 1000:1) in toluene and (b) the same with added styrene.

**Table 2. Styrene Polymerization Results for $Cp^*TiCl_{2-3}$ with MAO:Ti Ratios 500:1 and 1000:1**

| system | MAO/Ti ratio | [Ti] ($10^3$ M) | wt % conv | $M_w$ ($M_w/M_n$) |
|---|---|---|---|---|
| $Cp^*TiCl_2$/MAO | 500:1 | 3 | 5.5 | $47.0 \times 10^3$ (1.8) |
| $Cp^*TiCl_2$/MAO | 1000:1 | 1.5 | 38.0 | $74.6 \times 10^3$ (2.1) |
| $Cp^*TiCl_3$/MAO | 500:1 | 3 | 3.3 | $36.1 \times 10^3$ (1.5) |
| $Cp^*TiCl_3$/MAO | 1000:1 | 1.5 | 5.1 | $33.0 \times 10^3$ (1.6) |

systems. After the EPR spectra were recorded, addition of the 1 mL samples to an excess of acidified methanol yielded very small amounts of s-PS.

The EPR spectrum of $Cp^*TiCl_2$ activated with MAO at an Al/Ti ratio of 1000:1 ([Ti] = 0.0015 M) exhibited two major peaks at $g = 1.975$ and $g = 1.997$, as mentioned above, but also several weaker peaks and a great deal more fine structure (Figure 6a). The EPR spectrum of an identically prepared sample of $Cp^*TiCl_3$ and MAO was virtually identical to the spectrum produced by the same compound at an Al/Ti ratio of 500:1; one weak, broad peak at $g = 1.995$ and a stronger peak at $g = 1.975$ were the only resonances present although the shoulder at $g = 1.986$ was not visible (Figure 7a). Titanium(III) concentrations were very similar under these conditions in both samples, with ~2% of the initial titanium in the $Cp^*TiCl_3$ sample present as observable titanium(III) species and ~3% of the initial titanium in $Cp^*TiCl_2$ present as observable paramagnetic species. The addition of styrene (0.1 mL) to the solutions resulted in decreases in the intensity of the upfield resonance in both cases, indeed almost completely in the spectrum of $Cp^*TiCl_3$/MAO, with the downfield resonance remaining essentially unchanged (Figures 6b and 7b). The titanium(III) concentrations decreased accordingly, by approximately half in each case. Both EPR samples, upon addition to an excess of acidified methanol, yielded very small amounts of s-PS. The polymer yield obtained when the Al/Ti ratio was increased to 1000:1 did not change significantly for the $Cp^*TiCl_3$ system, but the yield obtained with $Cp^*TiCl_2$ increased dramatically at this Al/Ti ratio, the reasons for which are not yet clear.

The results of styrene polymerizations utilizing $Cp^*TiCl_2$ and $Cp^*TiCl_3$ activated by MAO are shown in Table 2. The polymeric materials were in all cases highly syndiotactic, as judged from the $^{13}C\{^1H\}$ spectra (*o*-dichlorobenzene at 135 °C), which exhibit sharp singlets at $\delta$ 41.2, 44.4, 125.5, 127.8, and 145.4 (Figure 8).[13] However polymer yields are surprisingly low for

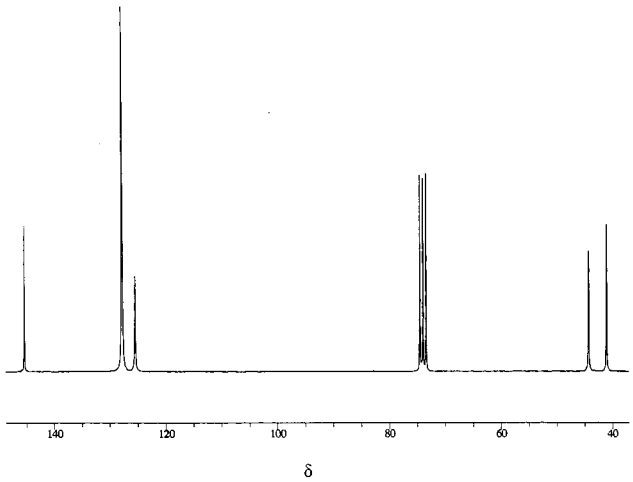


**Figure 8.** A typical $^{13}C\{^1H\}$ NMR spectrum of s-PS.

both systems at a MAO:Ti ratio of 500:1 and are much lower than has been previously reported for $Cp^*TiCl_3$/MAO.[13] As with the $Cp^*Ti(OMe)_2$/MAO and $Cp^*Ti(OMe)_3$/MAO systems,[3d] only marginal improvement is observed with the titanium(III) precursor on increasing the MAO:Ti ratio (to 1000:1), and all yields are strikingly lower than has been observed with the $Cp^*TiMe_3/B(C_6F_5)_3$ system.[7] However, as with the $Cp^*Ti(OMe)_{2,3}$/MAO systems,[3d] the differences in activities between the titanium(III) and -(IV) systems at two different MAO:Ti ratios are not substantial. Molecular weight data are also listed in Table 2, but here we have no literature data with which to make comparisons. No molecular weight data were given in the only other work that has dealt with the $Cp^*TiCl_3$/MAO system,[13] but data are given therein for the $CpTiCl_3$/MAO system and similar molecular weights and molecular weight distributions were obtained. Although the activity of the $Cp^*TiCl_2$/MAO (MAO:Ti = 1000:1) is higher than that of the corresponding titanium(IV) catalyst, the very close similarities in molecular weight distributions (Table 2) and degrees of syndiotacticity for the four batches of s-PS described in Table 2 suggest that very similar catalytic species are active in all four cases although the EPR results show clearly that the addition of MAO to $Cp^*TiCl_2$ and $Cp^*TiCl_3$ does *not* produce *identical* distributions of titanium(III) products. Thus, MAO-induced styrene polymerizations appear to be particularly complex.

Moreover, as outlined above, our results are difficult to reconcile completely with apparently similar systems reported elsewhere, and it seems likely that different samples of MAO from different sources may exhibit different properties. A report that appeared as this manuscript was being written shows also that the nature of the EPR-active titanium(III) species in the $CpTiCl_3$/MAO system varies with MAO:Ti ratio, temperature, and extent of aging,[16a] parameters which have apparently not been exhaustively investigated for the Cp*Ti systems. A subsequent study attempted a correlation of the titanium(III) species detected with activities for s-PS formation, finding inter alia that the system is very variable at temperatures much above ambient.[16b] These results are consistent with our findings that the EPR spectra varied little with time at room temperature; we would presumably observe a much richer chemistry at higher temperatures but have not explored these avenues in this investigation, the purpose of which

was to study the various Cp*Ti(IV) catalyst systems at room temperature.

## Summary and Conclusions

We have compared and contrasted four different Cp*Ti complexes which catalyze the polymerization of styrene to syndiotactic polystyrene, finding that they exhibit quite variable physical and chemical behavior. Indeed, while it might be anticipated that the $Cp^*TiMe_3/B(C_6F_5)_3$ and $Cp^*TiCl_3$/MAO catalyst systems, for instance, would show similar polymerization capabilities,[2] such is definitely not the case, and subtle ligand changes to these Cp*Ti-based catalytic systems can have quite major effects on the ultimate result. Addressing the issue of the role(s) of titanium(III) species in the polymerization processes, it is clear that titanium(IV) catalysts or catalyst precursors may be reduced to at least the III oxidation state and that in many cases more than one such complex is formed. In addition, the reduced systems are often quite labile with respect to processes involving ligand exchange and/or varying degrees of electron spin coupling between titanium(III) centers.

To date, most of the evidence taken to indicate the role(s) of titanium(III) complexes in the polymerization process has involved EPR spectroscopy, a technique that is generally difficult to interpret in terms of precise molecular structures but that is sufficiently sensitive[8] that traces of paramagnetic compounds far below concentrations likely to affect a chemical process may be detected. In this paper we report complementary EPR, $^1$H NMR, and $^{13}C\{^1H\}$ NMR spectroscopic studies, carried out to provide both comparisons of very similar styrene polymerization catalysts and information on the nature of the various species present in solution. However, there is a natural exclusion principle in effect here since the long electronic $T_1$ values that are necessary for narrow EPR resonances to be observed are expected to result in extremely broadened NMR resonances, especially of ligand atoms bonded directly to the metal ion.[17] In contrast, short electronic $T_1$ values, which may arise for example from intermolecular electron spin-exchange processes, have the opposite effect and result in observable NMR spectra of paramagnetic compounds but often greatly broadened EPR resonances.[17] It follows that all of the reasonably well-resolved titanium(III) EPR resonances observed here and elsewhere[4−6] must be assigned to dilute spin, fully paramagnetic ($S = {}^1/_2$) titanium(III) complexes which should not exhibit well-resolved NMR spectra. Interestingly, they must also therefore differ substantially from $Cp^*TiCl_2$, for which we have observed a not severely broadened Cp* resonance in solution $^1$H NMR spectra. The latter observation implies significant shortening of the electronic spin−lattice relaxation time, possibly through intermolecular electronic exchange.[17]

During our detailed study of the thermal "decomposition" of the $^{13}$C-enriched $Cp^*TiMe_3/B(C_6F_5)_3$ system, we observed well-resolved but rather complex $^1$H and $^{13}C\{^1H\}$ NMR spectra which exhibited total intensities comparable to those of all or most of the starting titanium complex during much of the experiment. The resonances must be attributed to either diamagnetic species or to titanium(III) complexes undergoing the type of rapid electronic exchange described above, a process which could induce sufficient EPR line broadening that detection of otherwise EPR-active titanium(III) species would be difficult. However, one might anticipate weakly electronically coupled titanium(III) systems to be readily cleaved on addition of the triphenylphosphine and pyridine ligands. Since this does not happen, it seems even more unlikely that styrene could coordinate and that the solutions contain nascent Ziegler−Natta catalysts for styrene polymerization.

The observation of $^{13}CH_3$ NMR resonances of species evidently containing all of the original $Ti-^{13}CH_3$ carbons is fully consistent with the dearth of EPR resonances, and while none (except for the methane resonance) of the $^{13}CH_3$ NMR resonances observed during and at the conclusion of the NMR experiments (Table 1) can be assigned to specific compounds, the chemical shifts of the majority are inconsistent with bonding of the $^{13}CH_3$ group to carbon in a diamagnetic compound. Instead, several are likely to be attributable to $^{13}CH_3$ groups bonded to spin-paired titanium(II) and/or titanium(IV) or even titanium(III) with very weak contact shifts.[17] Our results thus rule out participation by the putative monomeric $[Cp^*TiMe]^+$ as the major EPR-active species in solution. If this complex were present as ≥10% of total titanium,[4] its EPR resonance would be very obvious—it is not—and its presence would result in major loss in intensity early in the NMR experiments, which does not occur. Thus, all of our NMR and EPR results are completely *inconsistent* with the formation of major amounts of an $S = {}^1/_2$ spin system at any time during the thermal decomposition of $Cp^*Ti(CH_3)_2(\mu\text{-}CH_3)B(C_6F_5)_3$, $^{13}$C-enriched or not. While a role for titanium(III) species for s-PS formation in this and other catalyst systems cannot be ruled out, it is clear from the results presented here and elsewhere[5,6] that there are instances where polymerization processes cannot be correlated with the presence of EPR active titanium(III) species. Observation of an EPR resonance cannot be regarded as evidence requiring the intermediacy of titanium(III) catalytic species.[18]

We note finally that while the compounds $CpTiR_2$ (R = allyl, benzyl) have been synthesized,[11a] attempts to prepare the analogous $CpTiMe_2$ and $CpTi(CH_2SiMe_3)_2$ resulted in disproportionation to $CpTiMe_3$ or $CpTi(CH_2SiMe_3)_3$ and, presumably, EPR-inactive compounds of the $d^2$ ion, titanium(II).[19] Thus, reactions of MAO on CpTi(III) and Cp*Ti(III) compounds may well result in the formation the compounds $CpTiMe_2$ and $Cp^*TiMe_2$, which could undergo (reversible?) disproportion to titanium(II) products which may be catalytically active but and EPR-inactive. Little is know of the chemistry of organotitanium(II) compounds.

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