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Reductive Decomposition of Cationic Half-Titanocene(IV) Complexes, Precursors of the Active Species in Syndiospecific Styrene Polymerization

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Summary: Mixtures of Cp^*TiR_3 *(with* $Cp^* = C_5(CH_3)_5$ *and* $R = CH_3$, $^{13}CH_3$*) and equimolar amounts of* $B(C_6F_5)_3$ *or* $C(C_6H_5)_3B(C_6F_5)_4$*, active in the syndiospecific polymerization of styrene, have been investigated by means of ESR spectroscopy. At room temperature the formation of* Cp^*TiR^+ *complexes has been observed. Rapid insertion of styrene occurs in Ti−R bonds of these cationic Ti(III) complexes, strongly suggesting their role in the stereospecific polyinsertion.*

Half-titanocenes, as well as many other hydrocarbon-soluble titanium compounds, are suitable precursors of very efficient homogeneous catalysts promoting polymerization of 1-olefins,[1] conjugated diolefins,[2] styrene, and substituted styrenes.[3] The title catalysts can be prepared by allowing to react e.g. $CpTiCl_3$ or Cp^*TiCl_3 (where $Cp = C_5H_5$ and $Cp^* = C_5(CH_3)_5$) with a large excess of methylaluminoxane (MAO) or by reaction of Cp^*TiR_3 ($R = CH_3$, $CH_2C_6H_5$) with either a large excess of MAO or an equimolar amount of $B(C_6F_5)_3$[4] or $C(C_6H_5)_3B(C_6F_5)_4$.[5] The MAO- and borane-activated catalysts promote syndiotactic polymerization of styrene[3a,4] and aspecific polymerization of 1-olefins.[1] Either *cis*-1,4-polymerization[2a,b,d] or 1,2-syndiotactic[2c] polymerization of conjugated diolefins has been also reported. Binary copolymerizations of styrene with substituted styrenes,[6] and of styrene with conjugated diolefins,[7] afford sequentially homogeneous copolymers exhibiting almost random comonomer sequence distributions. In contrast, in attempts to copolymerize e.g. ethylene and styrene, the reaction products are not sequentially homogeneous at all, even when copolymerization is carried out with constant feed. Exhaustive extraction of the produced polymer samples with selective solvents affords at the same time, quite different fractions ranging from syndiotactic polystyrene to polyethylene and, in same cases, including *pseudo*-random ethylene−styrene copolymers.[8] These intriguing results can be hardly understood by accepting that the same cationic Ti(IV) organometallic complexes, which promote 1-olefin polymerization,[9] are also active in syndiotactic polymerization of styrene. This possibility seems to be even more unlikely when considering that both styrene and 1-olefin polymerizations proceed through a polyinsertion mechanism occurring with *cis* addition to the double bond, although with different regiospecificities,[10] and that in both cases the active species are powerful electrophiles.[6] On this matter, some evidence is reported in the literature suggesting that the active species promoting syndiotactic polymerization of styrene should be a cationic Ti(III) complex bearing a η^5 anionic ligand (Cp or Cp*) and the growing polymer chain.[6] Accordingly, electron spin resonance (ESR) analysis of MAO-activated catalytic systems did show that partial reduction of Ti(IV) to Ti(III) occurs under the polymerization conditions.[11] Also, the cationic $Cp^*Ti(CH_2C_6H_5)_2^+$ complex, highly active in ethylene polymerization, easily undergoes reduction to Ti(III) species.[12] In order to achieve some more information concerning reductive decomposition of cationic Ti(IV) complexes and the related activity in syndiospecific styrene polymerization, we investigated the $Cp^*TiR_3/B(C_6F_5)_3$ catalytic systems (where $R = CH_3$, $^{13}CH_3$) in chlorobenzene solution by ESR spectroscopy.[13]

The room-temperature ESR spectrum of equimolar amounts of $Cp^*Ti(CH_3)_3$ and $B(C_6F_5)_3$ (system **A**: [Ti] = 0.01 M; B/Ti molar ratio 1) exhibits two signals at $g_{iso} = 1.979(3)$ and $g_{iso} = 1.977(3)$, with an approximately 1:5 intensity ratio (see Figure 1a).[14] Under the same

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(10) In the presence of the title catalysts insertion of the monomer is secondary for styrene and mainly primary for 1-olefins.

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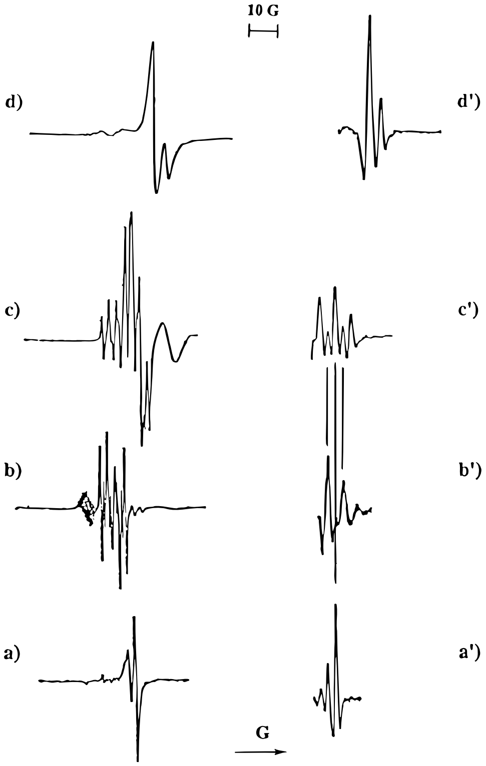
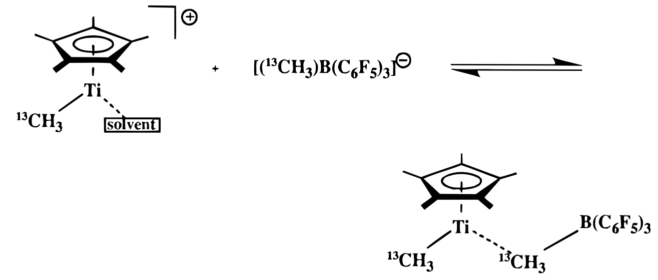


Figure 1. Room-temperature X-band ESR spectra of chlorobenzene solutions ([Ti] = 0.01 M; Ti/B molar ratio = 1) of (a) Cp*Ti(CH$_3$)$_3$ and B(C$_6$F$_5$)$_3$ (system **A**), (b) Cp*Ti(^{13}CH$_3$)$_3$ and C(C$_6$H$_5$)$_3$B(C$_6$F$_5$)$_4$ (system **B**), (c) Cp*Ti(^{13}CH$_3$)$_3$ and B(C$_6$F$_5$)$_3$ (system **C**), and (d) system **C** after the addition of *p*-chlorostyrene. In (a′)–(d′) are reported the second derivatives of the signals appearing in (a)–(d).

experimental conditions, the ESR spectrum of a mixture of the 100% ^{13}C-enriched methyl complex Cp*Ti(^{13}CH$_3$)$_3$ and C(C$_6$H$_5$)$_3$B(C$_6$F$_5$)$_4$ (system **B**) exhibits a doublet centered at $g_{\rm iso}$ = 1.977 and some additional downfield resonances (see Figure 1b).[15] In the ESR spectrum of Cp*Ti(^{13}CH$_3$)$_3$ and B(C$_6$F$_5$)$_3$ (system **C**), a doublet and a triplet resonating at $g_{\rm iso}$ = 1.977, both showing the same coupling constant of 6.2(0.5) G, have been observed (see Figure 1c). These findings can be explained by assuming that, under our experimental conditions, the Cp*Ti(CH$_3$)$_2^+$ cation, produced in the reaction of Cp*Ti(CH$_3$)$_3$ and B(C$_6$F$_5$)$_3$, slowly decomposes to produce the cationic Ti(III) complex Cp*Ti(CH$_3$)$^+$. As a matter of fact, the singlet at g = 1.977 observed in the ESR spectrum of system **A** appears as a doublet in the spectrum of the ^{13}C-enriched **B** system and a doublet plus a triplet in the ESR spectrum of system **C**. The doublet can be attributed to a Ti(III) nucleus coupled with one ^{13}C-enriched methyl ligand. The triplet, observed at the same g values, is probably due to the Cp*Ti(^{13}CH$_3$)$^+$(μ-^{13}CH$_3$)B(C$_6$F$_5$)$_3^-$ zwitterion, in which the bridging methyl accounts for the coupling of the Ti(III) nucleus with two ^{13}C-enriched methyl ligands instead of only one. This explanation arises when one considers that, in system **B**, the ^{13}C methyl migrates from titanium to trityl cation to produce the noncoordinating 1,1,1-triphenylethane, while in system **C** the methylborate moiety acts as a weakly coordinating counterion. On the other hand, in system **C,** an equilibrium between the solvent-separated and -associated ion pairs is likely anticipated in chlorobenzene at room temperature, accounting for the observed spectrum.[16] This equilibrium does not appear to be strongly temperature dependent. As a matter of fact, the relative amounts of the two species do not change in the range 253–300 K. Addition of *p*-chlorostyrene to the ESR tube containing systems **A**–**C** produces a darkening of the solution, and the resonances centered at g = 1.977 are replaced by a strong ESR signal showing two components at g = 1.974 and g = 1.968[17] (see Figure 1d). The area of the latter resonances is always larger than the total area of the signals at g =1.977, suggesting that the monomer itself accelerates reduction of Ti(IV).[18]

Scheme 1



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(13) X-Band electron spin resonance (ESR) spectra were recorded with an ER 200 D-SRC Bruker spectrometer operating at ν = 9.62 GHz using an HS Bruker rectangular cavity. The control of the operational frequency was obtained with a Hewlett-Packard X5-32 B wave meter, and the magnetic field was calibrated with a DPPH (diphenylpicrylhydrazyl) free radical as suitable field marker. The control of the temperature was obtained with a Bruker ER 4111 VT device (±1 K).

(14) The ESR resonances observed downfield from g = 1.977 are probably due to Ti(III) alkoxides and/or other products arising from oxygen traces and impurities present in the ESR tube. The relative intensities of these resonances erratically depend on the samples, and they seem unrelated to the polymerization catalysis (e.g., see Figure 1d). These resonances are observed in all the spectra reported in this communication and will not discussed any further.

(15) The downfield multiplet at g = 1.998 can be attributed to an organic radical, such as Ph$_3$C$^\bullet$, on the basis of the number and sharpness of the spectral lines (see Figure 1b).

(16) It is worth noting that the same equilibrium has been observed for the corresponding Ti(IV) complexes (see: Gillis, D. J.; Tudoret, M. J.; Baird, C. *J. Am. Chem. Soc.* **1993**, *115*, 2543).

(17) In the presence of a strongly immobilizing matrix, arising from active polymerization processes, the Ti(III) paramagnetic species undergoes molecular dynamics typical of rigid motion limits. As a consequence, the room-temperature ESR signal of the Ti(III) species displays a well-separated axial structure ($g_\parallel < g_\perp$) unresolved in both anisotropic regions due to significant line broadening of the two signals. By $S = {}^1/_2$ spin Hamiltonian computer simulation (SIM14), the "quasi-glassy" line shape exhibits g_i values different from the g_e one (2.0023):

$$g_\parallel = 1.968(3)$$

$$g_\perp = 1.974(3)$$

$$\langle g \rangle = {}^1/_3(g_\parallel + 2g_\perp) = 1.972(3)$$

suggesting that a significant orbital contribution of the unpaired electron affects the present spectral features.

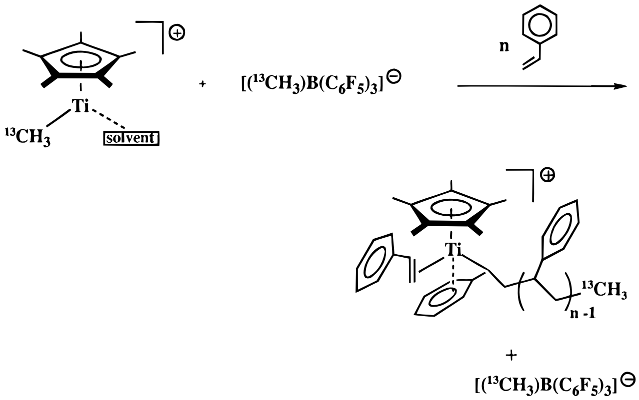
(18) A quantitative analysis of the Ti(III) ESR signals was carried out by comparing the areas with the areas of the ESR signals of standard TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy free radical) toluene solutions with a concentration in the range (1.0 × 10^{-3}) – (1.0 × 10^{-5}) M. In the ESR spectrum of the **A** system (see Figure 1a) the concentration of Ti(III) species has been evaluated as corresponding to 1% of the starting Ti. After the addition of *p*-chlorostyrene or styrene, the area of the ESR signal (see Figure 1d) at $\langle g \rangle$ = 1.972, corresponding to the supposed active species, is integrated for 50% of the starting Ti. In the ESR spectrum of toluene solutions of the same catalytic system with [Ti] = 0.001 M (this value approximately corresponds to the catalyst concentrations typically used in styrene and olefin polymerizations) the concentration of Ti(III) species was about 1% of the starting Ti. After the addition of styrene, the ESR resonance observed at $\langle g \rangle$ = 1.972 is integrated for about 10% of the starting Ti.

Similar results were previously reported by Cam[19] and Chien.[11] Furthermore, the anisotropic signals observed at $g = 1.974$ and $g = 1.968$ show a line width of about 5 G without any hyperfine structure. Surprisingly, the treatment of $B(C_6F_5)_3$ with an excess of $Cp^*Ti(^{13}CH_3)_3$ (Ti/B molar ratio 2, [Ti] = 0.01 M) produces a chlorobenzene solution that is ESR inactive. However, the intense resonances at $g = 1.974$ and $g = 1.968$ are still observed soon after the addition of *p*-chlorostyrene. This finding suggests that the excess $Cp^*Ti(CH_3)_3$ might possibly promote the formation of the binuclear cation $[Cp^*Ti(CH_3)_2(\mu\text{-}CH_3)TiCp^*(CH_3)_2]^+$, stabilizing titanium toward reduction.[20] Competitive coordination of *p*-chlorostyrene could promote dissociation of binuclear cations with displacement of $Cp^*Ti(CH_3)_3$, allowing the reduction reaction to occur. Of course it is also possible that under the reported experimental conditions Ti(III) ESR-silent species are formed. The NMR analysis of the polymer obtained in the ESR tube containing the ^{13}C-enriched precursor (system **C**) shows that it consists of a mixture of atactic and syndiotactic poly(*p*-chlorostyrene).[21] The ^{13}C NMR spectrum of the stereoregular fraction exhibits, in addition to the resonances diagnostic for syndiotactic poly(*p*-chlorostyrene), a resonance at 9.8 ppm which has been previously assigned to $-CH(Ph)CH_2CH(Ph)CH_2{}^{13}CH_3$ polymer end groups.[22] The chemical structure of this end group is in agreement with previously reported evidence[23] that the polymer growing chain arises from a secondary polyinsertion of styrene monomers into the titanium−carbon bond.

It is worth noting that the stereoirregular polymer fraction produced by **A**−**C** systems is absent in the polymer samples produced by the $Cp^*Ti(CH_2C_6H_5)_3/B(C_6F_5)_3$ system.

In conclusion this communication provides substantial evidence that (a) slow decomposition of $Cp^*Ti(CH_3)_2^+$ to $Cp^*Ti(CH_3)^+$ occurs under the polymerization conditions, (b) addition of styrene increases the rate of the reduction reaction of the Ti(IV) complexes, and (c) $Cp^*Ti(CH_3)^+$ reacts with styrene with removal of the methyl ligand from the titanium coordination sphere, possibly by styrene insertion. Most likely the addition of styrene to the Ti−CH_3 bond represents the initiation reaction of the syndiotactic polymerization of styrene (see Scheme 2). Finally, the catalytic systems were investigated in chlorobenzene solution and *p*-chlorostyrene instead of styrene was used for testing the activity. This somewhat esoteric choice is simply due to the higher solubility of the catalytic systems in chlorobenzene and the lower reactivity of *p*-chlorostyrene in comparison with styrene.[2a,6] Actually, when the catalyst is prepared in toluene solution ([Ti] = 0.01 M), after a few minutes a broad ESR resonance without any hyperfine structure is observed at $g = 1.977$; after about 30 min a red oil settles on the bottom of the ESR tube and the aforementioned signal is not detectable any longer in the supernatant toluene solution. Apparently the signal observed after a short time is due to a microemulsion of the catalyst in toluene, and after settling of the oil, the concentration of the titanium compound in toluene becomes too low in comparison with the sensitivity of the ESR spectrometer. At the present, the mechanism of the reduction of the cationic Ti(IV) precursors, either by themselves or in the presence of styrene, is not clear and requires further investigation.

Scheme 2



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Supporting Information Available: Figure giving the ^{13}C NMR spectrum of a poly(*p*-chlorostyrene) sample obtained in an ESR tube containing ^{13}C-enriched catalytic system **C** (1 page). Ordering information is given on any current masthead page.

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[19] Dam, C.; Sartori, F.; Maldotti, A. *Macromol. Chem. Phys.* **1994**, *195*, 2818.

[20] When an excess of metallocene is added to $B(C_6F_5)_3$ at room temperature, the formation of stable binuclear cationic CH_3-bridged complexes of general formula $Cp'_2M(CH_3)(\mu\text{-}CH_3)M(CH_3)Cp'_2$ has been reported (e.g. with M = Zr and Cp′ = C_5H_5: Haselwander, T.; Beck, S.; Brintzinger, H. H. In *Ziegler Catalysts*; Fink, G., Mulhaupt, R., Brintzinger, H. H., Eds.; Springer-Verlag: Berlin, 1995; p 181. With M = Ti and Cp′ = indenyl see: Bochmann, M.; Lancaster, S. J. *J. Organomet. Chem.* **1992**, *434*, C1).

[21] In the polymer samples obtained with the **B** and **C** systems the atactic polystyrene production could be related to some organometallic byproducts that are present with $Cp^*Ti(^{13}CH)_3$ in the catalytic systems. As a matter of fact, the synthesis of the ^{13}C-enriched titanium complex afforded an impure product which was used in the polymerization runs without further purification.

[22] Ammendola, P.; Tancredi, T.; Zambelli, A. *Macromolecules* **1986**, *19*, 307. The chemical shift of the signal is referred to hexamethyldisiloxane, used as internal reference.

[23] (a) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 277. (b) Pellecchia, C.; Pappalardo, D.; Oliva, L.; Zambelli, A. *J. Am. Chem. Soc.* **1995**, *117*, 6593.