

Monotitanocene catalysts: an ESR study of Ti(III) derivatives formed in presence of MAO and other organoaluminium compounds

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Abstract

Mixtures of monocyclopentadienyltitaniumtrichloride derivatives [$\text{Cp}'\text{TiCl}_3$, $\text{Cp}' = \text{C}_5\text{H}_5 = \text{Cp}$ (**1**), $\text{C}_5\text{Me}_5 = \text{Cp}^*$ (**2**), $\text{Me} = \text{CH}_3$] and methyl-aluminoxane (MAO), well known catalytic systems for olefins, styrene and dienes polymerisation, were characterised by ESR spectroscopy. The assignment of the observed signals to defined structures was carried out by comparison with the systems: **1**, **2**/ AlMe_3 ; **1**/ $\text{Al}(\textit{iso-butyl})_2\text{hydride}$, **2**/ AlEt_3 , **2**/ $\text{AlMe}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$.

In all the analysed mixtures titanium is partially reduced to the trivalent state and, generally, **1** shows a higher tendency to reduction than **2**.

At low Al/Ti ratio ($R = 10$) both in the presence of AlMe_3 or MAO, **1** and **2** produce similar Ti(III) compounds: the bimetallic trinuclear complex $\text{Cp}'\text{Ti}[(\mu\text{-Cl})_2\text{AlMe}_2]_2$ (A and A* for **1** and **2**, respectively).

At higher ratio ($R = 300, 500$), new species are observed, at higher g -values, compatible with a alkylation of the metal centre. In the system **1**/MAO a rather unstable new species C appears initially at $g = 1.977$, and is progressively converted to a stable titanium hydride compound (D).

In the system **2**/MAO ($R = 300, 500$) the species C^* ($g = 1.975$) and C_1^* ($g = 1.977$) are observed. C^* and C_1^* form in the system $\text{Cp}^*\text{TiCl}_3/\text{AlMe}_3/[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$ as well, i.e. in the presence of the ionising agent $[\text{CPh}_3][\text{B}(\text{C}_6\text{F}_5)_4]$, which is also employed to activate the half-metallocene precursors for styrene polymerisation, pointing to the formation of common species in the two catalytic systems.

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1. Introduction

Half-metallocene complexes $\text{Cp}'\text{TiCl}_3$ in combination with MAO or boron compounds have proved to be effective in promoting olefins, styrene and diene polymerisation [1–9]. Such a wide application spectrum stimulated many efforts to characterise these catalytic systems. In particular, ESR studies have been carried out since 1960s as a consequence of the fact that the Ti(IV) chlorinated precursors, which are ESR silent, exhibit a catalytic activity in the presence of suitable organoaluminium compounds (OAC), which promotes the reduction to Ti(III), where the unpaired electron makes the complexes paramagnetic.

First studies on metal complexes with cyclopentadienyl ligands concern Cp_2TiX_2 derivatives in combination with chloro alkyl aluminium compounds [10,11]. Later, on

the basis of an accurate ESR and UV–Vis investigation, Mach et al. [12,13] studied in detail the molecular structure of the products generated in the reaction of variously substituted mono-Cp complexes $\hat{\text{C}}\text{pTiCl}_3$ ($\hat{\text{C}}\text{p} = \text{C}_5\text{H}_5, \text{C}_5\text{H}_4\text{Me}, \dots, \text{C}_5\text{Me}_5$) with $\text{AlEt}_x\text{Cl}_{3-x}$ ($x = 1, 3$).

The spectroscopic [14,15] and catalytic [15] behaviours of **1**, **2** [14] and $\text{Cp}(\text{OR})_3$ [15] in the presence of MAO were then studied by Chien. Among others, the formation of a titanium hydride species was observed and its reactivity towards styrene was demonstrated. Moreover, with the aid of a special apparatus for electro dialysis, it was concluded that the hydride is a neutral species, active in the polymerisation of syndiotactic polystyrene.

In the literature, however, the discussion concerning the charge and even the oxidation state of the catalytically active species is still open.

In fact, recently, Grassi et al. [16] showed the formation of the cationic species $[\text{Cp}^*\text{TiCH}_3]^{+\bullet}$ solvent in the catalytic system based on $\text{Cp}^*\text{Ti}(\text{CH}_3)_3$ in combination with

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$B(C_6F_5)_3$ or $[CPh_3][B(C_6F_5)_4]$ in chlorobenzene solution. This species is reactive towards *p*-chlorostyrene, yielding a new one at $g_{ave} = 1.971$. This last signal was observed also in the system $Cp^*TiCl_3/MAO/p$ -chlorostyrene [17] and was assigned to the active species during styrene polymerisation. On the basis of these observations and of the coincidence of the concentration values of Ti(III) adducts and of the active species [18], the authors argue that the active site in both catalytic processes is the cationic complex $Cp^*Ti(III)CH_3^+$.

On the other side, Baird and co-workers [19,20] claim that titanium can hardly be in the oxidation state III in the species active for styrene polymerization, considering that, in disagreement with the above mentioned authors, they could find only traces of Ti(III) adducts in the ionic catalytic systems based on the mono-Cp precursors $Cp(Cp^*)Ti(CH_3)_3$.

Recently, in the system Cp^*TiCl_3/MAO'' (where MAO'' refers to vacuum treated MAO), with Al/Ti = 700, Bryliakov et al. [21] observed a Ti(III) concentration up to 10% of total titanium, mainly due to a species at $g = 1.970$, together with a titanium(III)hydride. On the basis of a detailed ^{13}C NMR study, Bryliakov et al. also show the formation of the cation-like species $Cp^*Ti(IV)Me_2^+ \leftarrow Me \cdots Al \equiv (MAO)$, which is the main reaction product generated from $CpTiMe_3$ precursor, in presence of MAO''.

Finally, some ESR studies were recently carried out on the system $CpTiCl_3/MMAO$ (MMAO = modified MAO including 11.5% isobutyl and 87.5% methyl groups) both in absence [22] and presence [23] of styrene. An accurate quantitative evaluation of the results evidenced the possible occurrence of interaction between Ti(III) sites, along with the correlation between Ti(III) concentration and styrene conversion.

Therefore, a unique description of these catalytic systems and a clear identification of the active species is still lacking. Indeed, some further complexity is added by the possible effect of the solvent, which is not the same in all experiments (toluene in [14,15,21–23], Cl-benzene in [16–18] and both chlorobenzene and toluene in [19,20]).

In this work we aimed to the characterisation of the paramagnetic reaction products of **1** and **2** in combination with $AlMe_3$ or MAO. In particular, we intended to point out similarities and differences in the reactive behaviour of the two precursors. We explored different reaction conditions including variable Al/Ti ratio ($R = 10$ –500), Ti concentration and temperature and the presence of styrene, in order to reproduce the catalytic environment. Even if the mixtures of **1** and **2** with $AlMe_3$ do not represent catalytically active systems, their characterisation is important in the study of MAO based ones, since free $AlMe_3$ is present in MAO and some common reaction products are formed in both cases. Moreover, in order to discuss the assignment of some of the observed signals, they were compared with those registered on the reaction products of **1** in combination with DiBAH or **2** in combination with $AlEt_3$ and $AlMe_3/[CPh_3][B(C_6F_5)_4]$.

In the reaction with $AlMe_3$ and MAO at low Al/Ti molar ratio (10) similar chemical species were generated from the two precursors, differing only by the presence of the methyl groups on the cyclopentadienyl ring. It was therefore possible to investigate the spectroscopic differences caused by the methylated ring compared to the unsubstituted one. Conversely, at high Al/Ti molar ratio, besides the similar ones, different reaction products were observed as well.

2. Experimental

2.1. General procedures

All experiments were performed under argon atmosphere by using standard Schlenk techniques. Toluene (Carlo Erba) was distilled under nitrogen over calcium hydride and stored in flasks under activated molecular sieves 4A.

Cyclopentadienyltitaniumtrichloride, $CpTiCl_3$ (**1**) and pentamethylcyclopentadienyltitaniumtrichloride, Cp^*TiCl_3 (**2**) were purchased from STREM and used as-received. Methyl-aluminoxane, MAO (10 wt.% solution in toluene), triethyl aluminium, $AlEt_3$, di-isobutylaluminium hydride, *i*-Bu₂AlH were purchased from Aldrich and used as-received. Tetra(pentafluorophenyl) boron triphenyl methyl $[C(Ph)_3][B(C_6F_5)_4]$ was synthesised in our laboratory.

dMAO was obtained by treating the commercial product under vacuum in order to remove some of the trimethylaluminium (TMA) present. 1H NMR spectroscopy was used for the estimation of the TMA content which is 26.7% (w/w) in the commercial product and 15.8% (w/w) in dMAO.

The cyclopentadienyl derivative solution was always added to the organoaluminium compound (OAC) one. When the effect of styrene was considered, this was added last.

2.2. ESR analysis

The ESR measurements were recorded in the X-band at room temperature or 35 °C on a Bruker ESP300-E spectrometer, equipped with a variable temperature unit. The *g*-values are determined within ± 0.001 by comparison with the signal of the 2,2-diphenyl-1-picrylhydrazyl (dpph) standard ($g_{iso} = 2.0036$) inserted in the cavity inside a capillary close to the sample tube. For quantitative evaluation, the double integral of the first derivative spectrum was compared with that of the standard $VO(acac)_2$ (*acac* = acetylacetonate) (0.001 M in toluene).

2.2.1. Calculations

All DFT calculations were performed using Amsterdam Density Functional program 2.3.0 (ADF) [24–26], using the integration scheme of te Velde et al. The electronic configurations of the molecular systems were described by unrestricted double- ζ basis sets with polarisation functions. The $1s^2$ configuration on carbon and aluminium, $1s^2$ and

Table 1
Full list of the analysed mixtures (OAC: organoaluminium compound)

Precursor	OAC	[Ti] (M)	[OAC]/[Ti] (M/M)	Observed species	[Ti(III)] _{ESR} (% M/M) ^a
CpTiCl ₃ (1)	AlMe ₃	0.01	10	A, C (aged sample)	12
		0.01	10	A, C	7–10
	MAO	0.001	10	A, C	3–5
		0.001	300	C, D	16
		0.001	500 (35 °C)	C, D	26–24
Cp*TiCl ₃ (2)	AlMe ₃	0.01	10	A*	7–8
		0.01	10	A*, D*	4
	MAO	0.001	300	C*, D*, L	4–5
		0.001	500 (35 °C)	C*, C ₁ *, D*, L	7–14
		0.001	300, 1000	C ₂ *	48–55
	MAO styrene	0.001	300, 1000	C*, C ₁ *, L	4–7
	dMAO	0.001	300, 1000	C ₂ *	50–57
	dMAO styrene	0.001	300, 1000	C ₂ *	34–33
AlEt ₃	0.01	10	B		

^a Titanium(III) percentage with respect to the total titanium content in the sample. The reported range of values is referred to the variation within the first hour of reaction.

2s² on aluminium and chlorine, and 1s² 2s² 2p⁶ on titanium were assigned to the core and treated by the frozen-core approximation. Unrestricted calculations were carried out for all the molecules including a titanium atom. A full geometry optimisation was carried out, using BFGS energy minimisation algorithm [27]. The Vosko–Wilk–Nusair [28] (VWN) local correlation potential (LDA) were applied to evaluate the density functionals. The computations were then performed recalculating the energies of the VWN optimised structures including electron exchange and electron correlation [29–31], through single point gradient-corrected self-consistent calculations.

3. Results and discussion

The full list of the analysed systems is reported in Table 1. We will discuss in the order the results obtained by mixing **1** and **2** with AlMe₃ then with MAO at low ratio ($R = 10$) and, finally, with MAO at high ratio ($R = 300, 500$) where the two precursors exhibit a remarkably different behaviour.

3.1. Reaction with AlMe₃

The solutions of the Ti(IV) precursors **1** and **2** are obviously ESR silent because of the absence of paramagnetic species, but, upon contact with the AlMe₃, they become ESR active. The spectra registered at Al/Ti = 10, [Ti] = 0.01 M are reported in Fig. 1. They show a constant shape during the first hours of reaction with minor quantitative variations. In both cases a simple ESR spectrum is observed, which can be assigned to single species (A and A* in the case of **1** and **2**, respectively), whose magnetic parameters are reported in Table 2. The signals show the hyperfine structure due to the interaction of the unpaired electron with the two titanium isotopes with nuclear spin $\frac{5}{2}$ (⁴⁷Ti, natural abundance = 7.4%) and $\frac{7}{2}$ (⁴⁹Ti, natural abundance = 5.4%). On the basis of

the titanium hyperfine pattern and the g -value, they were assigned to Ti(III) species [32]. Ti(III) fraction is higher in the reaction of **1** (12%, constant during the first 3 h of reaction) with respect to **2** (from 7 to 8% in same time interval). This behaviour can be explained assuming that the presence of the more electron-rich ligand Cp* in the latter case could limit the expected tendency of the Ti atom to increase its electron density by reduction (formally Ti(IV) + e⁻ → Ti(III)).

A molecular structure can be assigned to A and A* by comparison with the species B* which forms in the analogous system AlEt₃/Cp*TiCl₃ (Fig. 1), as described in the literature [12,13] and is assigned to Cp*Ti(μ-Cl)₄AlEt₄:

In the species A* and B* the titanium isotropic coupling and the g -values are the same within the experimental error; only the line width is larger in the former case (11.6 G) than in the latter (9.6 G). Therefore, it is very likely that they have similar structures, only differing by the kind of alkyl group on the aluminium. In particular, the coincidence of the g -values together with the higher stability of chlorine bridges with respect to methyl ones, induce to exclude Ti–X–Al

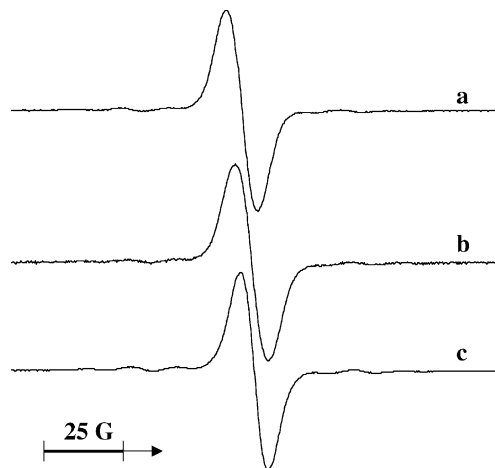
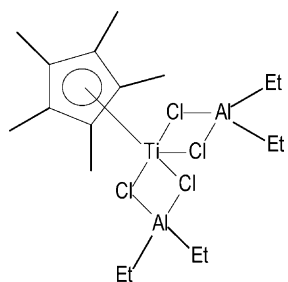


Fig. 1. ESR spectra registered on the mixtures: (a) AlMe₃/1; (b) AlMe₃/2; (c) AlEt₃/2; $R = 10$, Ti = 0.01 M, 5 min after the contact.

Table 2
List of the observed species with the relative magnetic parameters

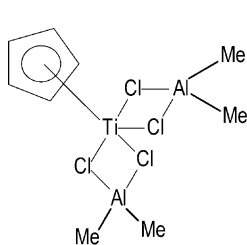
Species	g_{iso} (0.0002)	ΔH , peak–peak (G)	$a_{iso}(\text{Ti})$ (G)	$a_{iso}(\text{H})$ (G)	$a_{iso}(\text{Al})$ (G)
A	1.9724	10.7	15.3		
C	1.977	9.3			2.2 ^a
D	1.989	2.9	8.6	7.2	
D [†]	1.9847	2.9		5.4	
O [†]	1.9874	~2		3.7	3.7
A*	1.9701	11.6	15.6		
C*	1.975	12.3			
C ₁ *	1.977	5.1	14		
C ₂ *	1.973	8			
D*	1.991	5.5		20	
B	1.9701	9.6	15.6		
L	1.991	5			

^a Obtained from the simulation with the Public EPR Simulation Program WinSIM of NIEHS.

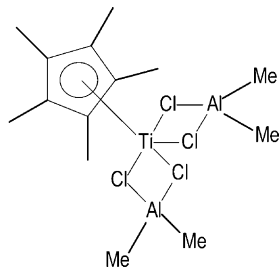


B*

nearest bridging atoms other than chlorine. Therefore, the following structures can be assigned to A and A*:



A



A*

As reported for B*, the coupling to aluminium is not observed in A and A*. In fact, the eleven-line superhyperfine multiplet due the presence of two aluminium atoms is observed in this kind of adduct only if all the terminal ligands are chlorine atoms (i.e. Cp*Ti(μ-Cl)₄Al₂Cl₄ [11,12]). When one or more terminal chlorine atoms are replaced by alkyl groups (i.e. Cp*Ti(μ-Cl)₄Al₂Cl_{4-x}Et_x) the multiplet shows as a broad single line whose peak to peak line width ΔH progressively decreases as an effect of the reduced $a_{iso}(\text{Al})$, while g_{iso} is shifted towards the free electron value g_e [12]. Both such variations can be rationalised considering that aluminium is involved in progressively more covalent bonds, so that a lower hyperfine interaction with the aluminium nuclei and a higher spin delocalisation can be expected.

In a similar way the difference in ΔH between A* and B* (11.6 G versus 9.6 G) can be explained considering that the ethyl is a more electron-releasing group with respect to the methyl group [33]. Analogous variations are observed also in A* with respect to A: the g -value is shifted away from g_e and the ΔH value (which is correlated with $a_{iso}(\text{Al})$) is slightly higher, pointing to a higher localisation. This can be explained assuming that the alkylation of the cyclopentadienyl reduces the “spread” of the unpaired electron on the ring and slightly increases its interaction with aluminium. As it is shown below, also in the reaction with MAO, similar effects were observed on products differing only by the alkylation of the ring.

Concerning the reaction mechanism of reduction, a similar one to that proposed in the literature [12] in the reaction of **1** or **2** with AlEt₂Cl can be hypothesised: the homolytic dissociation of the Ti-alkyl bond in the reaction intermediate Cp'Ti(IV) [(μ-Cl)₂AlEt₂][(μ-Cl)₂AlEtCl]Et.

Indeed, we verified by DFT calculations that the energetic costs of the reactions: Cp'Ti[(μ-Cl)₂AlMe₂]₂Me → Cp'Ti[(μ-Cl)₂AlMe₂]₂• + Me• are of only 6 and 5 kcal/mol, respectively, for Cp and Cp* derivatives, i.e. fully consistent with the occurrence of some reduction at r.t. Analogous calculations about the reaction: Cp'TiCl₂Me → Cp'TiCl₂• + Me• yield the energetic cost of 47 kcal/mol, pointing out the destabilisation of the Ti–R bond by the presence of di-μ-chloroalane ligands. Indeed it is reported that, on the contrary of CpTi(IV)[(μ-Cl)₂AlEt₂][(μ-Cl)₂AlEtCl]Et, CpTiCl₂Et is a stable product [34].

3.2. Reaction with MAO at low Al/Ti ratio

By mixing **1** or **2** with MAO ([Ti] = 0.01 M and R = 10) the formation of the same Ti(III) reaction products obtained with AlMe₃ (A and A*, respectively) was observed during 24 h contact time (see Figs. 2 and 3, respectively). Their formation could be ascribed to the presence of some free AlMe₃ in MAO. In fact, the initial Ti(III) concentrations are lower with respect to the reaction with AlMe₃: 7 and 4% in-

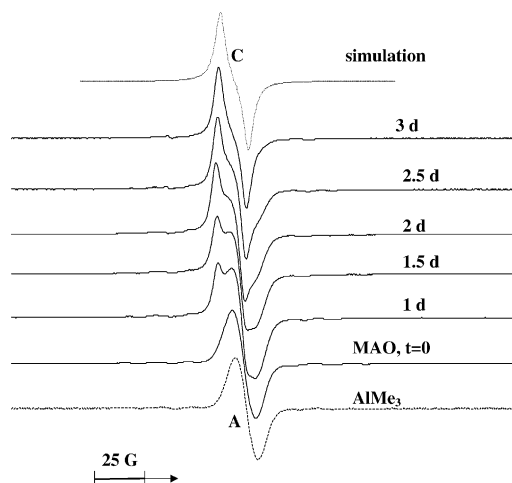


Fig. 2. ESR spectra registered on the mixtures: $\text{AlMe}_3/\mathbf{1}$ (bottom, broken line) and $\text{MAO}/\mathbf{1}$ at increasing times after contact (continuous line); $R = 10$, $[\text{Ti}] = 0.01 \text{ M}$. The upper spectrum is the simulated spectrum generated by WinSIM simulation program with the following magnetic parameters: $g = 1.977$, $a_{\text{iso}}(\text{Al}) = 2.22$, $\Delta H = 3.16 \text{ G}^1$ (correlation coefficient 0.998).

stead of 12 and 7% in cases **1** and **2**, respectively. In the case of **1**, however, an increase of $[\text{Ti(III)}]$ is observed with time. As in the reaction with AlMe_3 , **1** is reduced more than **2**.

In the reaction mixture $\mathbf{1}/\text{MAO}$ aged one day, a new species **C** appears, whose amount increases continuously during the following time of observation (48 h) while **A** is progressively consumed (Fig. 2). **C** is characterised by the g_{iso} value of 1.977 and does not show the hyperfine pattern of titanium, but a peculiar inflection point due to the unresolved interaction with some nuclei with non-zero nuclear spin. Considering the observed easy formation of Ti–Al adducts with chlorine bridges in the reaction of **1** with AlMe_3 , it is probably due to the interaction with one or more aluminium atoms. Indeed, the spectrum can be simulated with the following parameters: $g = 1.977$, $a_{\text{iso}}(\text{Al}) = 2.22$,

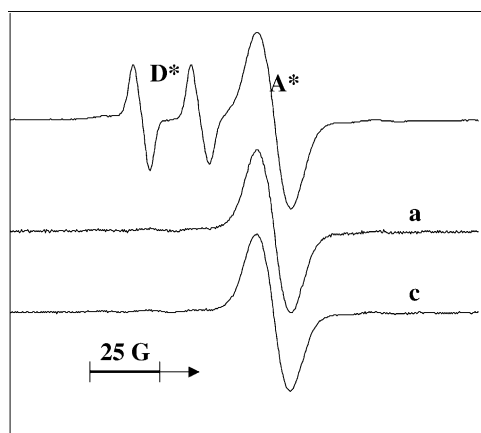
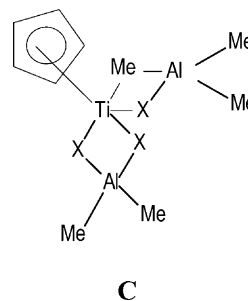


Fig. 3. ESR spectra registered on the system $\text{MAO}/\mathbf{2}$ 10/1 ($[\text{Ti}] = 0.01 \text{ M}$) immediately after the contact (a) and after 2 days ageing (b). For comparison the spectrum registered on $\text{AlMe}_3/\mathbf{2}$ is also reported (c).

$\Delta H = 3.16 \text{ G}^1$ (correlation coefficient = 0.998), as shown in Fig. 2. Concerning the g -value, it is possible that the observed shift towards g_e from the value 1.9724 of **A** to 1.977 of **C** could be due to the alkylation of titanium. Indeed, a similar variation has been observed in the bis-Cp derivatives from Cp_2TiCl ($g_{\text{iso}} = 1.980$) to Cp_2TiCH_3 ($g_{\text{iso}} = 1.986$) [33]. In conclusion we suggest the following structure for **C**: where some of the X ligands could be Cl or Me and where



the rather unstable [33] Ti-alkyl bond could gain some stability from the bridging structure.

A completely different behaviour was observed for the $\mathbf{2}/\text{MAO}$ mixture: neither an increase of the Ti(III) fraction, nor the formation of any other species occurs. After 2 days ageing, however, a doublet D^* appears at $g = 1.991$, with a spacing of 20 G (Fig. 4). Comparing these values with magnetic parameters reported in literature for the complex $\text{Cp}_2\text{TiH}^*\text{THF}$ ($g = 1.992$ and $a(\text{H}) = 11.6 \text{ G}$) [35] or the $\text{Ti(III)}\text{--Ti(IV)}$ dimer $(\text{Cp}_2\text{TiH})_2\text{H}$ ($g = 1.994$, $a_1(\text{H}) = 9.7$, $a_2(\text{H}) = 15.6$) [36], it was assigned to a titanium hydride, in agreement with Bryliakov et al. [21].

In conclusion at $R = 10$, the initial reactivity of both precursors is dominated by the reaction with AlMe_3 , while the effects of ageing are different. Elapsing time promotes the conversion of **A** to a probably alkylated species **C** and yields an hydride in the reaction mixture with **2**.

3.3. Reaction with MAO at high Al/Ti ratio

3.3.1. $\mathbf{1}/\text{MAO}$

In the case of $\mathbf{1}/\text{MAO}$ mixture, by raising the R value to 300 the initial concentration of Ti(III) increases up to 16% ($[\text{Ti}] = 0.001 \text{ M}$). The spectrum shows the immediate formation of the species **C**, already observed at $R = 10$ in the aged sample, and of a doublet, described in literature [14], at $g_{\text{iso}} = 1.989$ (species **D**) with a spacing of 7.2 G and the hyperfine pattern of $^{47,49}\text{Ti}$ nuclei ($a_{\text{iso}}(\text{Ti}) = 8.5 \text{ G}$) (Fig. 4a).

For longer reaction times the total Ti(III) concentration remains stable, but **C** changes to **D**. Increasing R up to 500 and T to 35°C , such a transformation becomes remarkably faster and in these conditions **C** totally disappears in 20 min

¹ The magnetic parameters were optimised with the Public EPR simulation program WinSIM of NIEHS.

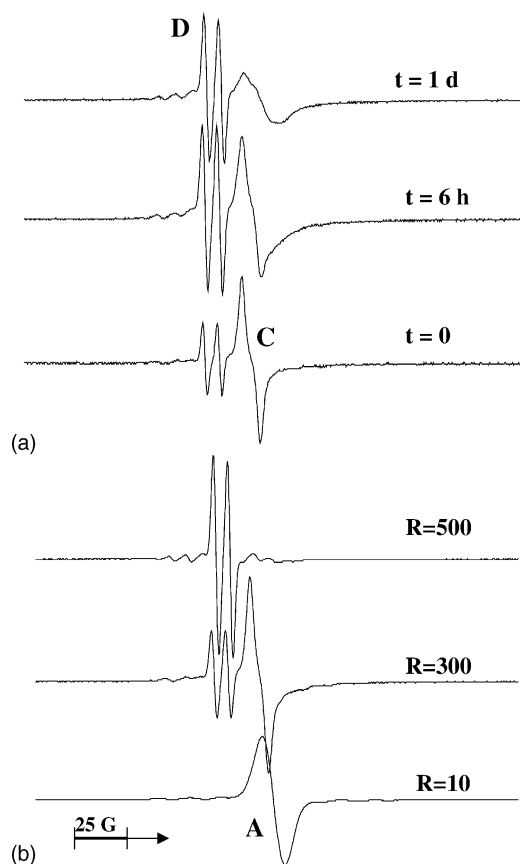


Fig. 4. ESR spectra of the system MAO/1 (a) $R = 300/1$; $[\text{Ti}] = 0.001$, at increasing times from contact; (b) $R = 10, 300, 500$, at 20 min from the contact (spectra not to scale).

(Fig. 4). The initial Ti(III) concentration grows to 26% and later slowly decreases with time, reaching 22% after 3 h.

Therefore, the increase in the Al/Ti molar ratio, not only raises the reduction to Ti(III), but also affects the distribution of the reaction products, accelerating the transformation to the final ones (Fig. 4b): on the time scale of catalytic interest, some species are formed only for high R values (300 or more). These observations could be correlated to the high R values required to observe catalytic activity.

Concerning the assignment of the doublet D, the first choice should fall on a Ti hydride [14]. In order to clarify the possible structure of this adduct, the reaction of **1** with $\text{Al}(i\text{-But})_2\text{H}$ ($i\text{-But} = \text{CH}_2\text{CH}(\text{CH}_3)_2$, $R = 10$, $[\text{Ti}] = 0.01 \text{ M}$) was studied, and, on the basis of the obtained results, we suggest that in both cases the unpaired electron is partially delocalised on a hydrogen bridging Ti and Al atoms.

The reaction of **1** with $\text{Al}(i\text{-But})_2\text{H}$ induces the formation of a multiplet (species O^\dagger) and of a doublet (species D^\dagger), whose magnetic parameters are reported in Table 2. The spectra registered at 1 h and 2 days of ageing are reported in Fig. 5, showing that O^\dagger is unstable with respect to D^\dagger . On the basis of comparison with analogous patterns reported in the literature [37–39], concerning the spectra of the

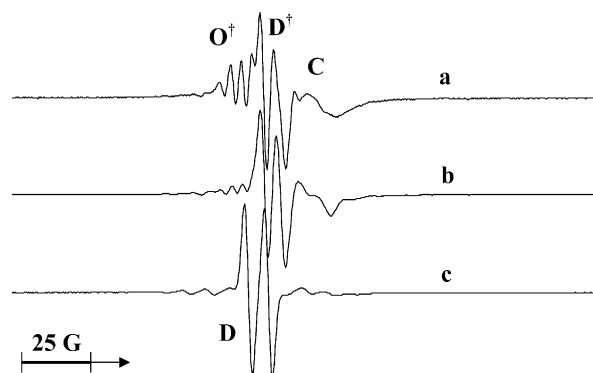


Fig. 5. ESR spectra registered on the system DiBAH/1 10:1 at 1 h (a) and 2 days (b) of ageing and on the system MAO/1 10:1 (c) ($[\text{Ti}] = 0.01 \text{ M}$).

systems $\text{Al}(i\text{-But})_2\text{H}/\text{Cp}_2\text{TiCl}_2$ and $\text{Al}(i\text{-But})_3/\text{Cp}_2\text{TiCl}_2$, D^\dagger and O^\dagger are to be assigned to two titanium–aluminium adducts where the two metals are bonded through a mixed chlorine–hydrogen bridge and double hydrogen bridge respectively. In fact:

- (1) in the species D^\dagger the splitting in two components of the main line of the titanium hyperfine pattern could arise from the superhyperfine interaction of the unpaired electron with one proton ($a(\text{H}) = 5.4 \text{ G}$); obviously the splitting is present also on the weaker lines, but it is not experimentally observed;
- (2) concerning O^\dagger , the observed multiplet is superimposed on the first lines of a sextet of triplets, that Allen et al. [39] were able to isolate in the mixture $\text{Cp}_2\text{TiCl}_2/\text{Al}(i\text{-But})_3$. This pattern was explained [37] in terms of the interaction of the unpaired electron with an aluminium nucleus (sextet with $a_{\text{iso}}(\text{Al}) = 3.7 \text{ G}$) and two equivalent protons (triplet with $a(\text{H}) = 3.7 \text{ G}$) in the adduct $\text{Cp}_2\text{Ti}(\mu\text{-H})_2\text{AlCl}_2$.

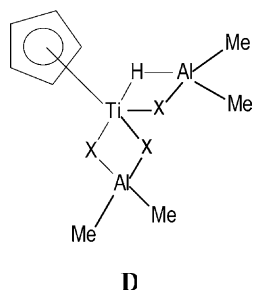
Similar signals are therefore observed in the reaction of bis- and mono-cyclopentadienylyl titanium precursors with OAC, showing a similar tendency to generate $(\mu\text{-H})$ and $(\mu\text{-Cl})$ bridge bonds with Al.

The comparison between the rather close values of the hydrogen coupling in the species D ($a(\text{H}) = 7.2 \text{ G}$) and D^\dagger ($a(\text{H}) = 5.4 \text{ G}$) (Fig. 5) induces to assign to D an analogous $\text{Ti}(\mu\text{-H})\text{Al}$ bridged structure. The shift of the g -value towards g_e in D with respect to D^\dagger could be due to the alkylation of titanium. In conclusion the following structure can be proposed for the species D: where some of the X ligands could be Me and the others are chlorine ones.

3.3.2. 2/MAO

The spectra registered on 2/MAO mixture at $R = 300$ (r.t.) and $R = 500$ (35°C) ($[\text{Ti}] = 0.001 \text{ M}$) are reported in Fig. 6.

The Ti(III) concentration is generally lower than in the reaction of **1** in analogous conditions: 4% (constant) for $R = 300$ and from 7 to 18% in 3 h for $R = 500$ and $T = 35^\circ\text{C}$.



In general, as already observed for **1**, both the increase of reaction time and R induce a shift of the resonant absorption towards lower fields, that is an enrichment in species with g -values closer to g_e .

When $R = 300$ the main signal ($g = 1.975$, species C^*) shows the characteristic inflection already observed in the C signal and interpreted as an unresolved hyperfine splitting to aluminium, so that an analogous $Cp^*Ti[(\mu-Cl)(\mu-Me)AlMe_2][(\mu-Cl)_2AlMe_2]$ structure can be hypothesised.

As already observed in the comparison of A with A^* , the permethylated derivative C^* shows a g -value closer to g_e and a higher ΔH , i.e. a lower delocalisation, than the unsubstituted C.

At lower fields the species D^* can be observed, together with an other absorption L at $g = 1.991$, also reported in the literature [20] which becomes stronger at $R = 500$. In principle the formation of species shifted towards g_e can be considered as an indication of a further alkylation of the metal centre [33,40].

As it can be seen in Fig. 6, at $R = 500$ the shape of the absorption about C^* becomes asymmetrical with time because of the convolution of C^* with an increasing signal at $g = 1.977$ (species C_1^*), which is superimposed on its lower component. C_1^* has the same g -value reported in literature for

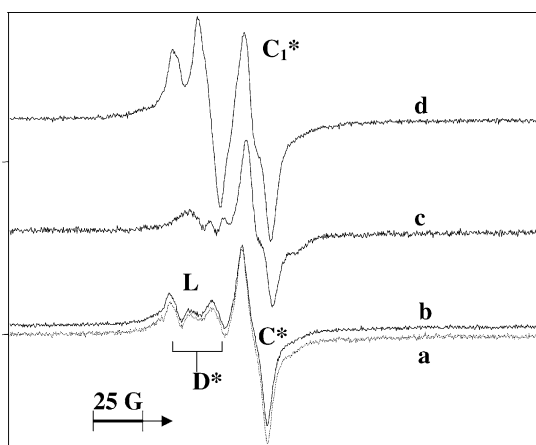


Fig. 6. ESR spectra registered on the mixtures MAO/2 300/1 (r.t.) and 500/1 (35 °C) at different reaction times ([Ti] = 0.001) (a, dotted line) $R = 300$, $t = 0$; (b) $R = 300$, $t = 165'$; (c) $R = 500$, $t = 0$; (d) $R = 500$, $t = 165'$.

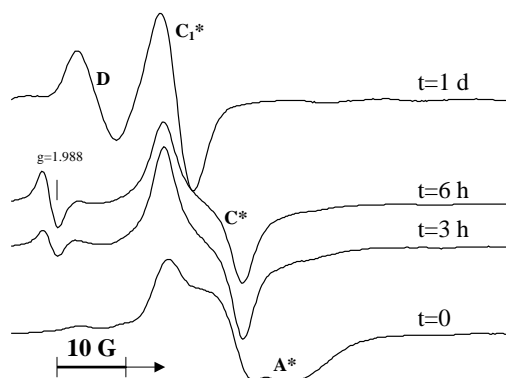


Fig. 7. ESR spectra registered on the mixture 2/AlMe₃/[CPh₃][B(C₆F₅)₄] 1/10/1 at increasing times from contact (Ti = 0.001 M).

the cationic species $[Cp^*TiCH_3]^{+*}$ (solvent), observed in low quantity (1%) in the system $Cp^*Ti(CH_3)_3/[CPh_3][B(C_6F_5)_4]$ [16] (chlorobenzene solution).

Therefore, in order to compare directly C_1^* with an ion pair deriving from **2**, the reaction mixture 2/AlMe₃/[CPh₃][B(C₆F₅)₄] was studied. Besides the ionising agent [CPh₃][B(C₆F₅)₄], AlMe₃ was added to the mixture, as an alkylating agent, since the formation of the cationic species has been reported in the reaction of an alkylated titanium(IV) complex.

On the mixture 2/AlMe₃/[CPh₃][B(C₆F₅)₄] (1/10/1, [Ti] = 0.001 M), a sequence of spectra was observed, with similar spectroscopic features observed on the system 2/MAO (see Figs. 7 and 8).

Initially, the species A^* and C^* are observed, with A^* slowly decreasing and C^* steadily increasing with time, until, after 3 h, A^* completely disappears. At the same time a rather weak, not assigned signal at $g = 1.988$ increases with time. Note that in presence of AlMe₃ only, the species C^* is not observed, not even upon ageing, but it only forms in the interaction with MAO. After 48 h C^* also disappears, leaving the strong resonance line of C_1^* and the doublet D^* , as shown in Fig. 7. A direct comparison between the system 2/MAO at $R = 500$ ($T = 35$ °C) and the aged system 2/AlMe₃/[CPh₃][B(C₆F₅)₄] is reported in Fig. 8, where the presence of C_1^* in both systems is shown. In this range of magnetic field, in the trace registered on the ionic system, the trityl radical² signal is also observable.

The comparison of C_1^* with the cationic species $Cp^*TiCH_3^+$ described in literature is not straightforward, since the two species were observed in different experimen-

² The presence of relevant amounts of the trityl radical is observable at any times in the reaction mixture, and, in traces, also in the [CPh₃][B(C₆F₅)₄] solution. It can be observed when the microwave power is low enough to avoid saturation (e.g. 0.2 mW). Its complex hyperfine pattern can be partially resolved lowering the modulation amplitude to 0.2 G. The signal can be satisfactorily simulated by the parameters: $g_{iso} = 2.013$, $a_{iso}(H_{para}) = 2.80$ G; $a_{iso}(H_{meta}) = 1.23$ G, $a_{iso}(H_{ortho}) = 2.55$. The presence at $g = 1.998$ of the multiplet due to the trityl radical has been described also in literature [16] in the system $Cp^*Ti(CH_3)_3/[CPh_3][B(C_6F_5)_4]$.

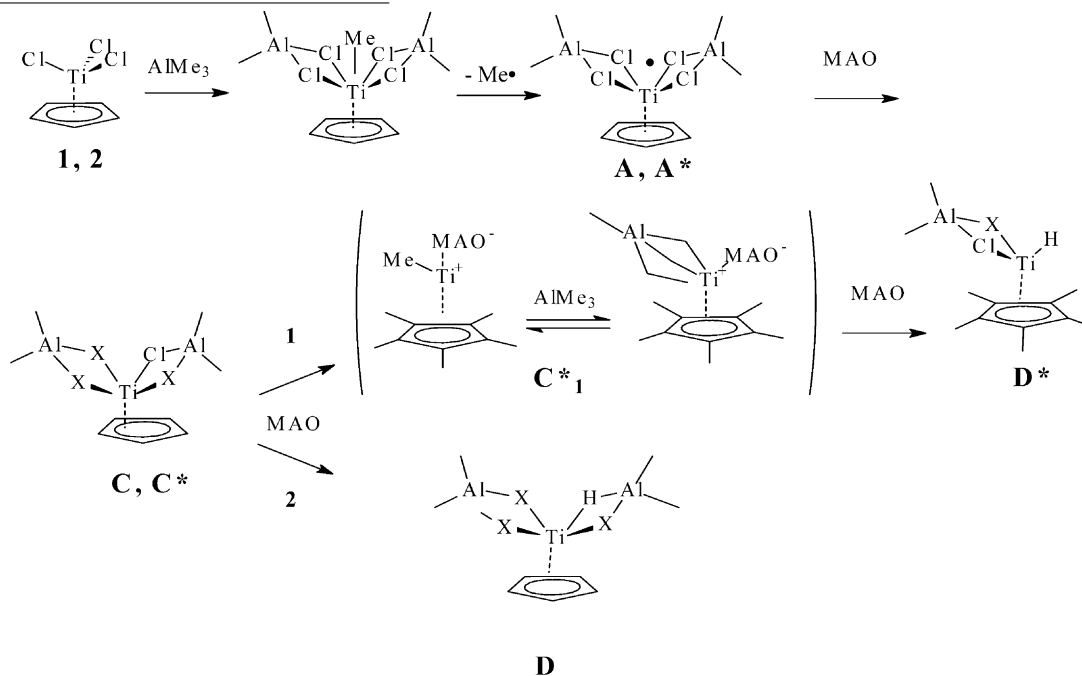
tal conditions. C_1^* was observed in this experimentation in toluene solvent and in presence of $AlMe_3$; in such conditions C_1^* forms at high concentration, with resolved hyperfine coupling to titanium (14 G) and a ΔH value of 5 G.

The cationic species $Cp^*TiCH_3^+$ was described in the literature both in absence [16] and presence [17] of $AlMe_3$ (Al:Ti = 3:1), always in chlorobenzene solution. No shift in the resonance position ($g = 1.977$) was observed, but its intensity is higher in the latter case. However, in that circumstance, the ^{13}C isotopically substituted products $Cp^*Ti(^{13}CH_3)_3$ and $Al(^{13}CH_3)_3$ were employed as reagents [17]. In these conditions, the absorption at $g = 1.977$ shows at 240 K an hyperfine pattern assigned to the interaction with three ^{13}C ($a(^{13}C) = 4.7$ G) and interpreted with the formation of the adduct $[Cp^*Ti(\mu-^{13}CH_3)_3Al(^{13}CH_3)]^+$. Its signal broadens at r.t. in a single line absorption with $\Delta H = 25$ G, with no hyperfine interaction to titanium. These results show that $AlMe_3$ interacts strongly with the

Finally, considering the catalytic relevance of lowering the free $AlMe_3$ content in MAO, it was examined the reaction of **2** with dMAO, obtained from the commercial product by vacuum treatment. The spectra have almost the same intensity as that observed with MAO activation (Ti(III) initial value = 7% at $R = 300$); however the relative intensity of the species C_1^* and L are slightly higher (Fig. 9).

In both cases, if styrene is added (molar ratio 1000:1 with respect to titanium) the initial Ti(III) concentration remarkably increases, up to about 50% in both systems, and slowly grows further with time. The species C^* is completely consumed, and an almost unique signal is present at $g = 1.974$ (Fig. 9), which is reported also in literature [20].

On the basis of the above observations, a possible reaction scheme able to rationalise the formation of the Ti(III) species starting from the **1** or **2** precursors is the following:



highly unsaturated cationic species $Cp^*TiCH_3^+$; since the spectroscopic effects depends on the kind of isotope present, the comparison is affected.

In conclusion, since the species C_1^* appears in the same position as $[Cp^*Ti(CH_3)]^+$ and it is also formed from Cp^*TiCl_3 in the presence of the alkylating agent $AlMe_3$ and the ionising compound $[CPh_3][B(C_6F_5)_4]$, we can put forward for C_1^* a structure like as the alkylated cationic species coordinated to $AlMe_3$ $[Cp^*Ti(\mu-^{13}CH_3)_3Al(^{13}CH_3)]^+$. It is also possible that, at r.t. the bimetallic adduct is in equilibrium with some dissociated products, as suggested by the line broadening described above. This observation is important since this cationic species $[Cp^*Ti(CH_3)_3]^+$ has been considered responsible of catalytic activity towards styrene polymerization in the ionic system as well as in the presence of MAO [17].

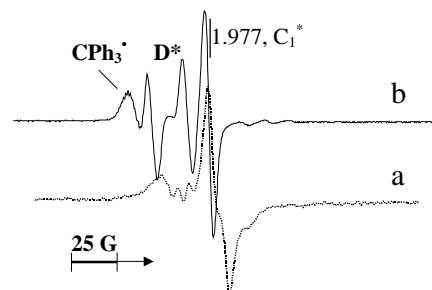


Fig. 8. ESR spectra registered on the system $2/AlMe_3/[CPh_3][B(C_6F_5)_4]$ 1/10/1 and on MAO/2 500/1 ([Ti] = 0.001 M).

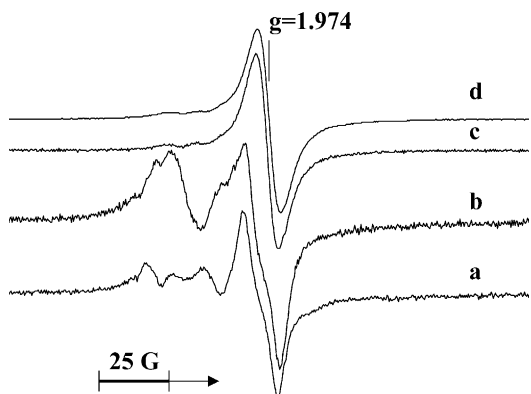


Fig. 9. ESR spectra registered on the mixtures: MAO/2 300/1 (a) and dMAO/2 300/1 (b) at 1 h 10' from contact and on the mixtures MAO/2/styrene 300/1/1000 (c) and dMAO/2/styrene 300/1/1000 ([Ti] = 0.001 M) (not to scale).

where some of the X ligands could be chlorine or Me ones. The shift of the reaction products distribution towards the latest ones is promoted by time and/or higher Al/Ti molar ratios. A common reactivity between **1** and **2** is observed until the one to last step, where the formation of the hydride D and of the species C₁^{*} was observed in cases **1** and **2**, respectively. An overview of the spectroscopic features of the two systems is reported in Fig. 10.

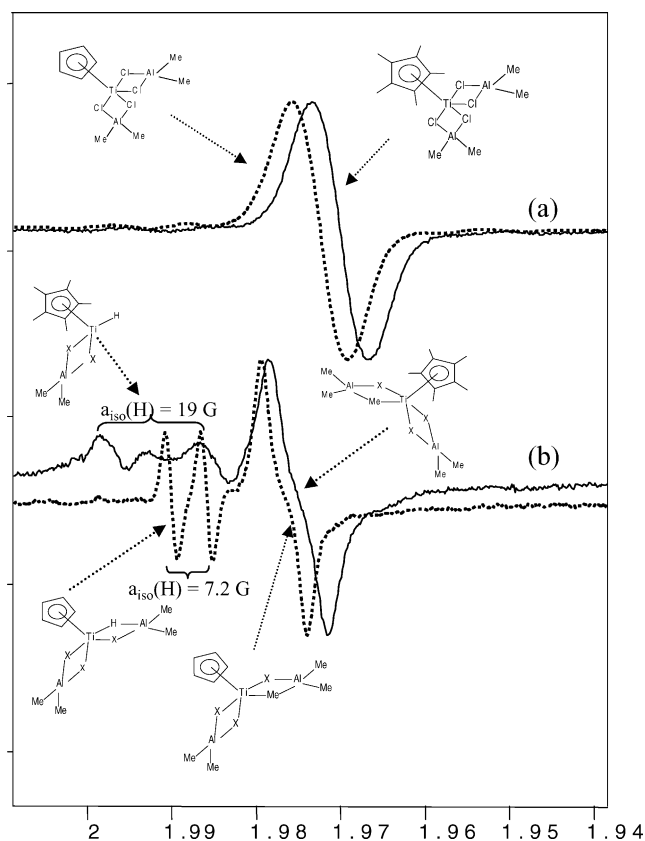


Fig. 10. ESR registered on the systems MAO/1 (broken line) and MAO/2 (continuous line) at $R = 10$ (a) and $R = 300$ (b) (not to scale).

4. Conclusions

It was shown that, for the same OAC and Al/Ti molar ratio, **2** has a lower tendency to reduction than **1**, likely because of the presence of a more electron-rich ligand on titanium (Cp^{*} versus Cp). This probably limits the further increase of the electron density on the metal induced by reduction. The reaction of **1** or **2** with both AlMe₃ and MAO at low $R = \text{Al/Ti}$ molar ratio ($R = 10$) yields initially the same Ti(III) product, the bimetallic adduct Cp^{*}Ti[(μ-Cl)₂AlMe₂]₂ (A and A^{*}). Therefore, in the presence of MAO, **1** and **2** react first with the free AlMe₃ fraction.

At higher Al/Ti molar ratio ($R = 300, 500$) the formation of new species was observed, with a shift of the resonant absorption towards lower fields, promoted by both the increase of reaction time and/or of R . This could be related to the need of employing similarly high R in order to achieve catalytic activity in polymerization.

At $R = 300$, in both systems it appears a species with a characteristic inflection that has been attributed to an unresolved hyperfine interaction with an aluminium nuclei (C and C^{*}). Moreover, C and C^{*} signals are shifted towards the free electron g -value g_e with respect to A and A^{*} ones, respectively. It was therefore hypothesised that the assignment of C and C^{*} to adducts where the titanium atom is partially alkylated: Cp^{*}Ti[(μ-CH₃)(μ-Cl)AlMe₂][(μ-Cl)₂AlMe₂] or Cp^{*}Ti[(μ-CH₃)₂AlMe₂][(μ-Cl)₂AlMe₂].

A^{*} and C^{*} are shifted away from g_e with respect to A and C, respectively, showing that the permethylated ring reduces the delocalisation on the unpaired electron, likely on the cyclopentadienyl ligand.

At increasing times C decays yielding a doublet D that has been assigned to a H-bridged titanium–aluminium adduct. Considering that it is generated by the erosion of C, possible assignments are: Cp^{*}Ti[(μ-H)(μ-Cl)AlMe₂][(μ-Cl)₂AlMe₂] or Cp^{*}Ti[(μ-H)(μ-CH₃)AlMe₂][(μ-Cl)₂AlMe₂].

The titanium hydride D is a stable species: it remains the only ESR active species for several days.

In the system **2**/MAO at high R , the spectra are more complex. In addition to the main species C^{*}, it can also be observed that a titanium hydride D^{*} ($g = 1.991, a(\text{H}) = 20 \text{ G}$), a species at $g = 1.991$ and one at $g = 1.977$ (C₁^{*}). This last one is at the same g -value as the cationic species Cp^{*}Ti(CH₃)⁺, claimed to be the active species promoting syndiospecific styrene polymerization [17,18], and as [Cp^{*}Ti(μ-Me)₃AlMe]⁺. Indeed it was verified that C₁^{*} also forms in the presence of an ionising agent, i.e. in the system: Cp^{*}TiCl₃/AlMe₃/[CPh₃][B(C₆F₅)₄]. These observations suggest that C₁^{*} is of the kind of the cited cationic species and reinforce the hypothesis [17,18] of charged catalytically active half titanocene species, both in ionic and MAO-activated systems.

It was also experimentally observed that C^{*} is reactive towards styrene: upon addition of the monomer it disappears, yielding a new stable species at $g = 1.974$ (C₂^{*}) with a

considerable increase in the Ti(III) concentration, up to 50% of the total approximately.

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