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# $^{13}\text{C}$ -NMR study of Ti(IV) species formed by $\text{Cp}^*\text{TiMe}_3$ and $\text{Cp}^*\text{TiCl}_3$ activation with methylaluminoxane (MAO)

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## Abstract

Using  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectroscopy, titanium(IV) species formed in the catalytic systems  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  and  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  ( $\text{Cp}^* = \text{C}_5(\text{CH}_3)_5$ ) in toluene and chlorobenzene were studied within the temperature range 253–293 K and at Al/Ti ratios 30–300. It was shown that upon activation of  $\text{Cp}^*\text{TiMe}_3$  with methylaluminoxane (MAO) mainly the ‘cation-like’ intermediate  $\text{Cp}^*\text{Me}_2\text{Ti}^+ \leftarrow \text{Me}^- - \text{Al} = (\text{MAO})$  (**2**) is formed. Three types of titanium(IV) complexes were identified in  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  catalytic system. They are methylated complexes  $\text{Cp}^*\text{TiMeCl}_2$  and  $\text{Cp}^*\text{TiMe}_2\text{Cl}$ , and the ‘cation-like’ intermediate **2**. Complex **2** dominates in  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  system in conditions approaching to those of practical polymerization (Al/Ti ratios more than 200). According to the EPR measurements, the portion of EPR active Ti(III) species in the  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  system is smaller than 1% at Al/Ti = 35, and is about 10% at Al/Ti = 700.

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## 1. Introduction

The discovery of syndiotactic polystyrene (sPS) was an important milestone in stereospecific polymerization [1]. Catalytic system  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  is one of the most effective for sPS production [2]. In spite of the extensive studies, the nature of the reactive intermediates of this catalytic system still remains uncertain.

EPR monitoring of the  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  system provided evidence for an EPR active Ti(III) complex [3]. The activity of the  $\text{Cp}^*\text{Ti}^{\text{III}}(\text{OMe})_2/\text{MAO}$  combination is greater than that of  $\text{Cp}^*\text{Ti}^{\text{IV}}(\text{OMe})_3/\text{MAO}$  [4]. In some cases, correlations of catalyst activities with the intensities of the Ti(III) EPR signals were observed [5]. Thus, the important role of Ti(III) species in syndiospecific polymerization of styrene is assumed. However, recent studies of  $\eta^5\text{-LTiCl}_3/\text{MAO}$  (where L = 2-Me-Ind,

1-Me-Ind, Ind, H<sub>4</sub>-Ind, Cp) catalysts show that all these catalysts are multisite, including Ti(IV) and Ti(III) active sites, the activity of the Ti(IV) catalyst being greater than that of Ti(III) catalyst [6]. The related catalytic systems  $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  and  $\text{Cp}^*\text{TiMe}_3/[\text{Ph}_3\text{C}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$  have been extensively studied by various research groups using NMR and EPR spectroscopy [7–13]. Grassi and co-workers anticipated that the  $[\text{Cp}^*\text{Ti}^{\text{III}}\text{Me}]^+$  cationic intermediate would be the true active species of sPS production [7–9], while Baird and co-workers concluded that observation of an EPR resonance could not be regarded as evidence requiring the intermediacy of Ti(III) catalytic species and called attention to the examples where polymerization process could not be correlated with the presence of EPR active Ti(III) species [10,12,13]. In recent work, Waymouth and co-workers examined the catalytic activity of Ti(III) and Ti(IV) complexes originated from  $\text{Cp}^*\text{Ti}(\text{C}_3\text{H}_5)_2$  and  $\text{Cp}^*\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_3$ , using stoichiometric amounts of  $[\text{C}_6\text{H}_5\text{NH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$  salt as the activator [14]. They have reported that in the presence of styrene/ $\alpha$ -olefin mixtures, catalysts derived from Ti(III) complexes

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exhibit chemoselectivity for styrene homopolymerization, whereas those from Ti(IV) precursors demonstrate complementary selectivity for  $\alpha$ -olefin polymerization. Thus, the nature of the active metal catalysts is a matter of extensive discussion, and neither the intermediacy of titanium(III) nor titanium(IV) cationic complexes in syndiospecific polymerization of styrene can be excluded.

Thus, it is important to elucidate the nature of titanium(IV) species formed upon activation of  $\text{Cp}^*\text{TiCl}_3$  and  $\text{Cp}^*\text{TiMe}_3$  with methylaluminoxane (MAO). This has not been done so far, though such data are available for  $\text{Cp}_2\text{ZrMe}_2/\text{MAO}$  and  $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$  catalytic systems [15,16].

In this work, we have undertaken a  $^{13}\text{C}$ - and  $^1\text{H}$ -NMR spectroscopic study of the Ti(IV) intermediates in  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  and  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  catalytic systems. The concentration of EPR active Ti(III) species in  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  system has also been monitored by EPR.

## 2. Experimental

### 2.1. Materials

MAO was purchased from Witco GmbH (Bergham) as toluene solution (total Al content 1.8 M, Al as  $\text{AlMe}_3$  0.5 M).  $\text{Cp}^*\text{TiMe}_3$  was prepared as in Ref. [17].

Toluene, toluene- $d_8$  and chlorobenzene were dried over molecular sieves (4A), purified by refluxing over sodium metal and distillation in dry argon. The distilled solvents were degassed in vacuo.

The solvents were stored and handled in vacuum. All experiments were carried out in sealed high vacuum systems using breakseal techniques to avoid undesired contact with atmosphere.

### 2.2. Preparation of MAO and $\text{Al}_2\text{Me}_6$ samples

MAO was obtained from commercial MAO (Witco) by removal of the solvent in vacuo at 20 °C. The solid product obtained (polymeric MAO with total Al content 40 wt.% and Al as residual  $\text{AlMe}_3$  ca. 5 wt.%) was used for the preparation of the samples.

$^{13}\text{CH}_3$ -labelled  $\text{Al}_2\text{Me}_6$  was prepared from 99%  $^{13}\text{C}$ -labelled  $\text{CH}_3\text{I}$  (Aldrich) by sequential treatments with Al metal at 80 °C and Na metal in  $\text{C}_{12}\text{H}_{26}$  at 100 °C. For this goal, dried glass ampoule was filled with argon and charged with 0.126 g (4.7 mmol) of Al metal powder, 1.0 g (7 mmol) of  $^{13}\text{CH}_3\text{I}$  (99%  $^{13}\text{C}$ ) and  $\text{I}_2$  (used as catalyst). The atmosphere was evacuated and the ampoule was sealed off from the vacuum line. The reaction mixture was kept at 80 °C for 10 h. The obtained suspension was mixed under vacuum with Na metal (0.170 g) suspended in dodecane. The obtained

mixture was stirred at 100 °C for 5 h. After that the product —  $^{13}\text{CH}_3$ -labelled  $\text{Al}_2\text{Me}_6$  (99%  $^{13}\text{C}$ ) was distilled in vacuo from the reaction mixture and used for  $^{13}\text{CH}_3$ -labelled MAO sample preparation.

$^{13}\text{CH}_3$ -labelled MAO was prepared by ligand exchange of  $^{13}\text{CH}_3$ -labelled  $\text{Al}_2\text{Me}_6$  (70 mol.% of total Me groups) and unlabelled MAO-2 (30 mol.% of total Me groups) in toluene solution. In a typical experiment, 0.12 g of polymeric MAO powder (total Al content 1.8 mmol) was dissolved in 5 ml of toluene and  $\sim 0.3$  ml ( $\sim 2$  mmol Al) of  $^{13}\text{CH}_3$ -labelled  $\text{Al}_2\text{Me}_6$  was added to the solution. The reaction mixture was stirred for 24 h at 25 °C and the liquid fraction  $\text{Al}_2\text{Me}_6$  (70%  $^{13}\text{C}$ ) was distilled in vacuum to give the sample of  $^{13}\text{C}$ -labelled MAO (70%  $^{13}\text{C}$ ) with desired  $\text{Al}_2\text{Me}_6$  content (total concentration of Al = 1.8 M, concentration of Al as  $\text{Al}_2\text{Me}_6$  = 0.5 M).

### 2.3. Preparation of $\text{Cp}^*\text{TiCl}_3$ ( $\text{Cp}^*\text{TiMe}_3$ ) + MAO ( $^{13}\text{CH}_3$ -labelled MAO) samples

Calculated quantities of  $\text{Cp}^*\text{TiCl}_3$  ( $\text{Cp}^*\text{TiMe}_3$ ), MAO and  $\text{Al}_2\text{Me}_6$  ( $\text{Al}_2(^{13}\text{CH}_3)_6$ ) were combined in toluene or chlorobenzene under vacuum in NMR tubes and sealed off from vacuum line. When using  $^{13}\text{C}$ -labelled samples, complete ligand scrambling was observed by  $^{13}\text{C}$ -NMR spectroscopy within several minutes needed for sample handling even at  $-25$  °C. Total Ti concentration was 0.02–0.001 M, and that of Al was 0.1–0.3 M, whereas Al/Ti ratios were in the range 5–300.

### 2.4. NMR measurements

The  $^{13}\text{C}$ -NMR spectra were recorded at 100.614 MHz on a Bruker MSL-400 NMR spectrometer, using cylindrical 5 and 10 mm glass sample tubes.

The typical operating conditions used for  $^{13}\text{C}$ -NMR measurements were the following: sweep width 25 kHz; spectrum accumulation frequency 0.2–0.02 Hz; number of transients 100–10 000, 45° pulse at 10  $\mu\text{s}$ . The data were accumulated with 32–16 K data points in the time domain.

$^{13}\text{C}$ -NMR measurements for the quantitative determination of the relative intensities of resonances in one and the same spectrum were made using inverse gated decoupling mode and long relaxation delays between the transients. The multiplicities and coupling constants were derived from analysis of gated decoupled spectra. Chemical shifts were calculated in parts per million, with positive values in the low field direction. For calculations of  $^{13}\text{C}$  chemical shifts, the resonance of  $\text{CH}_3$ -group of toluene solvent was taken as 22.25, and residual  $\text{CH}_3$ -group of toluene in chlorobenzene as 21.4. Sample temperature measurements uncertainty was smaller than  $\pm 2$  °C, and temperature reproducibility was within  $\pm 1$  °C.

## 2.5. EPR measurements

EPR spectra were recorded on a Bruker ER-200D spectrometer at 9.3 GHz, modulation frequency 100 kHz, modulation amplitude 10 G. Measurements were performed in glass tubes ( $d = 5$  mm) at room temperature. Periclase crystal (MgO) with impurities of  $Mn^{2+}$  and  $Cr^{3+}$ , which served as a side reference, was placed into the second compartment of the dual cavity. EPR signals were quantified by double integration with copper chloride ( $CuCl_2 \cdot 2H_2O$ ) as a standard.

## 3. Results and discussion

### 3.1. $Cp^*TiMe_3 + MAO$ in toluene

$Cp^*TiMe_3$  complex exhibits three  $^{13}C$  resonances due to  $C_5Me_5$  and Ti–Me moieties:  $-20^\circ C$ ,  $d_8$ -toluene:  $\delta = 123.2$  (Cp, 5C), 12.8 (Me–Cp, 5C, q,  $J_{CH}^1 = 127.5$  Hz), 62.1 (Ti–Me, 3C, q,  $J_{CH}^1 = 118.5$  Hz) (Table 1). The  $^{13}C$ -NMR spectrum of the system  $Cp^*TiMe_3$ /unlabelled MAO (Al/Ti = 35) does not display Ti–Me peaks due to their great widths (Fig. 1(b)). The same sample prepared with  $^{13}C$ -labelled MAO exhibits Ti–Me resonances of the intermediates 1–3 (Fig. 1(a)).

Species 1 is a weak complex of  $Cp^*TiMe_3$  with Lewis acidic sites of MAO:  $Cp^*Me_2Ti-Me \rightarrow Al \equiv MAO$  (1) (Fig. 1(a)). The exchange between free  $Cp^*TiMe_3$  and 1

Table 1

The  $^{13}C$  chemical shifts, line widths and  $J_{CH}^1$  coupling constants for Ti(IV) species formed upon interaction of  $Cp^*TiMe_3$  and  $Cp^*TiCl_3$  with MAO in toluene

Complex	Cp	Me–Cp	Ti–Me
$Cp^*TiMe_3$	123.2	12.8 $J_{CH}^1 = 127.5$ Hz	62.1 $J_{CH}^1 = 118.5$ Hz
1			63.2 $\Delta\nu_{1/2} = 200$ Hz
2		13.2 $\Delta\nu_{1/2} = 15$ Hz	83 $\Delta\nu_{1/2} = 400$ Hz
3			67.5 $\Delta\nu_{1/2} = 9$ Hz
$Cp^*TiCl_3^a$	138.0	14.8 <sup>b</sup> $J_{CH}^1 = 127.7$ Hz	
$Cp^*TiMeCl_2^a$	131.3	13.7 $J_{CH}^1 = 128.7$ Hz	79.4 $J_{CH}^1 = 127.4$ Hz
$Cp^*TiMe_2Cl^a$		13.2	73 $\Delta\nu_{1/2} = 200$ Hz
2 <sup>c</sup>		13.2	84 $\Delta\nu_{1/2} = 500$ Hz
3 <sup>c</sup>			64.5 $\Delta\nu_{1/2} = 5$ Hz

All parameters measured in toluene at  $-10^\circ C$  unless otherwise stated.

<sup>a</sup> At  $-20^\circ C$ .

<sup>b</sup> In the presence of  $Al_2Me_6$  14.1–14.2 ppm.

<sup>c</sup> Observed in  $Cp^*TiCl_3/MAO$  at Al/Ti = 30.

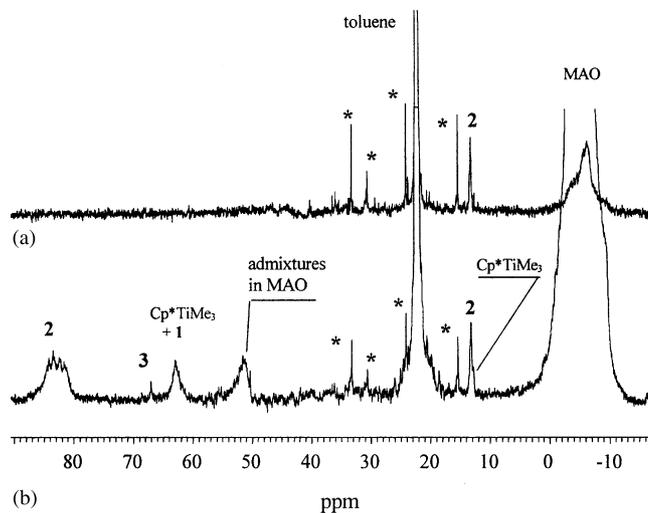


Fig. 1.  $^{13}C$ -NMR spectrum of  $Cp^*TiMe_3$  recorded 1 h after addition of MAO in toluene at  $-10^\circ C$ , Al/Ti = 35,  $[Cp^*TiMe_3] = 0.02$  M: (b)  $^{13}C$ -labelled sample of MAO, (a) unlabelled sample of MAO. Asterisks denote admixtures in toluene.

gives rise to dramatic increase of the line width and to downfield shift (ca. 1–2 ppm with respect to  $Cp^*TiMe_3$ ) of the resulting Ti–Me resonance. A similar weak complex was observed previously for  $Cp_2ZrMe_2$  and Lewis acidic sites of MAO [16].

Complex 2 exhibits broad Ti–Me peak centered at 83 ppm ( $\Delta\nu_{1/2} = 400$  Hz), and the peak at 13.2 ppm from Cp–Me groups which overlaps with the corresponding peak of 1. The broad peak at 83 ppm is a superposition of several more sharp signals (Fig. 1(a)). Chemical shift of Ti–Me resonance of 2 ( $\delta = 81$ –84 ppm) is close to that of the terminal Ti–Me resonance of cationic complex  $[Cp^*TiMe_2]^+[MeB(C_6F_5)_3]^-$  ( $\delta = 80$ –81 ppm) [12]. Most probably, complex 2 is the ‘cation-like’ intermediate  $Cp^*Me_2Ti^+ \leftarrow Me^- - Al \equiv MAO$  (Fig. 2). Unfortunately, we have not succeeded in detection of Ti–Me–Al resonance of complex 2. For related ‘cation-like’ intermediate  $Cp_2MeZr^+ \leftarrow Me^- - Al \equiv MAO$ , both Zr–Me and Zr–Me–Al resonances were observed at 42 and 9 ppm, respectively. The Zr–Me–Al signal was much broader than the Zr–Me one ( $\Delta\nu_{1/2} = 500$  and 120 Hz, respectively) [16]. Thus, one can expect that Ti–Me–Al signal in complex 2 is much broader than the Ti–Me one ( $\Delta\nu_{1/2} = 400$  Hz) and can hardly be detected. The existence of several Ti–Me peaks of 2 ( $\delta = 81$ –84 ppm) is caused by nonuniformity of MAO oligomers

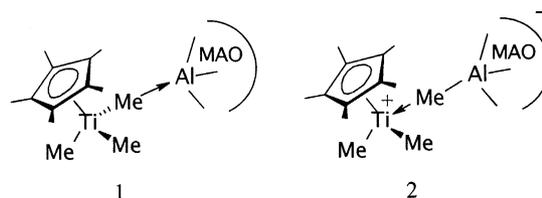


Fig. 2. The structures proposed for the intermediates 1 and 2.

and by fairly slow exchange of  $[\text{Cp}^*\text{Me}_2\text{Ti}]^+$  cations between various  $\text{Me}^-$ -MAO counter ions.

It is worth noting that for most zirconocene/MAO systems, the intermediate  $[\text{L}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$  exhibiting sharp NMR peaks dominates in the reaction system at high Al/Zr ratios [18]. It is tempting to assume that complex **3** displaying a weak and sharp Ti–Me resonance at 67.5 ppm is the cationic intermediate  $[\text{Cp}^*\text{TiMe}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$ . Better solubility of titanium species in chlorobenzene allowed to determine  $J_{\text{CH}}^1 = 115$  Hz for Ti–Me resonance of complex **3** in chlorobenzene. The sharp resonance with the same  $J_{\text{CH}}^1 = 115$  Hz was observed earlier for Zr–Me–Al carbon atom of the heterodinuclear cationic complex  $[\text{Cp}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+[\text{Me-MAO}]^-$ . However, NMR investigations have so far failed to provide evidence for the formation of cationic species  $[\text{Cp}^*\text{TiMe}(\mu\text{-Me})_2\text{AlMe}_2]^+$  in boron based systems, and thus the structure of **3** remains unclear. Fortunately, as it will be shown below, cationic intermediate **2** with proposed structure  $\text{Cp}^*\text{Me}_2\text{Ti}^+ \leftarrow \text{Me}^- - \text{Al} \equiv \text{MAO}$  strongly dominates in  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  and  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  systems in conditions approaching to real polymerization (Al/Ti more than 200). The relative concentrations of complexes **1**, **2** and **3** in the sample of Fig. 1(a) are about 10:30:1.

### 3.2. $\text{Cp}^*\text{TiCl}_3 + \text{Al}_2(\text{CH}_3)_6$ in toluene

$\text{Cp}^*\text{TiCl}_3$  exhibits two  $^{13}\text{C}$  resonances due to  $\text{C}_5\text{Me}_5$  moiety:  $-20^\circ\text{C}$ ,  $d_8$ -toluene,  $^{13}\text{C}$ :  $\delta = 138.0$  (Cp, 5C), 14.8 (Me, 5C,  $J_{\text{CH}}^1 = 127.7$  Hz) (Table 1).

The system  $\text{Cp}^*\text{TiCl}_3/\text{Al}_2(\text{CH}_3)_6$  (1:5) prepared by combining toluene solutions of  $\text{Cp}^*\text{TiCl}_3$  and  $\text{Al}_2(\text{CH}_3)_6$  at  $-20^\circ\text{C}$  (concentration of  $\text{Cp}^*\text{TiCl}_3$  was 0.005 M) displays additional  $^{13}\text{C}$ -NMR peaks, besides those of  $\text{Cp}^*\text{TiCl}_3$ , due to the formation of  $\text{Cp}^*\text{TiMeCl}_2$ :  $-20^\circ\text{C}$ ,  $\delta = 131.3$  (Cp, 5C), 79.4 (Ti–Me, 1C, q,  $J_{\text{CH}}^1 = 127.4$  Hz), 13.7 (Cp–Me, 5C, q,  $J_{\text{CH}}^1 = 128.7$  Hz) (Fig. 3(a), Table 1). The displacement of only one chlorine atom in  $\text{Cp}^*\text{TiCl}_3$  by Me group is evident from the relative intensities of Ti–Me and Cp–Me resonances of  $\text{Cp}^*\text{TiMeCl}_2$  (the enrichment of Ti–Me resonance by  $^{13}\text{C}$  isotope was taken into account).

In order to monitor formation of dimethylated complex  $\text{Cp}^*\text{TiMe}_2\text{Cl}$ , the sample  $\text{Cp}^*\text{TiCl}_3/\text{Al}_2(\text{CH}_3)_6 = 1:50$  ( $[\text{Cp}^*\text{TiCl}_3] = 0.02$  M in toluene) was prepared. The ordinary  $\text{Al}_2\text{Me}_6$  was used for preparation of this sample due to limited amount of isotopically enriched  $\text{Al}_2\text{Me}_6$  available. Nevertheless,  $^{13}\text{C}$ -NMR spectrum (range of Cp–Me carbons) clearly shows, that besides the peaks of  $\text{Cp}^*\text{TiCl}_3$  and  $\text{Cp}^*\text{TiMeCl}_2$  at 14.2 and 13.7 ppm, the new peak at 13.2 ppm appears that might be reasonably assigned to  $\text{Cp}^*\text{TiMe}_2\text{Cl}$  (Fig. 3(b)).

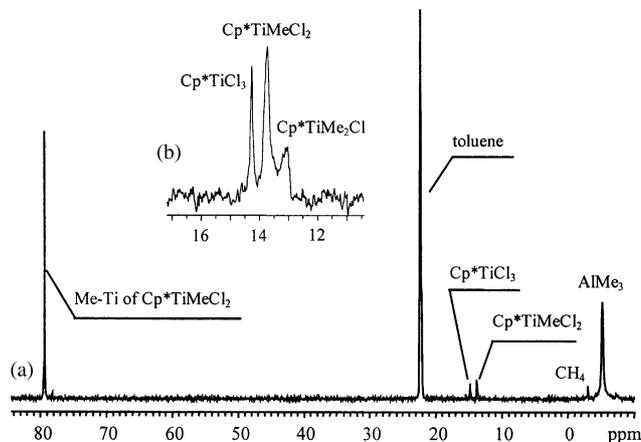


Fig. 3.  $^{13}\text{C}$ -NMR spectrum of  $\text{Cp}^*\text{TiCl}_3 + \text{Al}_2(^{13}\text{CH}_3)_6$  in toluene at  $-20^\circ\text{C}$ , Al/Ti = 5,  $[\text{Cp}^*\text{TiCl}_3] = 0.02$  M (a).  $^{13}\text{C}$ -NMR spectrum (range of Cp–Me carbons) of  $\text{Cp}^*\text{TiCl}_3 + \text{Al}_2(\text{CH}_3)_6$  in toluene at  $+20^\circ\text{C}$ , Al/Ti = 50,  $[\text{Cp}^*\text{TiCl}_3] = 0.02$  M (b).

### 3.3. $\text{Cp}^*\text{TiCl}_3 + ^{13}\text{C}$ -labelled MAO in toluene

The system  $\text{Cp}^*\text{TiCl}_3/^{13}\text{C}$ -labelled MAO (Al/Ti = 35) at  $-20^\circ\text{C}$  just after sample preparation exhibits  $^{13}\text{C}$ -NMR spectrum shown in Fig. 4(a). The peaks observed belong to complexes  $\text{Cp}^*\text{TiMeCl}_2$  and  $\text{Cp}^*\text{TiMe}_2\text{Cl}$  (Table 1). As it was expected, the chemical shift of the Ti–Me resonance of  $\text{Cp}_2\text{TiMe}_2\text{Cl}$  at 73 ppm ( $\Delta\nu_{1/2} = 200$  Hz) has intermediate value between those of  $\text{Cp}^*\text{TiMe}_3$  (62 ppm) and  $\text{Cp}^*\text{TiMeCl}_2$  (79 ppm). Its position and width markedly differ from those of the ‘cation-like’ species  $\text{Cp}^*\text{Me}_2\text{Ti}^+ \leftarrow \text{Me}^- - \text{Al} \equiv \text{MAO}$  (**2**) (81–84 ppm,  $\Delta\nu_{1/2} \sim 400$  Hz). Cp–Me peaks of  $\text{Cp}^*\text{TiMeCl}_2$  and  $\text{Cp}^*\text{TiMe}_2\text{Cl}$  in the sample  $\text{Cp}^*\text{TiCl}_3/^{13}\text{C}$ -labelled MAO have the same chemical shifts as corre-

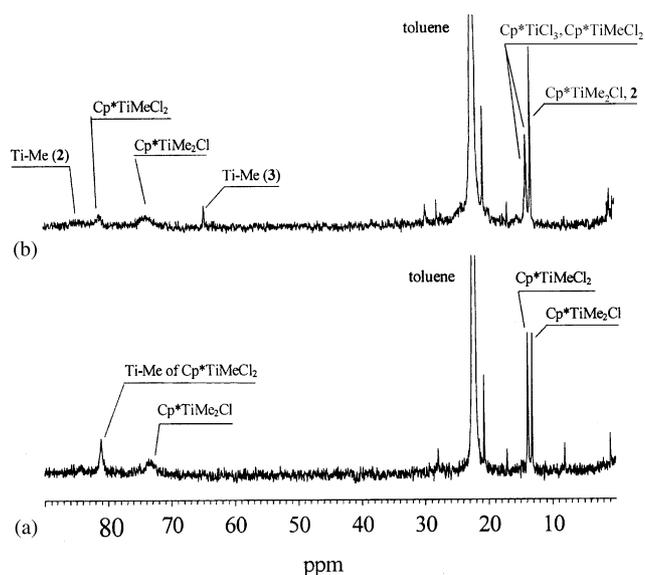


Fig. 4.  $^{13}\text{C}$ -NMR spectrum of  $\text{Cp}^*\text{TiCl}_3 + ^{13}\text{C}$ -labelled MAO in toluene, Al/Ti = 30,  $[\text{Cp}^*\text{TiCl}_3] = 0.005$  M: (a) 1 h after sample preparation at  $-20^\circ\text{C}$ , (b) 1 h after storing the sample at  $-10^\circ\text{C}$ .

sponding species in the sample  $\text{Cp}^*\text{TiCl}_3/\text{Al}_2\text{Me}_6$  (Fig. 3(b)).

After storing the sample of Fig. 4(a) during an hour at  $-10^\circ\text{C}$ , the relative concentration of  $\text{Cp}^*\text{TiMeCl}_2$  decreases. Besides, a number of weak and broad peaks at 83–85 ppm resembling those of **2** can be observed, and sharp resonance at 64.5 ppm resembling that of **3** appears (Fig. 4(b)). It is reasonable to expect that at high Al/Ti ratios (about 300), cationic intermediates formed in  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  and  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  systems are similar, since high excess of  $\text{Al}_2\text{Me}_6$  gives rise to methylation of  $\text{Cp}^*\text{TiCl}_3$ . Indeed, with the increase of Al/Ti ratio up to 300 only one peak of Cp–Me carbons at 13.2 ppm is observed for  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  system as it was the case for  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  analog. This peak belongs to complex **2**. The corresponding Ti–Me signal was not detected due to low concentration of titanium.

The portion of complex **3** does not drastically increase with the growth of Al/Ti ratio. If this were the case, sharp Cp–Me peak of **3** would be detected at high Al/Ti ratios. However, no signals besides that of **2** were observed in the range of Cp–Me carbon atoms (Al/Ti ratios of 100–300,  $[\text{Cp}^*\text{TiCl}_2] = 0.001\text{--}0.003\text{ M}$ ). Thus, the major part of titanium exists in the catalytic systems  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  and  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  (Al/Ti = 300,  $[\text{Ti}] = 0.001\text{ M}$ ) in the form of complex **2**.

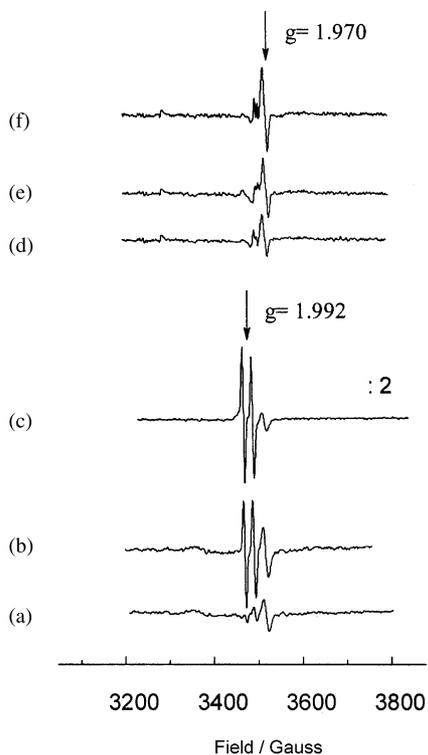


Fig. 5. EPR spectra ( $20^\circ\text{C}$ ) of the  $\text{Cp}^*\text{TiCl}_3+\text{MAO}$  mixture in toluene, Al/Ti = 35,  $[\text{Cp}^*\text{TiCl}_3] = 5.6 \times 10^{-3}\text{ M}$ : (a) immediately after mixing, (b) 2 h, (c) 10 h after mixing. EPR spectra ( $20^\circ\text{C}$ ) of the  $\text{Cp}^*\text{TiCl}_3+\text{MAO}$  mixture in toluene, Al/Ti = 700,  $[\text{Cp}^*\text{TiCl}_3] = 2.7 \times 10^{-4}\text{ M}$ : (d) immediately after mixing, (e) 8 min, (f) 40 min after mixing.

is far less stable than related complex  $\text{Cp}_2\text{MeZr}^+ \leftarrow \text{Me}^- - \text{Al} \equiv \text{MAO}$  in zirconocene/MAO systems. NMR peaks of **2** in the catalytic system  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  in toluene (Al/Ti = 300) disappear with half-life of 3–5 h at room temperature, while cationic species  $\text{L}_2\text{MeZr}^+ \leftarrow \text{Me}^- - \text{Al} \equiv \text{MAO}$  are stable during weeks at room temperature [18]. In contrast to zirconium based systems where outer-sphere ion pair  $[\text{L}_2\text{Zr}(\mu\text{-Me})_2\text{AlMe}_2]^+ [\text{Me-MAO}]^-$  dominates in the reaction solution at high Al/Zr ratios, for titanium system studied, inner-sphere ion pair  $\text{Cp}^*\text{Me}_2\text{Ti}^+ \leftarrow \text{Me}^- - \text{Al} \equiv \text{MAO}$  is the major species at high Al/Ti ratios. Further, it will be interesting to compare cationic intermediates formed in various titanium/MAO and zirconium/MAO systems. Until now there was only one example of  $^{13}\text{C}$ -NMR characterization of cationic species formed upon activation of titanium catalyst by MAO. Tritto et al. observed formation of cationic intermediates via reaction of  $^{13}\text{C}$  enriched  $\text{Cp}_2\text{TiMe}_2$  and  $\text{Cp}_2\text{TiClMe}$  with MAO. These intermediates displayed relatively sharp Ti–Me and Cp peaks in the range typical for cationic species and were tentatively assigned to ion pairs  $[\text{Cp}_2\text{TiMe}]^+ [\text{Me-MAO}]^-$  and  $[\text{Cp}_2\text{TiMe}]^+ [\text{Cl-MAO}]^-$  [19]. Further studies are needed for more precise identification of cationic intermediates formed in  $\text{Cp}^*\text{TiMe}_3/\text{MAO}$  and  $\text{Cp}_2\text{TiMe}_2/\text{MAO}$  systems.

#### 3.4. EPR monitoring of Ti(III) species in $\text{Cp}^*\text{TiCl}_3/\text{MAO}$ system in toluene

Upon interaction of  $\text{Cp}^*\text{TiCl}_3$  with MAO at room temperature, formation of paramagnetic Ti(III) complexes was detected by EPR (Fig. 5). At high Al/Ti ratios (ca. 700), an isotropic signal with  $g = 1.970$  is observed. The concentration of Ti(III) species exhibiting this signal reaches 10% of total titanium content 40 min after mixing  $\text{Cp}^*\text{TiCl}_3$  with MAO at room temperature (Fig. 5(d–f)). At low Al/Ti ratio (Al/Ti = 35), mainly EPR signal ( $g = 1.970$ ) is observed 0–1 h after sample preparation, whereas further, the doublet signal at  $g = 1.992$  with hyperfine structure ( $a = 20 \pm 1\text{ G}$ ) increases monotonically, and after 10 h the Ti(III) concentration amounts up to 1% of total titanium (Fig. 5(a–c)). The observed increase of the concentration of Ti(III) in  $\text{Cp}^*\text{TiCl}_3/\text{MAO}$  system with the increase of Al/Ti ratio is consistent with the results reported for  $\text{CpTiCl}_3/\text{MAO}$  system in the Ref. [20]. A doublet signal with hyperfine splitting of  $20 \pm 1\text{ G}$  was previously observed in a  $\text{Cp}^*\text{Ti}(\text{CH}_2\text{C}_6\text{H}_5)_3/\text{B}(\text{C}_6\text{F}_5)_3$  system in chlorobenzene [21], but was not assigned to a particular Ti(III) complex. According to the literature, the g-factor of 1.989–1.994 is typical for hydrido-Ti(III) species in  $\text{Cp}'\text{TiX}_3/\text{MAO}$ ,  $\text{Cp}' = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5, \text{X} = \text{Cl, OR}$  [22,23] and  $\text{Cp}^*\text{TiMe}_3/\text{B}(\text{C}_6\text{F}_5)_3$  [10] systems, whereas the observed value of splitting (20 G) is unexpectedly high with respect to the values  $a^{\text{H}} = 7.0\text{--}8.4\text{ G}$  reported

for hydrido-Ti(III) species [10,22,23]. Cp\*TiCl<sub>3</sub>/MAO system is active towards polymerization of styrene only at high Al/Ti ratios. Thus, a mononuclear Ti(III) species (ca. 10% of total Ti content) exhibiting a singlet at  $g = 1.970$  is observed in the reaction solution in conditions close to real polymerization. Further, it will be interesting to correlate the intensities of NMR peaks of **2** and the EPR signal at  $g = 1.970$  with polymerization activity of Cp\*TiCl<sub>3</sub>/MAO system in order to elucidate the role of Ti(IV) and Ti(III) species in syndiospecific polymerization of styrene.

#### 4. Conclusions

By means of <sup>13</sup>C and <sup>1</sup>H-NMR spectroscopy, Ti(IV) species formed upon activation of Cp\*TiMe<sub>3</sub> and Cp\*TiCl<sub>3</sub> with MAO were characterized for the first time. They are: Cp\*TiMeCl<sub>2</sub>, Cp\*TiMe<sub>2</sub>Cl and Cp\*Me<sub>2</sub>Ti<sup>+</sup> ← Me<sup>-</sup>–Al≡(MAO) (**2**). In conditions close to practical polymerization (high Al/Ti ratios) mainly complex **2** is present in Cp\*TiCl<sub>3</sub>/MAO system. Concentration of EPR active Ti(III) species in Cp\*TiCl<sub>3</sub>/MAO system at Al/Ti ratio of 700 reaches 10% of total titanium content. Further studies are needed to elucidate a particular role of Ti(III) and Ti(IV) species in styrene polymerization.

#### 5. Supplementary material

The material is available from the author on request.

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