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Synthesis, characterization and catalytic activity of the complex titanium bis(dimethylmalonate)–bis(diethylamido) in the polymerization of propylene

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Abstract

In this account we present the synthesis, characterization and catalytic activity in the polymerization of propylene of a bis(dimethyl malonate) titanium bis(diethylamine) complex (**1**). The complex exhibits in solution a dynamical isomerization following an internal Bailar twist. The activation of complex **1** was obtained by its reaction with methylalumoxane (MAO). The activated complex in solution shows a different dynamic process involving an equilibrium between a monodentate η^1 and bidentate η^2 binding of the dimethylmalonate ligand to the metal center. This equilibrium is responsible for the formation of, at least, two active species for the polymerization reaction bearing major symmetry differences. The monodentate coordination (opened form) of the ligand was found to be the major form of the active species of the complex when activated with MAO, most probably due to a strong interaction of the oxygen atoms in the ligand with the strong Lewis acid co-catalyst. The active species in the polymerization were studied by NMR and ESR spectroscopies. The resulting polypropylene showed elastomeric properties with low tacticites.
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1. Introduction

Since the pioneering work of Ziegler and Natta showing the catalytic activities of systems such as $TiCl_4/AlClEt_2$ for the formation of high-density polyethylene [1] or polypropylene [2,3], the field of the polymerization of α-olefins has widened its scope by the discovery of homogeneous "single-site" metallocene-type catalyst systems [4]. For early transition complexes, the metals generally belong to groups 3 or 4. High activities in the polymerization process can be achieved with the use of co-catalysts such as methylalumoxane (MAO) [5], perfluoroarylboranes [6–8], perfluoroarylborates and aluminates [9,10], or mixtures of alkyl aluminum and perfluoroaryl borane and borate [11–13]. The polymers obtained by these systems are generally highly stereoregular and display narrow polydispersities.

The symmetry of the precatalyst shows a major influence on the microstructure of the polymer and by a careful control of this structure, the properties of the obtained polymers can be tailored [4,14,15]. The symmetry of the complex is a structural feature of particular importance, when complexes exhibiting C_2 symmetry usually produce stereoregular isotactic polypropylene [16] and higher symmetries will induce atactic polymers [17].

During the last decade, large amount of research has focused on non-metallocene related complexes such as borrolides [18], phosphinimides [19], and guanidinate type ligands [20] (where the steric and electronic properties of the ligand are similar to cyclopentadienyl) and ligands such as constrained geometry ligands (CGC) [21–29], diamides [30–32], phenoxyimine (FI) [33,34] amidinates [35,36], and β-diketiminates [37–39] which have been successfully used.

Finding new catalytic systems which can promote the formation of elastomeric polyolefins has been a major

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challenge in recent years, these polymers show both the physical properties of elastomers and the processing properties of thermoplastics and therefore are expected to find wide scopes of applications [40–42]. The first example of elastomeric polypropylene was proposed by Natta [43,44] and was described as a succession of alternating atactic–isotactic stereoblocks in the polymer chain. Elastomeric materials are characterized by low degrees of crystallinity and their elastic properties were attributed to two major structural features: A high molecular atactic polymer, where the polymeric chains in the amorphous domains entangle creating a physical network, and crystalline lamellae formed by isotactic domains in the amorphous matrix that give the polymer its elastic properties. Numerous studies have proposed precatalyst–co-catalyst systems for the formation of high molecular atactic polymers [45–50], binary mixtures of compatibilized isotactic–atactic polypropylene [51], polypropylene with isotactic–atactic microstuctural blocks [52–54], isotactic polypropylene with stereoerror sequences [55,56] producing in all these systems elastomeric polypropylene.

Recently, our group have reported the use of benzamidinate complexes for the catalytic polymerization of α-olefins. It was shown that these complexes, in the presence of an appropriate activator (MAO or $B(C_6F_5)_3$), produce a highly active catalyst [57] for the polymerization of propylene and produce elastomeric polymers. These results have raised the question of the potential use of other bulky heteroallylic octahedral C_2 group 4 complexes. Inexpensive racemic bis-acetylacetonate titanium and zirconium complexes were also successfully presented in our laboratory for the polymerization of propylene [58,59]. By an appropriate choice of the metal and the solvent, the properties of the polymer could be tailored, allowing the formation of either elastomeric or highly isotactic polypropylene. The steric and electronic properties of the ligands can be conceptually easily modified by the choice of a β-diesterate backbone instead of the β-diketonate. We therefore expected to further tailor the properties of the polymers obtained by using a simple modification in the structure of the complex.

In this paper we report the synthesis, characterization and solid state structure of a simple non-metallocene racemic octahedral complex based on the dimethyl malonate ligand. We present as well the formation of the cationic species of the complex when activated by MAO and its catalytic activity in the polymerization of propylene. The electronic properties of the ancillary ligand shows a strong influence on the polypropylene obtained as compared to the similar β-diketonate complex.

2. Experimental

All manipulations of air sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flamed Schlenk-type glassware on a dual-manifold Schlenk line, or interfaced to a high-vacuum (10^{-5} Torr) line, or in a nitrogen-filled Vacuum Atmospheres glovebox with a medium-capacity recirculator (1–2 ppm of O_2). Argon and nitrogen gases were purified by passage through a MnO oxygen-removal column and a Davison 4 Å molecular sieve column. Ether solvents were distilled under nitrogen from potassium benzophenone ketyl. Hydrocarbon solvents were distilled under nitrogen from Na/K alloy. All solvents for vacuum-line manipulations were stored in vacuo over Na/K alloy in resealable bulbs or freshly distilled prior to use.

NMR spectra were recorded on a Bruker Avance 300 spectrometer and a Bruker Avance 500 spectrometer. Chemical shifts for ^{1}H NMR and ^{13}C NMR spectra are referenced to the internal solvent resonance and reported relative to tetramethylsilane.

Molecular weight determinations of the polymers were measured on a Waters Alliance 2000 GPC instrument using 1,2,4-trichlorobenzene as a solvent at 140 °C. Polystyrene standards were used for the standard calibration curve of the GPC.

ESR spectra were recorded on a Bruker EMX-10/12 X-band ($v = 9.4$ GHz) digital ESR spectrometer equipped with Bruker N_2-temperature controller. All spectra were recorded at microwave power 6.4 mW, 100 kHz magnetic field modulation of 1.0 G amplitude. Digital field resolution was 2048 points per spectrum, allowing all hyperfine splitting to be measured directly with an accuracy better than 0.1 G. Spectra processing and simulation were performed with Bruker WIN-EPR and SimFonia Software.

2.1. Crystal structure determination – general procedure

Single crystals immersed in Paraton-N oil were quickly fished with a glass rod and mounted on a KappaCCD diffractometer under a cold stream of nitrogen at 230 K. Data collection was carried out with monochromatized Mo Kα radiation using omega and phi scans to cover the Ewald sphere [60]. Accurate cell parameters were obtained with complete collections of intensities and these were corrected in the usual way [61,62]. The structures were solved by direct methods and completed using successive Fourier difference maps [63]. Refinements were performed anisotropically with respect to the nonhydrogen atoms [64,65]. Hydrogens were placed at calculated positions and refined using the riding model until convergence was reached.

2.2. Synthesis of Ti(NEt₂)₄

Ti(NEt₂)₄ was prepared by a modification of known procedures of Bradley [66] and Petersen [67]. n-BuLi (90 ml, 1.6 M in hexane, 0.144 mol) was syringed into a solution of freshly distilled NHEt₂ (distilled over BaO under reduced pressure; 15 ml, 144 mmol) in 19 ml dry toluene. The solution was stirred overnight then 20 ml of dry toluene were added. TiCl₄ · 2THF (12.0 g, 36 mmol) (which was prepared according to a known procedure [68]) was added in portions affording a brown solution, which was

refluxed overnight. A white suspension could then be observed. The product was distilled from the bulk at low pressure (10^{-3} Torr) with constant heating of the distillation apparatus with a high temperature air-blower (300 °C). The distilled fraction was collected in a vessel cooled with liquid nitrogen. The total yield of the reaction was 72.2% (8.47 g, 26 mmol).

^{1}H NMR: [benzene-d_6, 293 K, δ]: 3.58 (q, 2H, $^2J_{HH}$ = 7.0 Hz, NCH$_2$CH$_3$) 1.11 (t, 3H, $^2J_{HH}$ = 7.0 Hz, NCH$_2$CH$_3$). ^{13}C NMR: [benzene-d_6, 293 K, δ]: 45.0 (NCH$_2$CH$_3$), 15.2 (NCH$_2$CH$_3$).

2.3. Synthesis of complex 1

Ti(NEt$_2$)$_4$ (1.29 g, 3.8 mmol) and dimethyl malonate (1.01 g, 7.7 mmol) were added in the glovebox to a frit containing 14 ml of dry hexane. The solution was stirred for 96 h at room temperature affording a brown-reddish solution. The solution was filtered to remove insoluble impurities and half of the hexane evaporated. The temperature was gradually lowered to −10 °C and crystals of the product were obtained after 48 h. The crystals were isolated by filtration and the solvent was vacuum removed. The total yield of the reaction was 57.0% (0.98 g, 2.2 mmol).

^{1}H NMR: [THF-d_8, 294 K, δ]: 4.36 (s, 2H, methine), 3.82 (m, 4H NCH$_2$CH$_3$), 3.80 (m, 4H, NCH$_2$CH$_3$), 3.74 (s, 6H, OCH$_3$), 3.44 (s, 6H, OCH$_3$), 1.03 (dd, 12H, $^3J_{HH}$, 7.0 Hz, NCH$_2$CH$_3$). ^{13}C NMR: [THF-d_8, 294 K, δ]: 175.7 (OCO), 175.5 (OCO), 68.0 (methine), 52.2 (OCH$_3$), 51.2 (OCH$_3$), 49.1 (NCH$_2$CH$_3$), 14.6 (NCH$_2$CH$_3$).

2.4. Polymerization procedure

The polypropylene samples were prepared in a stainless steel reactor equipped with a magnetic stirrer. The reactor was charged with 4 mg (8.8×10^{-3} mmol) of complex 1 and with the required amount of solvent and co-catalyst. The mixture was stirred for 5 min. Purified propylene gas was then condensed in excess (35 ml) into the reactor vessel. The polymerization was conducted with strong stirring for the required reaction time and at the required temperature.

The polymerization was quenched by opening the reaction vessel in a hood and adding 30 ml of a 5:1 H$_2$O:acetylacetone solution. The solution was decanted and the polymer was washed with three 30 ml portions of acetone. The polymer samples were vacuum-dried at 50 °C.

2.5. Isomerization procedure

The isomerization reaction of allyl benzene was performed in a J-Young type NMR tube. Complex 1 (4 mg, 8.8×10^{-3} mmol), a molar ratio of 50:1 of MAO and about 0.01 ml (7.5×10^{-2} mmol) of allylbenzene were transferred into an NMR tube in a glovebox. Benzene-d_6 was vacuum transferred into the tube and the solution was allowed to react for the desired time at room temperature. The reac-

tion was followed by NMR spectroscopy and the products were compared to those in the literature [69].

2.6. Estimation of the entropy of activation

The estimation of the entropy of activation for the dynamic processes taking place in complex 1 was calculated according to the ^{1}H NMR line shape analysis. The approximation used for the rate constant is $k = \pi(W - W_o)$, where W_o = width of signal (in hertz) at half height at the slow rate limit, W = width of signal (in hertz) at half height at a given temperature. The entropy of activation was derived from Eyring's equation

$$\ln(k/T) = \frac{-\Delta H^{\ddagger}}{RT} + \ln\frac{k_B}{h} + \frac{\Delta H^{\ddagger}}{R},$$

where k = reaction rate, T = temperature (K), $\Delta H^{\ddagger}$ = enthalpy of activation (J/mol), R = gas constant (J/mol K), k_B = Bolzmann constant, h = Planck's constant, $\Delta S^{\ddagger}$ = entropy of activation (J/mol K).

3. Results

3.1. Synthesis and characterization of complex 1

The reaction of 2 equiv of dimethyl malonate with the homoleptic titanium tetrakis diethyl amine in hexane at room temperature afforded the desired complex 1.

$$\text{Ti(NEt}_2)_4 + 2\,\text{CH}_2(\text{COOCH}_3)_2 \xrightarrow[\text{96 hours}]{\text{hexane}}$$

(1)

1

+ 2 HNEt$_2$
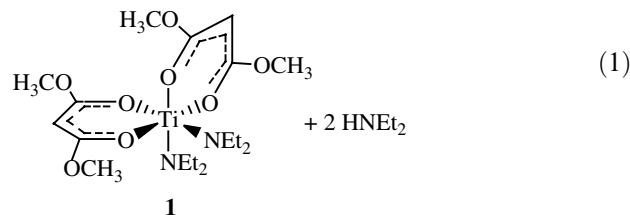
The titanium complex was successfully crystallized from a concentrated cold solution of hexane (−10 °C). Suitable single crystals were characterized by X-ray diffraction, ^{13}C NMR and ^{1}H NMR spectroscopy. The cell unit contains three similar and independent molecules. The ORTEP plot of the complex 1 is shown in Fig. 1, representative bond lengths and angles are presented in Table 1 and crystallographic data with structure refinement details are listed in Table 2. The crystalline structure of complex 1 shows an octahedral structure with a slightly distorted C_2 symmetry. The complex displays two cis-diethyl amido ligands (N(2A)–Ti(1)–N(1A) = 96.1°) and exhibits normal Ti–N bonds (Ti(1)–N(2A) = 1.902(5) Å and Ti(1)–N(1A) = 1.919(5) Å) corresponding to the formation of an anionic ligand as can be observed in similar Ti(IV) bis-amido complexes [70]. Interestingly the C–N–C and Ti–N–C angles around the nitrogen atoms indicate that these atoms display some sp$_2$ character, thus implying a slight multiplicity
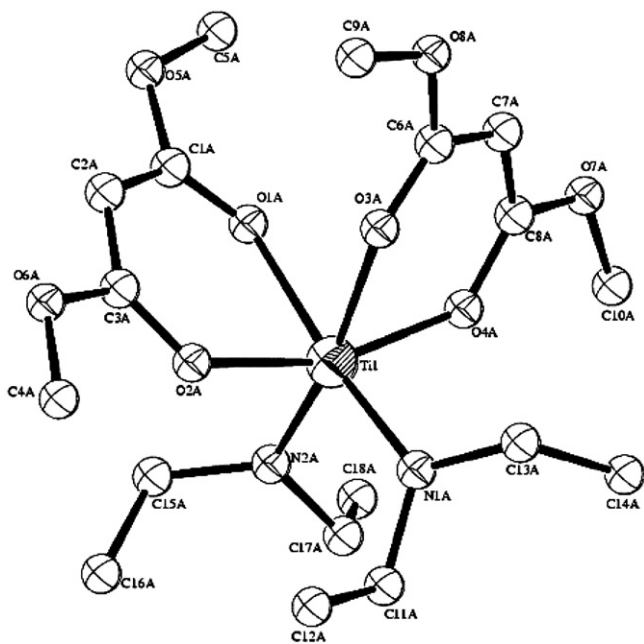
Fig. 1. ORTEP diagram (50% probability ellipsoid) of the titanium complex **1**. Hydrogens were omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complex **1**

Ti(1)–N(2A)	1.902(5)
Ti(1)–N(1A)	1.919(5)
Ti(1)–O(4A)	2.012(4)
Ti(1)–O(2A)	2.025(4)
Ti(1)–O(3A)	2.124(4)
Ti(1)–O(1A)	2.153(4)
N(2A)–Ti(1)–N(1A)	96.1(2)
Ti(1)–N(2A)–C(15)	125.6(4)
Ti(1)–N(2A)–C(17)	121.0(4)
C(15)–N(2A)–C(17)	113.4(5)
O(4A)–Ti(1)–O(2A)	161.94(18)
O(2A)–Ti(1)–O(1A)	82.46(17)

Table 2
Crystal data collection for complex **1**

Identification code	Complex **1**
Empirical formula	$C_{54}H_{102}N_6O_{24}Ti_3$
Formula weight	1363.12
T (K)	230(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$\bar{P}$
Unit cell dimensions	
a (Å)	11.458(2)
b (Å)	12.816(3)
c (Å)	24.525(5)
α (°)	90.91(2)
β (°)	99.99(3)
γ (°)	96.29(3)
Volume (Å^3)	3523.2(13)
Z	2
D_{calc} (mg/m^3)	1.285
Absorption coefficient (mm^{-1})	0.407
$F(000)$	1452
Crystal size (mm)	$0.27 \times 0.24 \times 0.03$
θ Range for data collection (°)	1.78 to 25.05
Limiting indices	$0 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-29 \leqslant l \leqslant 28$
Reflections collected/unique (R_{int})	29204 / 11989 (0.0970)
Completeness to θ	96.0% ($\theta = 25.05$)
Absorption correction	none
Refinement method	full-matrix least-squares on F^2
Data/restraints/parameters	11989/0/784
Goodness-of-fit on F^2	0.768
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0542$, $wR_2 = 0.1177$
R Indices (all data)	$R_1 = 0.2289$, $wR_2 = 0.1768$
Largest differences in peak and hole (e Å^{-3})	0.336 and -0.261

of the Ti–N bond. The two dimethyl malonate ligands are also positioned in *cis*-like structure where two oxygen are *trans* (O(4A)–Ti(1)–O(2A) = 161.94(18)°) one to another in the apical position. The oxygen bonds *trans* to the nitrogen atoms display longer bond lengths (Ti(1)–O(3A) = 2.124(4) Å and Ti(1)–O(1A) = 2.153(4) Å) as compared to the bond lengths of the two *trans* oxygen (Ti(1)–O(4A) = 2.012(4) Å and Ti(1)–O(2A) = 2.025(4) Å) as expected from the corresponding *trans* effect. Similar *trans* bond lengths have been observed for a diacetate titanium tetrachloride complex [71].

The proton NMR spectrum of complex **1** displayed signals that were not expected from the X-ray structure. Upon varying the temperature, two dynamic processes in complex **1** were observed. The dynamic behavior was studied by variable temperature following the proton in toluene-d_8. The spectra were measured in the temperature range from 253 to 355 K and representative temperatures are presented in Fig. 2. The analysis of the spectra at various temperatures indicates the presence of two different fluxional processes. The first process involves the diethylamido ligand (see **A** in Fig. 2). At temperatures lower than 330 K, the methylene hydrogens are differentiated and two multiplets are observed. At a temperature of approximately 330 K the signals coalesce and one broad signal is observed. At temperatures higher than 355 K this signal splits into a quartet, corresponding to the normal coupling to the methyl group of the diethylamine ligand. This dynamic process is produced by the internal rotation of the diethylamine ligand. The rotation rate of the methylene moiety is expected to be lowered by a slight agostic interaction with the metal center and by the partial multiplicity of the Ti–N bond (as observed in the crystal structure of complex **1**). Long enough residence time leading to the differentiation of the hydrogen atoms within a methylene moiety can already be observed at temperatures lower than 330 K. At high temperatures, the rotation is faster than the time-scale of the NMR experiment, thus leading to a normal splitting pattern for an ethyl group. The methyl groups display lower energy barrier for the rotation, therefore no major differentiation between the methyl hydrogens is observed. Recently, a similar dynamical process for a (diethylamido)(diphosphineamido) titanium complex has been reported [54].
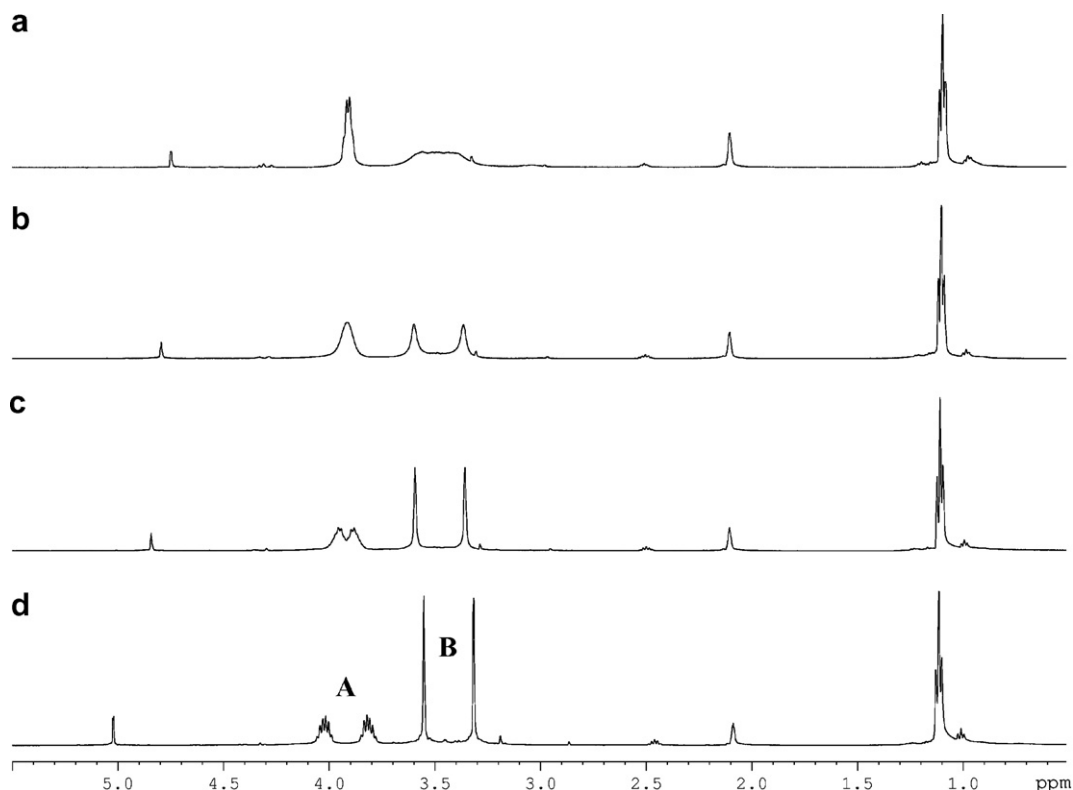
Fig. 2. Variable temperature proton-NMR spectrum of complex **1** at (a) 355 K, (b) 333 K, (c) 314 K, (d) 253 K.

A second interesting dynamic process taking place in the complex involves two signals corresponding to the methoxy groups in the dimethylmalonate ligand (**B** in Fig. 2). At temperatures lower than 355 K, two singlets corresponding to the OCH_3 of the dimethylmalonate ligand are exhibited, which coalesces at 355 K. In the X-ray of the complex, a clear differentiation between the methoxy groups can be observed as to the atom holding the *trans* position in the complex (nitrogen (N1A for O5A–C5A) or oxygen (O4A for O6A–C6A) in Fig. 1). The dynamic behavior of **1** with temperature can be instigated either by an internal twist, known as Bailar twist, which is often encountered in organometallic complexes [72,73] or via the dynamic opening-closing of the dimethylmalonate ligand ($\eta^2 \leftrightarrow \eta^1$) (see Fig. 3). These two processes can be differentiated by the nature of their transition states. A negative $\Delta S^{\ddagger}$ is expected for the Bailar twist (decrease of degrees of freedom due to increase of symmetry – from C_2 to C_{2v}) and a positive value for the entropy of activation ($\Delta S^{\ddagger}$) is expected for the second process (increase of degree of freedom in the opening process). The entropy of activation was calculated with line shape analysis which gives a simple mathematical relationships for rate constants at temperatures where the slow exchange between two equally populated sites takes place [74].

The value for the entropy of activation obtained from an Eyring's analysis is presented in Fig. 4. The value obtained ($\Delta S^{\ddagger} = -56.78$ J/mol) points to an internal Bailar twist as the major pathway responsible for the dynamic process taking place in complex **1**.

Bailar twist mechanism:
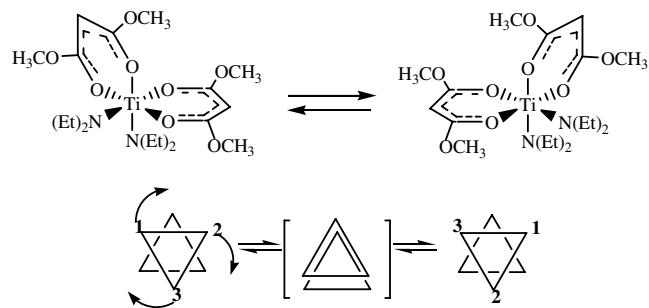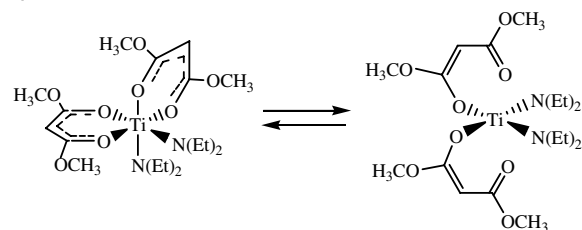

η^1-η^2 equilibrium:

Fig. 3. Two alternatives for the dynamic processes taking place in complex **1**.

3.2. Reaction of complex **1** with MAO

As will be presented below, in all of our polymerization reactions of propylene with complex **1** activated by MAO, an elastomeric polypropylene is the major component
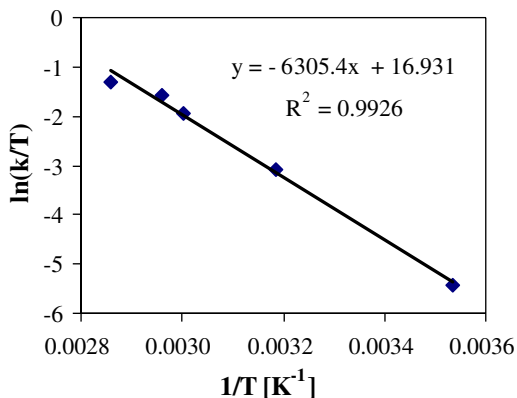
Fig. 4. Eyring's equation for the dynamic process observed in complex **1**.

obtained (>96%) in addition to a small amount (<4%) of a stereoregular isotactic polymer. Although the characterization (X-ray diffraction, ^{1}H NMR, ^{13}C NMR, COSY spectra) of the neutral complex **1** is unambiguous in the solid state and in solutions of toluene and tetrahydrofuran it was very important to understand its activation by MAO and to correlate the new complex/es formation with the type of polymers obtained. Recently, we have shown that when MAO reacts with a diphenylphosphinamido titanium complex two active species are formed. The first complex, exhibiting open ligands where the complex retains a C_2v symmetry, affords the atactic polypropylene, whereas the second form, in which the ligands are chelating to the metal center giving a C_2-symmetry complex, is responsible for the stereoregular polymer [16]. A similar feature was proposed for the bisacetylacetonate titanium complex [75,76]. In order to check the possibility that such an equilibrium exists also in complex **1** and that various active sites can be observed in the presence of the MAO co-catalyst, we

have studied solutions of complex **1** with different amounts of MAO following the reaction by NMR spectroscopy. The reaction mixture of complex **1** with MAO (cat:-MAO = 1:50) in THF-d_8 dissolved thoroughly and produced a homogeneous yellow-brown solution.

The reaction taking place can be divided into three stages that are observed in both proton and carbon NMR spectroscopy. In the first step, a coordination of the Lewis acid aluminum moieties of MAO to the nitrogen and oxygen atom in the complex induces slight changes in the spectrum producing probably complex **2** (Fig. 5). The signals corresponding to the diethylamido ligands in complex **1** (^{13}C: 14.6, 49.1 ppm; ^{1}H: 1.03, 3.81 ppm) were shifted slightly upfield in the carbon (14.3 and 48.9 ppm) and downfield in the proton (1.10 ppm (triplet) and 4.08 ppm (broad)) spectra. Regarding the methoxy signals, prior to the addition of MAO, two signals were observed in the ^{1}H NMR spectrum, at 3.44 and 3.74 ppm correlating to signals in the ^{13}C NMR spectrum at 51.24 and 52.20 ppm, respectively. These signals moved downfield upon addition of MAO and two new signals were observed at 3.72 and 3.78 ppm correlating to the carbon signals at 53.3 and 53.7 ppm, respectively. The new signals show a similar pattern to the neutral complex and imply that the complex must still be found at this stage in the closed form. The differentiation between the methoxy groups derives from the different *trans* positions of these groups in the complex (see **2** in Fig. 5). In addition, the methine signals of the carbon α to the carbonyl groups (68.0 ppm) and of its hydrogen (4.36 ppm) in the complex were replaced by new signals (70.0 ppm and broad 4.63 ppm, respectively) upon addition of MAO.

The second step of the reaction, which happens after about 3 h is the abstraction of an amido ligand and its replacement by a methyl group from MAO forming com-
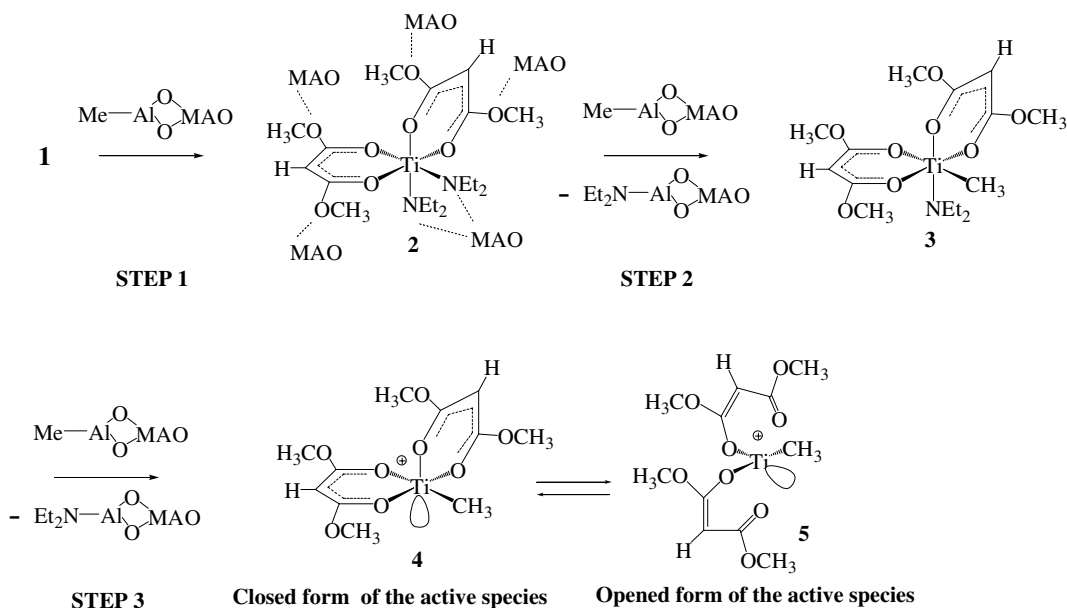

Fig. 5. Plausible reaction path for the reaction of complex **1** with MAO and subsequent formation of putative active species in the polymerization of propylene.

plex **3** (Fig. 5). A second set of signals corresponding to a new diethylamido moiety were observed both in the carbon (15.0 and 44.4 ppm) and the proton (1.19 (triplet) and 3.91 ppm (quartet)) spectra. In addition, two new signals for OCH_3 groups appear at 3.76 and 3.78 ppm (the latter overlapping the similar signal in complex **2**). These results allow to imply that in this step, the complex may be as well found in its closed form. Moreover, a new signal corresponding to a Ti–Me signal is observed and characterized at 1.00 ppm. Interestingly, a similar Ti–Me signal has been recently characterized for a labeled $L_2TiCl^{13}CH_3$ (L = *N*-3-*tert*-butylsalicylidene-2,3,4,5,6-pentafluoroanilinate) from the reaction of L_2TiCl_2 with MAO [77]. In parallel to the formation of this complex **3**, a triplet emerged at 1.10 ppm and a quartet at 2.86 ppm in the proton NMR spectrum (the correlating signals in carbon NMR spectrum are at 12.4 and 40.5 ppm, respectively) corresponding to a Al–NEt_2 moiety confirming the abstraction of one amido ligand from the complex [54].

The third step of the activation involves the abstraction of the second diethyl amido ligand and the putative formation of a cationic methyl complex forming presumably complexes **4** and **5** (Fig. 5). Two broad signals corresponding to the methine protons (4.60 ppm in ^{1}H NMR spectrum correlated to a broad signal 74.3 ppm in ^{13}C spectra) and to the OCH_3 (3.82 ppm in ^{1}H NMR spectrum correlated to broad signal at 53.6 ppm in ^{13}C spectra) are displayed. It is important to note that the signal of the Ti–CH_3 group disappeared and the formation of the cationic Ti–Me signal is not observed probably due to overlap of signals. Ti–CH_3 signals in cationic complexes have been reported especially with boranes and borates as activators, and the reported values are in the range of 0.5–1.5 ppm for proton NMR, which in our case are overlapping with MAO signals [8]. It is important to point out the drastic decrease (disappearance) of the signals corresponding to the putative neutral titanium-amido complexes (**2** and **3**) accompanied by a constant increase of the Al–NEt_2 and of the new methine and methoxy signals as a function of time. The broad signals observed for the cationic complex indicates an equilibrium process, which we propose to be between the opened and the closed form of the dimethylmalonate ligands (vide infra) (**4** and **5** in Fig. 5).

We have allowed the reaction to stir for 7 days and no changes were observed in the ^{1}H and ^{13}C spectra. In order to validate the assumption that the complexes we observe in the presence of MAO are indeed mainly in the cationic form and that both the amido ligands have been abstracted, we added a supplementary amount of MAO (cat:MAO = 1:100) to the solution and again, no further changes in the signals corresponding to the methyl, methylene and methoxy region of the spectra were observed. In similar experiments we studied the reactions of complex **1** and MAO directly at a 1:100 and 1:200 ratios. We could observe a faster formation of the signals we attributed to the Et_2NAl moiety and to the active species **4** and **5**.

In order to provide evidence of our claim regarding the dynamic nature of the active species, we have also performed a variable temperature experiment of the active species. A THF solution containing complex **1** and MAO at a 1:100 ratio was studied by proton NMR spectroscopy in a range of temperatures from 298 K to 240 K. This experiment showed that upon cooling the broad signal (3.82 ppm) corresponding to the OCH_3 moiety in the active species split into two signals (coalescence observed at 280 K). In parallel, we observe the splitting of the broad signal at 4.60 ppm corresponding to the methine hydrogen. A large positive value for the entropy of activation ($\Delta S^{\ddagger} = 144.2$ J/mol K) for the dynamic process at the methoxy signal was calculated by line shape analysis (Fig. 6). This results indicates that the dynamic equilibrium undergoes through a less ordered transition state as expected for an equilibrium between the closed (**4**) and opened (**5**) forms of the complex. It is important to note that the polymerization reaction takes place at higher catalyst:MAO ratio than the ratio used in the variable temperature experiment. It is most likely that the opened form of the complex is greatly stabilized in the presence of higher amount of MAO, leaving it as the main form present under the polymerization conditions.

In order to exclude MAO-induced ligand abstraction we have reacted dimethylmalonate with MAO (ligand:MAO ratio = 1:10, respectively). The ^{1}H and ^{13}C NMR signals corresponding to the free dimethylmalonate disappeared upon addition of MAO and the obtained new signals were inconsistent with the ones we observed in the reaction of complex **1** with MAO, thus excluding the ligand abstraction and further catalysis of propylene polymerization by an aluminium dimethylmalonate moiety.

The addition of propylene at atmospheric pressure at **1**:MAO ratios of 1:50 and 1:100 did neither induce an insertion of the propylene in the Ti–CH_3 bond nor polymerization. However, when a similar reaction was undertaken at a **1**:MAO ratio of 1:200, all the propylene reacted thoroughly. The reaction at atmospheric pressure is much slower than at high pressure of propylene where
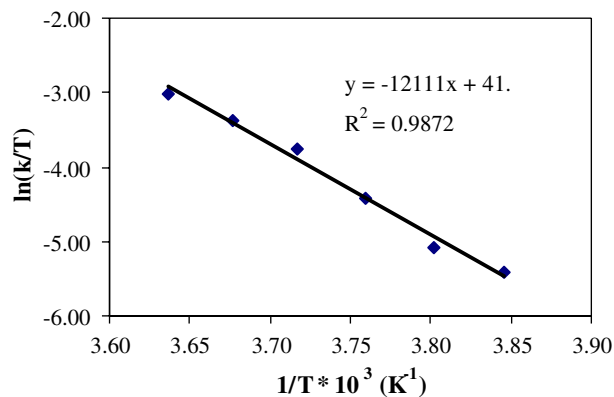

Fig. 6. Eyring's plot for the dynamic process observed in the active species of complex **1** with MAO.

the polymerization takes place with good activity (see Table 3). Moreover, the active species detected by NMR spectroscopy at lower MAO ratios are able to polymerize propylene only at high pressure.

In order to establish if the two proposed forms of the cationic complex **1** are responsible for the polymerization, we have looked for the presence of reduced forms (Ti(III)) of the complex by monitoring the reaction of the complex with the co-catalyst at a **1**:MAO ratio of 1:200 in toluene-d_8. The ESR spectra of the paramagnetic intermediates were measured at room temperature. When complex **1** was activated by MAO, the ESR spectrum at 290 K (Fig. 7a) showed a superposition of at least three (**Ti-1**, **Ti-2**, **Ti-3**) asymmetrical signals with up field-shifted g-factors (compared to organic radicals) at $g = 1.991–1.972$. Such low values of g-factor are typically exhibited by paramagnetic Ti^{3+} complexes [78–80]. An additional signal with a hyperfine structure [a (3H) = 3.43 G, g = 2.0017] was observed. The observed splitting pattern of this signal is clearly corresponding to a Ti–Me moiety as previously reported for Cp_2Ti^{3+}–Me [a (3H) = 4.4 G] [81] (see Fig. 7a and b). Upon addition of an aliquot of propylene, this Ti^{3+}–Me signal disappeared and the intensity of **Ti-1** increased (Fig. 7c). Further addition of propylene aliquot leads to a decrease in intensity of **Ti-2** (Fig. 7d and e). Signals **Ti-1** (line width ∼10 G) and **Ti-3** (line width ∼13 G) were found to have a weak anisotropy of the g-factor in frozen glass (at 150 K) in contrast with typical Ti^{3+} paramagnetic complexes [82–85]. This may be the result of an agglomeration of various titanium non-catalytic reactive species and spin exchange processes within the agglomerate [82,86].

We have excluded the existence of radical polymerization by these paramagnetic species by performing the polymerization in the presence of a solution of fullerene (C_{60}) in toluene (2 mg fullerene in 1 ml toluene). A large amount of weakly conjugated bonds in fullerene makes it an excellent radical trapping agent [87–92]. Furthermore, fullerene has been used successfully as inhibitor for radical polymeriza-

tion processes [82,93]. The analysis of the polypropylene obtained (see entry 11 in Table 3), confirm that the presence of the radical trap does not influence drastically the nature of the polymer (% mmmm, MWD, M_n). Moreover, the ^{13}C NMR spectrum of the polymer obtained does not display typical branching caused by the presence of radicals on the polymeric chain [94]. We can therefore conclude that if the paramagnetic species are active they play a minor role in the polymerization reaction.

3.3. Polymerization of propylene

The formulation of the active complexes, **4** and **5**, is expected to induce either one polymeric fraction or two polymeric fractions if a rapid or a slow equilibrium between the complexes is operative, respectively. Since we have obtained a minor (4%) isotactic fraction, and a major elastomeric fraction (96%), it is apparent that a slow equilibrium between the complexes is operative. In addition we can infer that complex **4** is responsible for the isotactic fraction (vide infra) and complex **5** is responsible for the elastomeric polymers similar as was found for the phosphinamide complexes [54]. The proposed complex **5** bears a methylester functionality which is not bound to the titanium atom. The oxygen atoms of this functionality coordinated to the aluminium atoms of MAO give rise to a fluxional active species with pseudo C_{2v} symmetry at the metal. The polymers obtained in the presence of this complex are therefore expected to display atactic properties. In contrast, the closed conformation of the proposed complex **4** with C_2 symmetry is expected to behave as a "single site" catalyst leading to the formation of stereoregular polypropylene. In order to characterize the catalytic activity of complex **1** in the polymerization of propylene, a series of polymerizations under different conditions were performed. The effects of temperature, time, catalyst:MAO ratios, and solvent on the nature of the polymers obtained are summarized in Table 3. The carbon NMR spectra of all the polymer samples show signals of considerable intensi-

Table 3
Data for the polymerization of propylene with complex **1** – variation of polymerization parameters

Entry	**1**:MAO[a]	Time (h)	T (°C)	Activity[b]	Mmmm (%)	M_n	MW	MWD
1	1:750	1	25	72000	7.8	20000	69000	3.47
2	1:750	2	25	93000	7.9	21000	64000	3.27
3	1:750	4	25	96000	7.9	25000	79000	3.24
4	1:750	18	25	54000	7.5	27000	78000	2.93
5	1:200	1	25	46000	12.4	15000	38000	2.64
6	1:400	1	25	94000	11.6	29000	58000	2.30
7	1:1000	1	25	52000	8.0	17000	49000	2.91
8	1:750	1	0	18000	10.8	52000	263000	5.16
9	1:750	1	50	277000	6.7	36000	109000	3.06
10[c]	1:750	1	25	391000	5.5	13000	39000	3.01
11[d]	1:750	1	25	61000	8.7	29000	92000	3.17

[a] 4 mg catalyst.
[b] In units of (g polymer) (mol cat.)$^{-1}$ (h)$^{-1}$.
[c] Polymerization performed in the absence of solvent.
[d] Polymerization performed in the presence of 2.5 ml of a fullerene solution (2 mg fullerene/1 ml toluene).
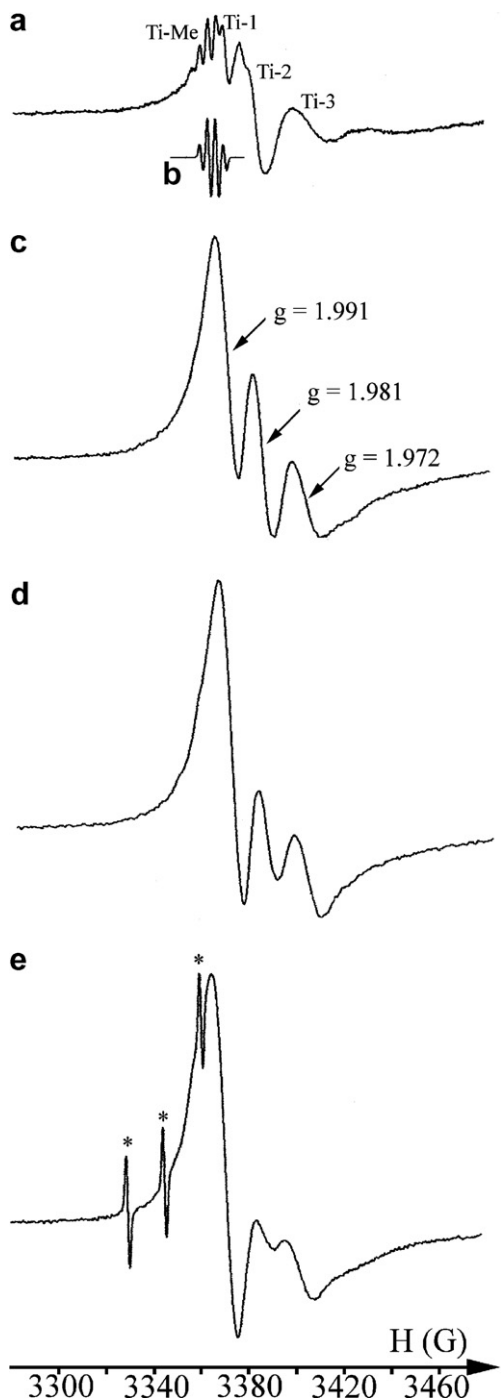
Fig. 7. ESR monitoring of complex **1** with MAO and propylene: (a) ESR spectrum of complex **1** activated by MAO in toluene at room temperature, (b) simulated ESR spectrum of paramagnetic species containing Ti–Me fragment (c) addition of one aliquot of propylene (roughly 1 mmol propylene), (d) addition of four aliquots of propylene (e) addition of seven aliquots of propylene (for determination g-factors ESR spectrum recorded with TEMPO marked by ∗, g = 2.0059).

ties in the region of 15–18 ppm and 30–45 ppm, which are known to be related to misinsertions of propylene of the "2,1" and "1,3" type (Fig. 8) [95].

The influence of time on the activity of the complex and the polymers properties was studied under constant condi-

tions (compare entries 1–4). The activity of the complex increases with the reaction time reaching a maximum after 4 h. After this optimized amount of time, the activity of the complex dropped presumably due to diffusion problems of the monomer caused by the raising viscosity of the reaction medium [16]. The molecular weight increased in a similar fashion during the first 4 h. After this amount of time only a small increment on the M_n is observed.

The catalyst:MAO ratio influence on the polymers properties was studied by varying the amount of MAO while the concentration of complex **1** was kept constant (compare entries 1 and 5–7). It was found that at a **1**:MAO ratio of 1:400 the catalytic system reached the maximum activity. Larger MAO amounts induced a decrease in the activity presumably via an equilibrium process towards the deactivation of the catalytic system as observed for other catalytic systems [59,96]. A similar trend was observed in the molecular weights of the polymers. A **1**:MAO ratio higher than 1:400 leads to the formation of polymers with reduced molecular weight due to an active participation of MAO in the termination process. We have found that for complex **1** a chain transfer to aluminium is the main active termination process of the polymerization above a catalyst:MAO ratio of 1:400. The presence of only isobutyl end groups in the carbon NMR spectrum of the polymers obtained at these ratios corroborates with the termination pathway [97,98]. Interestingly, a decrease in tacticity was observed with higher amounts of MAO. This result supports the assumption that the opened form of the complex (**5**) is stabilized by the aluminium atoms from the MAO, inducing the production of the atactic polymer.

The effect of temperature on the polymerization was studied at a **1**:MAO ratio of 1:750 (entries 1, 8 and 9), a ratio in which we found that the principal termination process at room temperature is a chain transfer to aluminium. At lower ratios, a competition among several termination mechanisms is observed. At 0 °C low activity of the catalysts induces high polydispersity of the polymer however, the tacticity of the polymer was the highest at this temperature. At the low temperature the lability of the dimethylmalonate ligand is lowered, hence, the closed form of the complex (**4**) is expected to produce a slightly stereoregular polymer. The number average molecular weight (M_n) showed two opposite trends when compared at different temperatures. From 0 to 25 °C the molecular weight decreased then a raise was observed from 25 to 50 °C. This phenomenon is an outcome of the difference in the rates of termination and insertion as a function of temperature for both bimolecular processes (vide infra).

When the polymerization was performed in bulk with no solvent a high polymerization activity was obtained (see entry 10). This result indicates that the monomer can insert faster when no competitive solvent coordination to the metal is present. In addition a lower degree of tacticity and a higher amount of misinsertions were observed for the bulk polymerization. We have previously shown that the dimethyl bisacetylacetonate titanium complex displays
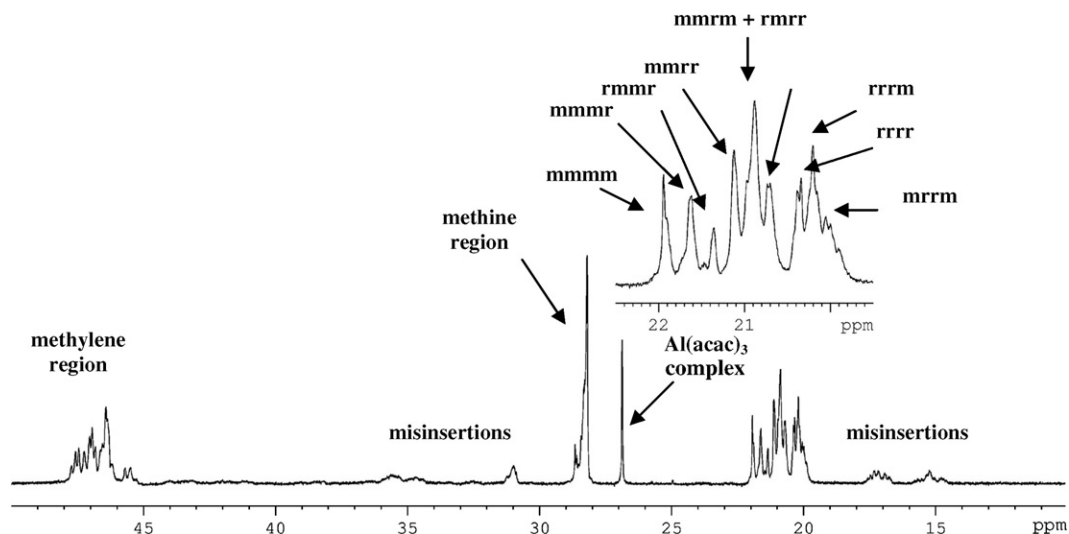
Fig. 8. Typical carbon NMR spectrum of polypropylene prepared with complex **1** and MAO.

lower activities in the presence of polar or coordinating solvents (such as toluene) due to a coordination of the solvent to the free orbital of the cationic metal and stabilization of the active species [99]. This solvent interaction allowed a better discrimination of the monomer enantiofaces and the formation of a more isotactic polymer. When no solvent is present, the active site is more accessible to the monomer. The lack of solvent allows a less sterically hindered approach of the monomer and the formation of more stereoerrors, thus increasing the atactic character of the obtained polymer. The drastic decrease in molecular weight indicates that the bulk polymerization enhance the rate of termination as compared to the rate of insertion.

An interesting trend is to follow the rates of insertion and termination as presented in Eq. (2). The calculated rate values derived from the data in, ($T = 25\,°C$, reaction time = 1 h; **1**:MAO = 1:750) are presented in Table 4 and Fig. 9. We have observed that a decrease in the insertion rate occurs merely after 4 h while a decrease in the termination rate occurs already after 2 h, thus explaining the continuing raise in activity up to a polymerization time of 4 h. The feature is explained by the stronger influence of the viscosity of the medium on the mobility of the large growing polymer chain involved in the termination process (for all termination mechanisms) as compared to the mobility of the small propylene molecule (involved in the insertion rate). The degree of polymerization (DP = number of monomeric units in an average polymer chain at a
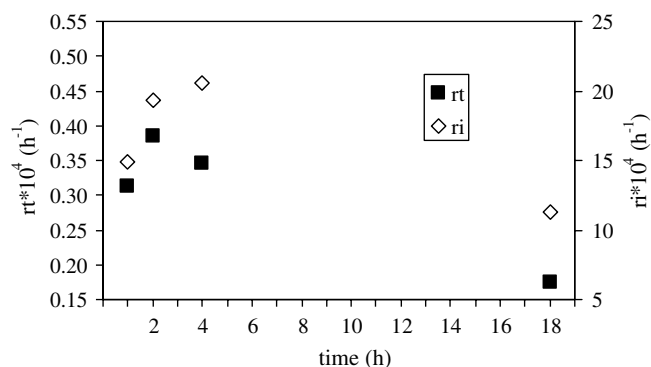

Fig. 9. Insertion and termination rates as function of reaction time.

given reaction time) shows that most of the insertions take place in the first hour of the reaction (476 units), in the second hour only 24 units are added. One hundred and sixty-seven units are added in the next 17 h with an average of about 10 monomeric units per hour.

Eq. 2: Calculated termination and insertion rates

$$r_i = \frac{m/\mathrm{MW}}{t}$$
$$r_t = \frac{m/M_n}{t} \tag{2}$$

r_i = rate of insertion; r_t = rate of termination; M_n = number average molecular weight; m = mass of the polymer (g); MW = molecular weight of propylene = 42 g/mol; t = polymerization time (h).

All the polymers obtained in Table 3 are elastomers and are "quasi-atactic". In order to confirm the existence of at least two active species giving rise to a mixture of polymers, we have performed a fractionation in boiling diethylether of a sample bearing a relatively high degree of tacticity. The resulting polymers were analyzed and the results are presented in Table 5 (entries 11 and 12). The majority of the polymer (96%) was found to be soluble in ether. It

Table 4
Degree of polymerization as a function of time

Reaction time (h)	Degree of polymerization DP = r_i/r_t
1	476
2	500
4	595
18	643

($T = 25\,°C$, reaction time = 1 h; **1**:MAO = 1:750).

Table 5
Data for the fractionalization of entry 6 in boiling diethylether

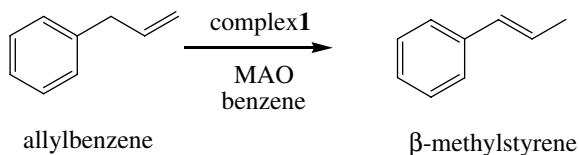| Entry	Solubility in ether	Fraction (%)	Mmmm (%)	M_n	MWD
11	Soluble	96.0	9.7	19 000	2.41
12	Insoluble	4.0	71	373 000	2.13

Fig. 10. Isomerization reaction of allylbenzene in the presence of complex **1** and MAO.

has a low degree of tacticity, relatively high molecular weight, and shows elastomeric properties. The second fraction (4%) is insoluble in ether and it is higher in tacticity (mmmm = 71%) and high molecular weight (M_n = 373 000).

These results corroborate our assumption that two active species are present during the polymerization process. The proposed closed (**4**) and opened (**5**) complexes are in line with the nature of the polymers obtained. The methylester functionality in **5** undergoes a strong interaction with MAO inducing the subsequent formation of a low symmetry complex with fluxional structures. The resulting polypropylene is atactic with relatively low molecular weight. The closed conformation **4** affords a highly stereoregular polymer with a narrow polydispersity that corresponds more to a more "single-site" type catalytic system. The results obtained show that the equilibrium between species **4** and **5** is slow as compared to the insertion rate of the monomer thus giving raise to two fractions.

Besides the misinsertions of the type 2,1 and 3,1, the presence of stereoerrors in the polymer has raised the question of the occurrence of a process competing with the polymerization. We have found that in benzamidinate and acetylacetonate complexes, the polymerization of propylene is accompanied by a competing intramolecular epimerization reaction of the last inserted monomer unit [57]. Two mechanisms for the epimerization have been proposed by Busico [100,101] and by Resconi [102]. In order to learn if our catalytic system induces such an epimerization we have studied the isomerization of allylbenzene in the presence of **1** and MAO to form β-methylstyrene (Fig. 10). The reaction of allylbenzene in benzene-d_6, in the presence of **1**:MAO (1:50) was followed by ^{1}H NMR and ^{13}C NMR spectroscopy yielding 95% β-methyl styrene in 20 h. The results indicate that besides the polymerization, a possible epimerization process is operative inducing the stereoerrors in the polymer and enhancing its atactic character.

3.4. Polymerization in the presence of trityltetra(pentafluorophenyl)borate salt

In an attempt to stabilize the closed form of the active complex **4** and to promote the formation of an isotactic propylene, we have performed the polymerization reaction in the presence of a stochiometric amount of trityl tetra(pentafluorophenyl)borate salt. This conceptual experiment does not take into account the misinsertions (inducing low isotacticity) as observed for example via the epimerization mechanism.

Borate salts are known to activate the polymerization in complexes of the type TiMe₂L₂ (L = ancillary ligand). The expectation was that the borate anion will not interact with the oxygens of the opened ligand in complex **5** as MAO. Although the borate salt did not react with complex **1**, we activated the complex by adding a small amount of MAO (that amount alone with complex **1** does not induce activation) to produce in situ the corresponding titanium dimethyl complex. The three components of the reaction were added simultaneously prior to solvent addition. Interestingly, the polymerization reaction with this mixed system showed higher activity and molecular weights than with MAO alone similar to our recent results obtained with benzamidinate complexes [36]. The small excess amount of MAO used was expected to form besides the dimethyl complex, a smaller fraction of the opened form of the complex (giving rise to the atactic fraction of the polymer) as compared to regular polymerization conditions in the presence of a large amount of MAO. The fractionation in boiling diethylether of the polymer obtained with the borate/MAO system provided a low molecular weight (M_n = 4000) soluble atactic fraction (49.82%; 6.41% mmmm) and a second non-soluble fraction (42.44%) showing a larger tacticity (23.42% mmmm) and higher molecular weight (M_n = 143 000) as compared with the reaction using MAO alone. The low molecular weight of the atactic fraction is in agreement with the low amount of MAO used (compare M_n in entries 5–7 in Table 3) and most probably is the result of a direct activation of complex **1** and stabilization of a small amount of the opened active complex **5** by MAO itself. Interestingly, the same amount of MAO alone with complex **1** did not induce polymers, hence an activation via the boron co-catalysts should be operative. The high molecular weight ether insoluble polymer is different from the insoluble fraction obtained with MAO alone, hence it arises from a different active species, presumably with a boron co-catalyst instead of MAO. These results implicate that the borate alone does not govern the stereoregularity of the polymer and that parameters other than the co-catalyst give the polymer its features [4].

4. Conclusions

We have shown that complex **1** reacts with MAO to give mainly a cationic mono-methyl species as the main active

species for the polymerization of propylene. This complex displays a slow equilibrium between open and closed forms, each of them responsible for a different type of polymer. The closed form of the active complex is responsible for the high molecular weight isotactic polymer, whereas the open form gives the low molecular weight "quasi atactic" elastomeric polymer. The atactic character of this polymer is enhanced by the occurrence of an epimerization process. Ti(III) paramagnetic species were formed upon addition of MAO but these species were found not to have an important role in the polymerization process. The use of trityl tetra(pentafluorophenyl)borate salt activated by a small amount of MAO afforded a smaller atactic fraction than with MAO alone, thus reinforcing our assumption that MAO stabilizes the opened form of the active complex **5**. Moreover the nature of the co-catalyst was found not to be the sole factor conferring the polymer its characteristics.

Acknowledgements

Appendix A. Supplementary material

CCDC 627256 contains the supplementary crystallographic data for complex **1**. These data can be obtained free of charge via htpp://www.ccdc.cam.ac.uk/conts/retrieving. html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +(44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem. 2006.10.031.

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