

Spectroscopic and voltametric studies in titanium tris(pyrazolyl)borate catalysts

Marcelo P. Gil^a, J.H.Z. dos Santos^a, O.L. Casagrande Jr.^{a,*},
Lílian M. T. Simplício^b, Zênis N. da Rocha^b

^a *Laboratory of Molecular Catalysis, Instituto de Química, UFRGS, Av. Bento Gonçalves, 9500 Porto Alegre, RS 91509-900, Brazil*

^b *Instituto de Química da Universidade Federal da Bahia, Campus de Ondina, Salvador 40170-290, Brazil*

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Abstract

The ethylene polymerization using $\text{Tp}^{\text{Ms}*}\text{TiCl}_3$ (**1**) ($\text{Tp}^{\text{Ms}*} = \text{HB}(3\text{-mesitylpyrazolyl})_2(5\text{-mesitylpyrazolyl})^-$) and $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ (**2**) ($\text{Tp}^{\text{Ms}} = \text{HB}(3\text{-mesitylpyrazolyl})_3^-$) was performed in toluene or hexane at 60 °C in the presence of MAO or TiBA/MAO (1:1) as cocatalysts. Higher activities were found for the polymerization reactions carried out in hexane, and using a combination of TiBA/MAO as cocatalysts. Absorciometric measurements in the UV–vis region and cyclic voltammetric have shown that such complexes when activated by MAO were not stable. Measurements carried out in the presence 1-hexene have demonstrated the necessity to add the cocatalyst in the presence of an olefin, i.e., ethylene or hexene-1 in order to stabilize the active species. Furthermore, these studies have revealed that after the activation process most of Ti remains as Ti^{IV} .

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1. Introduction

Polyolefins, such as polyethylene and polypropylene, have increasingly being widely used. Worldwide production volume of polyolefins has grown to more than 80,000,000 tonnes per year and is predicted to rise continuously at a high-rate. Besides the Ziegler–Natta and metallocene catalysts, several generations of non-metallocene compounds have been successfully used in olefin polymerisation [1]. Among them, that one based on Group 4 tris(pyrazolyl)borate ligands has been the subject of intense research activity in our group [2]. In particular, the Ti^{IV} and Zr^{IV} complexes containing sterically hindered Tp' ligand ($\text{Tp}' = \text{HB}(3\text{-mesitylpyrazolyl})_2(5\text{-mesitylpyrazolyl})^-$ ($\text{Tp}^{\text{Ms}*}$), $\text{HB}(3\text{-mesitylpyrazolyl})_3^-$ (Tp^{Ms})) have presented comparable activities related to the standard metallocene

Cp_2ZrCl_2 [2a,c]. The special features displayed by these catalyst systems prompted us to prepare a set of novel $\text{Tp}'\text{MCl}_3$ complexes ($\text{M} = \text{Ti}, \text{Zr}$; $\text{Tp}' = \text{HB}(3\text{-neopentylpyrazolyl})_3^-$ (Tp^{Np}); $\text{HB}(3\text{-tert-butylpyrazolyl})_3^-$ (Tp^{tBu}); $\text{HB}(3\text{-phenylpyrazolyl})_3^-$ (Tp^{Ph})) [2d] in order to investigate if the presence of bulky groups at 3(5) position of the pyrazolyl ring would be a key requirement to design novel high-active catalyst species. However, the very low-activities displayed by them strongly suggest that besides the steric features, others should be driving their catalytic behaviour.

As a part of a continuing effort to understand the effects of the Tp' ligands with diverse steric properties on the activity we report here some studies on $\text{Tp}'\text{TiCl}_3$ ($\text{Tp}' = \text{Tp}^{\text{Ms}*}, \text{Tp}^{\text{Ms}}, \text{Tp}^*$) ($\text{Tp}^* = \text{HB}(3,5\text{-dimethylpyrazolyl})_3^-$), using UV–vis spectroscopy, cyclic voltammetry, electrolysis measurements and spectroelectrochemistry. Studies related to the influence of solvent and cocatalyst on the activity for $\text{Tp}^{\text{Ms}*}\text{TiCl}_3$ and $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ are also reported.

* Corresponding author. Tel.: +55 51 3316 6300; fax: +55 51 3316 7304.
E-mail address: osvaldo@iq.ufrgs.br (O.L. Casagrande Jr.).

2. Experimental

2.1. Materials

All manipulations were carried out under argon atmosphere using the standard Schlenk tube techniques. Toluene and hexane were dried with Na/benzophenone, distilled and stored under argon. Acetonitrile (Merck, spectroscopic grade) used as solvent in the cyclic voltammetry experiments was dried in molecular sieve and distilled. Tetrabutylammonium tetrafluoroborate (Merck) was used without further purification. The catalysts $\text{Tp}^{\text{Ms}*}\text{TiCl}_3$ (**1**), $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ (**2**) and Tp^*TiCl_3 (**3**) were prepared according to the literature [2a]. Ethylene (polymer grade), provided by White Martins Company, and argon were deoxygenated and dried through columns of BTS (BASF) and activated molecular sieves (13 Å) prior to use. MAO (Witco, 5.21 wt.% toluene solution which contains ca. 20 wt.% TMA, trimethylaluminum), TiBA (Akzo, gently supplied by Ipiranga Petroquímica, 8.0 wt.% hexane solution) were used as received.

2.2. Polymerization reactions

Ethylene polymerization experiments were carried out in a 2 L Büchi glass reactor equipped with a magnetic driven mechanical stirrer and temperature measurement indicator. Under argon atmosphere, the suitable amounts of hexane or toluene, and cocatalyst solution were sequentially introduced and then the system was saturated with ethylene. After complete thermal equilibration of the system, the catalyst precursors **1–3** were added as solids and the reactor was quickly pressurized (5.2 atm) with stirring. The total volume of the reaction mixtures was 1 L for all polymerizations. The total pressure was kept constant by a continuous feed of ethylene. The polymerization runs were stopped by cooling, degassing the reactor, and introducing 1 mL of methanol. The polymers were washed with acidic ethanol, then ethanol and water, and dried in a vacuum oven at 40 °C for 12 h. On the basis of the results of multiple runs, we estimate the accuracy of these numbers to $\pm 8\%$.

2.3. Catalyst characterization

UV–vis spectroscopic analyses were performed in a Shimadzu spectrophotometer using an experimental apparatus similar to that described by Coevoet et al. [3]. The cyclic voltammograms (CV) and constant potential electrolysis (coulometry) measurements were taken with a potentiostat/galvanostat (PARC, model 273). All experiments were carried out using a conventional three electrodes cell. Glassy carbon was used as working electrode for CV and platinum gauze for coulometry. An Ag/AgCl electrode was used as the reference electrode and a platinum wire as the auxiliary electrode. Electrochemical data were obtained using 0.1 mol L⁻¹ acetonitrile solutions of tetrabutylammonium tetrafluoroborate as supporting electrolyte. In the cyclic voltammograms,

neither anodic nor cathodic peaks were observed in the absence of titanium complexes in the potential range studied. All solutions were deaerated by bubbling high-purity argon. The cocatalyst solutions were prepared with different [Al]/[Ti] molar ratios between 0 and 10 and the cyclic voltammograms were recorded with scan rate of 100 mV s⁻¹. The reported E_f values are the arithmetic mean of E_{ap} (anodic peak potential) and E_{cp} (cathodic peak potential) values. The spectroelectrochemical measurements were carried out using a gold mini-grid working electrode, Ag/AgCl as reference and platinum wire as an auxiliary electrode and quartz cell with 0.030 cm optical path. The electronic absorption spectra were recorded using Hewlett Packard Model 8453. Successive spectra were recorded during the redox process of the complexes.

2.4. Polymer characterization

Polymer melting points (T_m) and crystallinities (χ_c) were determined on a Thermal Analysis Instruments DSC-2010 calibrated with Indium, using a heating rate of 10 °C min⁻¹ in the temperature range 40–200 °C. The heating cycle was performed twice, but only the results of the second cycle are reported, since the former is influenced by the mechanical and thermal history of the samples. The intrinsic viscosity was determined in a modified Ostwald capillary viscometer, at 135 °C in decaline, using concentrations of 0.1 g dL⁻¹. Based on the experimental intrinsic viscosity values $[\eta]$, it was possible to calculate the viscometric molar mass according to the formula $[\eta] = k(\bar{M}_v)^\alpha$ for $k = 6.7 \times 10^{-4}$ dL g⁻¹ and the $\alpha = 0.67$ [4]. For gel permeation chromatography (GPC) analysis, 2 mg of polyethylene was dissolved in 4 mL of 1,2,4-trichlorobenzene (TCB) in the oven at 180 °C for 1 h. Molar masses and molar mass distributions were investigated with a Waters GPCV 2000 high-temperature GPC instrument, equipped with viscometric detector and four columns (107, 107, 106E, 140). TCB was used as solvent at a flow rate of 1 mL min⁻¹. The analyses were performed at 140 °C. The columns were calibrated with standard narrow molar mass distribution polystyrenes and with linear low-density polyethylenes and polypropylenes.

3. Results and discussion

3.1. Catalyst activity

The ethylene polymerization behavior of **1** and **2** was studied in toluene or hexane at 60 °C using methylaluminoxane (MAO) or a mixture of triisobutylaluminum (TiBA) and MAO (1:1) as cocatalysts. The polymerization results are summarized in Table 1.

The ethylene polymerization results show that both catalyst precursors are highly active under these experimental conditions with the activities varying from 5.4 to 16.6×10^3 kg of PE/mol[Ti]·h. Higher activities were found

Table 1
Ethylene polymerization results using the catalytic precursors **1** and **2**^a

Entry	Complex	Cocatalyst	Solvent	Activity ^c ($\times 10^{-3}$)
1	1	MAO	Toluene	11.9
2	1	MAO	Hexane	13.8
3 ^b	1	TiBA/MAO ^d	Hexane	16.6
4	2	MAO	Toluene	5.4
5	2	MAO	Hexane	10.1
6	2	TiBA/MAO ^d	Hexane	16.1

^a Büchi glass reactor (2 L); $P_{\text{ethylene}} = 5.2$ atm; Al/Ti = 1000; polymerization time = 5 min.

^b polymerization time = 3 min.

^c kg[PE]/mol[Ti]·h.

^d TiBA:MAO = 1:1.

in hexane using TiBA/MAO (1:1) cocatalyst system. It seems that under these polymerization conditions, the combination of MAO in suitable Al content, combined with the scavenger properties of TiBA affords better conditions to stabilize the active species. Besides, TMA, which is present in commercial MAO, can act as a poison in the polymerization reaction. In recent studies involving **1**, Jordan and co-workers have suggested that the TMA present in MAO coordinates to active species disfavoring the monomer coordination [2a,5]. Therefore, the higher activity observed in the case of TiBA/MAO (1:1) could also be due to the lower nominal amount of MAO which was employed in the polymerization reaction. Nevertheless, we cannot neglect the coordination capacity of toluene to titanium [6], which might engender a competition between the coordinating olefin and the solvent itself.

The polymer properties have been evaluated by means of differential scanning calorimetry (DSC), intrinsic viscosity measurements, and gel permeation chromatography (GPC). Characteristics of the resulting polymers are shown in Table 2.

According to Table 2, most of the melting temperatures (T_m) of the polyethylenes are higher than 136 °C, approaching to that usually observed in the case of linear ultra high-molecular weight polyethylene (UHMWPE). In addition, most of the resulting polymers presented high-crystallinities. Only two polymers were soluble under standard GPC analysis condition, both of them presenting broad molecular weight distribution (Mw/Mn). According to viscometric measurements, molecular weight remained comprised

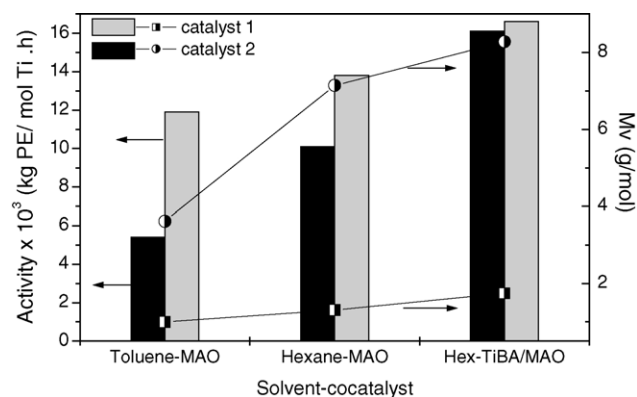


Fig. 1. Catalyst activity and polyethylene viscometric molecular weight relationship.

between 1.0 and 8.3×10^5 g mol⁻¹. Fig. 1 represents the correlation between catalyst activity and viscosity average molecular weight (\bar{M}_v).

3.2. UV and visible spectroscopy analysis

The UV–vis spectroscopy has become an important tool for olefin polymerization catalysts due to the useful information that this technique can provide on the metal complex electronic structure [3,7]. Furthermore, this spectroscopic technique was found to be very effective for the observation of the successive elementary steps yielding cationic active species generated during the polymerization reaction. In this context, and aiming at getting some insights into the stability and electronic properties of the catalytic species originated from reaction of $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ and Tp^*TiCl_3 with MAO, we have performed an UV–vis spectroscopic study in toluene at 25 °C.

As shown in Figs. 2 and 3, the absorption spectra of the **2** and **3** recorded under argon atmosphere show low-energy bands at 313 and 328 nm which can be assigned, respectively, to $\text{Tp}^{\text{Ms}} \rightarrow \text{Ti}$ and $\text{Tp}^* \rightarrow \text{Ti}$ transitions according to the results reported by Traverso and co-workers [8]. The addition of MAO ([Al]/[Ti] = 300) to toluene solution containing **2** or **3** engendered immediately the disappearance of those peaks suggesting that a decomposition process of the titanium species took place. Similar behavior was already reported in the literature for **1** [2d]. On the other hand, if

Table 2
The DCS, intrinsic viscosity and GPC analysis results of produced polyethylene

Entry	Complex	T_m (°C)	χ_c (%)	η (dL g ⁻¹)	\bar{M}_v ($\times 10^{-5}$)	Mw ($\times 10^{-5}$)	Mw/Mn
1	1	137	81	1.50	1.0	0.96	10.6
2	1	139	68	1.80	1.3	1.64	7.7
3	1	134	84	2.18	1.8	nd ^a	–
4	2	137	79	3.55	3.6	nd	–
5	2	136	59	5.60	7.1	nd	–
6	2	136	65	6.18	8.3	nd	–

^a Insoluble in trichlorobenzene.

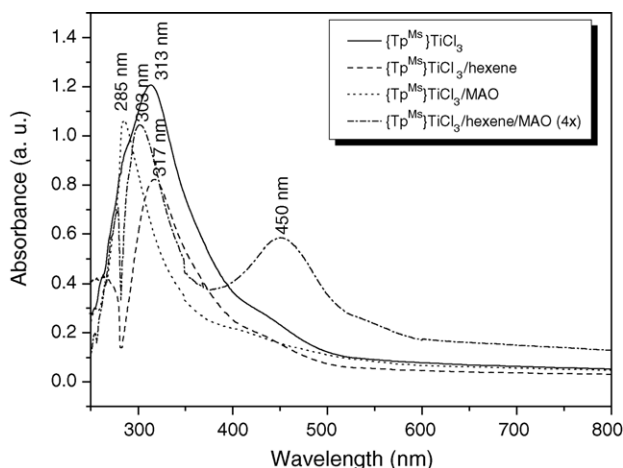


Fig. 2. UV–vis absorption spectra of $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ and $\text{Tp}^{\text{Ms}}\text{TiCl}_3/\text{MAO}$ catalytic system in toluene at 25 °C ($[\text{Ti}] = 5 \mu\text{mol}$; $[\text{Al}]/[\text{Ti}] = 300$; $[\text{hexene-1}] = 0.38 \text{ M}$).

the interaction of **2** or **3** with MAO is performed in the presence of 1-hexene, the formation of absorption bands (dash dot line) centered at 450 and 382 nm, respectively, are observed. The UV–vis studies performed by Deffieux and co-workers [9], using $(\alpha\text{-diimine})\text{NiBr}_2/\text{MAO}/\text{hexene-1}$ catalyst system, showed the formation of an absorption band at 510 nm which has been ascribed to the generation of active species. The available data for $\text{Tp}'\text{TiCl}_3/\text{MAO}/\text{hexene-1}$ systems catalysts ($\text{Tp}' = \text{Tp}^{\text{Ms}}, \text{Tp}^*$) are very limited at present, however, based on the Ni-diimine results, we speculate that the absorption band at 450 nm for **1** and 382 nm for **2** may be also associated to the formation of the active species.

Furthermore, it is worth noting that the UV–vis spectra of the studied Ti^{IV} complexes show the absence of any absorption peak between 500 and 800 nm (dash dot line in Figs. 2 and 3) indicating that after the activation process most of Ti remains as Ti^{IV} [8]. These data are corroborated by the

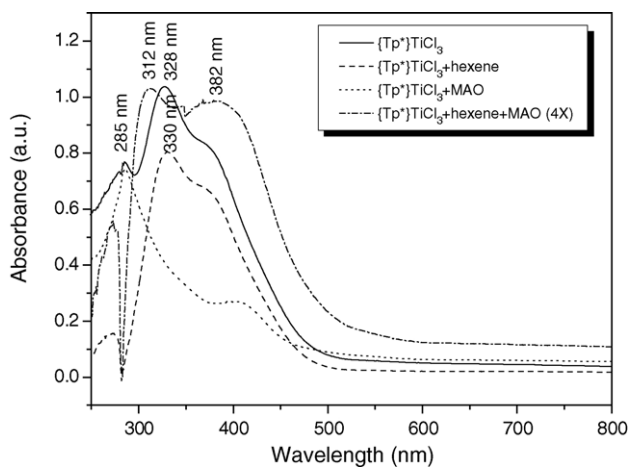


Fig. 3. UV–vis absorption spectra of Tp^*TiCl_3 and $\text{Tp}^*\text{TiCl}_3/\text{MAO}$ catalytic system in toluene at 25 °C ($[\text{Ti}] = 5 \mu\text{mol}$; $[\text{Al}]/[\text{Ti}] = 300$; $[\text{hexene-1}] = 0.38 \text{ M}$).

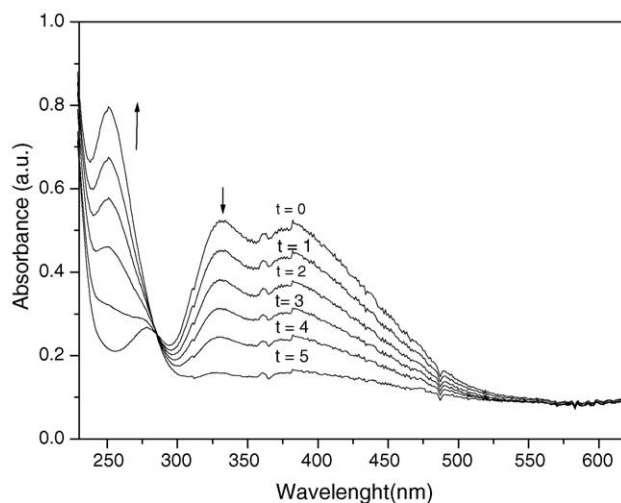


Fig. 4. Successive spectra during reduction of Tp^*TiCl_3 .

XPS results involving **1** [2b]. The stabilization of Ti^{IV} species against reduction can be attributed to the electronic properties of the Tp ligands which are known to stabilize transition metal complexes in high-oxidation state [10]. Recently, Jordan et al. reported the synthesis and structural characterization of stable Ti^{III} species, $\text{K}[\text{Tp}^{\text{Ms}*}\text{TiCl}_3]$, by reaction of **1** with a strong reduction agent, potassium, in toluene. This pale blue compound shows an absorption band at 615 nm [11].

In order to find further evidences related to the non-generation of stable Ti^{III} species during the activation process by MAO, the following experiments were performed: (i) electrolysis at controlled potential and recording of the cyclic voltammogram of the resulting product; (ii) electrochemical reduction followed by spectroscopic monitoring in the UV–vis region (spectroelectrochemistry) under ethylene atmosphere. The UV–vis spectra, recorded during electrochemical reduction of **3** at ethylene atmosphere show decrease of the band at 328 nm (Fig. 4). This spectral change shows bleaching of the LMCT absorption at 328 nm in consequence of the decomposition of **3**. Based on these results, the process $\text{Ti}^{\text{IV}}/\text{III}$ can be ruled out.

These catalytic systems were further evaluated by cyclic voltammetry as discussed in the following.

3.3. Cyclic voltammetry measurements

The cyclic voltammogram of **1** (Fig. 5) depicts a pair of peaks at +25 mV (E_{cp1}) and +95 mV (E_{ap1}) with E_f at 60 mV and $\Delta E = 70 \text{ mV}$. Similar current–potential profile was observed for **2**. In this case, this pair of peaks was observed at +5 mV (E_{cp1}), +80 mV (E_{ap1}) with E_f at 40 mV and $\Delta E = 75 \text{ mV}$. For both cases, these pair of peaks are attributed to the electrode process that involves one electron whereas the $\text{Tp}'\text{Ti}^{\text{IV}}\text{Cl}_3$ complexes ($\text{Tp}' = \text{Tp}^{\text{Ms}*}, \text{Tp}^{\text{Ms}}$) are reduced generating Ti^{III} species, $[\text{Tp}'\text{Ti}^{\text{III}}\text{Cl}_3]^-$. The cathodic peaks at negative potential at –1280 and –1470 mV and

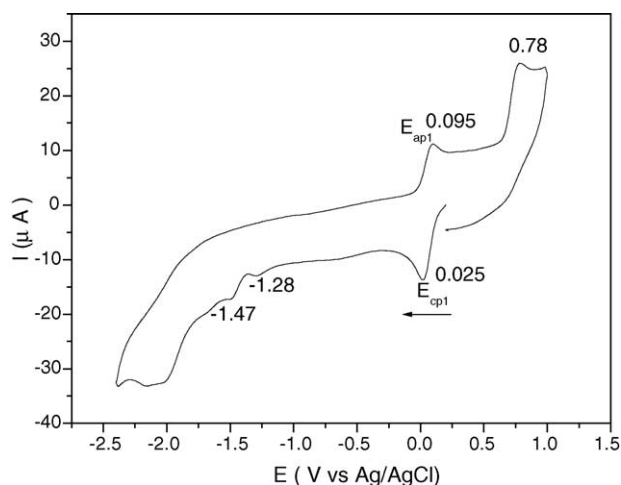


Fig. 5. Cyclic voltammogram of the $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$.

anodic peak at +780 mV, probably involve the ligand, since the redox process in similar potential values is shown in the cyclic voltammogram of uncoordinated ligand.

For comparative reasons, the cyclic voltammogram of **3** was also performed. For **3** the pair of peaks occurs at +110 mV (E_{cp1}), +180 mV (E_{ap1}) with E_f at 145 mV and $\Delta E = 70$ mV. The cathodic peaks at negative potential and E_{ap} around +800 mV may be associated to the redox process of the Tp^* ligand.

For **1** and **3**, the cyclic voltammogram scan in rates from 0.05 to 0.5 V s^{-1} in potential range from -100 to $+700$ mV starting at 200 mV were recorded. The peak current ratio $I_{\text{a}}/I_{\text{c}}$ shows a range of 0.95–0.78 for **1** (Fig. 6) and 1.00–0.81 for **3** with a diffusion coefficient D_0 , for the oxidized species, of 1.7×10^{-7} and $2.5 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively. The D_0 values were obtained from the $I_{\text{pc}} \times v^{1/2}$ plots and the Randles–Sevcick equation [12]. The diagnostics tests were in agreement with the reversible systems with couple reac-

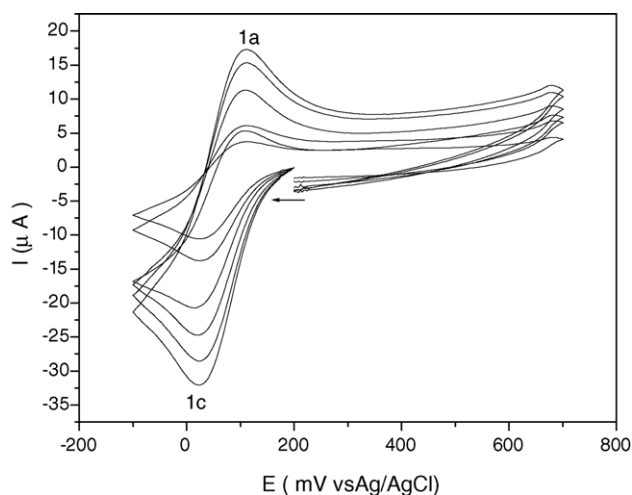


Fig. 6. Cyclic voltammogram of the $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ at scan rates: 50–500 mV s^{-1} .

Table 3

Relevant data extracted from cyclic voltammograms recorded on solutions containing $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$, $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ and $\text{Tp}^*\text{TiCl}_3^{\text{a}}$

	$\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$	$\text{Tp}^{\text{Ms}}\text{TiCl}_3$	Tp^*TiCl_3
E_{cp1} (mV) vs. Ag/AgCl	+25	+5	+110
E_{ap1} (mV) vs. Ag/AgCl	+95	+80	+180
E_f (mV)	60	40	145
ΔE (mV)	70	75	70
$I_{\text{a}}/I_{\text{c}}^{\text{a}}$	0.78–0.95	–	0.81–1.00
D_0 ($\text{cm}^2 \text{ s}^{-1}$) ^b	1.7×10^{-7}	–	2.5×10^{-6}

^a E_f = arithmetic mean on E_{pa} and E_{pc} values.

^b Scan rates: 0.05–0.5 V s^{-1} .

tion. The results extracted from the cyclic voltammograms of $\text{Tp}'\text{TiCl}_3$ complexes ($\text{Tp}' = \text{Tp}^{\text{Ms}^*}$, Tp^{Ms} , Tp^*) are collected in Table 3.

In order to investigate the electrochemical behavior of **1** in presence of MAO, we carried out the cyclic voltammetric experiments under ethylene atmosphere, using $[\text{Al}]/[\text{Ti}]$ molar ratios of 1, 5 and 10. The cyclic voltammograms are presented in Fig. 7.

The potential run begins at +200 mV and goes toward negative potential showing one cathodic peak at -900 mV, which is absent in the cyclic voltammogram of **1** as can be seen in Fig. 5. The appearance of a cathodic peak at more negative suggests that the substitution of one chloride atom by a methyl group took place. This result is reasonable since the substitution of an electron withdrawing chloro atom by a donating methyl group from the cocatalyst (MAO) increases the electronic density on the Ti^{IV} and consequently the reduction process is shifted to a more negative potential.

The successive cyclic voltammograms at 200 mV s^{-1} show that current peak at -900 mV for 1/MAO ($[\text{Al}]/[\text{Ti}] = 10$) decreases with time probably due to the instability of these active species in solutions as can be seen in Fig. 8.

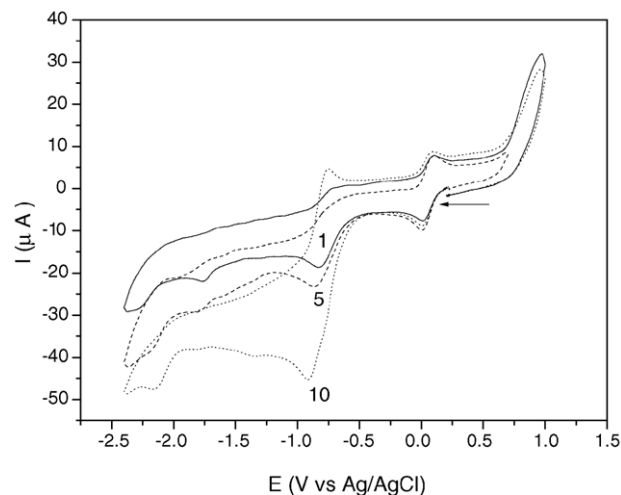


Fig. 7. Cyclic voltammograms of the $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ at $[\text{Al}]/[\text{Ti}] = 1, 5$ and 10 molar ratios.

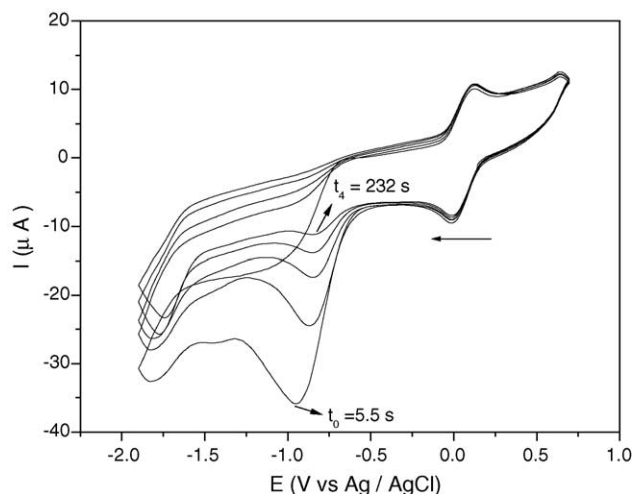


Fig. 8. Successive cyclic voltammograms of the $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ at $\text{Al/Ti} = 10$ with $v = 200 \text{ mV s}^{-1}$.

4. Conclusions

The catalytic performance of $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$ and $\text{Tp}^{\text{Ms}}\text{TiCl}_3$ was shown to be dependent on the nature of the cocatalyst/solvent system. Higher activity was obtained in hexane using a combination of cocatalyst MAO/TiBA. Absorciometric measurements in the UV–vis region, cyclic voltammetry, coulometry and spectroelectrochemistry were shown to be useful tools in the investigation of the nature of catalytic species. The cyclic voltammograms of $\text{Tp}'\text{TiCl}_3$ complexes showed a pair of peaks which is attributed to the electrode process that involves one electron where Ti^{IV} are reduced leading Ti^{III} species, $[\text{Tp}'\text{TiCl}_3]^-$. UV–vis spectroscopic studies revealed the necessity of a coordinating olefin in order to stabilize the active species originated by reaction of $\text{Tp}'\text{TiCl}_3$ with MAO.

Furthermore, absence of any absorption peak between 500 and 800 nm indicated that after the activation process most of Ti remains as Ti^{IV} . The stabilization of Ti^{IV} species against reduction can be attributed in part to the electronic properties of the Tp ligands which are known to stabilize transition metal center in high-oxidation state.

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