

# Titanium and zirconium complexes containing sterically hindered hydrotris(pyrazolyl)borate ligands: synthesis, structural characterization, and ethylene polymerization studies <sup>☆</sup>

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## Abstract

The synthesis, characterization and ethylene polymerization behavior of a set of  $\text{Tp}'\text{MCl}_3$  complexes (**4**,  $\text{M} = \text{Ti}$ ,  $\text{Tp}' = \text{HB}(3\text{-neopentyl-pyrazolyl})_3^- (\text{Tp}^{\text{Np}})$ ; **5**,  $\text{M} = \text{Ti}$ ,  $\text{Tp}' = \text{HB}(3\text{-tert-butyl-pyrazolyl})_3^- (\text{Tp}^{\text{tBu}})$ ; **6**,  $\text{M} = \text{Ti}$ ,  $\text{Tp}' = \text{HB}(3\text{-phenyl-pyrazolyl})_3^- (\text{Tp}^{\text{Ph}})$ ; **7**,  $\text{M} = \text{Zr}$ ,  $\text{Tp}' = \text{HB}(3\text{-phenyl-pyrazolyl})_3^- (\text{Tp}^{\text{Ph}})$ ; **8**,  $\text{M} = \text{Zr}$ ,  $\text{Tp}' = \text{HB}(3\text{-tert-butyl-pyrazolyl})_3^- (\text{Tp}^{\text{tBu}})$ ) is described. Treatment of these tris(pyrazolyl)borate Group IV compounds with methylalumoxane (MAO) generates active catalysts for ethylene polymerization. For the polymerization reactions performed in toluene at 60 °C and 3 atm of ethylene pressure, the activities varied between 1.3 and  $5.1 \times 10^3$  g of PE/mol[M] · h. The highest activity is reached using more sterically open catalyst precursor **4**. The viscosity-average molecular weights ( $\bar{M}_v$ ) of the PE's produced with these catalyst precursors varying from 3.57 to  $20.23 \times 10^5$  g mol<sup>-1</sup> with melting temperatures in the range of 127–134 °C. Further polymerization studies employing **7** varying Al/Zr molar ratio and temperature of polymerization showed that the activity as well as the polymer properties are dependent on these parameters. In that case, higher activity was attained at 60 °C. The viscosity-average molecular weights of the polyethylene's decreases with increasing Al/Zr molar ratio.

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**Keywords:** Tris(pyrazolyl)borate ligands; Titanium and zirconium; Ethylene; Polymerization

## 1. Introduction

The chemistry of the non-metallocene catalysts has grown considerably over the past decade, largely due to the remarkable variety of non-cyclopentadienyl ligands available and their high-performance in olefin polymerization [1]. Many contributions have thus been made concerning this topic, especially using Group 4 metals [2]. Among them, the most part is related to the titanium and zirconium compounds containing a wide variety of ancillary ligands including those ones based on tris(pyrazolyl)borate [3]. Tris(pyrazolyl)borate ligands (Tp) have

been widely used in coordination and organometallic chemistry as stabilizing groups in high-oxidation state transition metal complexes considering their strong electron donor ability. Furthermore, the steric and electronic properties of the pyrazolyl donors can be modified by variation of the 3 and 5 substituents determining attractive properties for the Tp-metal complex [4]. In the recent years, we have been interested in exploring the chemistry of Group 4 complexes that containing sterically hindered tris(pyrazolyl)borate ligands with the goal of developing novel olefin polymerization catalysts [5]. Our studies have demonstrated that the presence of mesityl substituents at the 3(5)-position of pyrazolyl rings establishes the formation of highly active catalyst species for ethylene polymerization. These compounds of general formula  $\text{Tp}'\text{MCl}_3$  ( $\text{M} = \text{Ti, Zr}$ ;  $\text{Tp}' = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^- (\text{Tp}^{\text{Ms*}})$ ,  $\text{HB}(3\text{-mesityl-pyrazolyl})_3^- (\text{Tp}^{\text{Ms}})$ ) exhibit much higher activities than those

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displayed by titanium and zirconium compounds bearing Tp ligands with low steric hindrance such as HB(pyrazolyl)<sub>3</sub><sup>-</sup> (Tp) or HB(3,5-dimethylpyrazolyl)<sub>3</sub><sup>-</sup> (Tp\*) [3]. In this context, the contrasting performance of these species in ethylene polymerization have prompted us to synthesize some Ti(IV) and Zr(IV) complexes containing sterically hindered Tp ligands in order to evaluate if the presence of bulky groups at 3(5) position of the pyrazolyl ring is a key requirement for design high-active catalysts. Herein, we describe the syntheses and characterization of Tp' MCl<sub>3</sub> (M = Ti, Zr; Tp' = HB(3-neopentyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>Np</sup>), HB(3-phenyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>Ph</sup>), HB(3-*tert*-butyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>tBu</sup>)) and their use in ethylene polymerization. Studies related to the influence of the Al/Zr molar ratio and polymerization temperature on the activity and on polyethylene characteristics are also described.

## 2. Results and discussion

### 2.1. Synthesis and characterization of tris(pyrazolyl)borate Tp' MCl<sub>3</sub> complexes (4–8)

The general procedure for the synthesis of the tris(pyrazolyl)borate titanium (IV) and zirconium compounds (4–8), by displacement of a chloride group, involves the simple reaction between the tris(pyrazolyl)borate ligands 1–3 and MCl<sub>4</sub> (M = Ti, Zr) in CH<sub>2</sub>Cl<sub>2</sub> or toluene as solvent. Thus, the Tp' ligands 1–3 reacts with an equimolar amount of MCl<sub>4</sub> to give, after work, up, the Tp' MCl<sub>3</sub> complexes (4, M = Ti, Tp' = HB(3-neopentyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>Np</sup>); 5, M = Ti, Tp' = HB(3-*tert*-butyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>tBu</sup>); 6, M = Ti, Tp' = HB(3-phenyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>Ph</sup>); 7, M = Zr, Tp' = HB(3-phenyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>Ph</sup>); 8, M = Zr, Tp' = HB(3-*tert*-butyl-pyrazolyl)<sub>3</sub><sup>-</sup> (Tp<sup>tBu</sup>)) as orange to yellow solids in 50–92% yield. These compounds are air-stable and soluble in most of polar solvents such as dichloromethane, THF, and toluene. The

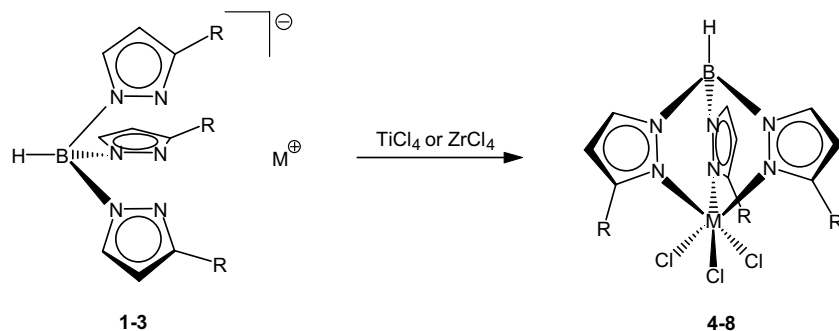
structures of 4–8 were assigned on the basis of elemental analysis, IR, multinuclear (<sup>1</sup>H, <sup>13</sup>C) NMR data, and by X-ray structural determination carried out for 4 (see Scheme 1).

The elemental analyses of 4–8 are in agreement with the proposed formula Tp' MCl<sub>3</sub>. The NMR spectra are consistent with the expected C<sub>3v</sub>-symmetric structures in which the three 3-R-pyrazolyl groups are equivalents. In all cases, the <sup>1</sup>H NMR spectra contain two set of doublet in the region of 8.44–7.49 and 7.05–6.13 ppm corresponding to the H-5 and H-4 resonances of the pyrazolyl group, besides the characteristic peaks corresponding to the neopentyl, phenyl and *tert*-butyl groups. In addition, the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of 4–8, show the 5-C and 4-C resonances of the pyrazolyl ring in the region of 159.4–151.3 and 104.9–103.3 ppm, respectively.

### 2.2. Molecular structure of {Tp<sup>Np</sup>}TiCl<sub>3</sub> (4)

Single crystals of compound 4 suitable for X-ray diffraction analysis were obtained from toluene solution at –20 °C. Crystal data for 4 is summarized in Table 1, refinement details are discussed in Section 3, and selected bond distances and angles are listed in Table 2. Molecular geometry and atom-labeling scheme are shown in Fig. (1). Compound 4 crystallises in the monoclinic space group P2<sub>1</sub>/m.

The crystal structure of 4 (Fig. 1) confirms both the monomeric nature of the complex and κ<sup>3</sup>-coordination of the Tp<sup>Np</sup> ligand with the neopentyl groups being all in the 3-position. This configuration is consistent with <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, indicative of the molecule being stereochemically rigid at room temperature. The titanium center possesses distorted octahedral geometry as evidenced by the *cis* L–Ti–L angles (96.76(13)–89.30(16)°). As expected, the N–Ti–N angles formed from the pyrazolyl ring donor atoms are all less than 90° allowing the face formed by three chloride ligands to



	1	2	3	4	5	6	7	8
M	Ti	K	K	Ti	Ti	Ti	Zr	Zr
R	Np	Ph	tBu	Np	Ph	tBu	Ph	tBu

Scheme 1.

Table 1  
Summary of crystallographic data for **4**

<b>4</b>	
Formula	C <sub>24</sub> H <sub>40</sub> BCl <sub>3</sub> N <sub>6</sub> Ti
fw	577.68
T (K)	173(2)
Cryst system	Monoclinic
Space group	P2 <sub>1</sub> /m
a (Å)	7.799(4)
b (Å)	17.625(9)
c (Å)	11.378(6)
α (deg)	90
β (deg)	109.73(1)
γ (deg)	90
V (Å <sup>3</sup> )	1472.0(13)
Z	2
d (calc.), g cm <sup>-3</sup>	1.303
abs coeff, mm <sup>-1</sup>	0.587
F(000)	608
Crystal color, morphology	Orange, plate
Cryst size, mm	0.17 × 0.08 × 0.02
θ range for data collen (deg)	1.90–25.13
Unique reflcns colled	8785
Observed data [I > σ(I)]	2704 [R <sub>(int)</sub> = 0.1184]
Data/params	2704/197
Goodness-of-fit on F <sup>2</sup>	1.002
Final R indices [I > σ(I)]	R <sub>1</sub> = 0.0672, wR <sub>2</sub> = 0.1471
R indices (all data)	R <sub>1</sub> = 0.1143, wR <sub>2</sub> = 0.1738
Δρ (max,min), e Å <sup>-3</sup>	0.473 and -0.289 e Å <sup>-3</sup>

Table 2  
Selected bond lengths (Å) and angles (°) for compound **4**

Bond lengths	
Ti–N(1)	2.162 (8)
Ti–N(3)	2.167 (6)
Ti–N(3)*	2.167 (6)
Ti–Cl(1)	2.245 (3)
Ti–Cl(2)	2.252 (2)
Ti–Cl(2)*	2.252 (2)
Angle lengths	
N(1)–Ti–Cl(1)	170.8 (3)
N(1)–Ti–Cl(2)	89.45 (18)
N(1)–Ti–Cl(2)*	89.45 (18)
N(1)–Ti–N(3)	84.5 (2)
N(3)–Ti–Cl(1)	88.63 (16)
N(3)–Ti–Cl(2)	171.42 (18)
N(3)–Ti–Cl(2)*	89.30 (16)
N(3)*–Ti–N(1)	84.5 (2)
N(3)*–Ti–N(3)	84.1 (3)
N(3)*–Ti–Cl(1)	88.63 (16)
N(3)*–Ti–Cl(2)	89.30 (16)
N(3)*–Ti–Cl(2)*	171.42 (18)
Cl(1)–Ti–Cl(2)	96.66 (9)
Cl(1)–Ti–Cl(2)*	96.66 (9)
Cl(2)–Ti–Cl(2)*	96.76 (13)

open considerably. The Ti–N (Ti–N<sub>av</sub> = 2.165 Å, range 2.162(8)–2.167(6) Å) and Ti–Cl (Ti–Cl<sub>av</sub> = 2.250 Å, range 2.245(3)–2.252(2) Å) bond distances are comparable to those found in similar titanium compounds having Tp ligands with low steric hindrance such as

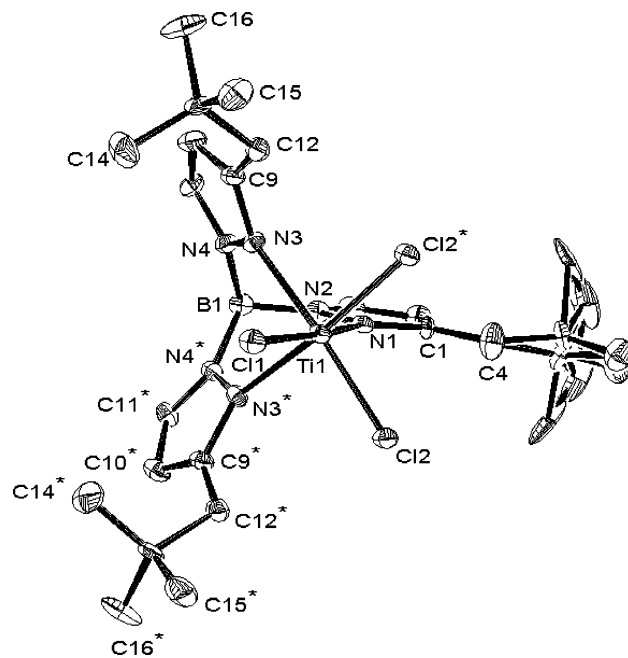


Fig. 1. Molecular structure of compound **4** drawn at the 30% probability level (hydrogen atoms omitted for clarity).

{Tp\*}TiCl<sub>3</sub> (Ti–N<sub>av</sub> = 2.168 Å; Ti–Cl<sub>av</sub> = 2.262 Å), [6] and Tp<sup>Menth</sup>TiCl<sub>3</sub> (Ti–N<sub>av</sub> = 2.152 Å; Ti–Cl<sub>av</sub> = 2.261 Å) [7]. However, the longer Ti–N distance bonds found for titanium complexes having sterically hindered tris(pyrazolyl)borate ligands such as Tp<sup>Ms</sup>TiCl<sub>3</sub> (Ti–N<sub>av</sub> = 2.219 Å), [8] Tp<sup>Ms\*</sup>TiCl<sub>3</sub> (Ti–N<sub>av</sub> = 2.191 Å) [8] related to those observed in **4**, suggest that the presence of less sterically demanding R groups at 3-position of the pyrazolyl ring determines a stronger coordination of the Tp ligand to the metal center.

### 2.3. Ethylene polymerization

It is interesting to compare the performance of Tp'MCl<sub>3</sub> complexes (**4–8**) in ethylene polymerization in order to obtain insights concerning to the effects of the steric hindrance on the activity and polymer properties of the catalytic system. For that, the polymerization reactions were carried out in toluene in the presence of methylaluminoxane (MAO) as cocatalyst. The polymerization results are summarized in Table 3.

The ethylene polymerization reactions performed at 60 °C, and using Al:M molar ratio of 500 show that all Tp'MCl<sub>3</sub> complexes (**4–8**) are active under these polymerization conditions. Furthermore, the polymerization results demonstrate that changing the R substituents at 3-position of the pyrazolyl ring affects the activity that varied from 1.3 to 5.1 × 10<sup>3</sup> g of PE/(mol[M]·h·atm). The sterically open catalyst precursor **4** exhibited highest activity (5.1 × 10<sup>3</sup> g of PE/(mol[Ti]·h·atm)) followed by the zirconium compound (**7**) with activity of 4.0 × 10<sup>3</sup> g of PE/(mol[Ti]·h·atm).

Table 3  
Results of ethylene polymerization using  $\text{Tp}^i\text{MCl}_3$  complexes (**4–8**)<sup>a</sup>

Entry	Complex	Polymer yield (g)	Activity <sup>b</sup> ( $\times 10^{-3}$ )	$T_m$ (°C)	$\chi$ (%)	$[\eta]^c$ (dL/g)	$\bar{M}_v$ ( $\times 10^{-5}$ )
1	<b>4</b>	0.153	5.1	132	21	–	–
2	<b>5</b>	0.085	2.8	132	20	3.52	3.57
3	<b>6</b>	0.071	2.4	127	55	4.79	5.66
4	<b>7</b>	0.120	4.0	132	42	11.25	20.23
5	<b>8</b>	0.038	1.3	134	18	4.18	4.62

<sup>a</sup> Polymerization conditions: Fischer Porter bottle (100 ml),  $[\text{M}] = 10 \mu\text{mol}$ , toluene = 60 ml, polymerization time = 1 h,  $[\text{Al}]/[\text{M}] = 500$ , temperature = 60 °C,  $\text{P}_{\text{C}_2\text{H}_4} = 3.0 \text{ atm}$ , blank MAO runs were carried out every 5 normal runs, MAO as activator.

<sup>b</sup> g of PE/mol $[\text{M}] \cdot \text{h} \cdot \text{atm}$ .

<sup>c</sup> Calculated from the experimental intrinsic viscosities ( $[\eta]$ , decaline at 135 °C) according to the  $[\eta] = k(\bar{M}_v)^\alpha$  with  $k = 6.7 \times 10^{-4} \text{ dl/g}$  and  $\alpha = 0.67$ .

The catalyst precursors **6** and **8** that contain sterically larger *tert*-butyl group displayed lowest activities of 2.4 and  $1.3 \times 10^{-3}$  g of PE/mol $[\text{M}] \cdot \text{h} \cdot \text{atm}$ , respectively. In that case, the lower activities of these compounds can be rationalized considering the higher cone angle (251°) and lower wedge angle (29°) presented by  $\text{Tp}^{\text{tBu}}$  ligand [9] which provide significant steric crowding around the  $\text{MCl}_3$  unit diffculting the coordination of ethylene to the metal center. Nevertheless, the much higher activities displayed by the tris(pyrazolyl)borate titanium(IV) species containing steric crowded Tp ligands such as  $\text{Tp}^{\text{Ms}^*}\text{TiCl}_3$  [ $\text{Tp}^{\text{Ms}^*} = \text{HB}(3\text{-mesityl-pyrazolyl})_2(5\text{-mesityl-pyrazolyl})^-$ ;  $105.4 \times 10^3$  g of PE/mol $[\text{Ti}] \cdot \text{h} \cdot \text{atm}$ ] and  $\text{Tp}^{\text{Ms}}\text{TiCl}_3$  [5] [ $\text{Tp}^{\text{Ms}} = \text{HB}(3\text{-mesityl-pyrazolyl})_3^-$ ;  $93.2 \times 10^3$  g of PE/mol $[\text{Ti}] \cdot \text{h} \cdot \text{atm}$ ] in the polymerization reactions carried out under the same conditions, suggest that besides the steric effects other features including the electronic ones are determining different activity tendencies.

The polyethylene's (PE's) produced by **4–8** were found to exhibit melt transitions ( $T_m$ 's) between 127 and 134 °C, with crystallinities varying from 18% to 55%. The viscosity–average molecular weights ( $\bar{M}_v$ ) of the PE's produced range from ultrahigh for that using **7** ( $20.23 \times 10^5 \text{ g mol}^{-1}$ ) to high for those using with **4–6** and **8** ( $3.57\text{--}5.66 \times 10^5 \text{ g mol}^{-1}$ ).

In order to examine the influence of the Al/Zr molar ratio and the polymerization temperature on activity and polymer properties, we performed a series of polymerization reactions using **7**. Table 4 summarizes the polymerization results. The polymerization studies cor-

responding to the effect of Al/Zr molar ratio on the activity showed that **7** is active using Al/Zr molar ratio as low as 100:1. Maximum activity was attained using Al/Zr molar ratio of 500 ( $4.0 \times 10^3$  g of PE/mol $[\text{Zr}] \cdot \text{h} \cdot \text{atm}$ ). Increasing the MAO concentration to 1000 resulted in lower activity ( $2.2 \times 10^3$  g of PE/mol $[\text{Zr}] \cdot \text{h} \cdot \text{atm}$ ).

As expected, the polymerization reaction varying the Al/Zr molar ratio provokes strong influences on  $\bar{M}_v$  as can be verified comparing the entries 4, 6 and 9 (4). For instance, the viscosity–average molecular weight drops from  $\bar{M}_v = 33.94 \times 10^5 \text{ g mol}^{-1}$  when the polymerization reaction was carried out employing Al/Zr = 100 to  $\bar{M}_v = 18.88 \times 10^5 \text{ g mol}^{-1}$  using Al/Zr = 1000. The decrease of the molecular weight can be rationalized assuming the predominant chain transfer process to Al as demonstrated in previously polymerization studies involving similar Group 4 tris(pyrazolyl)borate-based complexes [5].

By varying the polymerization temperature between 30 °C and 90 °C to a constant Al/Zr molar ratio of 500, it was observed that the activity of the catalyst precursor **7** is dependent on the temperature increasing from 30 to 60 °C (compare entries 4 and 7). At higher polymerization temperature 90 °C the activity decreases suggesting a partial catalyst deactivation (entry 8). The viscosity–average molecular weights of the polyethylenes are slightly dependent of the polymerization temperature varying from  $26.86 \times 10^5 \text{ g mol}^{-1}$  when the polymerization reaction was performed at 30 °C to  $20.45 \times 10^5 \text{ g mol}^{-1}$  at 90 °C. It is should be pointed out

Table 4  
Results of ethylene polymerization using  $\text{Tp}^{\text{Ph}}\text{ZrCl}_3$  complex (**7**)<sup>a</sup>

Entry	Al/Zr	Temperature (°C)	Polymer yield (g)	Activity <sup>b</sup> ( $\times 10^{-3}$ )	$T_m$ (°C)	$\chi$ (%)	$[\eta]^c$ (dL/g)	$\bar{M}_v$ ( $\times 10^{-5}$ )
6	100	60	0.045	1.5	131	38	15.91	33.94
7	500	30	0.017	0.6	134	44	13.60	26.86
4	500	60	0.120	4.0	133	42	11.25	20.23
8	500	90	0.029	1.0	133	47	11.33	20.45
9	1000	60	0.064	2.2	127	48	10.74	18.88

<sup>a</sup> Polymerization conditions: Fischer–Potter-reactor (100 ml),  $[\text{Zr}] = 10 \mu\text{mol}$ , toluene = 60 ml, polymerization time = 1 h,  $\text{P}_{\text{C}_2\text{H}_4} = 3.0 \text{ atm}$ , blank MAO runs were carried out every five normal runs, MAO as activator.

<sup>b</sup> g of PE/mol $[\text{M}] \cdot \text{h} \cdot \text{atm}$ .

<sup>c</sup> Calculated from the experimental intrinsic viscosities ( $[\eta]$ , decaline at 135 °C) according to the  $[\eta] = k(\bar{M}_v)^\alpha$  with  $k = 6.7 \times 10^{-4} \text{ dl/g}$  and  $\alpha = 0.67$ .

that even at high polymerization temperature as 90 °C, this catalyst precursor still making PE with ultrahigh molecular weight.

### 3. Experimental

#### 3.1. General procedures

All manipulations were performed using vacuum-line or Schlenk techniques under a purified argon atmosphere. Solvents stored under argon or vacuum prior to use. Toluene and hexane were distilled from Na/benzophenone ketyl, and CH<sub>2</sub>Cl<sub>2</sub> was distilled from P<sub>2</sub>O<sub>5</sub>. TiCl<sub>4</sub> were purchased from Merck and a 1.02 M solution in toluene was prepared prior to use. The tris(pyr-azoly)borate ligands TITp<sup>Np</sup> (**1**), [10] KTp<sup>Ph</sup> (**2**), [11] KTp<sup>tBu</sup> (**3**) [11] were prepared by literature procedures. 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 (5.21 wt.% Al, in toluene, average molar mass 900 g mol<sup>-1</sup>) was purchased from Witco and used without further purification. Infrared spectra were performed on a Bomem B-102 spectrometer. NMR spectra were recorded on a Varian Inova 300 spectrometer in Teflon-valved NMR tubes at ambient probe temperature. <sup>1</sup>H and <sup>13</sup>C chemical shifts are reported versus Me<sub>4</sub>Si and were determined by reference to the residual <sup>1</sup>H and <sup>13</sup>C solvent peaks. Coupling constant are reported in hertz. Elemental analyses were performed by Central Analítica IQ/UFRGS (Porto Alegre, Brazil).

#### 3.2. Tp<sup>Np</sup>TiCl<sub>3</sub> (**4**)

A solution of TiCl<sub>4</sub> in toluene (0.70 ml, 1.02 M, 0.71 mmol) was added dropwise by syringe to a solution of TITp<sup>Np</sup> (0.45 g, 0.71 mmol) in toluene (50 ml) at 0 °C. The resulting orange slurry was warmed to room temperature and stirred for 20 h. The reaction mixture was filtered by cannula, and the filtrate was dried under vacuum to afford an orange solid. The product can be crystallized in CH<sub>2</sub>Cl<sub>2</sub>/hexane. (0.18 g, 50% based on TITp<sup>Np</sup>). Anal. Calc. for C<sub>24</sub>H<sub>40</sub>BCl<sub>3</sub>N<sub>6</sub>Ti: C, 49.42; H, 6.99; N, 14.45; Found: C, 49.32; H, 6.90; N, 14.38. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.57 (d, 3H; <sup>3</sup>J<sub>HH</sub> = 2.2; 5-H pz); 6.20 (d, 3H; <sup>3</sup>J<sub>HH</sub> = 2.2; H-4 pz); 3.33 (s; 2H; CH<sub>2</sub> Np); 1.02 (s; 9H; Me Np). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ (ppm) 157.7; 134.8; 104.9 (C-3, C-5 e C-4 pz); 42.9 (CH<sub>2</sub> Np); 30.3 (CH<sub>3</sub> Np). IR (KBr): ν<sub>B-H</sub> 2507 cm<sup>-1</sup>.

#### 3.3. Tp<sup>Ph</sup>TiCl<sub>3</sub> (**5**)

A solution of KTp<sup>Ph</sup> (0.59 g, 1.22 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (50 ml) was cooled to -30°C, and a solution of TiCl<sub>4</sub>

(1.20 ml, 1.02 M, 1.22 mmol) in toluene was added dropwise by syringe within 15 min. The cloudy orange solution was warmed to room temperature and stirred for 20 h. The reaction mixture was filtered by cannula, and the filtrate was dried under vacuum to afford an orange solid. The product can be crystallized in hot toluene (0.67 g, 92 % based on KTp<sup>Ph</sup>). Anal. Calc. for C<sub>27</sub>H<sub>22</sub>BCl<sub>3</sub>N<sub>6</sub>Ti: C, 54.45; H, 3.72; N, 14.11. Found: C, 54.37; H, 3.65; N, 13.95. <sup>1</sup>H NMR (acetone): δ (ppm) 8.44 (d; 3H; <sup>3</sup>J<sub>HH</sub> = 2.6; H-5 pz); 8.20 (m; 6H; phenyl); 7.53 (m; 9H; phenyl); 7.05 (d; 3H, <sup>3</sup>J<sub>HH</sub> = 2.6; H-4 pz). <sup>13</sup>C{<sup>1</sup>H} NMR (acetone): δ (ppm) 151.3; 141.3; 105.9 (C-3, C-5 e C-4 pz); 131.5; 130.5; 128.5; 127.8 (C-1, C-2, C-3, C-4 phenyl). IR (KBr): ν<sub>B-H</sub> 2517 cm<sup>-1</sup>.

#### 3.4. Tp<sup>tBu</sup>TiCl<sub>3</sub> (**6**)

This compound was prepared according to the method described for **5** using a solution of TiCl<sub>4</sub> in toluene (0.90 ml, 1.02 M, 0.92 mmol) and **3** (0.39 g, 0.92 mmol). This compound was isolated as a yellow solid. (0.39 g, 79% based on KTp<sup>tBu</sup>). Anal. Calc. for C<sub>21</sub>H<sub>34</sub>BCl<sub>3</sub>N<sub>6</sub>Ti: C, 47.09; H, 6.40; N, 15.69. Found: C, 46.87; H, 6.25; N, 15.53. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.50 (d; 3H; <sup>3</sup>J<sub>HH</sub> = 2.3; H-5 pz); 6.15 (d; 3H, <sup>3</sup>J<sub>HH</sub> = 2.3; H-4 pz); 1.44 (s; 27H; Me, *t*-Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ (ppm) 159.3; 138.9; 103.6 (C-3, C-5 e C-4 pz); 32.5 (CCH<sub>3</sub>) 30.7 (Me, *t*-Bu). IR (KBr): ν<sub>B-H</sub> 2502 cm<sup>-1</sup>.

#### 3.5. Tp<sup>Ph</sup>ZrCl<sub>3</sub> (**7**)

This compound was prepared according to the method described for **5** using ZrCl<sub>4</sub> (0.29 g; 1.24 mmol) and **2** (0.59 g, 1.24 mmol). This compound was isolated as a white solid. The product can be crystallized in CH<sub>2</sub>Cl<sub>2</sub>/hexane. (0.50 g, 63% based on KTp<sup>Ph</sup>). Anal. Calc. for C<sub>27</sub>H<sub>22</sub>BCl<sub>3</sub>N<sub>6</sub>Zr: C, 50.76; H, 3.47; N, 13.15. Found: C, 50.63; H, 3.36; N, 13.08. <sup>1</sup>H NMR (acetone): δ (ppm) 8.11 (d; 3H; H-5 pz); 8.04 (m; 6H; phenyl); 7.50–7.39 (m; 9H; phenyl); 7.02 (d; 3H, H-4 pz); <sup>13</sup>C{<sup>1</sup>H} NMR (acetone): δ (ppm) 150.5; 133.4; 103.3 (C-3, C-5 e C-4 pz); 130.1; 129.0; 128.2; 126.9 (C-1, C-2, C-3, C-4 phenyl). IR (KBr): ν<sub>B-H</sub> 2521 cm<sup>-1</sup>.

#### 3.6. Tp<sup>tBu</sup>ZrCl<sub>3</sub> (**8**)

This compound was prepared according to the method described for **5** using ZrCl<sub>4</sub> (0.28 g; 1.20 mmol) and **3** (0.50 g, 1.20 mmol). This compound was isolated as a white solid. (0.43 g, 62% based on KTp<sup>tBu</sup>). Anal. Calc. for C<sub>21</sub>H<sub>34</sub>BCl<sub>3</sub>N<sub>6</sub>Zr: C, 43.57; H, 5.92; N, 14.52. Found: C, 43.81; H, 6.05; N, 14.59. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ (ppm) 7.65 (d; 3H; H-5 pz); 6.24 (d; 3H, H-4 pz); 1.44 (s; 27H; CH<sub>3</sub>, *t*-Bu); <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ (ppm)

159.4, 138.5, 103.3 (pz C-3, C-5 and C-4); 31.1 (C, *t*-Bu); 30.7 (CH<sub>3</sub>, *t*-Bu). IR (KBr):  $\nu_{\text{B-H}}$  2511 cm<sup>-1</sup>.

### 3.7. Polymerization procedures

All polymerization reactions were performed in Fisher–Porter bottle (100 ml) equipped with a magnetic stirrer bar and a stainless steel pressure head fitted with inlet and outlet needle valves, a septum-capped ball valve for injections, and a pressure gauge. Under an ethylene atmosphere, the proper amounts of toluene and MAO solution were introduced sequentially. After complete thermal equilibration, the catalyst precursor was added as toluene solution with stirring. The total volume of the reaction mixture was 60 ml for all polymerization runs. The total pressure (3 atm.) was kept constant by a continuous feed of ethylene. The polymerization runs were stopped introducing 1 ml of methanol. The polymers were washed with acidic ethanol, then ethanol and water, and dried in a vacuum oven at 70 °C for 6 h. On the basis of the results of multiple runs, we estimate the accuracy of these numbers to 8%.

### 3.8. Polymer characterization

Melting temperatures were determined by means of differential scanning calorimetry (DSC) with a Thermal Analysis Instruments DSC-2010 using a heating rate of 10 °C/min after twice previous heating to 180 °C and cooling to 40 °C at 10 °C/min. One-point intrinsic viscosities were measured with a Cinevisco viscosimeter in decalin at 135 °C, at concentrations of 0.1 dL/g.

### 3.9. Crystal structure determination of compound 4

Suitable single crystals of titanium compound was placed onto the tip of a 0.1 mm diameter glass capillary and mounted on a Bruker SMART CCD area detector diffractometer for a data collection at 173(2) K. The data collection was carried out using Mo K $\alpha$  radiation (graphite monochromator) with a frame time of 80 s and a detector distance of 4.92 cm. A randomly oriented region of reciprocal space was surveyed to a resolution of 0.77 Å. The intensity data were corrected for absorption and decay (SADABS) [12]. Final cell constants were calculated from the *xyz* centroids of 1390 strong reflections from the actual data collection after integration (SAINT 6.01, 1999) [13]. The crystal structure was solved and refined using SHELXL-86 and SHELXL-97 [14]. A direct-methods solution was calculated in *P*<sub>2</sub><sub>1</sub>/*m* which provided most non-hydrogen atoms from the E-map and shows clearly the presence of mirror(*m*). Full-matrix least squares/difference Fourier cycles were performed and all non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were either placed in ideal positions or

found for from the E-map(H1b) and refined with individual (or group for the methyl groups) isotropic displacement parameters. The neopentyl group of the pyrazolyl ring on the mirror was disordered over two positions. The hydrogen atoms of C4, C6, C7, and C8 have not refined but kept in geometrically ideal positions. The large thermal displacement parameters of the *t*-butyl group are due to correlations with the symmetry equivalents and the position close to the mirror.

## 4. Conclusions

In summary, this work extends the family of Group 4 tris(pyrazolyl)borate-based complexes by the synthesis of Ti(VI) and Zr(IV) compounds having bulky R groups at 3-positions of the pyrazolyl ring that are fully characterized including single-crystal X-ray diffraction studies carried out for **4**. All compounds are easily prepared, air-stable, and can be isolated in moderate to good yields. The complexes were active in ethylene polymerization in the presence of MAO; however the very low activities displayed by them, in comparison with those found for the parent compounds containing Tp<sup>Ms</sup> and Tp<sup>Ms\*</sup> ligands, indicate that besides the steric features, another ones should be driven their catalytic activity.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 220247 for compound **4**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK [Fax. (int code) +44(1223) 336-033, or E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk) or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)

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