Tris(pyrazolyl)methane–chromium(III) complexes as highly active catalysts for ethylene polymerization

Ivan García-Orozco[a,*], Raúl Quijada[a,b,*], Karen Vera[c], Mauricio Valderrama[c,*]

[a] *Centro para la Investigación Interdisciplinaria Avanzada en Ciencia de los Materiales, Santiago, Chile*
[b] *Departamento de Ingeniería Química, Facultad de Ciencias Físicas y Matemáticas, Universidad de Chile, Beauchef 850, Casilla 2777, Santiago, Chile*
[c] *Departamento de Química Inorgánica, Facultad de Química, Pontificia Universidad Católica de Chile, Casilla 306, Santiago 6094411, Chile*

Abstract

Reaction of complex $CrCl_3(THF)_3$ with the tris(pyrazolyl)methane ligands, $HC(Pz)_3$, $HC(3,5\text{-}Me_2Pz)_3$ and their substituted derivatives $RC(Pz)_3$ (R = Me, CH_2OH, CH_2OSO_2Me) in THF lead to the formation of neutral complexes of the types $[RC(Pz)_3CrCl_3]$ and $[RC(3,5\text{-}Me_2Pz)_3CrCl_3]$. After reaction with methylalumoxane (MAO) these complexes are active in the polymerization of ethylene. The substituent on the methane central carbon atom of the ligand has some influence in polymerization behavior. This compounds present higher activities than similar chromium complexes, in the ethylene polymerization reaction.

Keywords: Chromium complexes; Tris(1-pyrazolyl)methane complexes; Synthesis; Ethylene polymerization; Polyethylene

1. Introduction

The tris(pyrazolyl)borate ligand has been widely used in organometallic and coordination chemistry since their initial development by Trofimenko in the late 1960s [1]. These types of ligands are very attractive because they coordinate strongly with early transition metals in a tridentate fashion, and the steric and electronic properties of the pyrazolyl donor can be modified by changing the 3- and 5-substituents [2]. Interestingly, Group 4 complexes containing sterically hindered tris(pyrazolyl)borate ligands are highly active species for ethylene polymerization reactions [3].

The isoelectronic tris(pyrazolyl)methane ligands have received much less attention because their synthesis is more difficult than that of their tris(pyrazolyl)borate analogs. Improvement of the synthetic procedure for tris(pyrazolyl)methane and its derivatives, including functionalization of the central methine carbon atom has meant an important development of chemistry in this area [4]. Substitution of the methine proton by other functional groups can change the solubility characteristics of the ligands and their metal complexes, including the possibility of obtaining complexes soluble and stable in water [5]. The organometallic and coordination chemistry of these types of ligands has been reviewed [6]. Furthermore, the complexes tris(pyrazolyl)methanechromium(III) trichloride and tris(3,5-dimethyl-1-pyrazolyl)methanechromium(III) trichloride have been recently described as active and selective ethylene trimerisation catalyst in the presence on methylalumoxane (MAO) as co-catalyst at high ethylene pressure [7].

Recently we reported the synthesis, structural characterization and activity in ethylene polymerization of the anionic chromium(III) complex $[CrCl_3\{HB(Pz)_3\}]^-$, which shows a moderate activity and a wide molecular weight distribution associated with the presence of more than one active species [8]. In the search for related new polymerization catalysts and the influence of structure on catalyst performance, we now report the synthesis of neutral chromium(III) complexes containing tris(pyrazolyl)methane and its derivatives, of general formula

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Abbreviations: Pz, pyrazolyl; MAO, methylalumoxane; TIBA, tri-isobutylaluminum; Al/Cr, molar ratio of aluminum in MAO or TIBA and a Cr complex; M_w, weight-average molecular weight; M_n, number-average molecular weight; PE, polyethylene; Cp, cyclopentadienyl

[*] Corresponding authors. Tel.: +56 2 6864417; fax: +56 2 6864744.
E-mail addresses: ivagarci@cimat.cl (I. García-Orozco), raquijad@ing.uchile.cl (R. Quijada), jmvalder@puc.cl (M. Valderrama).

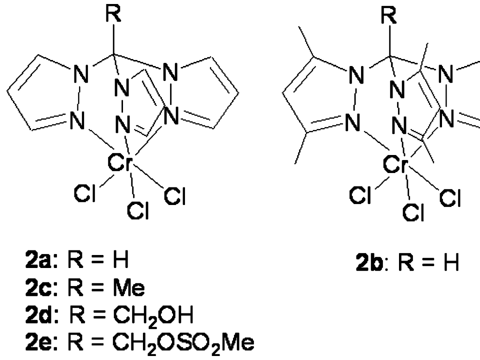


Fig. 1. Proposed molecular structure of complexes **2a**–**2e**.

$[CrCl_3\{(Pz)_3CR\}]$ (R = H, Me, CH_2OH, CH_2OSO_2Me) and $[CrCl_3\{(3,5\text{-}Me_2Pz)_3CH\}]$ (Fig. 1). These compounds present higher activities than similar chromium complexes in the ethylene polymerization reaction.

2. Experimental

2.1. Reagents and general techniques

All manipulations were routinely performed in an inert atmosphere using standard glove box and Schlenk-tube techniques. All reagent-grade solvents were dried, distilled, and stored under a nitrogen atmosphere. The starting compounds, $CrCl_3(THF)_3$, pyrazole and 3,5-dimethylpyrazole, from Aldrich, were used as received. The ligands $HC(Pz)_3$ (**1a**), $HC(3,5\text{-}Me_2Pz)_3$ (**1b**), $MeC(Pz)_3$ (**1c**) and $HOCH_2C(Pz)_3$ (**1d**) were prepared as described in the literatures [4e,9]. Elemental analyses (C, H and N) were carried out with a Fisons EA 1108 microanalyzer. FTIR spectra were recorded on a Bruker Vector-22 spectrophotometer using KBr pellets. NMR spectra were recorded on Bruker AC-200P and Avance-400 spectrometers. Chemical shifts are reported in ppm relative to $SiMe_4$. Magnetic measurements were carried out at room temperature (293 K) on a Johnson Matthey Magnetic Susceptibility Balance MSB MK1.

2.2. Synthesis of ligand $MeSO_2OCH_2(Pz)_3$ (1e)

To a solution of 1,1,1-tris(pyrazolyl)ethanol (**1d**) (150 mg; 0.37 mmol) and Et_3N (0.1 mL; 0.63 mmol) in CH_2Cl_2 (15 mL) cooled to 0 °C, $MeSO_2Cl$ (0.05 mL; 0.63 mmol) was added. After heating the reaction under reflux for 4 h the mixture was treated with H_2O/CH_2Cl_2 (30/15 mL). The organic layer was separated and dried over sodium sulfate. The mixture was filtered, the solvent removed by evaporation and the pale-yellow solid obtained was dried under vacuum. Yield 120 mg (99%). m.p. 118–119 °C. Anal. Found: C, 44.4; H, 4.2; N, 25.7; S, 10.3%. $C_{12}H_{14}N_6O_3S$ requires: C, 44.7; H, 4.4; N, 26.1; S, 10%. ^1H NMR ($CDCl_3$): δ 7.70 [d, 3H, $J_{HH} = 1.3$ Hz, H_3 (Pz)], 7.31 [d, 3H, $J_{HH} = 2.6$ Hz, H_5 (Pz)], 6.39 [dd, 3H, $J_{HH} = 1.3, 2.6$ Hz, H_4 (Pz)], 5.75 [s, 2H, CH_2], 2.95 [s, 3H, Me]. $^{13}C\{1H\}$ NMR ($CDCl_3$): δ 142.00 [C_3(Pz)], 130.50 [C_5(Pz)], 107.30 [C_4(Pz)], 88.46 [$C(Pz)_3$], 71.09 (CH_2), 37.54 (Me).

2.3. Synthesis of complexes **2a**–**2e**

General procedure: a solution of the tris(pyrazolyl)methane ligand [$HC(Pz)_3$ (**1a**), HC $(3,5\text{-}Me_2Pz)_3$ (**1b**), $MeC(Pz)_3$ (**1c**), $HOCH_2C(Pz)_3$ (**1d**), $MeSO_2OCH_2(Pz)_3$ (**1e**), 0.4 mmol] in THF (15 mL) was added via syringe to a solution of $CrCl_3(THF)_3$ (150 mg; 0.4 mmol) in THF (15 mL). The resulting mixture was stirred and refluxed for 4 h. The green solid formed was filtered off, washed with THF and diethyl ether, and dried under vacuum. The complexes formed with the ligands $MeC(Pz)_3$ and $MeSO_2OCH_2(Pz)_3$ were purified by dissolving in DMSO, filtered and precipitated by adding diethyl ether.

(**2a**) $[CrCl_3\{(Pz)_3CH\}]$, yield 93%. Anal. Found: C, 33.0; H, 2.8; N, 22.7%. $C_{10}H_{10}Cl_3CrN_6$ requires: C, 32.2; H, 2.7; N, 22.6%. IR (KBr, cm^{-1}): ν 3123 s, 2983 m, 1629 w (br), 1512 m, 1443 m, 1410 s, 1277 s, 1248 m, 1096 m, 1064 s, 991 m, 863 m, 777 s, 604 m, 405 m, 357 s, 330 m. $\mu_{eff} = 3.6\ \mu_B$.

(**2b**) $[CrCl_3\{(3,5\text{-}Me_2Pz)_3CH\}]$, yield 93%. Anal. Found: C, 41.8; H, 5.0; N, 18.2%. $C_{16}H_{22}Cl_3CrN_6$ requires: C, 42.1; H, 4.9; N, 18.4%. IR (KBr, cm^{-1}): ν 2927 s, 1627 w (br), 1565 s, 1460 s, 1409 m, 1393 s, 1384 s, 1301 s, 1262 s, 1049 s, 918 m, 861 m, 703 s, 493 w, 345 s. $\mu_{eff} = 3.7\ \mu_B$.

(**2c**) $[CrCl_3\{(Pz)_3CMe\}]$, yield 68%, crystallized from dimethyl sufoxide–diethyl ether. Anal. Found: C, 34.2; H, 3.1; N, 21.7%. $C_{11}H_{12}Cl_3CrN_6$ requires: C, 33.2; H, 3.1; N, 20.8%. IR (KBr, cm^{-1}): ν 3132 s, 3011 w, 1626 w (br), 1510 m, 1419 m, 1402 s, 1328 s, 1237 s, 1090 s, 1061 s, 980 m, 765 s, 601 m, 395 m, 351 s. $\mu_{eff} = 3.8\ \mu_B$.

(**2d**) $[CrCl_3\{(Pz)_3CCH_2OH\}]$, yield 83%. Anal. Found: C, 33.0; H, 3.1; N, 19.8%. $C_{11}H_{12}Cl_3CrN_6O$ requires: C, 32.8; H, 3.0; N, 20.9%. IR (KBr, cm^{-1}): ν 3410 s, 1513 m, 1423 s, 1408 m, 1339 s, 1316 m, 1230 s, 1080 s, 974 m, 875 m, 766 s, 615 m, 599 m, 351 s. $\mu_{eff} = 3.8\ \mu_B$.

(**2e**) $[CrCl_3\{(Pz)_3CCH_2OSO_2Me\}]$, yield 89%. Anal. Found: C, 29.4; H, 2.8; N, 16.1; S, 6.3%. $C_{12}H_{14}Cl_3CrN_6O_3S$ requires: C, 30.0; H, 2.9; N, 17.5; S, 6.7%. IR (KBr, cm^{-1}): ν 3141 m, 3105 m, 1418 m, 1339 s, 1232 m, 1183 s, 1084 m, 1029 m, 886 m, 802 m, 764 s, 518 m, 423 m, 355 s. $\mu_{eff} = 3.6\ \mu_B$.

2.4. Ethylene polymerization

Polymerization was carried out in a 1 L Pyrex glass reactor connected to a constant temperature circulator and equipped with mechanical stirring. Toluene and cocatalyst (MAO 10% or TIBA) were introduced into the reactor under an inert nitrogen atmosphere. Solvent volume was adjusted to a total of 120 or 240 mL, as required. Mechanical stirring was kept constant at 1000 rpm and ethylene pressure was adjusted to 4 bar before introducing the pre-catalyst, which was dissolved in toluene and pumped into the reactor to initiate the polymerization. Ethylene pressure and reactor temperature (60 °C) were kept constant throughout the polymerization. The reaction was stopped by addition of an HCl/ethanol solution (5 vol.%). The polymer was recovered by filtration, washed with ethanol and dried overnight at room temperature.

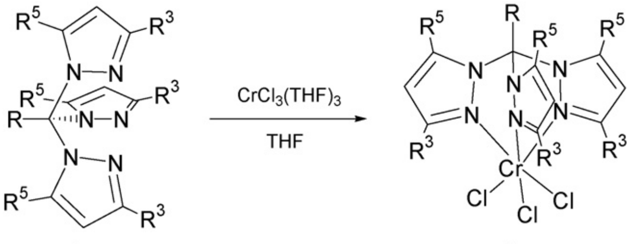
2.5. Polymer characterization

The polymers were characterized by Fourier transform infrared spectroscopy (FTIR), gel permeation chromatography (GPC) and differential scanning calorimetry (DSC). Molar mass distribution was obtained with a Watters (Alliance GPC 2000) high-temperature GPC instrument equipped with three Styragel HT-type columns (HT3, HT5 and HT6E). 1,2,4-Trichlorobenzene was used as solvent, at a flow rate of 1 mL/min and a temperature of 135 °C. A universal calibration curve was used to obtain weight-average molecular weight (M_w) and polydispersity index (M_w/M_n). Polymer melting points (T_m) were measured on a TA Instruments model DSC 2920 differential scanning calorimeter at a rate of 10 °C/min for two cycles using a temperature range from −10 to 170 °C. Reported results are those obtained on the second scan.

3. Results and discussion

3.1. Synthesis and ethylene polymerization activities of complexes **2a**–**2e**

The tris(pyrazolyl)methane ligands, $HC(Pz)_3$ and $HC(3,5\text{-}Me_2Pz)_3$, are commonly prepared by phase transfer reaction of the appropriate pyrazol with a large excess of Na_2CO_3 [4e]. Starting from the $HC(Pz)_3$ ligand is possible to functionalize the apical carbon to form $MeC(Pz)_3$ and $HOCH_2C(Pz)_3$ [9]. The substitution of alcohol proton in the latter compound yields a new substituted ligand. The reaction of 1,1,1-tris(pyrazolyl)ethanol with $MeSO_2Cl$ in the presence of Et_3N produces the $MeSO_2OCH_2C(Pz)_3$ compound. The ligand obtained was fully characterized by analytical and spectroscopic methods (see Section 2). When the chemical shifts of the $MeSO_2OCH_2C(Pz)_3$ ligand and potassium tris(pyrazolyl)methanesulfonate [5a] were compared some similarities were founded. The chemical shifts of the carbon atom in the pyrazole moiety (107.3, 130.5 and 142.0 ppm) are similar to those of tris(pyrazolyl)methanesulfonate compound (108.4, 132.9 and 142.7 ppm). Thus the pyrazole rings show a subtle electronic influence from the apical position substituent. However, the important differences in the H_5 proton chemical shifts (7.31 versus 7.60 ppm) may be due to a large sterically hindered CH_2OSO_2Me group [3b,9].



1a-e

2a-e

	R	R^3	R^5
a	H	H	H
b	H	Me	Me
c	Me	H	H
d	CH_2OH	H	H
e	CH_2OSO_2Me	H	H

Scheme 1. Synthesis of tris(pyrazolyl)methane–chromium complexes **2a**–**2e**.

The reaction of $CrCl_3(THF)_3$ with the tris(pyrazolyl)methane ligands in refluxing THF leads to the formation of green solids, characterized as neutral complexes of the type $[CrCl_3\text{-}\{RC(Pz)_3\}]$ (Scheme 1).

Complexes **2a**–**2e** are stable in air at room temperature and show low solubility in organic solvents. Elemental analysis, FTIR and magnetic moments were used to characterize the isolated complexes. The solid state IR spectra in KBr pellets show strong absorption bands in the 1510–1565 and 345–360 cm^{-1} ranges, assigned to ν (CN) and ν (Cr–Cl), respectively [4f,10]. Compounds **2a** and **2c**–**2e** show the ν (Cr–Cl) vibration around 350 cm^{-1}. In compound **2b** this vibration appeared at 345 cm^{-1} showing a lower Cr–Cl bond strength. This is probably due to steric hindrance due to the proximity of the methyl substituent to the chloride atom. The spin state of the complexes was confirmed by magnetic susceptibility measurements ($\mu_{eff} \approx 3.7\ \mu_B$) which indicate the presence of three unpaired electrons on the chromium center. All attempts to obtain a monocrystal of compounds **2a**–**2e** failed because of their low solubility in common solvents. However, the spectroscopic and analytical data are consistent with the proposed formulation.

Complexes **2a**–**2e** in the presence of MAO were used as initiators for ethylene polymerization. The catalytic behavior and properties of the polymers are summarized in Table 1. Analysis of the data showed that these new compounds have high activities

Table 1
Ethylene polymerization reactions by complexes **2a**–**2e** using MAO as cocatalyst in toluene

Entry	Complex	Polymer (g)	Activity[a]	M_w	M_w/M_n	T_{m_1} (°C)
1	2a	11.0	360	1900	1.3	128.3
2	2b	10.5	330	1900	1.2	126.2
3	2c[b]	21.0	640	2150	1.3	126.1
				64400	1.3	
4	2d[b]	1.5	50	1600	1.2	132.3
				93700	2.1	
5	2e[b]	20.0	620	1850	1.2	132.5
				52000	1.6	

Reaction condition: 8 µmol of Cr, $Al_{MAO}/Cr = 1000$, solvent: toluene (100 ml), $T = 60$ °C, $t = 60$ min, ethylene pressure = 4 bar, $\Omega = 1000$ rpm.

[a] In units: kg PE/mol Cr bar h.

[b] Bimodal distribution from GPC analyses.

compared to other chromium complexes [11], and in particular to the related anionic hydro-tris(pyrazolyl)borate–chromium(III) complex [8].

It was found that the activity of the catalysts depends on their structure. Complexes **2a** and **2b** showed similar activities, indicating that methyl substitution on the pyrazole moiety has minimal influence on ligand donor ability. However, a substituent on the central methine carbon atom of the ligand has a major influence on the ethylene polymerization reaction. A methyl group (**2c**) increases the activity up to twice, while a CH_2OH group (**2d**) decreases it dramatically. One possible reason for the low activity of complex **2d** is the coordinative interaction of the OH group with other metal centers or with the MAO cocatalyst. When the hydroxyl group is protected with a SO_2Me functionality, the activity becomes similar to that of compound **2c**. A constrained effect on the tripodal ligand for the steric hindrance of the substituent on the central methine carbon atom should be the cause of the greater activity of the catalyst [4f]. Several close contacts have been proposed on the proton in the five-position of the pyrazolyl ring and the group in the apical carbon position. In the same way, the proton chemical shift of such protons is more affected by hindered than electronic effect of the group on the central methine carbon atom [4e,9].

The polymers obtained in the polymerization were characterized by FTIR, GPC and DSC. The FTIR spectra do not show the vibration associated with terminal double bonds. This suggests that the predominant chain transfer mechanism is alkyl exchange with MAO [12]. The GPC analyses of the polymers obtained with compounds **2a**–**2b** show a monomodal molecular weight distribution (Fig. 2) with an average molecular weight of about 1980 g/mol. For the polymers from compounds **2c**–**2e** the GPC analyses show a bimodal distribution of molecular weights, with average molecular weights of 1900 and 70,000 g/mol. The contribution of the high molecular weight fraction to the polymer molecular weight increases in compounds **2d**–**2e** with an electron deficiency induced by the –OH and $–OSO_2Me$ groups. It is worth mentioning that regardless of the substituent, in all cases the low fractions have similar average molecular weights and molecular weight distributions.

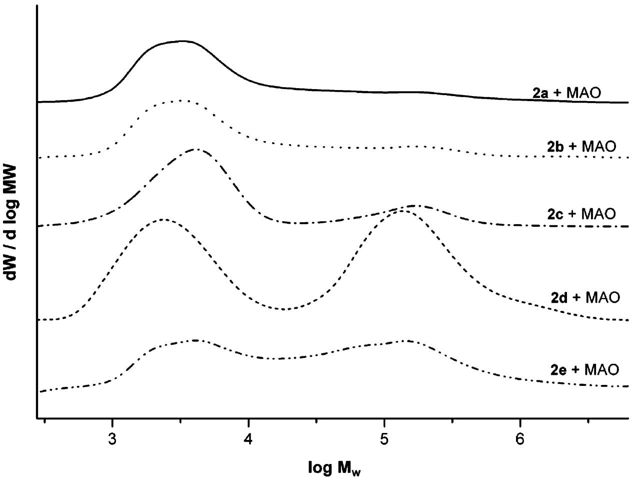


Fig. 2. GPC analyses of polymers obtained by compounds **2a**–**2e** with MAO.

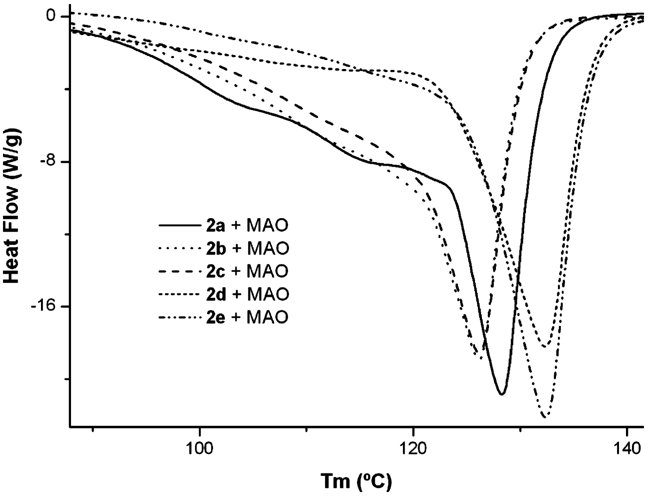


Fig. 3. DSC analyses of polymers obtained by compounds **2a**–**2e** with MAO.

The DSC analyses (Fig. 3) have a peak around 130 °C. The polymers obtained from compounds **2a**–**2c** show a broad shoulder at lower temperatures. The observed T_m values of compounds **2d** and **2e** are similar to that of high density polyethylene around 132 °C. The contribution of the high molecular weight fraction in the GPC analyses is also in agreement.

It is noteworthy to mention that compounds **2a** and **2b** yield only low molecular weight polyethylene. These compounds were showed as active and selective ethylene trimerisation catalyst [7]. The polymerization reaction was carried out at different conditions than trimerisation. The ethylene pressure of the polymerization (4 bar) is lower than that of trimerisation (40 bar). It had been showed that ethylene trimerisation reaction was second order with respect to ethylene [13] thus polymerization should be favored to lower pressures. The polymerization was carried out at a temperature of 60 °C and the trimerisation works well at higher temperatures (>80 °C). Lower reaction temperatures promote more PE and lower 1-hexene selectivity [14]. The catalyst and MAO are pre-contacted during 30 min before the addition of ethylene in the trimerisation reaction [7]. This step produces Cr(I) compounds, which are the active specie proposed for the trimerisation [15]. The MAO-catalyst pre-contact is not present in the polymerization reaction afterward the trimerisation active specie is unfavored. All this conditions probably cause the lower selectivity of the catalyst toward 1-hexene and the increase of the amount of PE obtained.

3.2. Study of ethylene polymerization conditions

As seen above, the highest activities were reached with compounds **2c** and **2e**. The main difference between them is the greater contribution of the high molecular weight fraction achieved with compound **2e**. However, compound **2c** is a better option than **2e** because of its undemanding synthesis. In order to obtain more insight with respect to the ligand structure, further polymerization experiments were carried out with compounds **2c** and **2a**, with the aim of studying the influence of the substituent on the central methine carbon atom on the dif-

Table 2
Ethylene polymerization reactions by complexes **2c** using MAO as cocatalyst in toluene

Entry	Al_{MAO}/Cr	Time (min)	Polymer (g)	Activity[a]	M_w[b]	M_w/M_n	T_{m_1} (°C)	T_{m_2} (°C)
1	1035	30	6.5	400	188400	2.25	128.8	116.6
					1930	1.35		
2	2070	30	17.3	1080	59200	1.13	126.8	117.9
					1600	1.27		
3	3100	30	31.4	1960	54700	1.31	125.5	116.3
					1380	1.18		
4	4140	30	40.7	2540	77700	1.43	123.3	115.7
					1590	1.21		
5	3100	60	42.1	1300	67900	1.41	128.1	112.8
					1580	1.21		
6	3100	15	13.4	1670	71500	1.50	127.7	102.9
					1200	1.15		
7	3100	15[c]	15.6	1950	73200	1.30	123.7	112.7
					1400	1.21		

Reaction condition: 8 μmol of Cr, solvent: toluene (100 ml), $T = 60\,^{\circ}C$, ethylene pressure = 4 bar, $\Omega = 1000$ rpm.

[a] In units: kg PE/mol Cr bar h.

[b] Bimodal distribution from GPC analyses.

[c] MAO pre-activation.

Table 3
Ethylene polymerization reactions by complexes **2c** using TIBA as cocatalyst

Entry	Al_{TIBA}/Cr	Polymer (g)	Activity[a]	M_w	M_w/M_n	T_m (°C)
1	1006	14.7	910	1070	1.10	95.4
2	2070	18.3	1140	940	1.06	90.3
3	3017	7.2	450	840	1.04	66.5

Different ratios Al_{TIBA}/Cr in toluene. Reaction condition: 8 μmol of Cr, Solvent: toluene (240 ml), $T = 60\,^{\circ}C$, $t = 30$ min, ethylene pressure = 4 bar, $\Omega = 1000$ rpm.

[a] In units: kg PE/mol Cr bar h.

ferent polymerization conditions. These results are summarized in Tables 2–4.

The polymerization conditions studied in these systems were temperature, the Al/Cr ratio, reaction time, and the effect of the cocatalyst. In the case of compound **2c** using the same conditions of former experiments (vide infra), the best polymerization temperature was found to be 60 °C. The activity decreases one order of magnitude at 40 °C. At temperatures higher than 60 °C reactor fouling occurred.

With the purpose of evaluating the effect of MAO concentration on the ethylene polymerization of compound **2c**, different Al_{MAO}/Cr ratios were studied. The catalytic behavior and properties of the polymers are summarized in Table 2 (entries 1–4). Catalyst activity increases with Al_{MAO}/Cr ratio up to $Al_{MAO}/Cr = 4140$, when the reaction reaches the highest yield.

The GPC analyses of the polymers obtained show the predominance of low molecular weights with Al_{MAO}/Cr ratios. The

Table 4
Ethylene polymerization reactions by complexes **2a** using MAO as cocatalyst in toluene

Entry	Al_{MAO}/Cr	Time (min)	Polymer (g)	Activity[a]	M_w[b]	M_w/M_n	T_{m_1} (°C)	T_{m_2} (°C)
1	1035	30	2.6	160	180740	2.35	127.1	120.6
					1937	1.34		
2	2070	30	4.5	280	180840	1.71	126.1	115.7
					1670	1.29		
3	3100	30	5.2	320	59150	1.31	127.0	113.4
					1332	1.19		
4	4140	30	9.0	560	135170	1.78	126.8	112.2
					1284	1.17		
5	4140	60	13.4	415	79729	1.62	127.0	112.3
					1299	1.19		
6	4140	90	23.9	494	64567	1.42	127.6	114.0
					1413	1.22		

Reaction condition: 8 μmol of Cr, Solvent: toluene (240 ml), $T = 60\,^{\circ}C$, ethylene pressure = 4 bar, $\Omega = 1000$ rpm.

[a] In units: kg PE/mol Cr bar h.

[b] Bimodal distribution from GPC analyses.

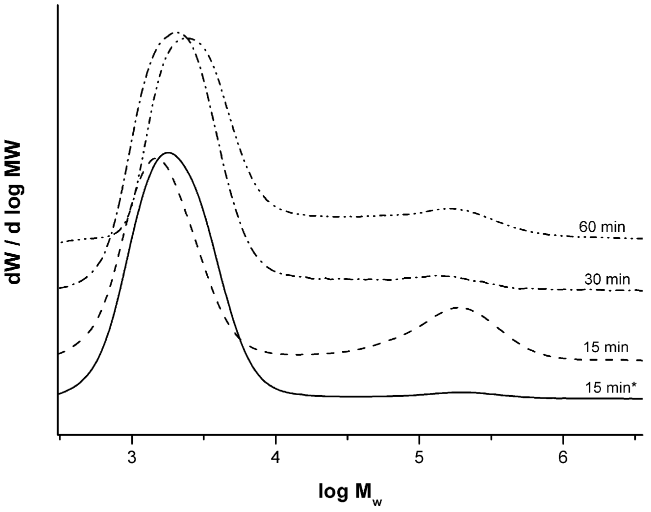


Fig. 4. GPC analyses of polymers obtained by compounds **2c** at different times.

DSC of the polymers obtained show the presence of a broad endotherm with a main peak centered at 126 °C and a broad shoulder toward 115 °C that increases whit the Al_{MAO}/Cr ratio.

The experimental conditions of the polymerization were evaluated at different times to study possible catalyst deactivation. Polymerization reaches a maximum activity value (1960 kg PE/mol Cr bar h) at 30 min (Table 2, entry 3). The catalyst becomes deactivated after 30 min of reaction. Between 30 and 60 min of reaction, the amount of polymer increases 25%, and after 60 min the catalyst is completely deactivated.

The FTIR spectra of the polymers obtained did not show the C=C vibration, therefore the main termination process was again chain transfer to MAO. In general, a bimodal distribution of molecular weight was seen in GPC analyses (Fig. 4), where the low fraction is larger than the high molecular weight fraction.

The DSC analyses of the polymer obtained at different reaction times show a broad endotherm with a main peak (T_{m_1}) around 127 °C and a broad shoulder (T_{m_2}) centered on 112 °C that become less important along time.

With the purpose of evaluating the cocatalyst effect and the MAO chain transfer as the polymer termination process, triisobutylaluminum (TIBA) was used instead of MAO in the polymerization with complex **2c**. The catalytic behavior and properties of the polymers are summarized in Table 3. The data show an increase in activity compared to the use of MAO when the Al_{TIBA}/Cr ratios are 1000–2000. Activity suddenly decreases at 450 kg PE/mol Cr bar h with the use of $Al_{TIBA}/Cr = 3017$. The IR spectra of the polymer obtained show C=C terminal groups. Thus β-hydrogen elimination becomes important when TIBA is used as co-catalyst confirming the Al chain transfer when MAO is used. GPC analyses show a monomodal distribution of low molecular weights (840–1070 g/mol) with lower polydispersity as that obtained with MAO. DSC analyses display a broad endotherm with a T_m around 90 °C.

Complex **2a** was studied in a similar way as complex **2c** to evaluate the influence of the central carbon atom substituent on the ligand. The activity of compound **2a** was evaluated at different Al/Cr ratios. The catalytic behavior and properties of the polymers are summarized in Table 4 (entries 1–4). In 240 mL of toluene and an Al/Cr = 4000, the catalyst reached its maximum activity (560 kg PE/mol Cr h bar). This value is five times less than those reached by compound **2c** under the same conditions.

The polymers obtained with complex **2a** were characterized by FTIR, GPC and DSC. In all cases the polymers behaved in a similar way as those obtained from compound **2c**. The FTIR spectra did not show the C=C vibration like the polymer obtained with compound **2c**. Likewise, the GPC show a bimodal distribution of molecular weights. The low fraction is predominant over the high fraction. The molecular weight of the low fraction decreases at greater Al/Cr values. The DSC of the polymer obtained within compound **2a** showed a broad endotherm with two clearly defined melting points, like that from compound **2c**.

Activity varied between 420 and 560 kg PE/mol Cr bar h from 30 to 60 min of reaction time (Table 4, entries 4–6). The GPC of the polymers obtained again showed a bimodal distribution with a predominant low fraction. The high molecular weight fraction decreased and the low molecular weight fraction increased with time. The DSC of the polymer obtained with compound **2a** also displayed a broad endotherm with slight changes in both T_m values with reaction time, similar to what happened with compound **2c**.

3.3. *The active catalytic species*

In the proposed polymerization mechanism of non-metalocene catalysts [16], the first step is halogen replacement by a methyl group from MAO. Some alkyl chromium compounds were prepared by reaction of $CrCl_3(THF)_3$ with organoaluminum compounds such as AlR_3 or AlR_2OEt [17]. In a compound with two chlorine atoms, the MAO promotes the replacement of one chloride by a methyl group and a vacant place for olefin coordination as has been proposed for Cp_2ZrCl_2 compounds [18]. Therefore, the metal acquires a positive charge stabilized by a $[MAO–Cl]^-$ counteranion.

Based on studies of mono(cyclopentadienyl)chromium(III) catalysts for the polymerization of ethylene [19], the presence of three chlorine atoms in the precatalyst compounds and the bimodal distribution shown by GPC, we propose the presence of two active species in the polymerization reaction: $[CrLMe_2]^+$ (**A**) and $[CrLMe]^{2+}$ (**B**), where L = tris(pyrazolyl)methane ligand.

Species **A** has two methyl groups from chloride exchange promoted by MAO, a vacancy, and a positive charge that favor ethylene coordination with the metal center. Species **B** has a methyl group, two vacancies and two positive charges that increase olefin affinity. However this species is possibly less stable due to the presence of a higher charge. Complexes of the type $[Cp^*CrMe]^+$, active in ethylene polymerization [20], should support the existence of active charged species with two vacancies.

The catalyst's structure has some influence on the predominance of both catalytic species that change in the different experimental conditions, as could be seen in the GPC analyses of the polymers obtained from **2a**–**2e** (Table 1, Fig. 2). The time resolved analyses of catalyst **2c** show that one catalytic center becomes deactivated with time (Fig. 3). An MAO preactivation was carried out before adding catalyst to the reactor and only low fractions were found in GPC analyses of the polymer (Table 2, Fig. 3). When the solvent used in the polymerization was changed by heptanes, the activity decreases drastically (60 kg/mol Cr bar h). The low dielectric constant of heptanes disfavors the presence of more charged species (as species **B**). The GPC analyses of the polymer obtained with heptanes show only the low molecular fraction. TIBA was used as cocatalyst instead of MAO, producing a polymer in which only the low molecular weight fraction was found (Table 3). The lower coordinating behavior of TIBA is well known, which produces less catalyst activity than MAO [21]. It is well know that isobutyl groups can be transferred to the polymer chain, decreasing the polymer's molecular weight by steric hindrance from the isobutyl groups on the growing chains.

4. Conclusions

In summary, this is the first example of ethylene polymerization by tris(pyrazolyl)methane–chromium(III) complexes **2a**–**2e**. These complexes are stable in air at room temperature and show low solubility in organic solvents. However, in the presence of MAO these compounds are active and produce bimodal molecular weight distribution where low molecular weight PE is predominant. The substituent in the central carbon atom of the ligand has more influence on polymerization activity than the pyrazole ring substituents, perhaps due to a steric hindrance effect. Higher molecular weight fraction was obtained in a major contribution to the molecular weight when the apical substituent is different than methyl group. Further studies are performed in this sense with the aim to increase of the higher molecular weight fraction of the polymer obtained.

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