

# Iron(II) and cobalt(II) tris(2-pyridyl)phosphine and tris(2-pyridyl)amine catalysts for the ethylene polymerization

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## Abstract

Polyethylene was synthesized using iron(II) and cobalt(II) complexes stabilized by tris(2-pyridyl)X (X=N, P) ligands in the presence of methylaluminoxane (MAO) as cocatalyst. The catalysts showed activities ranging from moderate to high. The iron complexes showed higher activities than the cobalt analogous and it was found that the bridgehead atom of the ligand tpX (X=P, N) did not affect significantly the activity of the active species as well as the molecular weight of the polymers. The polyethylenes obtained were classified as HDPE with linear structure and broad monomodal distribution.

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## 1. Introduction

Late transition metal catalysts for  $\alpha$ -olefins polymerization have been the attention center of the academic and industrial research, due to their tolerance to different functional groups and they allow better control over the physical properties of the resultant polymers [1–4]. After the discovery of iron and cobalt 2,6-bis(imino)pyridyl catalysts, the studies have been focused on the catalyst structure. The most modifications have been done by changing steric and electronic properties of the substituents on aromatic units of the imine framework, and by modification of the backbone of these catalysts [5–11]. Therefore, numerous variations of the original tridentate 2,6-bis(imino)pyridinyl ligand have been reported, many of them

maintaining the same core [N,N,N]-metal in the catalyst systems [1–4,12–15].

The success of  $\alpha$ -diimine and 2,6-bis(imino)pyridine catalyst systems in the production of high molecular weight polymers, instead of dimers or oligomers, is based on the protection of the bulky ortho substituents present in the ligands which is able to avoid chain transfer reactions and promotes high chain-growth rate on the metal center.

Going forward our interest in developing transition metal catalysts with [N,N,N] ligands, we have aimed at tripod ligands with a tridentate nitrogen-based because they present an inherent steric impediment around the metal center as consequence of their tripodal geometry. One of these tripod ligands is the tris(2-pyridyl)X (tpX; X=N, P, P=O, CH, COH, As), which coordination chemistry with early and late transition metals is well known [16], but its catalytic properties have not been fully studied. With the exception of a patent concerning to the ethylene polymerization by 3–11 transition metals with tris(2-pyridyl)amine ligands [17], catalyst systems with these kind of tripod ligands have not been reported in open literature. Consequently, in this work we describe a catalytic system for ethylene polymerization based on

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iron and cobalt tris(2-pyridyl)X (X = N, P) complexes activated with methylaluminumoxane (MAO) as cocatalyst.

## 2. Experimental

### 2.1. General procedure

All reactions and manipulations were carried out under argon atmosphere. Toluene was used as a solvent, dried over sodium, and deoxygenated prior to use. The ligands tris(2-pyridyl)amine (tpN) and tris(2-pyridyl)phosphine (tpP) were prepared according to reported procedures [18–20]. The salt precursors  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  and  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were dehydrated at 80 °C under vacuum for 8 h. MAO (12.6 wt%,  $\rho = 0.91$  g/mL at 30 °C Al, Akzo Nobel, USA) was used as a cocatalyst.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker AVANCE-300 or 500 MHz spectrometer in  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$  or 1,2,4-trichlorobenzene with the residual signal of solvent as internal standard at room temperature (25 °C) or 100 °C for polyethylene analysis. C, H and N analysis were measured on a Fisons EA 1108 analyzer. FAB mass spectra were obtained with a VG ZAB2SE high-resolution spectrometer, using 3-nitrobenzyl alcohol (NBA)/dimethyl sulphoxide (DMSO) as the matrix. The XPS measurements were made on a XL 220I VG Scientific Spectrometer, the collected data was referenced to an energy scale with  $\text{C}_{1s}$  binding energy (BE) at  $285.0 \pm 0.1$  eV. The oxidation state of the complexes was determined by comparison with the salts  $\text{FeCl}_2$  ( $\text{Fe}_{2p_{1/2}}$ : 723.2 eV;  $\text{Fe}_{2p_{3/2}}$ : 709.4 eV) and  $\text{CoCl}_2$  ( $\text{Co}_{2p_{1/2}}$ : 796.6 eV;  $\text{Co}_{2p_{3/2}}$ : 780.9 eV) which were used as standard.

### 2.2. Preparation of {tris(2-pyridyl)amine}FeCl<sub>2</sub> (1)

A solution of tris(2-pyridyl)amine (137 mg; 0.55 mmol) and  $\text{FeCl}_2$  (70 mg; 0.56 mmol) in *n*-butanol (10 mL) was stirred at 80 °C for 20 min to yield a yellow suspension. After, the suspension was cooled at room temperature. The solvent was filtered out and the yellow solid was washed one time with *n*-butanol and several times with *n*-hexane (6 × 20 mL). The yellow powder was filtered and dried under vacuum. Yield: 150 mg (73%). Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{FeCl}_2$ : C: 48.0; H: 3.2; N: 14.9. Found: C: 47.7; H: 3.2; N: 15.2. MS (FAB<sup>+</sup>):  $m/z$  339 ( $\text{M}^+ - \text{Cl}$ ). XPS, BE (eV):  $\text{Fe}_{2p_{1/2}}$ : 725.2,  $\text{Fe}_{2p_{3/2}}$ : 711.6.

Complexes 2–4 were prepared following the same procedure described above.

### 2.3. Preparation of {tris(2-pyridyl)phosphine}FeCl<sub>2</sub> (2)

A mixture of tris(2-pyridyl)phosphine (460 mg; 1.74 mmol) and  $\text{FeCl}_2$  (220 mg; 1.75 mmol) afforded an orange solid. Yield: 470 mg (69%). Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{N}_3\text{PFeCl}_2$ : C: 45.9; H: 3.1; N: 10.7. Found: C: 45.5; H: 3.4; N: 10.3. MS (FAB<sup>+</sup>):  $m/z$  356 ( $\text{M}^+ - \text{Cl}$ ). XPS, BE (eV):  $\text{Fe}_{2p_{1/2}}$ : 722.5,  $\text{Fe}_{2p_{3/2}}$ : 708.9.

### 2.4. Preparation of {tris(2-pyridyl)amine}CoCl<sub>2</sub> (3)

A mixture of tris(2-pyridyl)amine (325 mg; 1.31 mmol) and  $\text{CoCl}_2$  (170 mg; 1.31 mmol) afforded an aquamarine solid.

Yield: 400 mg (81%). Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{N}_4\text{CoCl}_2$ : C: 47.6; H: 3.2; N: 14.8. Found: C: 47.1; H: 3.5; N: 14.4. MS (FAB<sup>+</sup>):  $m/z$  342 ( $\text{M}^+ - \text{Cl}$ ). XPS, BE (eV):  $\text{Co}_{2p_{1/2}}$ : 796.1;  $\text{Co}_{2p_{3/2}}$ : 780.7.

### 2.5. Preparation of {tris(2-pyridyl)phosphine}CoCl<sub>2</sub> (4)

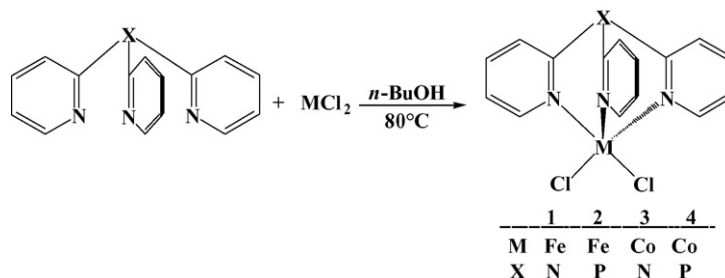
A mixture of tris(2-pyridyl)phosphine (142 mg; 0.54 mmol) and  $\text{CoCl}_2$  (70 mg; 0.54 mmol) afforded a grey solid. Yield 190 mg (89%). Anal. Calcd. for  $\text{C}_{15}\text{H}_{12}\text{N}_3\text{PCoCl}_2$ : C: 46.7; H: 3.2; N: 11.4. Found: C: 46.2; H: 3.0; N: 10.9. MS (FAB<sup>+</sup>):  $m/z$  359 ( $\text{M}^+ - \text{Cl}$ ). XPS, BE (eV):  $\text{Co}_{2p_{1/2}}$ : 796.0,  $\text{Co}_{2p_{3/2}}$ : 780.1.

### 2.6. Polymerization procedure

Runs were carried out in a 0.5 L thermostated Büchi autoclave, with a 500 mL glass vessel. The reactor was filled with 80 mL of dry and oxygen-free toluene and the appropriate amount of MAO (12.6% Al, in toluene, Al:M = 3000:1), pressurized with ethylene and thermostated to 60 or 80 °C. Cocatalyst solution was stirred for 10 min. Then, the selected amount of precatalysts in 20 mL of dry and oxygen-free toluene was transferred via cannula into the autoclave. The pressure was kept constant during the polymerization (5 bar) by a continuous admission of ethylene. After 0.5 h, the reaction was quenched with ethanol (2 mL) and the ethylene excess was vented. The resulting polymer was stirred with hydrochloric acid/water/ethanol mixture (5/85/10), washed several times with distilled water and finally vacuum dried at 60 °C.

### 2.7. Polymers characterization

Weight-average molecular weight and molecular weight distribution were determined by means of Gel Permeation Chromatography (WATERS Alliance GPCV 2000) at 135 °C with 1,2,4-trichlorobenzene as mobile phase, stabilized with 0.25 g/L of butylated hydroxytoluene (BHT). The results were analyzed using an universal calibration curve based on standards of polystyrene. Films for Fourier Transformed Infrared Spectroscopy (FTIR) analysis were molded at 190 °C for 5 min. FTIR spectra were obtained on a NICOLET Magna-IR 560 E.S.P. spectrometer with a resolution of about  $2\text{ cm}^{-1}$  and using 16 scans. The thermal analyses were performed on a Mettler Toledo DSC-822, calibrated with an indium standard. Samples (10–11 mg) were heated under nitrogen atmosphere from 25 to 170 °C at a heating rate of 20 °C/min and kept at 170 °C for 3 min, in order to erase the thermal history. Then, cooling was performed at 10 °C/min from 170 to 25 °C followed by a second heating from 25 to 170 °C at the same heating rate. The degree of crystallinity ( $X_c$ ) was determined from the heat evolved during crystallization using the following equation:  $X_c (\%) = \Delta H_c / \Delta H_m^0 \times 100$ , where  $\Delta H_c$  is the heat of crystallization and  $\Delta H_m^0$  is the heat of fusion for 100% crystalline PE (290 J/g) [21].

Scheme 1. Synthesis of (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes.

### 3. Results and discussion

#### 3.1. Synthesis and characterization

The (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes **1–4** were prepared in high yield (69–89%) according to Scheme 1, which is a modified method reported in the literature [19,22–24]. All the complexes are slightly air stable and are poorly soluble in polar and non-polar solvents.

The <sup>1</sup>H NMR spectra of the iron and cobalt complexes **1–4** showed broad peaks that were not possible to assign due to their paramagnetic nature. Additionally, was not possible to determine the magnetic moment of the complexes **1–4** by the Evans method [25] because these complexes have very low solubility in common solvents.

All the complexes **1–4** were characterized by X-ray photoelectron spectroscopy (XPS), FAB mass spectrometry (FAB-MS) and elemental analysis. The oxidation state of the metal center was determined by XPS. The iron complexes **1–2** showed signs for BE of Fe 2p<sub>3/2</sub> electron at 711.6 and 708.9 eV respectively, which are in good agreement with the BE found for FeCl<sub>2</sub> salt (Fe<sub>2p3/2</sub>: 709.4 eV) and for the iron complexes Py(PzR)<sub>2</sub>FeCl<sub>2</sub> (Fe<sub>2p3/2</sub>: 709.9 eV and 710.1 eV; Py(PzR)<sub>2</sub> = 2,6-bis(pyrazol-1-yl)pyridyl; R = H, Me) and Py(CH<sub>2</sub>)<sub>2</sub>(PzR)<sub>2</sub>FeCl<sub>2</sub> (Fe<sub>2p3/2</sub>: 709.7 eV and 709.4 eV; Py(CH<sub>2</sub>)<sub>2</sub>(PzR)<sub>2</sub> = 2,6-bis(pyrazol-1-ylmethyl)pyridyl; R = H, Me) reported in the literature [26]. On the other hand, the XPS spectra of cobalt complexes **3–4** showed peaks for BE of Co 2p<sub>3/2</sub> electron at 780.7 and 780.1 eV respectively. These values are in accordance with those for CoCl<sub>2</sub> salt

(Co<sub>2p3/2</sub>: 780.9 eV) and for the cobalt complexes Py(Pz)<sub>2</sub>CoCl<sub>2</sub> (Co<sub>2p3/2</sub>: 781.2 eV; Py(PzR)<sub>2</sub> = 2,6-bis(3,4,5-trimethyl-pyrazol-1-yl)pyridyl) and Py(CH<sub>2</sub>)<sub>2</sub>(PzR)<sub>2</sub>CoCl<sub>2</sub> (Co<sub>2p3/2</sub>: 780.8 eV; Py(CH<sub>2</sub>)<sub>2</sub>(Pz)<sub>2</sub> = 2,6-bis(3,4,5-trimethyl-pyrazol-1-ylmethyl)pyridyl) [26]. The XPS analysis confirms that the oxidation state for all complexes **1–4** is equal to 2, which is in conformity with the experimental (FeCl<sub>2</sub> and CoCl<sub>2</sub> salts) and reported references [26,27].

FAB-MS spectra of iron complexes **1–2** presented a main fragment with *m/z* of 339 (100%) and 356 (58%) respectively. Meanwhile, the cobalt complexes displayed *m/z* of 342 (100%) for complex **3**, and 359 (100%) for complex **4**. In all cases, the main fragment corresponded to [(tpX)MCl]<sup>+</sup> product, which suggests a M<sup>+</sup>–Cl fragmentation pattern. FAB-MS analyses indicated that molecular weight of (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes corresponds to the proposed molecular structure.

The elemental analysis for (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes are in good agreement with the expected molecular formula C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>MCl<sub>2</sub> and C<sub>15</sub>H<sub>12</sub>N<sub>3</sub>PMCl<sub>2</sub> (M = Fe, Co), with a maximum variation of 0.5%.

The coordination geometry of the iron and cobalt complexes **1–4** could not be determined by X-ray diffraction because monocrystals were not obtained. However, it is well known that the tripod tris-(2-pyridyl)X (X = N, CH, P) ligands are coordinated to metal in tripodal form through the nitrogen atom of the pyridine [19,22–24].

In order to determine whether all pyridine rings are coordinated to metal, the (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes were characterized by Fourier Transformed Infrared Spectroscopy (FTIR). Table 1 shows the character-

Table 1  
FT-IR data of ligands and (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes

Bands assignation	Py	tpP	tpN	(tpP)FeCl <sub>2</sub>	(tpP)CoCl <sub>2</sub>	(tpN)FeCl <sub>2</sub>	(tpN)CoCl <sub>2</sub>
Aromatic C–H stretch	3078(w)	3036(w)	3047(w)	3069(w)	3075(w)	3071(w)	3098(w)
	3030(w)	2957(w)	3001(w)	2917(w)	2918(w)	3053(w)	3062(w)
C=C, C=N ring stretching (skeletal bands)	1583(s)	1571(s)	1588(s)	1581(s)	1582(s)	1599(s)	1595(s)
	1482(m)	1562(s)	1567(s)	1457(s)	1458(s)	1564(s)	1566(s)
	1438(s)	1450(s)	1465(s)	1428(s)	1429(s)	1463(s)	1458(s)
		1420(s)	1424(s)			1429(s)	1437(s)
Ring-breathing	996(m)	985(m)	983(m)	1011(s)	1012(s)	1018(s)	1022(s)
C–H out-of-plane bending	749(s)	770(s)	774(s)	771(s)	770(s)	776(s)	792(s)
	705(s)	742(s)	738(s)	745(s)	744(s)	760(s)	761(s)

Py: pyridine; tpP: tris(2-pyridyl)phosphine; tpN: tris(2-pyridyl)amine; w: weak; m: medium; s: strong.

Table 2  
Ethylene polymerization by (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes

Entry	Complex	Temperature (°C)	Yield (g)	Activity (g PE mmol <sup>-1</sup> M h <sup>-1</sup> bar <sup>-1</sup> )
1	<b>1</b>	80	4.9	243
2	<b>1</b>	60	1.0	50
3	<b>2</b>	80	5.2	271
4	<b>2</b>	60	1.1	57
5	<b>3</b>	80	4.2	213
6	<b>3</b>	60	0.7	32
7	<b>4</b>	80	4.7	250
8	<b>4</b>	60	0.6	36

Conditions: Cocatalyst: MAO; Al<sub>MAO</sub>/M: 3000; ethylene pressure: 5 bar; polymerization time: 0.5 h; rpm: 600; precatalysts amount: 3 mg; solvent: toluene 100 mL.

istic absorption bands of the free ligands and the iron and cobalt complexes **1–4** respectively. The coordination mode of 2-substituted pyridine ligands in transition metal complexes has been determined by IR correlations. The four  $\nu(\text{C}=\text{C})$ ,  $\nu(\text{C}=\text{N})$  bands between 1600 and 1400 cm<sup>-1</sup>, a ring-breathing band near 990 cm<sup>-1</sup> and C–H out-of-plane bending between 800 and 700 cm<sup>-1</sup> are useful to determine the coordination mode of the ligand [28–30]. The tpX (X = N, P) ligands used in this work can be considered as a 2-substituted pyridine ligand; therefore, their coordination can be assigned using this kind of correlation. The (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes did not present more than four pyridine skeletal bands with higher wavenumber (1428–1595 cm<sup>-1</sup>) respect to free ligands. Besides, the ring-breathing band observed around 980 cm<sup>-1</sup> in the free ligands disappears in these complexes and it is replaced by a band between 1011 and 1022 cm<sup>-1</sup>. These changes are indicative that the all pyridine rings are coordinated to metal. The presence of only four pyridine skeletal bands (rather than eight) between 1600 and 1400 cm<sup>-1</sup> and the simple pattern showed by C–H out-of-plane bending (two bands rather than four) between 800 and 700 cm<sup>-1</sup> is indicative that the all pyridine rings are approximately equivalent.

### 3.2. Ethylene polymerizations

Once the (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes were characterized, their potential catalytic activity for the ethylene

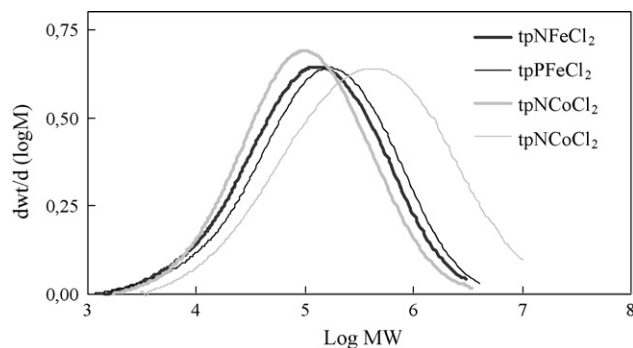


Fig. 1. Molecular weights distribution curves of polyethylenes obtained from (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co) complexes.

polymerization was explored using MAO as cocatalyst. The results are summarized in Table 2 and represent averages of three polymerization runs, which proved to have good reproducibility among them ( $\pm 10\%$ ).

The catalysts showed activities in the range of moderate to high (32–271 g mmol<sup>-1</sup> bar<sup>-1</sup> h<sup>-1</sup>) according to the catalysts performance classification for ethylene polymerization, previously reported [1]. As observed in the iron complexes **1–2** (entry 1 versus 3 and 2 versus 4) and cobalt complexes **3–4** (entry 5 versus 7 and 6 versus 8), the substitution of the nitrogen bridgehead atom by phosphorus in the ligand did not produce a significant increase of activity. The difference of activities observed for both type of catalysts are in the range of  $\pm 10\%$ .

On the other hand, the polymerization temperature has an important impact on both activity systems. In the case of complex **1**, a five times increase was observed by increasing the temperature from 60 to 80 °C (entry 2 versus 1). The analogous complex **3** showed a similar behavior, exhibiting an activity increase around six times (entry 6 versus 5).

Regarding the effect of the metal center during the polymerization, it was observed that the iron complexes **1–2** were slightly more active than the cobalt analogues **3–4**. These results were in accordance with the previous reports by Brookhart and Gibson [5–10].

Table 3  
Physical properties of PE obtained from (tpX)MCl<sub>2</sub> (X = N, P; M = Fe, Co)

Entry	Complex	$M_w$	$M_n$	$M_w/M_n^a$	$T_c^b$ (°C)	$T_m^c$ (°C)	$(X_c)^d$ (%)
1	<b>1</b>	272,289	43,682	6.2	112.7	140.5	52
2	<b>1</b>	434,133	72,198	6.0	112.6	140.7	44
3	<b>2</b>	304,897	47,903	7.1	112.9	139.5	41
4	<b>2</b>	612,942	101,445	6.0	113.3	138.9	39
5	<b>3</b>	222,323	42,838	5.2	115.3	138.5	58
6	<b>3</b>	330,042	70,008	4.7	113.0	140.5	54
7	<b>4</b>	255,129	47,165	4.7	113.0	140.3	40
8	<b>4</b>	429,341	79,311	5.4	112.6	141.7	50

<sup>a</sup> The molecular weights and polydispersities were determined by GPC using polystyrene as standards.

<sup>b</sup> Crystallization temperature.

<sup>c</sup> Melting temperature.

<sup>d</sup> Degree of crystallinity.

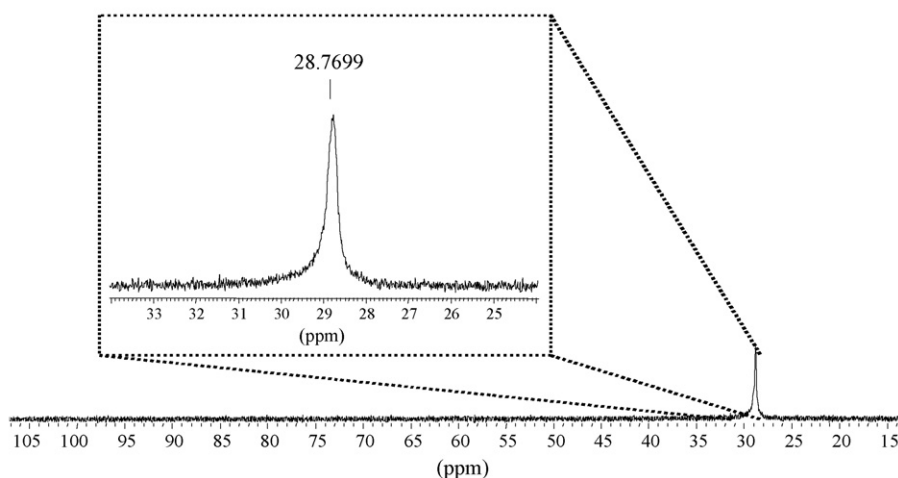


Fig. 2.  $^{13}\text{C}$  NMR of polyethylene produced by iron(II) complex **2**.

### 3.3. Polyethylene characterization

Table 4 shows the physical characterization of the polyethylenes. The polymers produced at  $80^\circ\text{C}$  by complexes **1–4**, have molecular weights ( $M_w$ ) in the range 222,000–304,000  $\text{g mol}^{-1}$  with polydispersities ( $M_w/M_n$ ) from 4.7 to 7.1. While at  $60^\circ\text{C}$ , the  $M_w$  increases up to 330,000–612,000  $\text{g mol}^{-1}$  with  $M_w/M_n$  from 4.7 to 6.0. The polydispersities of all polyethylenes synthesized in this work ( $M_w/M_n = 4.7–7.1$ ) were broad in comparison with the polymers obtained by other “single site” catalysts such as metallocenes, suggesting the presence of more than one active species. However, at the polymerization conditions employed in this work, the polyethylenes showed monomodal distribution (Fig. 1). Nevertheless, when tpN ligand is replaced by tpP ligand in the iron(II) complexes, **1–2** (entry 1 versus 3 and 2 versus 4) and in cobalt(II) complexes **3–4** (entry 5 versus 7 and 6 versus 8), an increase of  $M_w$  is produced. The same trend was observed when the cobalt(II) is changed by iron(II) (entry 5 versus 1, 6 versus 2, 7 versus 3 and 8 versus 4).

The thermal analysis for all polyethylenes prepared from complexes **1–4** showed melting temperatures ( $T_m = 138–141^\circ\text{C}$ ) characteristic for HDPE [21]. However, their crystallinity percent (Table 3) was lower than typical HDPE. It was attributed to the inherent diffusion problems of the polymer chains present in the high molecular weight polymers, due to the increase of entanglement density. In consequence, the polymer chains miscibility decreases and is more difficult to reach a complete lamellar growth [31].

The FTIR analysis of the polymers, showed the polyethylene characteristic absorption bands:  $720\text{ cm}^{-1}$  rocking vibration of linear carbon sequences;  $1465\text{ cm}^{-1}$  C–H deformation vibration of  $\text{CH}_2$ ;  $1375\text{ cm}^{-1}$  C–H symmetrical deformation vibration of  $\text{CH}_3$  and C–H stretching vibrations of  $\text{CH}_3$  ( $2962\text{ cm}^{-1}$ ,  $2872\text{ cm}^{-1}$ ),  $\text{CH}_2$  ( $2926\text{ cm}^{-1}$ ,  $2853\text{ cm}^{-1}$ ) of tertiary carbon

Table 4

$^{13}\text{C}$  NMR of PE obtained from  $(\text{tpX})\text{MCl}_2$  ( $\text{X} = \text{N}, \text{P}$ ;  $\text{M} = \text{Fe}, \text{Co}$ ) complexes

Entry	Complex	$\delta$ (ppm)
1	<b>1</b>	29.1
3	<b>2</b>	28.7
5	<b>3</b>	28.4
7	<b>4</b>	27.3

( $2890\text{ cm}^{-1}$ ). Absorption bands between  $850$  and  $1000\text{ cm}^{-1}$  were not observed, indicating the absence of vinyl groups ( $\text{RCH}=\text{CHR}'$ ,  $\text{RCH}=\text{CH}_2$ ,  $\text{RR}'\text{C}=\text{CH}_2$ ) [21].

The  $^{13}\text{C}$  NMR analyses of the polyethylenes (Table 4) indicated that all polymers have a linear structure. Fig. 2 shows an example of the  $^{13}\text{C}$  NMR spectrum of the polyethylene produced by complex **2**, which is a representative spectrum of the polymers obtained from all catalysts. Thus, the spectrum showed only methylene group ( $-\text{CH}_2-$ ) signal, which is an evidence of the high linearity of the chain. Signals corresponding to terminal methyl groups ( $-\text{CH}_3$ ) and methynyl groups ( $-\text{CH}-$ ) were not detected, due to their relatively low concentration compared to the methylene groups ( $-\text{CH}_2-$ ).

## 4. Conclusions

Iron(II) and cobalt(II) catalysts based on tris(2-pyridyl)amine and tris(2-pyridyl)phosphine ligands have been prepared, characterized and tested for ethylene polymerization. These catalysts precursor showed moderate to high catalytic activity. The iron complexes were slightly more active than the cobalt analogues. The type of bridgehead atom present on the ligand did not affect significantly the catalytic activity and the molecular weight. The polymerization temperature affects significantly on the catalyst activity and product properties. The polyethylenes synthesized were classified as HDPE with linear structure and broad monomodal weight distribution.

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