



Biphasic ethylene oligomerization using bis(imino)pyridine cobalt complexes in methyl-butylimidazolium organochloroaluminate ionic liquids

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ABSTRACT

Several bis(imino)pyridine cobalt (II) complexes have been synthesized and used in ethylene oligomerization in 1-methyl-3-butylimidazolium tetrachloroaluminate (BMI- AlCl_4) ionic liquid activated by methylaluminoxane (MAO). The ligand substitution pattern, with halogen, methyl or trifluoromethyl units in the *ortho*- and *para*-positions of the aromatic group, has a marked effect on activity and selectivity. The cobalt catalysts evaluated in this work exhibited activities in the range 4000–15,300 h^{-1} and selectivities towards ethylene dimerization to butenes above 90%. These catalysts also exhibited high selectivity to 1-butene formation, up to 87%.

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1. Introduction

The use of “green” solvents that allow catalyst recovery, low environmental impact and reduced production costs is a great challenge in industrial processes. A strategic approach is the use of biphasic catalysis using solvents that are immiscible with the reaction products and are efficient at immobilizing transition metal catalysts. The use of ionic liquids (ILs) allows for recycling of the catalyst by simple decantation of the catalyst solution from the products.

Since the pioneer reports by Chauvin et al. [1], concerning the utilization of ionic liquids for the immobilization of oligomerization catalysts, many efforts have been devoted to achieve a catalyst for the selective synthesis of linear α -olefins by ethylene oligomerization [2–8]. A great amount of the literature concerning the oligomerization reaction is devoted to nickel complexes [2–7], but examples of several other transition metal complexes that have been shown to promote carbon–carbon bond formation are known. Examples of a tungsten catalyst [8] and more recently, cobalt and iron complexes [9] have been reported.

A plethora of ligand structures are associated with transition metals and were studied in these reactions. Some relevant examples of nickel complexes are shown in Scheme 1, like bidentate [P,O] [2], structure A, α -diimine, structure B, bis(imino)pyridine [3], structure C, 1,2-diiminophosphorane [5], structure D, phosphines [6], bis-(salicylaldimine) [7], structure E.

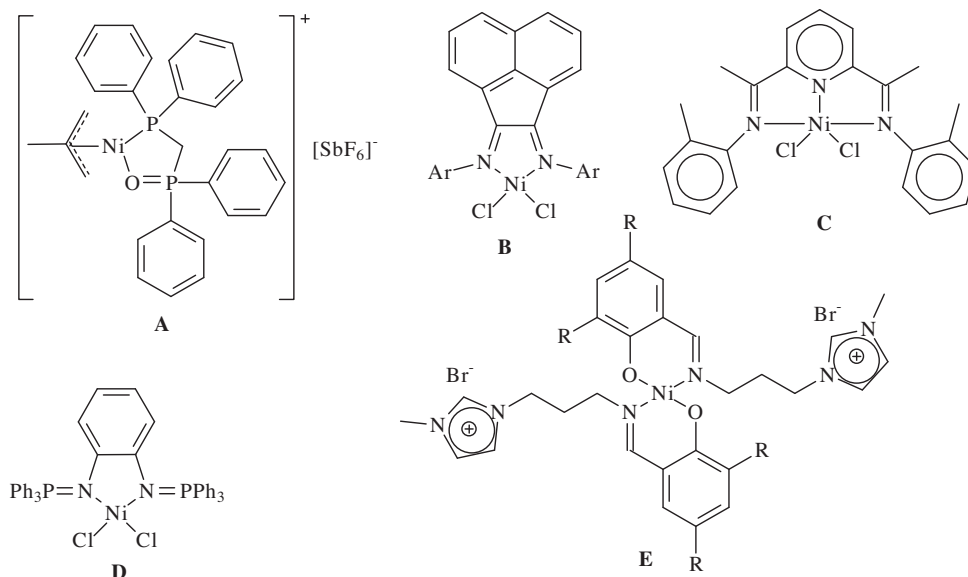
Despite efforts to develop more efficient oligomerization catalysts, limited success has been achieved in terms of systems active for the selective synthesis of linear α -olefins in ionic liquids [2]. As a matter of fact, nickel oligomerization catalysts immobilized in chloroaluminate ionic liquids present, in parallel with the oligomerization reaction, a high carbon–carbon double bond isomerization rate [3–7,9–13], generating internal and branched olefins. Another drawback of these ionic liquids observed in some studies was diminished selectivity during the oligomerization of olefin as a result of the abstraction ligand coordinated to the nickel by the aluminum species [5,14]. This aspect has been minimized by the addition of bases into the ionic liquid with an AlCl_3 /1-methyl-3-butylimidazolium chloride (BMICl) ratio higher than 1 [14,15].

Chloroaluminate ionic liquids show good abilities in immobilizing coordination compounds and incorporating organoaluminum co-catalyst due to their intrinsic characteristics. These characteristics of the dialkylimidazolium organoaluminates allows for a drastic reduction in catalyst and co-catalyst consumption. Some authors have evaluated reductions in catalyst consumption by a factor of ten and of the co-catalyst by a factor of at least two [16].

Complexes containing bis(imino)pyridine ligands have attracted much attention for their application in oligo/polymerization reactions [17–19]. Some of these complexes are able to convert ethylene with high oligomerization rates, producing a majority of α -olefins. The performance of these complexes in homogeneous catalysis, the strong coordination of this kind of ligand to transition metals [20] and the arrangement of its pyridine and N-aryl ring almost orthogonally to each other make them suitable candidates for tests in oligomerization of low molecular weight olefins when immobilized in chloroaluminate

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Scheme 1. Nickel complexes for ethylene oligomerization in ionic liquids.

ionic liquids. Herein, we describe the performance of a series of bis(imino)pyridine cobalt(II) complexes in an ethylene oligomerization reaction using as the ionic liquid BMI- AlCl_4 activated by MAO.

2. Experimental

All the manipulations were conducted under an argon atmosphere using Schlenk tube techniques. Anilines, 2,6-diacetylpyridine and silica-alumina grade-135 were purchased from Aldrich and used without further purification. Solvents were dried over Na and then distilled under an argon atmosphere. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dehydrated as described [21]. The $\text{CoCl}_2 \cdot (\text{THF})_{1.5}$ adduct was prepared as previously described [22]. The ionic liquid BMI- AlCl_4 was obtained by reacting 1-butyl-3-methylimidazolium chloride (BMICl) with aluminum chloride as described in the literature [23].

Elemental analyses were carried out in a Perkin Elmer M CHN/O Analyser, Model 2400, with a tolerance for carbon, hydrogen and nitrogen data of 0.4. The acquisition of ^1H NMR and ^{13}C NMR spectra was performed on an Inova 300 MHz (Varian), with the samples dissolved in CDCl_3 . The IR analyses of the ligands and complexes were performed on a Varian 640-IR spectrometer. Data was collected with 32 scans, resolution 4 cm^{-1} in a $400\text{--}4000\text{ cm}^{-1}$ range. Chromatographic analyses were performed on a Varian 3400 CX gas chromatograph, with a Petrocol DH capillary column: methyl silicone, 100 m long, 0.25 mm i.d., and 0.5 μm film thickness. Analytical conditions: 30 min at 36°C , heating rate of $5^\circ\text{C}/\text{min}$ until reach 250°C .

2.1. Ligands and complexes synthesis

Ligands 1 and 2 were prepared as described by Brookhart and co-workers [17]. The synthesis of these ligands was done by mixing 2,6-diacetylpyridine and the corresponding aniline in a 1:3 molar ratio in 20 mL of dichloromethane. Formic acid (0.4 mL) was added and the solution was stirred for four days. Dichloromethane was removed under reduced pressure and the ligand was precipitated by the addition of ethanol. The solution was filtered and the solid was washed with ethanol. The ligand was dissolved in hot ethanol and precipitated a second time, filtered and dried under reduced pressure.

Ligand 1: Yield 51%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.35 (2H, *m-H* Py), 7.87 (1H, *p-H* Py), 7.38 (4H, *m-ArH*), 7.12 (2H, *p-ArH*), 6.85 (4H, *o-ArH*), 2.41 (6H, $\text{CH}_3\text{-C=N}$). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 167.3 (C=N), 155.4 (*o-C* Py), 151.3 (*i-C* Ar), 136.8 (*p-C* Py), 129.0 (*m-C* Ar), 123.6 (*p-C* Ar), 122.3 (*m-C* Py), 119.2 (*o-C* Ar), 16.2 ($\text{CH}_3\text{-C=N}$). IR: C=N 1635 cm^{-1} .

Ligand 2: Yield 42%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.41 (2H, *m-H* Py), 7.89 (1H, *p-H* Py), 7.30–7.15 (4H, 3-*ArH*+5-*ArH*), 7.04 (2H, 4-*ArH*), 6.70 (2H, 6-*ArH*), 2.35 (6H, $\text{CH}_3\text{-C=N}$), 2.13 (6H, *o-CH}_3\text{Ar}*). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 166.8 (C=N), 155.4 (*o-C* Py), 149.9 (*i-C* Ar), 136.8 (*p-C* Py), 130.4 (3-*C* Ar), 127.1 (2-*C* Ar), 126.4 (5-*C* Ar), 123.6 (4-*C* Ar), 122.2 (*m-C* Py), 118.1 (6-*C* Ar), 17.8 (*o-CH}_3\text{Ar}*), 16.3 ($\text{CH}_3\text{-C=N}$). IR: C=N 1637 cm^{-1} .

Ligand 3 was prepared as described by Alt and co-workers [24]. To a stirred solution of 2,6-diacetylpyridine in 70 mL of benzene, 1 equivalent of *p*-toluenesulfonic acid was added. The 2,6-dimethylaniline compound was added in excess (2.2 equivalents to 2,6-diacetylpyridine). The mixture was refluxed and the water formed in the reaction was separated using *Dean-Stark* distillation. Refluxing was continued for 24 h and benzene was removed under reduced pressure. Dichloromethane (30 mL) was added and the ligand was neutralized in 30 mL of a solution saturated with Na_2CO_3 . The organic layer was separated and the aqueous phase was extracted twice with dichloromethane. The combined organic layers were evaporated to dryness. Ethanol was added to the dried residue and the ligand was filtered and dried under reduced pressure.

Ligand 3: Yield 62%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.49 (2H, *m-H* Py), 7.92 (1H, *p-H* Py), 7.09 (4H, *m-ArH*), 6.95 (2H, *p-ArH*), 2.25 (6H, $\text{CH}_3\text{-C=N}$), 2.06 (12H, *o-CH}_3\text{Ar}*). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 167.2 (C=N), 155.1 (*o-C* Py), 148.7 (*i-C* Ar), 136.8 (*p-C* Py), 127.9 (*m-C* Ar), 125.4 (*o-C* Ar), 123.0 (*p-C* Ar), 122.2 (*m-C* Py), 17.9 (*o-CH}_3\text{Ar}*), 16.4 ($\text{CH}_3\text{-C=N}$). IR: C=N 1645 cm^{-1} .

The ligands 4–7 were prepared as described by Qian et al. [25]. 2,6-Diacetylpyridine and 2.5 equivalents of the corresponding aniline were added to 40 mL of toluene. Silica-alumina grade-135 (80 g/mol of 2,6-diacetylpyridine) and 1.5 g of molecular sieves 4 Å were added. The mixture was stirred for four days. The suspension was filtered and the solid washed with four aliquots of 5 mL of toluene. The solvent was removed under reduced pressure and the ligand washed with ethanol and dried under reduced pressure.

Ligand 4: Yield 52%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.37 (2H, *m-H* Py), 7.92 (1H, *p-H* Py), 7.69 (2H, 3-*ArH*), 7.53 (2H, 5-*ArH*) 7.20 (2H, 4-*ArH*), 6.82 (2H, 6-*ArH*), 2.38 (6H, $\text{CH}_3\text{-C=N}$). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 168.5 (C=N), 154.9 (*o-C* Py), 149.6 (*i-C* Ar), 137.2 (*p-C* Py), 132.6 (5-*C* Ar), 126.5 (3-*C* Ar), 123.9 (CF_3), 123.2 (4-*C* Ar), 123.1 (*m-C* Py), 119.7 (6-*C* Ar), 119.5 (2-*C* Ar), 16.8 ($\text{CH}_3\text{-C=N}$). IR: C=N 1650 cm^{-1} .

Ligand 5: Yield 46%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.36 (2H, *m-H* Py), 7.92 (1H, *p-H* Py), 7.42 (2H, 3-*ArH*), 7.26 (2H, 5-*ArH*) 6.79 (2H, 6-*ArH*), 2.38 (6H, $\text{CH}_3\text{-C=N}$). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 169.5 (C=N), 158.5 (4-*C* Ar), 154.8 (*o-C* Py), 145.6 (*i-C* Ar), 137.2 (*p-C* Py), 123.2 (*m-C* Py), 123.0 (CF_3), 121.4 (6-*C* Ar), 120.7 (2-*C* Ar), 119.5 (5-*C* Ar), 113.8 (3-*C* Ar), 16.8 ($\text{CH}_3\text{-C=N}$). IR: C=N 1644 cm^{-1} .

Ligand 6: Yield 33%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.35 (2H, *m-H* Py), 7.92 (1H, *p-H* Py), 7.68 (2H, 3-*ArH*), 7.50 (2H, 5-*ArH*) 6.77 (2H, 6-*ArH*), 2.38 (6H, $\text{CH}_3\text{-C=N}$). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 169.2 (C=N), 154.6 (*o-C* Py), 148.0 (*i-C* Ar), 137.3 (*p-C* Py), 132.6 (5-*C* Ar), 128.7 (4-*C* Ar), 126.7 (3-*C* Ar), 123.3 (*m-C* Py), 123.0 (CF_3), 121.3 (6-*C* Ar), 120.9 (2-*C* Ar), 16.9 ($\text{CH}_3\text{-C=N}$). IR: C=N 1639 cm^{-1} .

Ligand 7: Yield 41%. ^1H NMR (300 MHz, CDCl_3): δ ppm 8.35 (2H, *m-H* Py), 7.92 (1H, *p-H* Py), 7.81 (2H, 3-*ArH*), 7.64 (2H, 5-*ArH*) 6.86 (2H, 6-*ArH*), 2.38 (6H, $\text{CH}_3\text{-C=N}$). ^{13}C NMR (75 MHz, CDCl_3): δ ppm 169.1 (C=N), 154.6 (*o-C* Py), 148.5 (*i-C* Ar), 137.3 (*p-C* Py), 135.6 (5-*C* Ar), 129.5 (3-*C* Ar), 124.8 (4-*C* Ar), 123.3 (*m-C* Py), 122.9 (CF_3), 121.6 (6-*C* Ar), 121.2 (2-*C* Ar), 16.9 ($\text{CH}_3\text{-C=N}$). IR: C=N 1643 cm^{-1} .

The bis(imino)pyridine cobalt (II) complexes were synthesized by reacting the corresponding ligand with $\text{CoCl}_2\cdot(\text{THF})_{1.5}$ in THF. The ligand and the cobalt adduct, 1.05 equivalents of the ligand to adduct, were dissolved in 10 mL of anhydrous THF. The solution was stirred for 24 h and then was filtered off, the solid washed with four aliquots of 5 mL of cold THF. The complexes were dried under reduced pressure. Scheme 2 shows the synthesis of the ligands and cobalt complexes.

Complex **1a**: Yield 77%. $\text{C}_{21}\text{H}_{19}\text{Cl}_2\text{CoN}_3$. CHN calculated: C = 56.91%; H = 4.32%; N = 9.48%. CHN found: C = 56.50%; H = 4.04%; N = 9.20%. IR: C=N 1590 cm^{-1} .

Complex **2a**: Yield 97% $\text{C}_{23}\text{H}_{23}\text{Cl}_2\text{CoN}_3\cdot 0.5$ THF. CHN calculated: C = 59.19% H = 5.36% N = 8.28%. CHN found: C = 59.00%; H = 5.75%; N = 8.08%. IR: C=N 1589 cm^{-1} .

Complex **3a**: Yield 96%. $\text{C}_{25}\text{H}_{27}\text{Cl}_2\text{CoN}_3\cdot 0.5$ H_2O . CHN calculated: C = 59.07%; H = 5.55%; N = 8.27%. CHN found: C = 59.28%; H = 5.49%; N = 7.42%. IR: C=N 1587 cm^{-1} .

Complex **4a**: Yield 87%. $\text{C}_{23}\text{H}_{17}\text{Cl}_2\text{CoF}_6\text{N}_3\cdot 0.5$ THF. CHN calculated: C = 48.80%; H = 3.44%; N = 6.83%. CHN found: C = 48.82%; H = 3.20%; N = 6.56%. IR: C=N 1589 cm^{-1} .

Complex **5a**: Yield 86%. $\text{C}_{23}\text{H}_{15}\text{Cl}_2\text{CoF}_8\text{N}_3\cdot 1$ THF. CHN calculated: C = 47.18%; H = 3.37%; N = 6.11%. CHN found: C = 47.17%; H = 3.13%; N = 6.11%. IR: C=N 1590 cm^{-1} .

Complex **6a**: Yield 70%. $\text{C}_{23}\text{H}_{15}\text{Cl}_4\text{CoF}_6\text{N}_3\cdot 0.5$ THF. CHN calculated: C = 43.89%; H = 2.80%; N = 6.14%. CHN found: C = 43.80%; H = 2.66%; N = 5.84%. IR: C=N 1588 cm^{-1} .

Complex **7a**: Yield 54%. $\text{C}_{23}\text{H}_{15}\text{Br}_2\text{Cl}_2\text{CoF}_6\text{N}_3\cdot 0.5$ THF. CHN calculated: C = 38.84%; H = 2.48%; N = 5.44%. CHN found: C = 38.95%; H = 2.25%; N = 5.29%. IR: C=N 1591 cm^{-1} .

2.2. MAO synthesis

The oligomerization tests of the cobalt catalyst were performed using methylaluminoxane (MAO) as the co-catalyst. The MAO was prepared as described by Reddy et al. [26]. A solution of 20.9 mL (0.218 mol) of TMA in toluene was added dropwise to a suspension 12.107 g (18.2 mmol) of $\text{Al}_2(\text{SO}_4)_3\cdot 18\text{H}_2\text{O}$ in toluene under vigorous stirring at -10°C . After the addition of trimethylaluminum, the solution was slowly heated to 30°C and maintained at this temperature for 4 h. The temperature was increased gradually to 50°C and

Table 1

Ethylene oligomerization performance of cobalt-bis(imino)pyridine catalysts in BMI-AlCl_4 .

Entry	Catalyst	Temperature ($^\circ\text{C}$)	Al/Co	TOF (h^{-1})	C_4 (%)	1- C_4 (%)	C_6 (%)
1	1a	30	600	4300	98.5	84.1	1.5
2	2a	30	600	6000	96.0	87.0	4.0
3	3a	30	600	5300	94.8	79.2	5.2
4	4a	30	600	9800	96.8	80.1	3.2
5	5a	30	200	4800	98.5	95.8	1.5
6	5a	30	400	8600	94.7	83.8	5.3
7	5a	10	600	6200	97.2	89.3	2.8
8	5a	30	600	15,300	95.6	80.1	4.4
9	5a	50	600	17,000	89.4	67.1	10.6
10	5a	30	800	5100	96.3	85.7	3.7
11	5a	30	1000	3000	98.3	95.2	1.7
12	6a	30	600	13,700	96.0	83.6	4.0
13	7a	30	600	10,400	96.5	83.2	3.5
14 ^a	1a	50	600	1200	63.7	96.9	36.3 ^b

Reaction conditions: complex: 10 μmol ; ionic liquid: 3 mL of BMI-AlCl_4 ; solvent: 20 mL of toluene; ethylene: 10 bar; co-catalyst: MAO; time: 30 min.

^a Without ionic liquid.

^b C_{10} products were detected.

maintained at this temperature for six more hours. The solution was filtered and used as prepared.

2.3. Oligomerization of ethylene

The catalytic runs were performed using a double-walled glass reactor equipped with magnetic stirring, a thermocouple, and with a continuous feed of ethylene at 10 bar. The reactor was fed with 10 μmol of the cobalt complex and 20 mL of toluene. The temperature was controlled by a thermostatic circulation bath. The system was initially purged with ethylene, then a solution of the cobalt catalyst dissolved in 3 mL of the ionic liquid BMI-AlCl_4 was added to the reactor. The reaction was started with the addition of the desired amount of MAO. The reaction was stopped after 30 min. The phases were allowed to separate and the organic phase was withdrawn by a cannula and analyzed by GC.

Chromatographic analyses were performed on a Varian 3400 CX, equipped with a Petrocol DH capillary column: methyl silicone, 100 m long, i.d. 0.25 mm, and film thickness 0.5 μm . Analysis conditions: 36°C for 15 min and a heating rate of $5^\circ\text{C}/\text{min}$ until 250°C . The productivity was expressed as turnover frequencies, TOF, defined as mol converted ethylene per mol pre-catalyst and by reaction time (in hours).

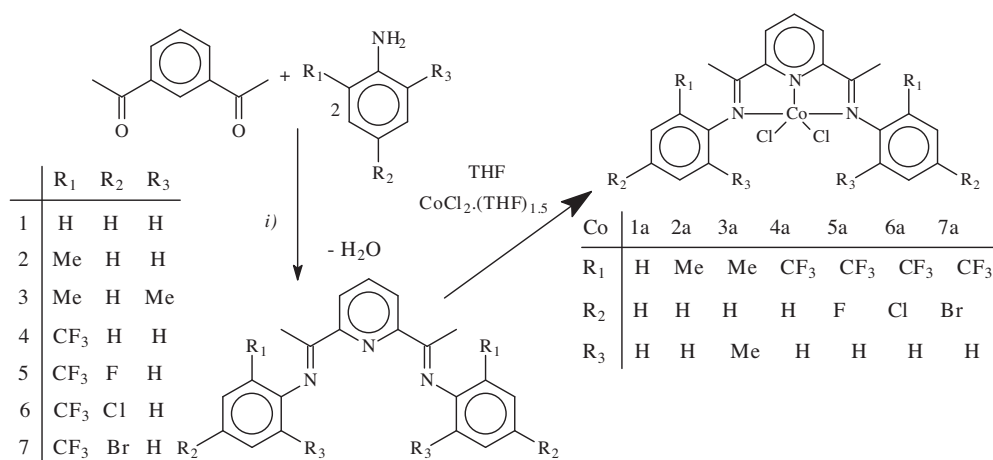
3. Results and discussion

Bis(imino)pyridine transition metal complexes have been showed as efficient catalysts for the oligomerization and/or polymerization of olefins, and this has become a subject of intense investigation [17–19]. More specifically, cobalt bis(imino)pyridine catalysts allow for the selective synthesis of linear α -olefins, but there are no available studies concerning their utilization under biphasic conditions in ionic liquids.

In the present study, several cobalt coordination compounds were synthesized and their catalytic performance in biphasic imidazolium–organoaluminates ionic liquids was evaluated. Table 1 shows the performance of selected complexes in the biphasic oligomerization of ethylene under different reaction conditions.

3.1. Effect of the Al/Co ratio

Compound **5a** was used for optimization of the effect of the aluminum/cobalt molar ratio Al/Co on the ethylene oligomerization ratio was evaluated. Values of Al/Co from 200 to 1000 were stud-



Scheme 2. Synthesis of the ligands and cobalt complexes.

ied [entries 5, 6, 8, 10 and 11]. The increase of the Al/Co molar ratio leads to an increase in the activity in the oligomerization rate, reaching a maximum for Al/Co = 600. This behavior indicates that an Al/Co ratio below 600 promotes the maximization of the number of active species, but a further increase in the Al/Co ratio results in the deactivation of the catalyst.

The selectivity in the formation of butenes is slightly dependent on the Al/Co molar ratio used in the catalytic runs. In all the Al/Co molar ratios tested, the selectivity towards butenes remained in the range of 94.7–98.5%. The selectivity for the formation of butene-1 changed with the Al/Co ratio in the range of 80.1–95.8%. As the co-catalyst should act only to activate the complex into the catalyst, no change on the selectivity from the catalyst should be expected. As expected, no change was observed into dimer selectivity. The same trend was not observed for the selectivity for butene-1. Increasing the amount of the co-catalyst should only increase the number of the active species until reach a maximum, without change the structure of the catalyst with the amount of the co-catalyst. In face of this observation, the change in the 1-butene selectivity is probably due the variation of the activity of the cobalt catalyst and not from Al/Co ratio, activity and 1-butene selectivity have the same trend with Al/Co ratio.

3.2. Effect of the reaction temperature

The reaction temperature showed a more pronounced influence in the activity of the oligomerization reaction of ethylene in BMI-AlCl₄. At 10 °C, the activity of the cobalt catalyst was restricted to 6200 h⁻¹ for the conversion of ethylene. Raising the reaction temperature to 30 °C, the activity increased to 15,300 h⁻¹. The temperature reaction of 50 °C showed no further substantial increase on the oligomerization activity. The activity for the cobalt complex **5a** at 50 °C was 17,000 h⁻¹. The selectivity for the dimerization of ethylene was high at 10 °C, 97.2%. An increase in temperature to 30 °C for oligomerization resulted in a low change in selectivity, 95.6% for the formation of C₄. A further increase of the oligomerization reaction to 50 °C showed a sharper decrease in selectivity in the formation of dimers to 89.4%.

The selectivity in the formation of butene-1 showed a strong dependence on the temperature at which the oligomerization reaction of ethylene was performed. At 10 °C, the catalyst had a selectivity of 89.3% for butene-1 of total butenes. The test performed at 30 °C showed selectivity for butene-1 of 80.1%, lower than that obtained at 10 °C. The reduction in selectivity was even more pronounced in the tests performed at 50 °C, with a selectivity of 67.1%. This profile is very similar to the decrease observed

with the cationic cobalt complex [9]. However, despite the same downward trend, the comparison of these data showed that the selectivities observed for bis(imino)pyridine cobalt catalysts were much higher to those observed for cationic cobalt complex, taking into account the temperature and especially when considering similar activities. For illustrative purposes, we compared the system Co-AlEtCl₂ activity 14,100 h⁻¹ and 48.8% of butene-1 [9], with **5a**-MAO activity of 15,300 h⁻¹ and 80.1% of butene-1, demonstrating the potential of this class of catalysts for selective dimerization of ethylene to butene-1.

3.3. Influence of the substitution pattern on catalyst activity

All the cobalt catalysts were active for the oligomerization of ethylene in BMI-AlCl₄. The activity for catalyst **1a** was low, 4300 h⁻¹. The presence of substitutions on the bis(imino)pyridine ligands proved to be beneficial for the activity of the cobalt catalysts, regardless of the electronic nature of the substituent group, as in entries 2–4, 8, 12 and 13. The presence of one methyl group at the ortho position on catalyst **2a** increased the activity to 6000 h⁻¹. When the CF₃ group was used as a substituent in the ortho position of the ligand, the complex of the cobalt catalyst was more active when compared to the **1a** complex and the **2a** complex. The activity for complex **4a** for ethylene oligomerization was 9800 h⁻¹ when immobilized in BMI-AlCl₄.

The substitution at the ortho position in bis(imino)pyridine ligands is beneficial for activity when this cobalt catalyst is immobilized in BMI-AlCl₄, regardless of the electronic nature of the substituent. The requirement of a substitution at the ortho position to improve the activity for oligomerization follows the same trend observed for homogeneous catalysis with cobalt bis(imino)pyridine catalysts [17,27,28]. Bazan and co-workers observed for nickel catalyst a relationship of activity with respect to the presence of a bulky substituent on the catalyst structure [29]. These authors observed that, as the bulk of the substituents increased, this was followed by a progressive decrease in the rate of ring rotation at the more crowded coordination sphere around nickel, increased monomer consumption activity [29].

Despite the increased oligomerization activity by the presence of a substituent in the ortho position, the insertion of a second methyl substituent proved useless for the activity of the catalyst. For the case of the **3a** complex, a decrease in oligomerization activity was observed when compared to the **2a** complex, with only one methyl substituent. This result suggests that although the presence of substituent in this position is important, the effect on activity is not only dependent on the spatial orientation of the ligand, but the

electronic component is probably the predominant aspect in the activity of a catalyst.

Gibson and co-workers showed that a cobalt catalyst, when substituted by a CF₃ group in the ortho position of aromatic ring of the ligand, could have its activity increased by the insertion of a fluorine atom in the ligand structure in the R₂ or R₃ position [30]. A similar trend in the activity of the oligomerization catalyst bis(imino)pyridine cobalt was observed by Lutz and co-workers [31]. These authors observed that the presence of a chlorine atom and a CF₃ group in the structure of the complex resulted in a more active catalyst compared to the one that just had CF₃ as a substituent. The cobalt complexes **5a**, **6a** and **7a** activated by MAO were shown to be the most active catalysts for the oligomerization of ethylene when immobilized in ionic liquid BMI-AlCl₄ and, among these catalysts, the activity for oligomerization was dependent on the electronegativity of the halogen present at R₂ position.

3.4. Influence of the substitution pattern on catalyst selectivity

The complexes of bis(imino)pyridine cobalt were selective for the dimerization of ethylene to butenes. It is remarkable that the selectivity for dimerization proved to be high regardless of the conditions under which the oligomerization tests were performed or the structure of the catalyst. These results are distinct from those observed with these catalysts in homogeneous medium in which they behave as catalysts for oligomerization with a Schulz–Flory distribution of 0.63 for catalyst **2a** [30] or oligo/polymerization catalysts [17,30,31]. There are other cases where the selectivity of the catalysts for oligomerization immobilized in ionic liquids was significantly directed to a shorter product distribution [3,32].

It has been demonstrated that the oligomerization reaction catalyzed by Co^{II} bis(imino)pyridine complexes activated by MAO shows a first-order dependence on monomer concentration [18,27], which is consistent with chain growth via a classic insertion mechanism. The chain end process for these cobalt catalysts has been studied by NMR spectroscopy and revealed a first order dependence of the reaction rate on the cobalt-alkyl species and a zero order dependence on the monomer concentration [33], suggesting an β -H elimination and formation of an intermediate metal hydride species.

It is known that the solubility of ethylene is lower in ionic liquids compared to organic solvents [32]. Based on experimental observations of the independence of the monomer concentration on the chain end process [33] and the low concentration of ethylene in ionic liquid, the chain end is favored compared to chain growth shifting to the formation of a shorter oligomer distribution. This observation is also supported by the results with the catalyst **1a**, comparing the selectivity of the reaction in ionic liquid with the selectivity of the same catalyst in toluene, entries 1 and 14. The reaction carried out in toluene showed and selectivity for the ethylene dimerization of 63.7, with C₁₀ formation. The reaction performed in ionic liquid was very selective for ethylene dimerization 98.5%.

All catalysts studied showed a high selectivity for the formation of butene-1. Complex **1a** showed selectivity for butene-1 at 84.1% of butenes. The presence of a methyl group at the R₁ position increased the selectivity for butene-1 to 87.0%. The catalyst **4a**, substituted with CF₃ at R₁ position and the catalysts **5a**, **6a** and **7a** substituted with CF₃ at R₁ position and F, Cl or Br at R₂ position showed a decrease in selectivity for butene-1 compared to catalyst **2a**. Possibly, the decrease in the selectivity was consequence of the low solubility of ethylene in the ionic liquid that might favor the isomerization of olefins under these conditions. Despite the decrease in selectivity for these catalysts, it still remained high (above 80%) for the most of the catalysts. It is worth to noting that the presence of electron-withdrawing groups such as CF₃, F, Cl, Br would reduce

the electron density on the metal sites and generate a more electrophilic Co center. Such increase in Co electrophilic character could favoring the isomerization as consequence of the catalyst activity increment, as observed with nickel catalysts [34]. For the cobalt catalyst studied, only a slight increase in isomerization rate of olefins was observed, suggesting that the product once formed remain on organic phase preventing their isomerization in larger scale.

It is worth noting that the bis(imino)pyridine cobalt (II) catalysts herein described, as far as we are concerned, show the best balance of activity and selectivity in the formation of α -olefin for a Ziegler–Natta oligomerization catalyst described in the literature [3–7,9].

4. Conclusions

Bis(imino)pyridine cobalt (II) catalysts activated by MAO were active for ethylene oligomerization under biphasic (BMI-AlCl₄) conditions. The cobalt catalysts evaluated in this work showed activities for ethylene conversion in a range of 4000–15,300 h⁻¹. The most active catalysts were those containing electron withdrawing groups CF₃ and F, Cl or Br in their structure. All the catalysts exhibited high selectivity for the dimerization of ethylene into butenes in an ionic liquid, above 90%. The major product was butene-1 for all the catalysts.

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