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Cobalt-β-diimine complexes for ethylene oligomerization

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¹ In memoriam

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Abstract

This work describes the synthesis of cobalt- β -diimine complexes as well as their application as ethylene oligomerization catalyst precursors. The ligands differ from each other by substituents on the aromatic rings. The catalytic precursors were tested in ethylene oligomerization, using EASC (Ethylaluminium sesquichloride, Et₂Al₂Cl₃) as co-catalyst, and toluene as solvent and displayed with TOF in the range of 0.8 to 34 s⁻¹. The catalytic systems were selective in the C₄-C₆ fraction, attaining 100% selectivity in C₄. It was observed that the ligands nature strongly influence the catalytic activity.

Keywords: oligomerization, ethylene, β-diimine, Schiff bases, cobalt

1. Introduction

The activity and selectivity of transition metal catalysts are dependent on the electronic nature and the steric environment of the central metal. So, the appropriated ligand choice is important for the catalyst performance and allows to drive the reaction to obtention of the desired products [1]. The use of a β -diimine as supporting ligand systems in both main and transition metals coordination chemistry has recently attracted considerable attention [2-5]. These ligands have several attractive features, including the possible tunability in both the Ar and R groups, which has a direct influence on the steric environment and the electron demand of the bound metal [6].

 β -Diimine ligands became more popular since the discovery by Feldman and co-workers of the "Brookhart type" nickel and palladium polymerization catalysts [7]. They synthesized the first cationic β -diimine palladium complex by the reaction between the so-called " β -iminoamine" and [Pd(MeCN)₄][BF₄]₂.

Studies on transition metal complexes with β -diimine ligand have greatly increased in the last few years, being 2007 the year with the largest number of publications on this field. These studies were initiated by Brookhart group with nickel and palladium catalysts [8] and developed simultaneously by Brookhart [9] and Gibson [10] with cobalt and iron complexes.

Since 2002 a lot of works on β -diimine complexes synthesis with several transition metals were reported in the literature. Some studies present metal and ligand similarities with the complexes synthesized in this work [6, 11-12].

Concerning the synthesis of N,N-bidentate cobalt(II) complexes there are, in the literature, the works reviewed by Sun and Redshaw [13] and other studies conducted by Sun [14].

Regarding to the studies that have employed specifically cobalt(II)-βdiimine complex as catalyst precursors, we found in the literature only one paper, published by Nagashima [1], which reports results obtained for ethylene polymerization.

Although the literature doesn't present results for oligomerization using β diimine complexes, some studies show oligomerization reaction conditions similar to those used in our catalytic tests specially the works from Sun [14-17]. The work that is the most similar to our study was published by Qian [18] in

2001, in which the authors presented ethylene oligomerization catalyzed by Co(II)- α -diimine complexes. There is also a repport from Gomes [19] concerning the polymerization of ethylene catalized by Co(II)- α -diimine complexes.

As far as we are concerned, the present results on the synthesis of homogeneous Co(II)- β -diimine complexes and their use in ethylene oligomerization reaction are unprecedented.

2. Experimental

2.1 Chemicals

All experiments and distillations were performed under an atmosphere of argon using standard Schlenk tube techniques. The solvents were deoxygenated by refluxing over appropriate drying agents (toluene, hexane, ethyl ether and benzene on sodium/benzophenone; dichloromethane and acetonitrile on phosphorous pentoxide) under argon and distilled immediately prior to use. Methanol, ethanol, were used without further purification. Celite was activated in an oven at 100° C for 2 h. 2,6-dimethylaniline and 2,4,6-trimethylaniline (Aldrich) were distilled prior to use. 4-methoxyaniline (Aldrich) and 2,4-pentanodione (Aldrich) were used without further purification. Sodium carbonate (Vetec) and thionyl chloride (Fluka) were used without further purification. Sodium Stark technique. Cobalt(II) chloride (Vetec) was previously dried according to methodology proposed by Pray [20]. EASC (Ethylaluminium sesquichloride, $Et_2Al_2Cl_3$) was supplied by Akzo Nobel and used with previous dilution in dry toluene (10% v/v).

2.2 Equipments

Elemental analyses were carried out in a Perkin Elmer M CHN/O Analyser, Model 2400. The ¹H NMR spectra were performed in an Inova 300 MHz Spectrometer, samples were dissolved in deuterated chloroform. Chromatographic analyses were performed on a Varian 3400CX Gas Chromatograph, equipped with a Petrocol DH capillary column (methylsilicone, 100 m long, i.d. 0.25 mm, and film thickness of 0.5 μ m). Analysis conditions: 36 °C (15 minutes) then heating rate of 5° C/minute until 250° C. The products were quantified using isooctane (0.43 mmol) as internal standard.

2.3 β-diimine ligands synthesis

Insert Fig. 1

Figure 1. Proposed structure of β -diimine ligands.

The synthesis and characterization of ligands, shown in figure 1, L1, 2-(2,6-dimethylphenyl)amine-4-(2,6-dimethylphenyl)imine-2-pentene and L2, 2-(2,4,6-trimethylphenyl)-amine-4-(2,4,6-trimethylphenyl)imine-2-pentene were previously described [2]. L3, 2-(4-methoxyphenyl)amine-4-(4methoxyphenyl)imine-2-pentene, was synthesized according to Budzelaar [21] using *p*-toluenesulfonic acid as catalyst. In a typical reaction, in a 250 mL flask, two equivalents of the required 4-methoxy-aniline (8.79 g, 71.4 mmol) were added to 2,4-pentanodione (3.5 mL, 34 mmol) and p-toluenesulfonic acid (5.8 g, 34 mmol) in benzene. The suspension was refluxed for 24 h, and the water formed was removed using a Dean-Stark. After, the solvent was removed under reduced pressure, and to the solid formed were added 60 mL of ethyl ether and 80 mL of a satured solution of sodium carbonate. The aqueous phase was extracted with ethyl ether (L3). The solvent was evaporated under vacuum, and the solid was recrystallized from methanol, yielding 7.18 g (68%).

Characterization: ¹H NMR (δ , ppm) 12.15 (s, 1H, *N*-H), 6.85 (s, 4H, *m*-ArH), 4.85 (s, 1H, β -CH), 2.25 (6H, s, *p*-CH₃Ar), 2.11 (s, 12H, *o*-CH₃Ar), 1.68 (s, 6H, α - CH₃). IR: C=N 1504 cm⁻¹. CHN (C₁₉H₂₂N₂O₂): Calculated C = 82.59% H = 9.04% N = 8.37%; Experimental: C = 82.68% H = 9.40 % N = 8.37%.

2.4 Cobalt(II)-β-diimine complexes synthesis

Insert Fig. 2

Figure 2. Proposed structure of cobalt- β -diimine complexes.

The proposed structures of the complexes are represented in figure 2 (based on reference [1]).

The methodology for the synthesis of the complexes, **C1**, dichlorido-1,5,4-bis(2,6-dimethylphenyl)pentanediiminecobalt(II), **C2**, dichlorido-1,5-

bis(2,4,6-trimethylphenyl)pentanediiminecobalt(II) and **C3**, dichlorido-1,5-bis(4methoxyphenyl)pentanediiminecobalt(II) as follows: in a 250 mL flask, one equivalent of the appropriated ligand (1.6 mmol) relatively to cobalt chloride (0.21 g, 1.6 mmol) was added to 30 mL of dry dichloromethane. The suspensions were stirred at room temperature for 72 h. After, they were filtered through Schlenk filter tubes and the solids were washed with THF. The solvent was evaporated under vacuum, and the blue (C1 and C2) and green (C3) solids recrystallized from cold hexane. Yields, after recrystallization: 650 mg (1.49 mmol, 93%), 528 mg (1.14 mmol, 71%) and 127 mg (0.29 mmol, 18%), respectively.

C1 Characterization: IR: C=N 1665 cm⁻¹. CHN ($C_{21}H_{26}CI_2CoN_2$): Calculated C = 57.81% H = 6.01% N = 6.42%; Experimental: C = 57.78% H = 5.77 % N = 6.22%.

C2 Characterization: ¹H NMR (CDCl₃, 400 MHz): 23.53, 20.86, 17,13, 9.71. Decomposes rapidly yielding increasing ligand peaks. IR: C=N 1558 cm⁻¹. CHN ($C_{23}H_{30}Cl_2CoN_2.CH_2Cl_2$): Calculated C = 52.48% H = 5.87% N = 5.10%; Experimental: C = 52.90% H = 6.12 % N = 5.01%.

C3 Characterization: CHN (($C_{19}H_{22}Cl_2CoN_2O_2$)₃.CH₂Cl₂): Calculated C = 49.56% H = 4.88% N = 5.98%; Experimental: C = 49.49% H = 4.70 % N = 5.95%.

Elemental analysis are consistent with the proposed constitution of the complexes. **C2** and **C3** seem to crystallize with dichloromethane: while **C2** seems to crystallize with a molecule of dichloromethane, each three molecules of **C3** seem to crystallize with one molecule of solvent. Unfortunately, no crystals could be obtained for X-ray diffraction analysis. The presence of CH_2Cl_2 in a solid structure, although may seem unusual, was already observed by X-ray diffraction [22] and elemental analysis [19, 22, 23].

2.5. Catalytic tests

Ethylene oligomerization experiments were carried out in a 450 mL Parr stainless steel autoclave equipped with magnetically driven mechanical stirring, thermocouple and a pressure gauge. The reaction temperature was kept at 30° C with a thermostatic bath. In a typical experiment, the reactor was charged with

a toluene solution containing the alkylaluminium cocatalyst added in amounts calculated to obtain an aluminium to cobalt molar ratio (Al/Co) of 1000. Then, the solution was saturated with ethylene and 2 or 6 µmol of the desired catalytic precursor was added. The pressure was raised up to 10 atm upon addition of ethylene and the system kept under continuous stirring. For all reactions, after 30 min the reaction was stopped, the mixture cooled to -30 °C and analyzed immediately by gas chromatography.

3. Results and Discussions

As the goal of this study was to evaluate the effect of ligand substituent in the catalytic activity, all complexes were investigated under the same conditions. Reactions were carried out using 2 µmol of the **C1**, **C2**, and **C3**. The choice of reaction conditions was based on the literature for similar systems based on nickel [2] with two exeptions. First, the catalyst quantities should be low because high activities of cobalt complexes. Second, Al/Co needs to be higher for cobalt than that for nickel precursors [24].

Table 1 exhibits the results obtained for ethylene oligomerization.

 Table 1. Oligomerization ethylene results obtained using the catalyst precursors

 C1-C3.^a

			Selectivity ^c				
Entry	Cat.	TOF (s ⁻¹) ^b	ΣC_4	1B	t-2B	c-2B	ΣC_6
1	C1	21	100	84	9	7	0
2	C2	34	74	76	14	10	26
3	C3	0.8	72	78	12	10	28

^a Reactional Conditions: 2 μ mol of catalytic precursor, 10 atm of ethylene, 60 mL of toluene, 30°C, 30 min, EASC, Al/Co = 1000

^b TOF = Turnover Frequency, mol of ethylene converted per mol of Co per second (s^{-1})

^c Determined by CG. ΣC_4 = total selectivity in butenes; 1-B = 1-butene; t-2B = *trans*-2-butene; c-2B = *cis*-2-butene; ΣC_6 = total selectivity in hexenes (selectivity on individual isomers not determinated). No heavier products were ever observed.

Variations on the imino substituents resulted in marked changes in the catalytic activity of each complex. The correlation between catalytic activity and substituents can be explained by the metal atom net charge correlation -MANCC. Sun and Yang [24] applied this correlation to study the catalytic activity of iron(II) bis(imino)pyridyl and iron(II) bis(imino)pyrimidyl complexes in ethylene oligomerization reactions. The authors concluded that the catalytic activity was more focused on the catalyst electronic configuration, especially in the electron density charge on the central metal atom rather than in the structural configuration. They proposed the existence of a turning point for the net charge versus the activity curve. Their results indicate an un-monotonous relation of the net charge and the activity for iron(II) catalysts. This seems to agree with what was observed in this study. The highest electron density of the metal center induces higher catalytic activity (for catalyst precursors that follow the oligomerization mechanism of metal-hydride). Since methoxy is a electronwithdrawing group, it should be expected complex C3 to display the weakest catalytic activity, which indeed happened [25]. Following this reasoning, it was also expected that C2 complex (containing three eletron donating methyl groups in each aromatic ring) should have catalytic activities higher than C1 complex, which contains two substituents in each aromatic ring, what was really observed. Thus, the catalytic activity increases in the order: R = methoxy (C3) < 2,6-dimethylphenyl (C1) < 2,4,6-trimethylphenyl (C2). This effects caused on the activity by the substituents can be justified taking into account other factors such as bond distances and angles, dihedral angle and steric hindrance, in addition to full charge on the metal center. There isn't a general model that explains such behavior. In most of the cases what is found is a set of factors in which each case presents its own features [26]. Within this context, it is suggested that the catalytic activity of any complex can be affected by the mobility of the aromatic rings of the β -diimine ligands, which hinders the access of the substrate to the metal center. It can be suggested that the presence of methyl groups in the aromatic rings of the complexes decrease the mobility of the ligand and facilitate the access to the active center of the catalyst precursor, allowing oligomerization. Figure 3 shows that the observations made with respect to steric hindrance may be further explored.

Insert Fig. 3

Figure 3. Chem3D representation for C1, C2 and C3 complexes.

Under the conditions studied and by EASC activation, the complexes showed high catalytic activity in ethylene oligomerization providing high selectivity on low molecular weight α -olefins and a higher prevalence of 1butene. The highest selectivity for α -olefins can be justified by the low isomerizating capacity presented by cobalt [27]. This result is in agreement with those reported in the literature for analogous cobalt complexes, which also exhibit selectivity for the obtention of light α -olefins. [15-18]. Complex **C1** produced only the C₄ fraction, complex **C2** showed the highest activity of all complexes studied whereas complex **C3** showed the lowest activity, the selectivity of complexes **C2** and **C3** remaining the same.

Comparing the results obtained in this study with others that have employed cobalt complexes in oligomerization reactions, we can observe that the activity values attained with Co(II)- β -diimine complexes are much higher than those previously reported in the literature [15-18]. Besides that, we observed that comparing Co(II)- β -diimine complexes with Ni(II)- β -diimine complexes activity in similar conditions (10 atm, 10 °C, toluene, EASC) cobalt complex presented higher activity (TOF = 34 s⁻¹) than nickel ones (TOF = 2.7 s⁻¹) [2].

4. Conclusions

Co- β -diimine complexes displayed very high activities (up to 34 s⁻¹), which is a result ten times higher than those reported in the literature. The complexes were also selective for the obtention of the C₄-C₆ fraction, reaching 100% of C₄ selectivity. It was observed that the different substituents present in the aromatic rings of β -diimine ligand strongly influence the activity of each catalyst precursor.

Acknowledgements

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KORTED MANUSCRIPT



	L1	L2	L3
R ₁	Me	Me	н
R ₂	н	Ме	OMe

Figure 1

d Karten ka tarten karten kart



NA





	C1	C2	C3
R ₁	Me	Me	н
R ₂	н	Me	ОМе

Figure 2





Graphic Abstract

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Highlights

- A new family of $Co-\beta$ -diimine complexes was synthetized.
- Co-_β-diimine complexes displayed very high activities in • ethylene oligomerization.
- Complexes produced mainly the C_4 - C_6 fraction. ٠
- Ligands strongly influence the activity of each catalytic ٠

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