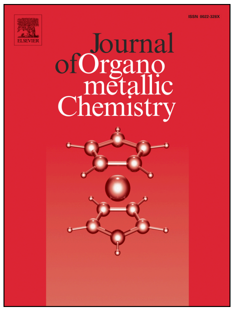

Catalytic ethylene oligomerization on cobalt(II) bis(imino)pyridine complexes bearing electron-withdrawing groups

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Catalytic ethylene oligomerization on cobalt(II) bis(imino)pyridine complexes bearing electron-withdrawing groups

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This work is dedicated to Prof. Armando J. L. Pombeiro for his prominent contribution to modern organometallic chemistry and on the occasion of his 70th birthday.

ABSTRACT

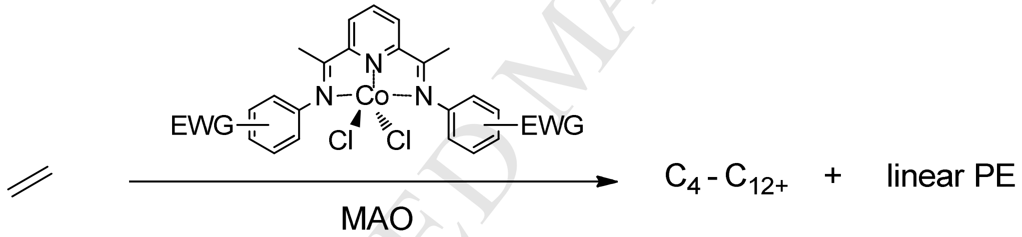
A series of novel bis(imino)pyridine cobalt(II) chlorides, $LCoCl_2$, with the bis(imino)pyridine ligands bearing one or several electron-withdrawing substituents (F, Cl, Br, CF_3) at the aniline moieties, have been prepared and characterized. In the presence of methylalumoxane (MAO), these complexes have demonstrated high ethylene oligo- and polymerization activity (up to $1.8 \cdot 10^7$ g products·(mol Co)$^{-1}$ h^{-1} bar^{-1}), affording products ranging from 1-butene and *Z,E*-2-butenes to strictly linear low-molecular-weight (M_n ~ 300…700) polyethylene. The dependence of the reaction outcome on the ligand structure is discussed.

Keywords: Ethylene; bis(imino)pyridine; cobalt; electron-withdrawing; oligomerization; polymerization

Highlights

- Novel cobalt(II) bis(imino)pyridine complexes bearing electron-withdrawing substituents
- High ethylene oligomerization/polymerization activities in the presence of MAO
- Ligand structure-catalytic behavior relationships

Graphical Abstract



1. Introduction

The milestone discoveries of Brookhart [1] and of Gibson [2] established the bis(imino)pyridine cobalt complexes as highly active post-metallocene catalysts of ethylene polymerization, affording highly linear polyethylene (PE) with narrow molecular weight distribution (MWD), characteristic of “single-site” catalysts [3-8]. The success of the bis(imino)pyridine ligand framework inspired further ligand modifications, retaining the N,N,N-donor chelating core, aimed at tuning the catalytic properties of cobalt complexes, as well as improving their thermal stability [9,10].

In the last years, we exploited a synthetic approach to single-site catalysts, relying on the introduction of electron-withdrawing substituents into the ligand structures, which was found to enhance the catalytic reactivities of nickel(II) complexes toward norbornene polymerization [11,12] and ethylene oligomerization [13], and provided a powerful tool to manipulate the relative rates of olefin enchainment and chain termination. Currently, we have been interested in designing highly-active single-site catalysts for selective ethylene dimerization, the crucial first step for further production of commodity plastics and value-added chemicals [14-20], as well as for the synthesis of strictly linear polyethylene with low molecular weight (PE waxes with narrow MWD), the precursors to food-grade paraffins, used as components of food coating compositions [21-24]. In this work, we have focused on bis(imino)pyridine Co based catalysts, owing to their high ethylene reactivity, sometimes matching that of their Fe counterparts, but leading to oligo- and polymeric products with lower molecular weight [1-10]. Another attractive feature of Co bis(imino)pyridine based catalysts is the absence of chain transfer to co-catalyst, chain termination operating exclusively by β-hydride transfer, thus ensuring stability of chain transfer rate over the polymerization course and hence narrow molecular-weight distribution (M_w/M_n down to 1.4) [8,9,25].

Herewith, we report designing a series of cobalt(II) bis(imino)pyridine complexes, bearing one or more electron-withdrawing substituents, their catalytic activities in ethylene dimerization/oligomerization/polymerization, and analyze the substituents effects on their catalytic behavior.

2. Experimental

General experimental details, preparation and characterization of bis(imino)pyridine ligands with electron-withdrawing substituents and the corresponding cobalt(II) complexes are reported in the Supporting Information.

2.1. Ethylene Oligomerization/Polymerization Procedure

The reaction was performed in a steel 0.3 L autoclave. The catalyst was introduced into the autoclave in a vacuum-sealed glass ampoule. The reactor was evacuated at 80 °C, cooled to 20 °C and charged with the solution of MAO (1 mmol Al) in toluene. After setting up the temperature and ethylene pressure, the reaction was started by breaking the ampoule with the complex. During the reaction, ethylene pressure, stirring speed and temperature were maintained constant. The experimental unit was equipped with an automatic computer-controlled system for ethylene feed and the ethylene consumption recording. The catalytic activity values were calculated based on the ethylene consumption.

2.2. Analysis of Oligomeric and Polymeric Products

After the catalytic experiment ended, an aliquot of the oligomerization products in toluene (0.6 ml) was quickly taken by a gastight syringe through a technical hole of the reactor lid, and was immediately transferred to the 5 mm o.d. glass NMR tube, capped with a septum stopper. The relative content of ethylene oligomers was determined by ^{13}C NMR. ^{1}H and ^{13}C NMR spectra of oligomeric mixtures were recorded on a Bruker DPX 250 MHz NMR spectrometer (at 250.130 and 62.90 MHz) at room temperature.

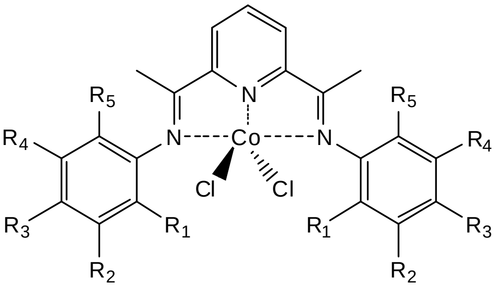
With regard to the polyethylene analysis, typically, 50-100 mg of dry polymer were dissolved in 3 ml of 1,2-dichlorobenzene at 140-150 °C. The ^{1}H and ^{13}C NMR spectra of linear polyethylene were recorded on a Bruker Avance-400 MHz NMR spectrometer (at 400.130 and 100.613 MHz, respectively) in 1,2-dichlorobenzene at 100 °C using 10 mm o.d. glass NMR tubes.

3. Results and Discussion

3.1. Synthesis and Characterization of Bis(imino)pyridine Ligands and Cobalt(II) Complexes

Cobalt(II) bis(imino)pyridine complexes were prepared in good yields (typically 62-95 %) by mixing the corresponding chelating ligands with $CoCl_2 \cdot 2H_2O$ in THF under an argon atmosphere for 5-24 h (SI). Overall, 13 cobalt complexes (Scheme 1) were synthesized and characterized by elemental analysis and ^1H NMR spectroscopy. All complexes contained cobalt(II) (d^7 configuration) in high-spin state ($S = 3/2$) and displayed well informative paramagnetic ^1H NMR spectra from the chelating ligands, with the paramagnetic shifts ranging from 100 to -65 ppm (Figure S1, SI). We notice that some cobalt(II) bis(imino)pyridine complexes containing alkyl [1,2,26-32] , bulky aromatic [33-37], both alkyl and electron-withdrawing [38-43], only electron-withdrawing [44-49] substituents at the aniline moieties, and supported cobalt(II) bis(imino)pyridine complexes [50-52] were reported previously by others and were studied as catalysts of ethylene polymerization or oligomerization in the presence of MAO, MMAO, $AlMe_3$, $B(C_6F_5)_3/AlMe_3$, $B(C_6F_5)_3/Al^iBu_3$, $AlEt_3/[Ph_3C][Al(OtBu^F)_4]$.

Complex	R_1	R_2	R_3	R_4	R_5
1	H	H	F	H	H
2	H	H	Br	H	H
3	Cl	H	F	H	H
4	F	H	H	H	H
5	H	Cl	H	Cl	H
6	CF_3	H	H	H	H
7	H	F	H	F	H
8	CF_3	H	F	H	H
9	H	CF_3	F	H	H
10	F	H	F	H	F
11	Cl	H	H	H	Cl
12	H	Cl	H	H	H
13	Br	H	H	H	H
14	Me	H	H	H	Me



Scheme 1. Structure of cobalt(II) complexes **1-14**.

3.2. Ethylene Oligomerization on Bis(imino)pyridine Cobalt(II) Complexes

The reactivity of complexes **1-13** toward ethylene was examined, using MAO as activator. For comparison, the 'reference' 2,6-dimethyl substituted complex **14** (Scheme 1) [1] was tested under the same conditions. The obtained data are summarized in Table 1.

Complexes **6**, **8**, and **11**, bearing either *o*-CF_3 substituent or two *o*-Cl substituents at each aromatic ring, demonstrated the highest catalytic activities, affording, predominantly, a mixture of C_4-C_{12+} oligomers (17-19 wt. %), along with low-molecular-weight polyethylene (81-83 wt. %, Table 1, entries 6, 8, 11, and Table 2, entries 1-3). In comparison, reference complex **14** showed somewhat lower activity, yielding higher-molecular-weight linear PE as the only reaction product (Table 1, entry 14, and Table 2, entry 4).

Table 1. Oligomerization of ethylene in the presence of cobalt complexes **1-14**. [a]

Entry	Catalyst	Time, min	Activity [b]	Products
1	**1**	6	$0.3\cdot10^6$	1-butene
2	**2**	15	$1.3\cdot10^6$	1-butene, *Z,E*-2-butene
3	**3**	15	$6\cdot10^6$	oligomers C_4
4	**4**	15	$2.5\cdot10^6$	1-butene , *Z,E*-2-butene
5	**5**	15	$1.8\cdot10^6$	1-butene , *Z,E*-2-butene
6	**6**	15	$7.1\cdot10^6$	oligomers C_4-C_{12+}, linear PE
7	**7**	15	$2.9\cdot10^6$	1-butene , *Z,E*-2-butene
8	**8**	15	$11.0\cdot10^6$	oligomers C_4-C_{12+}, linear PE
9	**9**	10	$1.4\cdot10^6$	1-butene , *Z,E*-2-butene
10	**10**	15	$0.6\cdot10^6$	1-butene
11	**11**	15	$18.2\cdot10^6$	oligomers C_4-C_{12+}, linear PE
12	**12**	15	$4.7\cdot10^6$	1-butene , *Z,E*-2-butene
13	**13**	15	$2.3\cdot10^6$	1-butene
14	**14**	15	$2.4\cdot10^6$	linear PE

[a] Conditions: Cobalt complex, 2 μmol, toluene, 50 mL, MAO (Al/Co = 500/1), ethylene pressure 2 bar, T = 35 ^oC. [b] In g products·(mol Co)$^{-1}$ h^{-1} bar^{-1}.

In all cases, the ratio of CH_3 and CH_2=CH polymer end groups was close to 1:1 (Table 2), thus witnessing that β-hydride transfer is the only chain termination pathway. The polyethylene M_n reduces when passing from **6** (one *o*-CF_3 substituent) to **8** (*o*-CF_3 substituent and *p*-F substituent) and further to **11** (two electron-withdrawing *o*-Cl substituents). Tentatively, this trend, dictated by the increasing propensity to β-H transfer in the order **6** < **8** < **11**, may be ascribed to an increase of overall cobalt electrophilicity in the same order. ^{13}C NMR analysis of the oligomeric fractions, obtained in the presence of complexes **6**, **8**, **11**, witnessed the presence of linear oligomers (Table 3). The share of 1-butene decreases in the order **6** > **8** > **11**.

Table 2. ^{13}C NMR characterization of PE obtained on complexes **6**, **8**, **11**, **14**.

Entry	Catalyst	m PE (g)	M_n[a]	End-groups (per PE molecule)[a]		PE/Oligomers (wt. %)
				CH_3	CH_2=CH	
1	**6**	1.28	690	1.1	0.9	17.5/82.5
2	**8**	2.07	390	1.1	0.9	19.3/80.7
3	**11**	3.32	300	1.0	1.0	17.7/82.3
4	**14**	2.66	1300	1.1	0.9	100/0

[a] Determined by ^{13}C NMR.

Table 3. Analysis of oligomeric products obtained on catalysts **6**, **8**, **11**.

Entry	Catalyst	1-Butene (mol. %)	1-Hexene (mol. %)	1-Octene (mol. %)	1-Decene (mol. %)	1-Dodecene^{+} [a] (mol. %)
1	**6**	29.5	22.0	14.5	10.0	24.0
2	**8**	22.0	21.0	15.5	12.0	29.5
3	**11**	16.0	20.5	17.5	14.5	31.5

[a] C_{12} and higher oligomers, soluble in toluene.

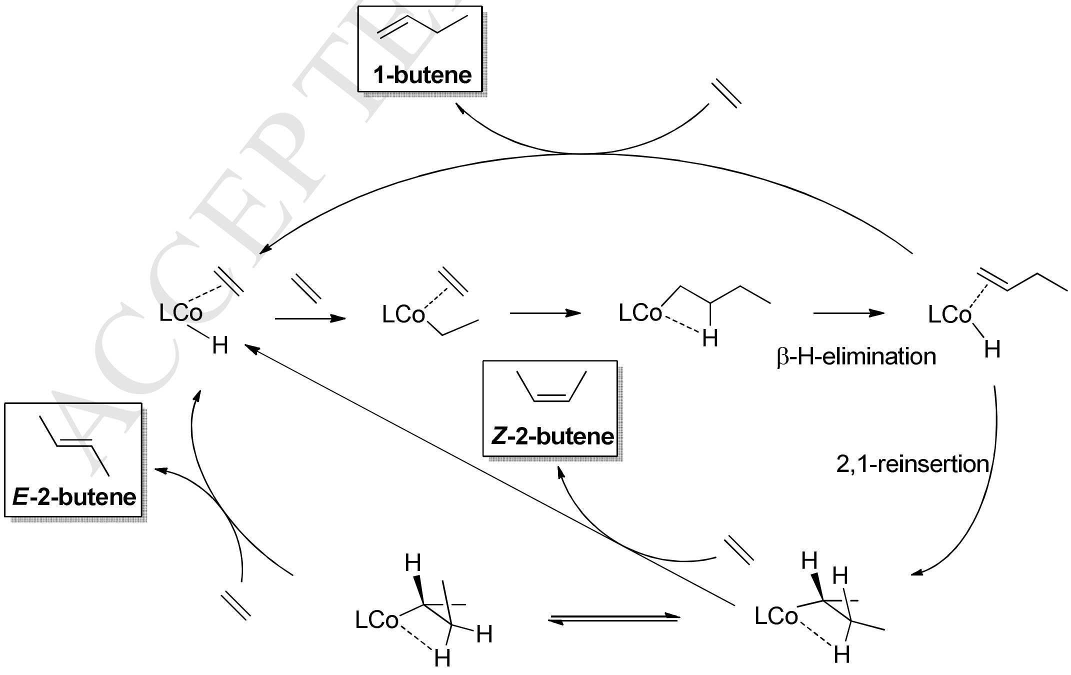
High activity was demonstrated by complexes **5**, **7**, **9**, **12**, bearing one or several electron-withdrawing *m*-substituents (Table 1), and by **3**, **4**, **13** (Table 1), having one *o*-halogen substituent. Complexes **1** and **2**, with *p*-halogen substituents, and **10**, with *o*,*p*-F substituted ligands (Table 1), were less active. In all cases, the only reaction products were C_4 oligomers, predominantly 1-butene (Table 4). Catalyst **13** was most selective for 1-butene (Table 4, entry 10); other complexes without *o*-substituents (**1**, **2**), one *o*-halogen substituent (**3**, **4**) or with *m*,*p*-substituents (**1**, **2**, **5, 9**) also showed high 1-butene selectivities (82-88.5 %) (Table 4, entries 1-5,7).

On the contrary, *m*-substituted complexes **7** and **12** afforded higher share of 2-butenes, with *E*-2-butene prevailing over *Z*-2-butene (Table 4, entries 6 and 9). This result shows that in case of less sterically demanding complexes **7** and **12**, 2,1-reinsertion of the initially formed 1-butene, with subsequent *cis*-*trans* conformational rearrangement and β-H elimination (Scheme 2), is substantially facilitated. At the same time, given the thermodynamic parameters of the geometrical isomerization of *Z*-2-butene to *E*-2-butene [53], the calculated equilibrium constant (corresponding to *E*-2-butene/*Z*-2-butene molar ratio) at +35 °C should have value of 3.0…3.1. The experimentally observed [*E*]/[*Z*] ratios, not exceeding 2.2 (Table 4), do not approach the predicted equilibrium value, which points to kinetic control of the proportion of *Z*- and *E*-2-butenes formed in our catalyst systems.

Table 4. Composition of C_4 fractions, obtained on cobalt complexes **1**, **2**, **3**, **4**, **5**, **7**, **9**, **10**, **12**, **13**. [a]

Entry	Catalyst	1-Butene (mol. %)	*Z*-2-Butene (mol. %)	*E*-2-Butene (mol. %)
1	**1**	n.d. [b]	n.d. [b]	n.d. [b]
2	**2**	88.5	6.5	5.0
3	**3**	87.0	9.5	3.5
4	**4**	82.0	11.5	6.5
5	**5**	85.0	6.0	9.0
6	**7**	71.0	10.0	19.0
7	**9**	85.0	6.5	8.5
8	**10**	n.d. [b]	n.d. [b]	n.d. [b]
9	**12**	58.5	13.0	28.5
10	**13**	≥98	≈2	-

[a] Results of ^{13}C NMR analysis of the reaction mixture. [b] Not determined: concentration of 1-butene and 2-butenes was insufficient for quantitative ^{13}C NMR measurements.



Scheme 2. Proposed scheme of 1-butene, *Z*-2-butene, and *E*-2-butene formation in the presence of Co complexes.

4. Conclusions

A family of cobalt(II) bis(imino)pyridine complexes, $LCoCl_2$, bearing electron-withdrawing substituents (F, Cl, Br, CF_3) at the aniline moieties, were prepared and found to exhibit high ethylene oligomerization/polymerization activities (up to $1.8\cdot10^7$ g products*(mol Co)$^{-1}$ h^{-1} bar^{-1}) in the presence of MAO. The highest catalytic activities were demonstrated by cobalt complexes with electron-withdrawing *o*-substituents (Cl, CF_3). Depending on the nature and number of the electron withdrawing groups, the process selectivity varies from dimerization (with the selectivity to 1-butene up to 98 %) to oligomerization (C_4–C_{12+}), with accompanying formation of strictly linear low-molecular-weight polyethylene (the share of PE approaching 19 wt. %). One of the complexes, **12**, bearing one *m*-Cl substituent at the aryl ring, catalyzed ethylene dimerization to a mixture of 1-butene and 2-butenes (58:42), reflecting significant contribution of double bond migration process. Analysis of polyethylene end groups gives evidence for β-hydride transfer as the only chain termination pathway.

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