

Iron(II) coordination compounds with ω -alkenyl substituted bis(imino)pyridine ligands: Self-immobilizing catalysts for the polymerization of ethylene

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Dedicated to Professor Max Herberhold's 70th birthday (August 02, 2006).

Abstract

Coordination compounds of iron(II)chloride with bis(imino)pyridine ligands bearing ω -alkenyl substituents were synthesized and characterized. They can be activated with methylalumoxane (MAO) and then be used as self-immobilizing catalysts for the polymerization of ethylene. The produced polyethylene has a monomodal molecular weight distribution which is in contrast to polyethylenes that are produced with the unsubstituted catalysts.

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Keywords: Bis(imino)pyridine; Iron; Catalysis; Polymerization; Self-immobilization

1. Introduction

Coordination compounds of late transition metals with bis(imino)pyridine ligands are known since the mid of the last century [1–3]. But their use as catalyst precursors for olefin polymerization was not discovered until Brookhart and Gibson first described such experiments in 1998 [4,5]. Because of the reduced sensitivity towards air and moisture compared to metallocene compounds and the expected tolerance towards polar functional groups, this class of catalyst precursors received much attention in the following years. The strong relations between substituents on the ligand backbone and the performance of the catalysts allow the tailoring of the catalyst precursors according to demands [6,7]. It is found that substituents on the aniline part of the ligand backbone show the strongest influence [8]. For instance, by changing the pattern of substitution from 2-alkyl to 2,6-alkyl, the catalysts no longer produce oligomers with 2–40 carbon atoms but high molecular weight polyethylene [9]. Unfortunately the bis(imino)pyridine complexes suffer from a problem known from other single site catalysts, the so

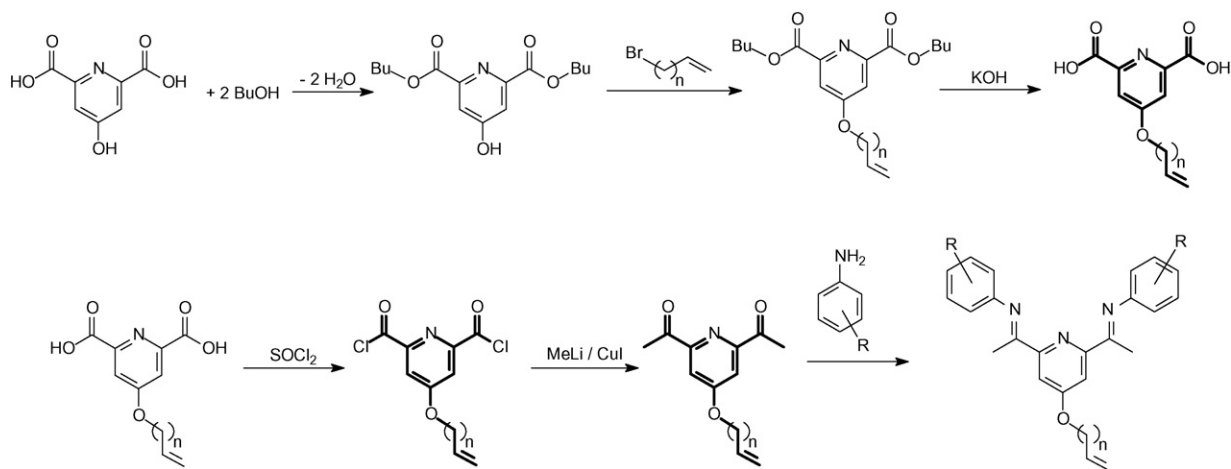
called reactor fouling [10]. This term describes the precipitation of the polymer on the walls of the reactor during the polymerization process. It is found in slurry as well as in gas phase reactors. The growing layer of polymer inhibits the reaction control and prevents a continuous process. In order to prevent reactor fouling many methods have been developed in order to heterogenize single site catalysts [11]. For instance, the approaches include the use of heterogeneous cocatalysts [12] or heterogenization of the catalysts on a support [13]. Concerning metallocene compounds Peifer and Alt developed a very elegant approach to prevent reactor fouling, the so called self-immobilization [14]. Here the catalyst precursor is functionalized with an ω -alkenyl substituent and as an olefin it can be copolymerized with the ethylene. The catalytic centers are immobilized in the growing polymer chain and therefore become heterogeneous preventing the reactor fouling. A first approach to transfer this idea to bis(imino)pyridine complexes was made by Herrmann and co-workers in 2002, who used ω -alkenyl substituents at the imino carbon atom [15].

2. Results and discussion

Because of the strong influence of substituents on the aniline part of the bis(imino)pyridine complexes, we have devel-

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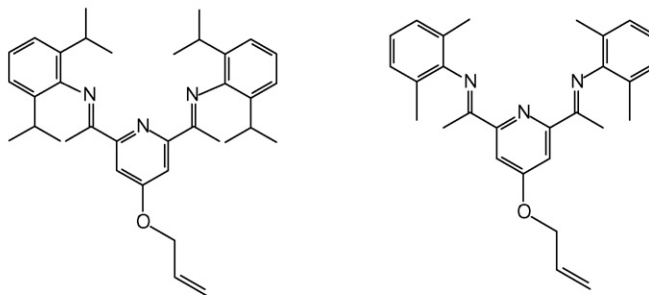
Scheme 1. Synthesis of the ω -alkenyl substituted ligand precursors.

oped a six step synthesis to place an ω -alkenyl substituent at position 4 of the pyridine ring. The reaction starts from cheilidamic acid which is esterified with butanol. The ω -alkenyl substituent is introduced via an ether bridge in position 4. The following steps are used to convert the ester groups first into acetyl functions and then by a double Schiff base condensation into the desired ligand precursor. Scheme 1 shows the reaction pathway.

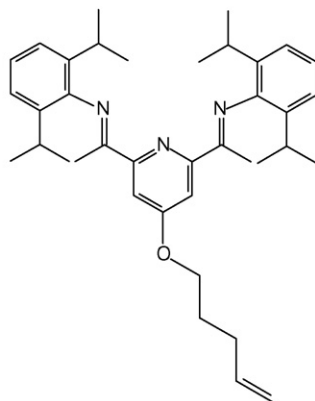
Using the synthetic route shown in Scheme 1 the following ligand precursors were synthesized (Scheme 2):

The characterization of the ligand precursors was performed by GC/MS analysis and NMR spectroscopy (see Section 4 for data). The ω -allyloxy substituted derivative with isopropyl substituents on the aniline parts was further characterized by X-ray diffraction. Fig. 1 shows the molecular structure.

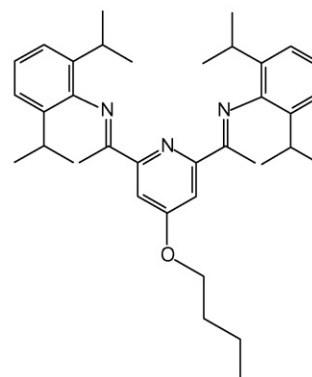
- with 4-allyloxy substituents:



- with a 4-(ω -pentenyloxy) substituent:



- with a 4-butyloxy substituent:



Scheme 2. Ligand precursors synthesized.

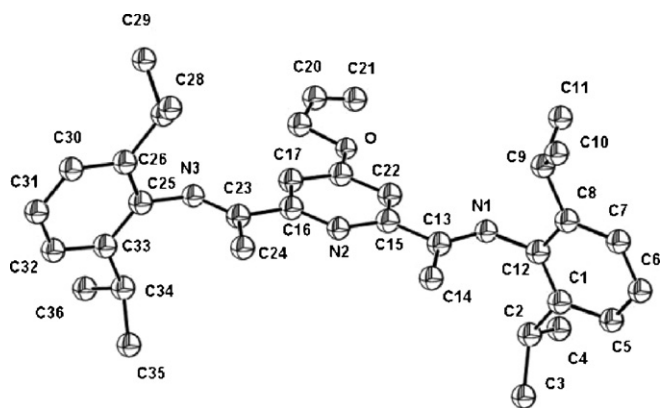


Fig. 1. Molecular structure of an ω -allyloxy substituted ligand precursor.

The X-ray data clearly shows that the ligand precursor crystallizes in the (E,E) conformation with typical C=N imino bond lengths of 1.271 and 1.275 Å. As may be seen by the high-temperature factors of the atoms of the strongly vibrating terminating group and by the relatively high R -values, the crystal quality was poor. So, the molecular structure of the ligand precursor could be well established but we will not discuss details (bond lengths and angles) of this compound (Fig. 2).

The ligand precursors with substituents in position 4 of the pyridine ring were applied for the coordination of iron(II)chloride. For reasons of comparison two ligand precursors were used which are known from literature [16] (Table 1).

Due to the paramagnetism of the iron complexes and their poor solubility in prevalent solvents used for NMR spectroscopy, the coordination compounds were characterized by mass spectrometry. The molecular structure of complex 5 was determined by X-ray analysis (Fig. 2).

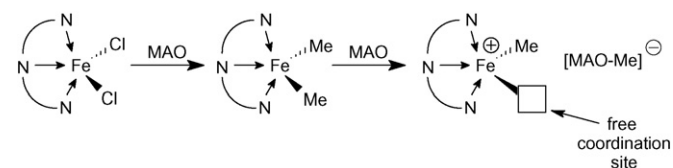
This structure is identical to structures already published except that the dimensions of the unit cell differ because of the inclusion of n -butanol [5,16]. Table 2 shows some selected data of the X-ray analysis.

Table 1
Coordination compounds synthesized

Number	R	R'	ML_n
1	2,6-Diisopropyl	Allyloxy	$FeCl_2$
2	2,6-Dimethyl	Allyloxy	$FeCl_2$
3	2,6-Diisopropyl	ω -Pentyloxy	$FeCl_2$
4	2,6-Diisopropyl	Butyloxy	$FeCl_2$
5	2,6-Diisopropyl	H	$FeCl_2$
6	2,6-Dimethyl	H	$FeCl_2$

Table 2
Data of the X-ray analysis of compound 5

Crystal data		Selected bond lengths			
Crystal system	Monoclinic	N1	Fe	2.205(22)	
Space group	$P 21/c$	N2	Fe	2.083(5)	
Unit cell	$a = 13.7871(28)$ Å	N3	Fe	2.191(6)	
	$b = 15.1742(30)$ Å	Fe	C11	2.247(27)	
	$c = 18.6711(37)$ Å	Fe	C12	2.351(25)	
	$\beta = 102.49(3)^\circ$				



Scheme 3. Activation of the coordination compounds.

All coordination compounds were activated with MAO according to Scheme 3 which is in agreement to the mechanism proposed for the activation of metallocene compounds [17,18] and is accepted for theoretical investiga-

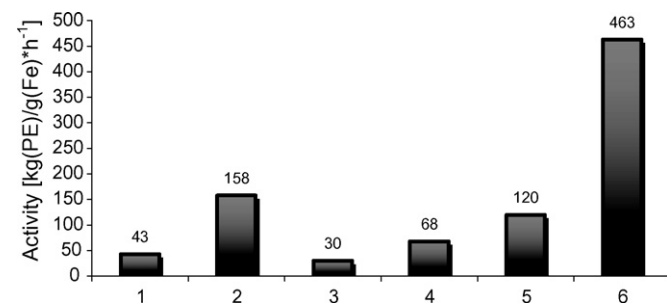


Fig. 3. Activities of the catalysts; polymerization conditions: catalyst precursor in 500 ml pentane, activation with MAO (Al: Fe = 2000:1), 10 bar ethylene pressure, 60 °C, 1 h.

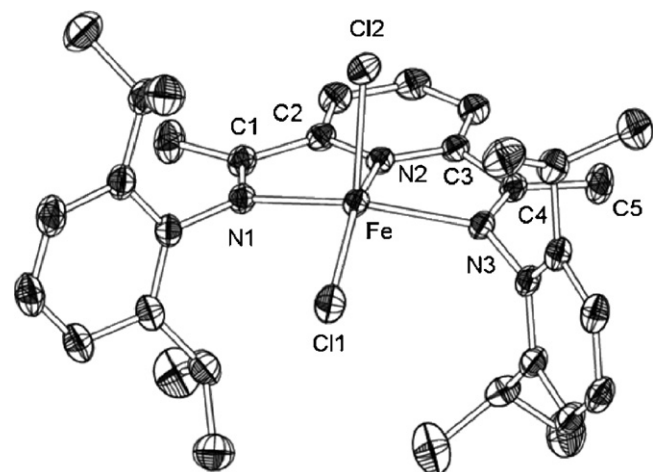


Fig. 2. Molecular structure of 5.

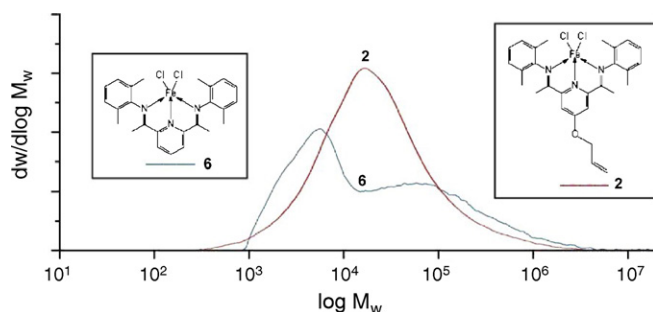


Fig. 4. HT-GPC data of polyethylenes obtained with catalyst precursors 2 and 6.

tions concerning the bis(imino)pyridine catalyst precursors [19,20].

The catalysts obtained were used for the polymerization of ethylene in a 1l autoclave. The reactions were conducted over 1 h, at a temperature of 60 °C and an ethylene pressure of 10 bar. Fig. 3 summarizes the results.

The series of polymerization experiments shows that the catalysts with substituents on position 4 of the pyridine ring have lower activities than the unsubstituted derivatives by a factor of 3.

With all the catalyst precursors tested it is found that the sterically more demanding isopropyl substituents on the aniline parts of the ligand backbone inhibit the coordination of ethylene leading to lower activities compared to the methyl substituted compounds [11]. With the series of coordination compounds differing only in the substituents on position 4 of the pyridine ring, the butyloxy substituted derivative shows the highest activity. The compound without the alkenyl function is not immobilized in the growing polymer chains as this catalyst shows reactor fouling. Only when using coordination compounds 1, 2 and 3 which have ω -alkenyl substituents the polymer does not precipitate on the reactor walls and the stirrer. Besides this advantage, the self-immobilization of the catalyst precursors also has an influence on the characteristics of the polymers produced. Fig. 4 compares the molecular weight distributions of polyethylenes obtained with catalyst precursors with and without an ω -allyloxy substituent in position 4 of the pyridine ring.

As can be seen from the HT-GPC analysis, the self-immobilized catalyst produces polyethylene with a monomodal molecular weight distribution. The average molecular weights are $M_n = 8902$ and $M_w = 70902$ g/mol and the polydispersity is 7.96. In contrast to this the non-functionalized derivative produces polyethylene with bimodal molecular weight distribution. In this case, the average molecular weights are $M_n = 6672$ and $M_w = 90950$ g/mol, with a polydispersity of 13.63. Since it is known, that the low molecular weight fraction of polyethylenes produced with late transition metal bis(imino)pyridine catalysts results from a chain transfer reaction to the aluminum centers of the cocatalyst [6], this behavior can be explained by the steric demand of the alkyl groups surrounding the self-immobilized catalysts. Because the active centers are incorporated in the growing chains, the interaction with the MAO counterions is sterically hindered and therefore the chain transfer is disfavored resulting in a monomodal molecular weight distribution [6].

3. Summary and conclusions

A suitable reaction pathway to synthesize coordination compounds with bis(imino)pyridine ligands bearing ω -alkenyl substituents was described starting from chelidamic acid. From the six step synthesis the desired ligand precursors are obtained in moderate yields and the coordination of iron(II)chloride proceeds almost quantitatively.

The polymerization experiments show that the introduction of ω -alkenyl substituents in position 4 of the pyridine rings generates catalyst precursors which are capable of self-immobilization and can prevent the reactor fouling efficiently. Due to the incorporation of the active centers into the growing chains the polymerization reaction shows lower activities and because of the inhibition of the chain transfer to the aluminum centers, polyethylenes with monomodal molecular weight distributions are obtained.

4. Experimental

4.1. General methods

All manipulations of air and water sensitive compounds were performed using standard Schlenk techniques. Therefore, argon was purified by passage over BTS catalyst and molecular sieves 4 Å. All solvents used were purchased in technical grade and purified by distillation over Na/K alloy under argon atmosphere. Methylalumoxane (MAO) was supplied by Witco GmbH, Bergkamen, as 30% solution in toluene (average molecular weight 1100 g/mol, aluminum content: 13.1%, 3.5% as trimethylaluminum). All other chemicals were commercially available or were synthesized according to literature procedures.

NMR spectra were recorded on a Bruker ARX 250 spectrometer at a temperature of 25 °C. CDCl_3 served as solvent. The chemical shifts (δ) in the ^1H NMR spectra are referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for chloroform) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for chloroform- d_1). MS spectra were recorded with a VARIAN MAT 8500 mass spectrometer (direct inlet system, electron impact ionization 70 eV). In addition, a Hewlett–Packard 5917A mass spectrometer was routinely used to record MS spectra and in combination with a Hewlett–Packard Series II 5890 gas chromatograph to record GC/MS spectra.

Molecular weight determinations of the polyethylene samples were performed using a Millipore Waters 150 C HT-GPC with refractometric detection (RI Waters 401). The polymer samples were dissolved in 1,2,4-trichlorobenzene (flow rate 1 ml/min) and measured at 150 °C.

4.2. Synthesis of the ω -alkenyl substituted ligand precursors

15.42 g (0.084 mol) chelidamic acid were dissolved in 600 ml toluene. Fifty millilitres 1-butanol and 3 ml concentrated sulfuric acid were added and the mixture was kept at reflux over

night. Afterwards neutralization was done by adding an aqueous NaHCO_3 -solution. The organic layer was separated and washed with water. After drying over Na_2SO_4 the solvent was removed by distillation in vacuo. The chelidamic acid dibutyl ester was obtained as a white powder with 87% yield. 3.22 g (0.045 mol) of it were dissolved in DMF and 18.35 g (0.133 mol) of potassium carbonate were added. After the drop wise addition of 0.045 mol of the desired bromide the mixture was heated to 65°C and stirred for 20 h. Afterwards the solvent was removed almost completely and the residue was suspended in water. This mixture was extracted three times with dichloromethane. The organic layers were combined and washed with water. Then they were dried over Na_2SO_4 and the solvent was removed by distillation in vacuo. The resulting substituted chelidamic acid dibutyl esters were suspended in 100 ml ethanol and 100 ml aqueous KOH solution were added. The mixture was kept at reflux for 2 h. After acidification with 5% HCl, the products were obtained by filtration as white powders. These were dried in vacuo and were mixed carefully with an excess of thionylchloride. After 2 h of refluxing the remaining SOCl_2 was distilled off and the products were obtained as white powders. In order to convert these diacidic dichlorides into the desired ketones a cuprate reaction analogous to the literature procedures of Paquette and co-workers [21] and Marino and Linderman [22] was chosen. Therefore, a suspension of 3.32 g (17.42 mmol) CuI in diethyl ether was cooled to 0°C and an equimolar amount of methyl lithium was added drop wise. 8.81 mmol of the corresponding diacidic dichloride were added drop wise as suspension in diethyl ether at 0°C . After this, the mixture was allowed to warm up to room temperature within 4 h. By addition of satu-

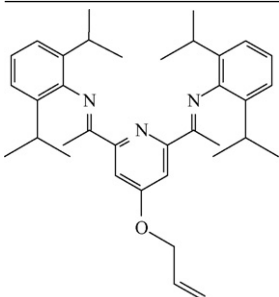
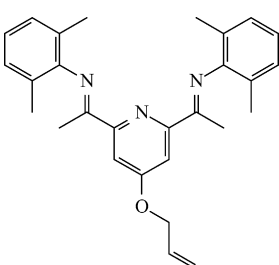
rated NH_4Cl solution, the reaction was quenched and the solvent was removed in vacuo. The remaining residue was extracted with dichloromethane several times and the extracts were combined and dried over Na_2SO_4 . After the removal of the solvent brown solids were obtained which were recrystallized from ethanol.

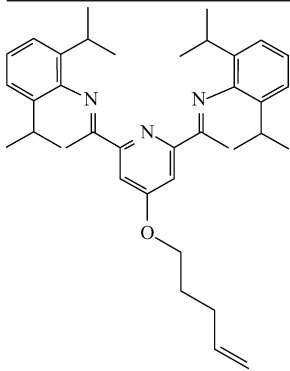
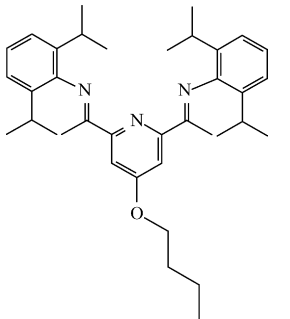
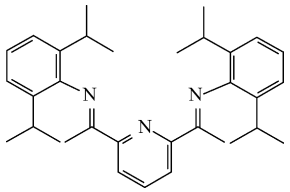
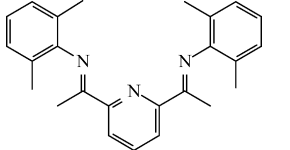
Substituent in position 4 of the pyridine ring	Yield (%)
Allyloxy	40
ω -Pentyloxy	38
Butyloxy	43

The corresponding 2,6-diacetylpyridine compound was dissolved in toluene and *p*-toluenesulfonic acid was added as a catalyst. A 2.5-fold excess of the desired amine was added and the solution was heated to reflux at a Dean–Stark trap. After the end of the reaction monitored by GC, the reaction solution was neutralized with aqueous NaHCO_3 solution. The organic layer was dried over Na_2SO_4 and the ligand precursors were crystallized at -20°C . The bis(imino)pyridine compound was recrystallized from absolute ethanol.

Substituent in position 4 of the pyridine ring	Substituent at the aniline moiety	Yield (%)
Allyloxy	2,6-Diisopropyl	71
Allyloxy	2,6-Dimethyl	62
ω -Pentyloxy	2,6-Diisopropyl	58
Butyloxy	2,6-Diisopropyl	29
None	2,6-Dimethyl	67
None	2,6-Diisopropyl	58

The compounds were characterized by NMR spectroscopy.

Compound	$^1\text{H-NMR}^a$	$^{13}\text{C-NMR}^b$
	8.12(s,2H), 7.16(m,6H), 6.09(m,1H), 5.43(dd,2H), 4.79(d,2H), 2.77(sept,4H, $^3J_{\text{HH}} = 2.5$ Hz), 2.27(s,6H), 1.17(d,24H, $^3J_{\text{HH}} = 2.5$ Hz)	C_q : 173.2, 165.9, 160.4, 142.9, 139.1; CH: 132.6, 123.4, 121.8, 104.3, 28.8; CH_2 : 118.1, 70.6; CH_3 : 23.7, 17.7
	8.19(s,2H), 7.04(m,6H), 6.07(m,1H), 5.51(m,2H), 4.82(m,2H), 2.27(s,6H), 2.08(s,12H)	C_q : 174.2, 162.7, 161.9, 150.2, 129.0; CH: 132.6, 128.1, 124.3, 103.6; CH_2 : 117.2, 68.7; CH_3 : 18.2, 16.9

Compound	¹ H-NMR ^a	¹³ C-NMR ^b
	7.10(m,6H), 5.86(m,1H), 5.74(s,2H), 4.91(m,2H), 3.82(t,2H, ³ J _{HH} = 6.2 Hz), 2.87(sept,4H, ³ J _{HH} = 2.3 Hz), 2.13(s,6H), 2.04(m,2H), 1.54(m,2H), 1.19(d,24H, ³ J _{HH} = 2.3 Hz)	C _q : 174.9, 166.7, 160.8, 142.9, 138.8; CH: 141.0, 123.8, 122.5, 103.4, 26.3; CH ₂ : 115.4, 67.9, 30.5, 28.9; CH ₃ : 23.3, 16.4
	7.09(m,6H), 5.81(s,2H), 3.97(t,2H, ³ J _{HH} = 6.3 Hz), 2.86(sept,4H, ³ J _{HH} = 2.4 Hz), 2.13(s,6H), 1.69(m,4H), 1.18(d,24H, ³ J _{HH} = 2.4 Hz), 0.99(t,3H, ³ J _{HH} = 7.3 Hz),	C _q : 174.8, 166.7, 160.7, 142.9, 138.9; CH: 124.8, 122.4, 103.6, 26.3; CH ₂ : 67.8, 31.2, 19.2; CH ₃ : 23.3, 16.4, 13.7
	8.31(d,2H, ³ J _{HH} = 7.18 Hz), 7.99(t,1H, ³ J _{HH} = 7.18 Hz), 7.18(m,6H), 2.96(sept,2H, ³ J _{HH} = 7.17 Hz), 2.33(s,6H), 1.19(d,24H, ³ J _{HH} = 7.17 Hz)	C _q : 167.7, 155.9, 147.3, 122.9; CH: 137.6, 136.6, 124.4, 123.8, 25.5; CH ₃ : 28.1, 21.9
	8.23 (d,2H), 7.86(t,1H), 7.04(d,2H), 6.81(t,2H), 6.52(d,2H), 2.35 (s,12H), 2.13(s,6H)	C _q : 167.2, 155.1, 148.7, 130.4; CH: 138.4, 127.9, 125.4, 123.0; CH ₃ : 18.0, 16.5

^a 250.13 MHz, 25 °C, in chloroform-d₁, δ [ppm] rel. chloroform (7.24).

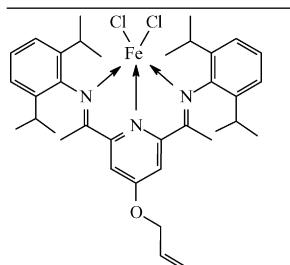
^b 62.9 MHz, 25 °C, in chloroform-d₁, δ [ppm] rel. chloroform-d₁ (77.0).

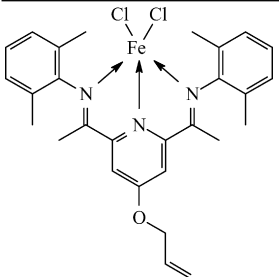
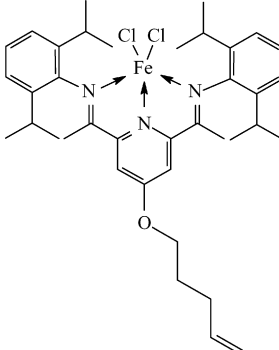
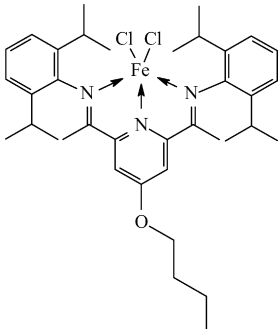
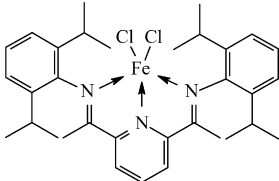
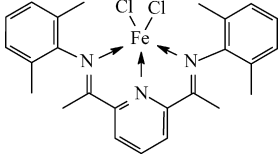
4.3. Synthesis of the coordination compounds

0.1–0.3 g of the corresponding ligand precursor were dissolved in dry *n*-butanol. One equivalent of iron(II)chloride was added and the mixture was stirred at room temperature.

The solution was concentrated in vacuo and the products were crystallized at –20 °C. After washing with pentane and drying the coordination compounds were obtained as blue powders.

The compounds were characterized by mass spectrometry.

Compound	Yield (%)	<i>m/z</i> (%)
	88	664(M ⁺ •), 629(17), 537(41), 522(100), 496(13), 364(6), 297(5), 237(6), 186(9), 174(5), 160(8), 144(3), 132(3), 122(2)

Compound	Yield (%)	<i>m/z</i> (%)
	89	552(M ⁺ •), 517(6), 425(53), 410(100), 384(29), 356(9), 326(5), 280(9), 239(11), 146(25), 131(12), 105(26), 77(12)
	90	692(M ⁺ •), 657(9), 566(47), 551(100), 523(11), 497(8), 405(9), 202(26), 186(13), 176(11), 160(17), 144(15), 122(18), 91(10)
	92	679(M ⁺ •), 644(5), 553(31), 538(100), 510(10), 496(8), 380(13), 202(17), 186(31), 122(20)
	86	608(M ⁺ •), 573(13), 558(7), 532(4), 481(37), 466(100), 309(12), 265(9), 249(32), 238(33), 202(73), 186(36), 177(61), 144(27), 132(21), 91(28)
	93	495(M ⁺ •), 460(3), 370(11), 369(38), 368(11), 355(27), 354(100), 224(15), 223(20), 209(28), 146(23), 105(23), 79(12), 77(11)

4.4. Activation of the catalyst precursors

An amount of 10 mg of the corresponding complex was suspended in pentane and activated with an excess of MAO (Al/Fe = 2000/1). The activated catalyst was used for ethylene polymerization within 15 min.

4.5. Polymerization of ethylene

The activated complex was added to a 1l steel autoclave (Büchi), filled with 500 ml *n*-pentane. The polymerizations were performed with constant ethylene pressure of 10 bar (99.98% ethylene, dried over aluminum oxide) and at a temperature of

60 °C. After a period of 1 h, the autoclave was cooled to room temperature and the pressure was reduced. The polymerization mixture was filtered. The remaining polymer was washed with half concentrated hydrochloric acid, dried and weighed.

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