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Iron(II)–ethylene polymerization catalysts bearing 2,6-bis(imino)pyrazine ligands Part I. Synthesis and characterization

L. Beaufort [a], F. Benvenuti [b], A.F. Noels [a,*]

[a] *Laboratory of Macromolecular Chemistry and Organic Catalysis (CERM), University of Liège, Sart-Tilman (B6a), 4000 Liège, Belgium*
[b] *Solvay S.A., rue de Ransbeek 310, 1120 Bruxelles, Belgium*

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Abstract

The synthesis of a new series of 2,6-bis(imino)pyrazinyl ligands, [Ar–N=C–Pyz–C=N–Ar] where the aryl groups Ar = naphtyl, 2,6-dimethylphenyl, 2,6-diisopropylphenyl, 2,4,6-trimethylphenyl, and their iron(II) complexes is described starting from monoacetylpyrazine.

Keywords: Tridentate ligands; Bis(imino)pyrazine; Iron(II) complexes; Diacetylpyrazine

1. Introduction

The world-wide demand for valuable products that can be produced in high yields and purities grows strongly year after year. The driving force is a strong economic incentive to find better and more cost effective catalyst systems that can produce these value-added products. New catalysts can provide the potential to shift the production of expensive products to value-added commodity products.

Beginning in the 1950s with the work and experiments of Ziegler et al. [1–3], and Natta et al. [4,5], the interest in olefin oligomerization and polymerization catalysts has grown dramatically over the years and still continues 50 years later. In addition to the development of metallocene technology [7], the search for catalysts that are more compatible with organic functionalities has led to the development of new catalyst systems based on late transition metals [6,8]. In 1995, Brookhart and co-worker's Nickel diimine complexes were synthesized and tested successfully as olefin polymerization and oligomerization catalysts [9–15] after activation with a co-catalyst such as methylaluminoxane (MAO) [16]. Then in 1998, Bennett and co-workers presented diiminopyridyl complexes of iron and cobalt [17] as oligomerization and polymerization catalysts after activation with MAO. These 2,6-bis(imino)pyridine type catalysts (Scheme 1) allowed the polymerization chemistry to enter the "iron age" as described by Gibson and Wass [18]. The two great advantages of these systems over existing homogeneous catalysts are their low cost and the ease with which chemists can derivatise the complexes. Here again, the catalyst structure is the key of the activity.

It was demonstrated by modelling results that the electronic density of a "Gibson's type" iron catalyst could be drastically altered by replacing the pyridine moiety by a pyrazine one. This could result in different polymerization activities. So, we report here on the synthesis of new tridentate bis(imino) Fe(II) complexes incorporating the pyrazinyl moiety. Part 2 of this series will describe the catalytic efficiency of these new precursors for ethylene polymerization upon treatment with different aluminium alkyls under homogeneous and heterogeneous conditions.

2. Results and discussion

The synthesis of the iron complexes of the 2,6-bis(imino)-pyrazine was envisaged in three steps, starting either from pyrazine or from the commercially available monoacetylpyrazine, according to the retrosynthetic route of Scheme 2. The first step is the synthesis of the 2,6-diacetylpyrazine backbone precursor (which contrary to 2,6-diacetylpyridine is

* Corresponding author.
E-mail address: AF.Noels@ulg.ac.be (A.F. Noels).

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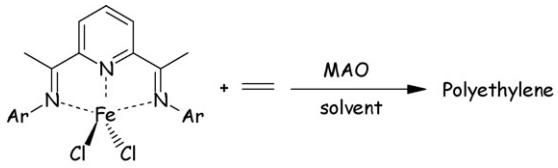


Scheme 1.

not commercially available). Next, Schiff base formation follows by reaction with differently substituted anilines. The last step consists in coordinating the metal ions.

It is well known that if the Friedel-Crafts acylation is a very useful method for the preparation of ketones in the benzenoid series, it is of little value for diazaaromatic compounds. Pyrazines (and especially pyrazine already substituted by an electron with growing (EWG) group) are particularly unsuited to direct electrophilic substitution due to the inductive effect of the ring nitrogen atoms, and to their possible quaternization by the Lewis acid catalyst [19]. In the past years, a variety of homolytic substitutions of heteroaromatic bases, leading to C–C bond formation were developed [20], which on the whole reproduce the Friedel-Crafts reaction, but with opposite reactivity and selectivity. We were inspired by a method reported by Minisci et al. [21] who developed a two-phase system suitable for pyrazine monoacylation. This system, based on the silver-catalyzed oxidative decarboxylation of a keto acid by persulfate has been adapted to the synthesis of 2,6-diacetylpyrazine. The acylation takes place through a redox chain process that is generally valid for substitution of heteroaromatic bases by nucleophilic carbon-centred radicals [22]. This process allows the use of mild reaction conditions that avoid decarbonylation of the acyl radicals.

Thus, we considered synthesizing 2,6-diacetylpyrazine through a direct diacylation of pyrazine by pyruvic acid and silver thiosulfate according to Scheme 3 [21]. As it appeared difficult to reach a maximum of conversion for the pyrazine ring while favouring the diacetylated product, the starting pyrazine product was then replaced by monoacetylpyrazine. So, the diacetylpyrazine synthesis was undertaken according to the same reaction protocol, in the presence of silver nitrate, pyruvic acid, ammonium persulfate and sulphuric acid. The experiments allowed us to isolate 2,6-diacetylpyrazine in about 50% yield after purification by column chromatography. The infra-red spectrum, mass spectroscopy, ^{1}H and ^{13}C NMR analysis confirmed that the diacetylation took place in the 2 and 6 positions of the pyrazine ring. In particular, the ^{1}H NMR shift fitted well the theoretical data obtained by simulation for the 2,6-isomer (i.e. 9.25 ppm for the 2,6-isomer versus 8.40 and 8.25 ppm for the 2,5- and the 2,3-isomers, respectively).

The 2,6-bis(imino)pyrazine ligands **1–5** were then prepared as yellow solids in good yields by the condensation of two equivalents of the appropriate aniline with one equivalent of 2,6-diacetylpyrazine (Scheme 4) according to the experimental details from the literature for the corresponding pyridine ligands [17,23,24]. All of the syntheses described on Scheme 4 were conclusive except the one with 2,4,6-tritertbutylaniline that did not afford the desired corresponding imine. Despite prolonged reaction times (more than 1 week in refluxing methanol), the use of various acid catalysts and a large excess of aniline, the diacetylpyrazine conversions remained lower than 5%. This poor reactivity is most probably due to the large steric hindrance induced by the two *ortho* tert-butyl groups of this aniline. Compounds **1–3** and **5** were characterised by NMR techniques, infra-red and melting point.

Complexes **6–8** were then synthesized in relatively good yields by refluxing a THF solution of the corresponding 2,6-bis(imino)pyrazinyl ligand with $FeCl_2$. All the iron complexes are air stable, paramagnetic solids, all intensively coloured. In particular, complexes **7** and **8** are blue in colour whereas complex **6** is green. Because of their paramagnetic character, no NMR spectra could be obtained for complexes **6–8** but elemental CHN analyses confirm their composition.

In conclusion, we present here a new synthesis of 2,6-diacetylpyrazine through a redox chain process. From this molecule, new 2,6-bis(imino)pyrazine ligands of different steric hindrance and their iron complexes can be readily synthesized in good to fair yields.

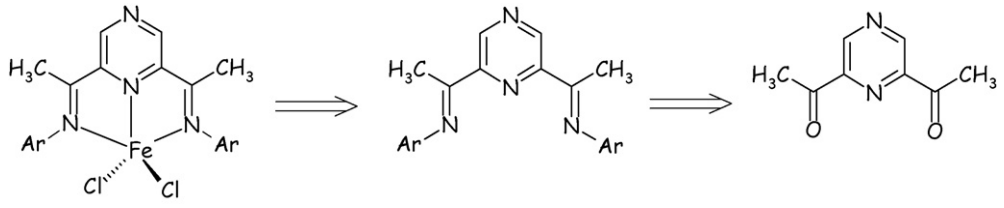
3. Experimental

All manipulations were carried out under an atmosphere of argon using standard Schlenk and cannula techniques. Argon was purified by passage through columns of BASF R3-11 catalysts and 4 Å molecular sieves. Solvents were refluxed over an appropriate drying agent and distilled under argon prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer FT-IR 1720X. Melting points (m.p.) were determined with an electrothermal apparatus without further correction. Anilines were used directly as purchased without further purification.

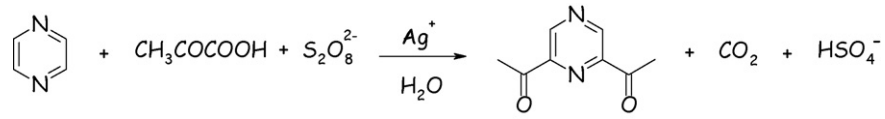
3.1. Synthesis of the 2,6-bis(imino)pyrazinyl ligands

3.1.1. Synthesis of the 2,6-diacetylpyrazine

In a three-necked 250 mL round-bottomed flask, one neck of which is closed by a septum, 1 g (8.19 mmol) of acetylpyrazine



Scheme 2.



Scheme 3.

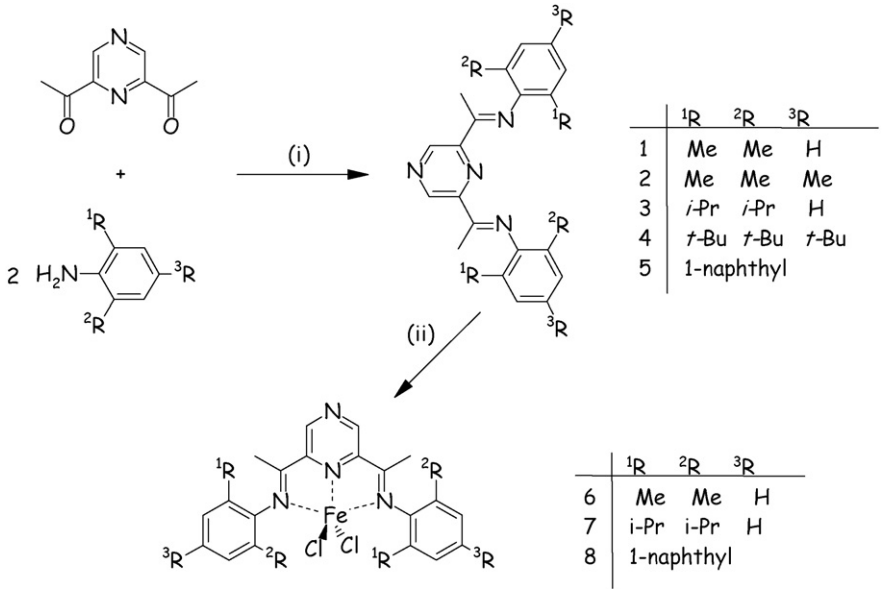
is introduced. The flask is flushed with argon and the acetylpyrazine is dissolved in 100 mL of deionized water. The solution is acidified by adding 0.87 mL (16.4 mmol) of 36 N sulphuric acid. The flask is protected from light by an aluminium sheet and 2.163 g (24.5 mmol) of pyruvic acid are added and the solution placed under magnetic stirring in a 50 °C oil bath. A solution of 0.11 g (0.65 mmol) silver nitrate in 10 mL of water and a solution of 5.6 g (24.5 mmol) of ammonium persulfate in 10 mL of water are then added separately dropwise and simultaneously. The solution becomes rapidly red coloured. The reaction mixture is cooled down, and the progress of the reaction checked by TLC for unreacted pyrazine. A further amount of pyruvic acid (2.16 g, 24.5 mmol), a solution of silver nitrate (0.11 g, 0.65 mmol in 10 mL of water), together with a solution of ammonium persulfate (5.6 g, 24.5 mmol in 10 mL of water) are again added simultaneously but separately. The mixture is heated at 50 °C for 2 h. After cooling down the reaction solution, the pH solution is adjusted to 12 by adding a 2 M solution of sodium hydroxide; the mixture becomes brown. The aqueous phase is extracted three times with portions of dichloromethane. The organic fractions are collected and then dried on $MgSO_4$. Filtration and evaporation of the solvent yield a yellow solid. The pure product is obtained by chromatography on silica (eluant: ethyl acetate/pentane = 4/6). Yield: 0.62 g (46%); m.p. (°C): 140; NMR ^{1}H ($CDCl_3$, ppm): 2.75 (s, 6H, CH_3), 9.25 (s, 2H, H pyrazine); NMR ^{13}C (CD_2Cl_2, ppm): 198.7 (s, C=O), 149.1 (s, C_2 pyrazine), 142.1 (s, C_3 pyrazine), 25.7 (s, CH_3); FT-IR (KBr, cm^{-1}): 3372.69, 3076.96, 2922.50, 1904.14, 1697.60, 1413.82, 1368.98, 1329.95, 1266.61, 1181.98, 1112.53, 1027.85, 937.76, 939.65, 647.76, 499.79, 431.05. Mass spectrum (*m/z*): 164 (molecular ion), 163, 135, 121, 120, 79, 78, 77, 52, 51, 50.

*3.1.2. 2,6-Diacetylpyrazinebis(2,6-dimethylanil) (**1**)*

In a 50 mL two-neck flask adapted with a condenser, 0.5 g (3.0 mmol) of diacetylpyrazine is dissolved into 30 mL of anhydrous MeOH; 0.92 g (7.6 mmol) of 2,6-dimethylaniline is added together with a few drops of acetic acid. The mixture is refluxed during 2 days; the solution turns yellow. After one night under reflux a solid appears in the solution and the progress of the reaction can be checked by GC. After all the starting material has reacted, the reaction mixture is cooled down. The mixture is then filtrated and the solid washed with cold pentane. The filtrate is then evaporated under vacuum and the yellow solid obtained is crystallized in hot MeOH and water. Yield: 0.8 g (77%); m.p. (°C): 160; NMR ^{1}H (CD_2Cl_2, δ, ppm): 9.6 (s, 2H, H pyrazine), 7.1 (d, 4H, C_3H et C_5H phenyl), 6.9 (m, 2H, C_4H phenyl), 2.2 (s, 6H, CH_3C=N), 2.0 (s, 12H, CH_3 phenyl); ^{13}C NMR (CD_2Cl_2, δ ppm): 166.0 (s, C=N), 151.1 (s, C_2 pyrazine), 148.3 (s, C_1 phenyl), 141.5 (s, C_3 pyrazine), 127.8 (s, C_2 phenyl), 125.1 (s, C_3 phenyl), 123.2 (s, C_4 phenyl), 17.5 (s, CH_3 phenyl), 16.2 (s, CH_3 imine); FT-IR (KBr, cm^{-1}): 3018 (s), 2921 (s), 2848 (s), 1635 (s), 1591 (s), 1470 (s), 1364 (d), 1253 (s), 1206 (s), 1167 (s), 1109 (s), 963 (s), 931 (s), 822 (s), 779 (s), 762 (s), 691 (s), 551 (s), 532 (s), 417 (s).

*3.1.3. 2,6-Diacetylpyrazinebis(2,6-diisopropylanil) (**3**)*

This product was synthesized following to the above procedure with 0.2 g (1.2 mmol) of diacetylpyrazine and 0.54 g



	^{1}R	^{2}R	^{3}R
1	Me	Me	H
2	Me	Me	Me
3	*i*-Pr	*i*-Pr	H
4	*t*-Bu	*t*-Bu	*t*-Bu
5	1-naphthyl		

	^{1}R	^{2}R	^{3}R
6	Me	Me	H
7	i-Pr	i-Pr	H
8	1-naphthyl		

Scheme 4. Reagents and conditions: (i) EtOH, H^+ and (ii) $FeCl_2$, THF.

(3.04 mmol) of 2,6-diisopropylaniline. The colour of the product is yellow. Yield: 0.28 g (48%); m.p. (°C): 191.1; NMR ^{1}H (CD_2Cl_2, δ, ppm): 9.58 (s, 2H, pyrazine), 7.2 (d, 4H, C_3H et C_5H phenyl), 7.12 (m, 2H, C_4H phenyl), 2.8 (m, 4H, CH isopropyl), 2.2 (s, 6H, CH_3C=N), 1.16 (d, 24H, CH_3 isopropyl); ^{13}C NMR (CD_2Cl_2, δ, ppm): 165.9 (s, C=N), 151 (s, C_2 pyrazine), 145.9 (s, C_1 phenyl), 141.6 (s, C_3 phenyl), 135.5 (s, C_2 phenyl), 123.9 (s, C_3 phenyl), 122.9 (s, C_4 phenyl), 28.32 (s, CH isopropyl), 22.9 (s, CH_3 isopropyl), 22.4 (s, CH_3 isopropyl), 16.9 (s, CH_3 imine); FT-IR (KBr, cm^{-1}): 3055 (s), 2960 (s), 1632 (s), 1587 (s), 1470 (s), 1434 (s), 1370 (s), 1273 (s), 1170 (s), 1109 (s), 1024 (s), 937 (s), 821 (s), 766 (s), 699 (s).

3.1.4. 2,6-Diacetylpyrazinebis(di-1-naphtylanil) (**5**)

This product was synthesized according to a procedure analogous to the one above with 0.1 g (0.60 mmol) of diacetylpyrazine and 0.22 g (1.5 mmol) of 2,6-naphtylamine. The colour of the product is yellow. Yield: 0.13 g (51%); m.p. (°C): 174.3; NMR ^{1}H (CD_2Cl_2, δ, ppm): 9.7 (s, 2H, pyrazine), 7.9 (d, 1H, C_4 naphtyl), 7.8 (d, 1H, C_5 naphtyl), 7.7 (d, 1H, C_8 naphtyl), 7.5 (m, 3H, C_7, C_6, C_3 naphtyl), 6.8 (d, 1H, C_2), 2.4 (s, 6H, CH_3); ^{13}C NMR (CD_2Cl_2, δ, ppm): 167 (s, C=N), 151.4 (s, C_2 pyrazine), 146.9 (C_1 naphtyl), 141.8 (s, C_3 pyrazine), 134.1 (s, C_5 naphtyl), 127.9 (6s, C naphtyl), 113.2 (s, C_2 naphtyl), 16.3 (s, CH_3 imine); FT-IR (KBr, cm^{-1}): 3043 (s), 1637 (s), 1572 (s), 1505 (s), 1470 (s), 1390 (s), 1368 (s), 1259 (s), 1231 (s), 1191 (s), 1109 (s), 1079 (s), 1046 (s), 1023 (s), 935 (s), 865 (s), 804 (s), 780 (s), 735 (s), 713 (s), 636 (s), 610 (s), 574 (s), 423 (s).

3.1.5. 2,6-Diacetylpyrazinebis(2,4,6-trimethylanil) (**2**)

This product was also synthesized according to the above procedure with 0.1 g (0.60 mmol) of diacetylpyrazine and 0.20 g (1.5 mmol) of 2,4,6-trimethylaniline. The colour of the product is yellow. Yield: 0.15 g (62%); m.p. (°C): 209.5; NMR ^{1}H (CD_2Cl_2, δ, ppm): 9.5 (s, 2H, pyrazine), 6.9 (s, 4H, phenyl), 2.3 (s, 6H, CH_3C=N), 2.2 (s, 6H, CH_3 *para* aniline), 1.9 (s, 12H, CH_3 *ortho* aniline); ^{13}C NMR (CD_2Cl_2, δ, ppm): 166.2 (s, C=N), 151.2 (s, C_2 pyrazine), 145.8 (s, C_1 phenyl), 141.5 (s, C_3 pyrazine), 132.5 (s, C_2 phenyl), 128.5 (s, C_3 phenyl), 124.9 (s, C_4 phenyl), 20.4 (s, CH_3), 17.5 (s, CH_3), 16.2 (s, CH_3 imine); FT-IR (KBr, cm^{-1}): 3003 (s), 2916 (s), 1639 (s), 1474 (s), 1372 (s), 1269 (s), 1214 (s), 1175 (s), 1143 (s), 1109 (s), 1021 (s), 852 (s), 787 (s), 688 (s).

3.2. Preparation of iron complexes

3.2.1. [2,6-Diacetylpyrazinebis(2,6-dimethylanil)]-$FeCl_2$ (**6**)

In a 50 mL Schlenk flask, equipped with a magnetic stirrer, 2,6-diacetylpyrazinebis(2,6-dimethylanil) (**1**), (368 mg; 0.993 mmol) and 126.1 mg (0.995 mmol) of activated iron dichloride are introduced under nitrogen atmosphere, followed by 30 mL of anhydrous THF. A ball condenser is then set on the Schlenk tube and the reaction medium is heated for 2 h under reflux and under agitation. After having cooling down the reaction medium at room temperature, the THF is evaporated under vacuum to the obtention of a dark green residue. This residue is suspended in hexane under agitation; the solid is finally filtered under nitrogen, rinsed with hexane and dried under vacuum. In this way, complex (**6**) is recovered as a green paramagnetic powder. Yield: 354.6 mg (0.731 mmol, 72%); NMR: not recorded due to the paramagnetic character of the complex. Anal. calc. for $C_{24}H_{26}N_4{\cdot}FeCl_2$: C, 58.0; H, 5.3; N, 11.3. Found: C, 60.1; H, 5.6; N, 11.9.

3.2.2. [2,6-Diacetylpyrazinebis(2,6-diisopropylanil)]-$FeCl_2$ (**7**)

In a 10 mL Schlenk, equipped with a magnetic stirrer, 2,6-diacetylpyrazinebisimine(2,6-diisopropylanil) (100 mg; 0.2075 mmol) and 26 mg (0.205 mmol) of activated iron dichloride are introduced under nitrogen atmosphere, followed by 10 mL of anhydrous THF. A ball condenser is then set on the Schlenk tube and the reaction medium is heated for 2 h under reflux and under agitation. After having cooling down the reaction medium at room temperature, the THF is evaporated under vacuum to the obtention of a dark blue residue. This residue is suspended in the hexane under agitation; the solid is finally filtered under nitrogen, rinsed with hexane and dried under vacuum. In this way, we recover the 2,6-diacetylpyrazinebisimine(2,6-diisopropylanil) complex as a very dark blue powder. Yield: 85 mg (0.1396 mmol) (68%); NMR: not recorded due to the paramagnetic character of the complex. Anal. calc. for $C_{32}H_{42}N_4{\cdot}FeCl_2$: C, 63.1; H, 6.9; N, 9.2%. Found: C, 63.7; H, 6.5; N, 8.6%.

3.2.3. [2,6-Diacetylpyrazinebis(dinaphtylanil)]-$FeCl_2$ (**8**)

In a 10 mL Schlenk, equipped with a magnetic stirrer, 2,6-diacetylpyrazinebis(di-1-naphtylanil) (**5**), (82 mg; 0.198 mmol) and 25 mg (0.197 mmol) of activated iron dichloride are introduced under nitrogen atmosphere, followed by 10 mL of anhydrous THF. A ball condenser is then set on the Schlenk tube and the reaction medium is heated for 2 h under reflux and under agitation. After having cooling down the reaction medium at room temperature, the THF is driven away under vacuum to the obtention of a dark blue residue. This residue is suspended in hexane under agitation; the solid is finally filtered under nitrogen, rinsed with hexane and dried under vacuum. In this way, complex (**8**) is recovered as a dark blue, paramagnetic powder. Yield: 59.7 mg (0.110 mmol, 56%). Anal. Calc. for $C_{28}H_{22}N_4{\cdot}FeCl_2$: C, 62.1; H, 4.1; N, 10.3%. Found: C, 63.2; H, 3.2; N, 9.8%.

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