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New iron-based bis(imino)pyridine and acetyliminopyridine complexes as single-site catalysts for the oligomerization of ethylene

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Abstract

New iron-based bis(imino)pyridine complexes **6**, **7** and the acetyliminopyridine complex **8a** are active catalysts together with the co-catalyst MAO for the oligomerization of ethylene. The ligands **1**–**4** with electron donating methoxy- and electron withdrawing trifluoromethyl-substituents react with $FeCl_2(thf)_2$ to the Fe(II) complexes **6**–**8a**. Especially *p*-methoxy substituents in **6b** increase the selectivity in the production of α-olefins. The distribution of oligomers obtained in the catalyzed ethylene oligomerization with **5**–**8a** follows Schulz–Flory rules for oligomers $>C_4$. The probability of chain propagation α is increased by lowering the reaction temperature, while higher pressure of the ethylene gas in the reaction has nearly no effect on the α-values.

Keywords: Oligomerization; Single-site catalysts; Ethylene; Bis(imino)pyridines; Acetylimino-pyridines

1. Introduction

The oligomerization of ethylene is one of the major industrial processes for the production of linear α-olefins [1–3]. Those oligomers in the range C_6–C_{20} are used as comonomers in the polymerization of ethylene to give linear low-density polyethylene (LLDPE) or for the preparation of detergents and synthetic lubricants. Catalysts currently used in industry for the shell higher olefin process (SHOP) [4–8] contain Ni(II) complexes bearing bidentate monoanionic ligands [1–8]. Also cationic Ni(II) α-diimine complexes were reported to be effective ethylene oligomerization catalysts [9], while iron-based bis(imino)pyridine catalysts were described as highly active compounds in the oligomerization of ethylene in combination with the co-catalyst MAO or MMAO [10–14]. Several modifications of the bis(imino)pyridine backbone are already described in the literature [15] which mostly lead to a decrease of catalytic activity. Recently fluoro-substituted bis(imino)pyridine complexes and their catalytic reactivity in ethylene oligomerizations were described [16].

We investigated the influence of electron donating methoxy- and electron withdrawing trifluoromethyl-groups attached to the imino phenyl substituents. We thus describe the synthesis of the bis(imino)pyridine ligands **1**, **2** and acetyliminopyridine ligand **3a** which react with $FeCl_2(thf)_2$ [17] to the ferric complexes **6**–**8a**. Additionally, the results of the catalytic oligomerization of ethylene with the pre-catalysts **6**–**8a** together with MAO as co-catalyst will be presented.

2. Experimental

All manipulations were carried out under an atmosphere of argon using standard Schlenk techniques. NMR spectra were recorded on a Bruker spectrometer 250 MHz (^1H) and 62.9 MHz (^{13}C) at 293 K. Mass spectra were obtained using electron ionisation (EI), electron spray ionisation (ESI) or field ionisation (FI). Oligomer products were analysed by GC with a flame ionisation detector, using a 50 m DB1 column, injector temperature 40 °C and the following temperature program: 40 °C/5 min, 40–300 °C, 5 °C/10 min^{-1}. The individual products were integrated, using *n*-tridecane as internal standard.

Materials: 2,6-bis[1-(phenylimino)ethyl]pyridine [18] was prepared according to the literature. MAO (10%

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solution in toluene) and all other anilines were purchased commercially and used as received.

2.1. Synthesis of ligands

2,6-Bis[1-(3-methoxyphenylimino)ethyl]pyridine (**1a**) [19]: 2,6-diacetylpyridine (0.74 g, 4.5 mmol) was stirred with *m*-anisidine (1.83 g, 15 mmol, 3.3 eq) in 20 ml of dry benzene at ambient temperature in the presence of 8.5 g of molecular sieves. The reaction was performed under argon in a closed flask for approximately 50 days. Then the reaction mixture was filtered, the solvent was removed under reduced pressure and a yellow oil was obtained. A few ml of *n*-hexane were added to the oil and the mixture was stored at 5 °C over night. A yellow precipitate formed which was filtered and washed with *n*-hexane. Yield: 1.1 g (3.0 mmol, 66%). ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2H, Py-H_m), 7.80 (t, 1H, Py-H_p), 7.22 (t, 2H, H_{aryl}), 6.61 (d, 2H, H_{aryl}), 6.38–6.34 (m, 4H, H_{aryl}), 3.76 (s, 6H, O*Me*), 2.34 (s, 6H, N=C*Me*); ^{13}C NMR ($CDCl_3$) δ 167.9, 160.7, 155.8, 153.1, 137.2, 130.3, 122 7, 111.9, 109.6, 105.3, 55.6, 16.6. EI$^+$-MS $m/z = 373$ (M^+); mp = 133 − 135 °C.

2,6-Bis[1-(4-methoxyphenylimino)ethyl]pyridine (**1b**) [20–22]: 2,6-diacetylpyridine (0.38 g, 2.3 mmol) and *p*-anisidine (0.67 g, 5.4 mmol, 2.3 eq) were dissolved in 16 ml of methanol under stirring. 0.3 ml of 97% formic acid were added to this solution and a beige precipitate slowly appeared from the brown solution. The reaction mixture was stirred for 8 h at room temperature, then the precipitate was collected by vacuum filtration and washed with methanol. The dried solid is a fluorescent greenish-yellow powder, yield: 0.78 g (2.1 mmol, 91%). ^{1}H NMR (THF-d_8) δ 8.35 (d, 2H, Py-H_m), 7.89 (t, 1H, Py-H_p), 6.85 (q, 8H, H_{aryl}), 3.78 (s, 6H, O*Me*), 2,42 (s, 6H, N=C*Me*); ^{13}C NMR (THF-d_8) δ 164.6, 154.6, 153.9, 141.3, 134.5, 119.8, 118.8, 112.0, 52.7, 13.1; EI$^+$-MS $m/z = 373$ (M^+); mp = 199 °C.

2,6-Bis[1-(3-trifluoromethylphenylimino)ethyl]pyridine (**2a**) [19]: 2,6-diacetylpyridine (0.82 g, 5.0 mmol) was stirred with 3-trifluoromethylaniline (1.62 g, 10 mmol, 2 eq) in 25 ml of dry benzene at ambient temperature in the presence of 2.8 g of molecular sieves. The reaction was performed under argon in a closed flask for 48 h. The molecular sieves were removed by filtration, the reaction mixture was concentrated and a few ml of dichloromethane were added. The obtained pale yellow crystals were filtered and dried, yield: 0.36 g (0.8 mmol, 16%). ^{1}H NMR ($CDCl_3$) δ 8.08 (d, 2H, Py-H_m), 7.89 (t, 1H, Py-H_p), 7.48-6.94 (m, 8H, H_{aryl}), 2.36 (s, 6H, N=C*Me*); EI$^+$-MS $m/z = 449$ (M^+).

2,6-Bis[1-(4-trifluoromethylphenylimino)ethyl]pyridine (**2b**) [23]: 2,6-diacetylpyridine (0.38 g, 2.3 mmol), 4-trifluoromethylaniline (2.4 g, 15 mmol, 6.5 eq) and a few milligrams of *p*-toluenesulfonic acid were heated under reflux in 50 ml of toluene for 15 h. Then the brown reaction mixture was concentrated and dissolved in a mixture of *n*-hexane/ethylacetate = 1:1. Filtration over silica-gel and removal of the solvents gave a brown oil which was stored at 5 °C over night. Colorless crystals of **2b** formed which were filtered and washed with *n*-hexane, yield: 0.08 g (0.18 mmol, 8%). ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2H, Py-H_m), 7.82 (t, 1H, Py-H_p), 7.53 (d, 4H, H_{aryl}), 6.82 (d, 4H, H_{aryl}), 2.31 (s, 6H, N=C*Me*); ^{13}C NMR ($CDCl_3$) δ 166.5, 153.5, 152.9, 135.6, 125.4 (q), 125.1 (q), 124.9 (q), 121.3, 117.8, 15.0. EI$^+$-MS $m/z = 449$ (M^+); FI$^+$-HR-MS: *m/z* 449.1327 (calcd.), found 449.1260 for $C_{23}H_{17}N_3F_6$, δ = 6.7 mDa; mp = 141 °C.

1-(6-{N-[3-(trifluoromethyl)phenyl]ethanimidoyl}pyridin-2-yl)ethanone (**3a**): 2,6-diacetyl-pyridine (1.63 g, 10 mmol) was stirred with 3-trifluoromethylaniline (1.61 g, 10 mmol) in 20 ml of dry benzene at room temperature in the presence of 11 g of molecular sieves. The reaction was performed under argon in a closed flask for approximately 80 days. Then the reaction mixture was filtered, the solvent was removed under reduced pressure and a yellow oil was obtained. The product was stored at 5 °C. Slowly a yellow precipitate formed which was filtered and washed with methanol. Yield: 2.1 g (7.0 mmol, 70%). ^{1}H NMR ($CDCl_3$) δ 8.38 (d, 1H, Py-H_m), 8.06 (d, 1H, Py-H_m), 7.88 (t, 1H, Py-H_p), 7.43 (t, 1H, H_{aryl}), 7.32 (d, 1, H_{aryl}), 7.04 (s, 1H, H_{aryl}), 6.94 (d, 1H, H_{aryl}), 2.71 (s, 3H, O=C*Me*), 2.35 (s, 3H, N=C*Me*); ^{13}C NMR ($CDCl_3$) δ 200.2, 168.3, 155.8, 152.8, 151.8, 137.8, 131.9 (q), 130.0, 125.1, 124.5 (q), 123.2, 122.9, 120.8 (q), 116.5 (q), 26.0, 16.6; EI$^+$-MS $m/z = 306$ (M^+); FI$^+$-HR-MS: *m/z* 306.0980 (calcd.), found 306.0917 for $C_{16}H_{13}N_3OF_3$, δ = 6.3 mDa; mp = 116 − 118 °C.

2.2. Synthesis of ferric complexes

General procedure for the synthesis of the ferric complexes (**5**–**8a**): the appropriate ligand was added to a suspension of $FeCl_2(thf)_2$ [17] in dry THF in a Schlenk-flask under argon. The mixture was stirred for 3 h at room temperature, then the solvent was removed and finally the product was dried in vacuum.

2,6-Bis[1-(phenylimino)ethyl]pyridyliron(II) chloride (**5**): 2,6-bis[(phenylimino)ethyl] pyridine (200 mg, 0.64 mmol), $FeCl_2(thf)_2$ (173 mg, 0.64 mmol), THF 30 ml. Compound **5** was obtained as a dark blue powder, yield 251 mg (0.56 mmol, 89%). FI$^+$-HR-MS: *m/z* 439.0305 (calcd.), found 439.0225 for $C_{21}H_{19}N_3Cl_2Fe$, δ = 8.0 mDa; $C_{21}H_{19}N_3Cl_2Fe$: calcd. C 57.30, H 4.35, N 9.54, found C 57.0, H 4.52, N 9.28.

2,6-Bis[1-(3-methoxyphenylimino)ethyl]pyridyliron(II) chloride (**6a**): 2,6-bis[1-(3-methoxyphenylimino)ethyl]pyridine **1a** (200 mg, 0.54 mmol), $FeCl_2(thf)_2$ (145 mg, 0.54 mmol), THF 30 ml. Compound **6a** was obtained as a dark blue powder, yield 208 mg (0.42 mmol, 77%). $C_{23}H_{23}N_3O_2Cl_2Fe$: calcd. C 55.22, H 4.63, N 8.40, found C 55.16, H 4.65, N 8.15.

2,6-Bis[1-(4-methoxyphenylimino)ethyl]pyridyliron(II) chloride (**6b**): 2,6-bis[1-(4-methoxyphenylimino)ethyl]pyridine **1b** (150 mg, 0.42 mmol), $FeCl_2(thf)_2$ (109 mg, 0.42 mmol), THF 30 ml. Compound **6b** was obtained as

a dark blue powder, yield 189 mg (0.38 mmol, 90%). FI^+-HR-MS: *m/z* 499.0517 (calcd.), found 499.0475 for $C_{23}H_{23}N_3O_2Cl_2Fe$, $\delta = 0.8$ mDa. $C_{23}H_{23}N_3O_2Cl_2Fe$: calcd. C 55.22, H 4.63, N 8.40, found C 55.44, H 4.92, N 8.11.

2,6-Bis[*1*-(*3-trifluoromethylphenylimino*)*ethyl*]*pyridyliron*(*II*) *chloride* (**7a**): 2,6-bis[1-(3-trifluoromethylphenylimino)ethyl]pyridine **2a** (54 mg, 0.12 mmol), $FeCl_2(thf)_2$ (33 mg, 0.12 mmol), THF 15 ml. Compound **7a** was obtained as a dark blue powder, yield 44 mg (0.08 mmol, 64%). FI^+-HR-MS: *m/z* 575.0053 (calcd.), found 575.0061 for $C_{23}H_{17}N_3F_6Cl_2Fe$, $\delta = 0.8$ mDa. $C_{23}H_{17}N_3F_6Cl_2Fe$: calcd. C 47.94, H 2.97, N 7.29, found C 47.50, H 3.02, N 7.03.

2,6-Bis[*1*-(*4-trifluoromethylphenylimino*)*ethyl*]*pyridyliron*(*II*) *chloride* (**7b**): 2,6-bis[1-(4-trifluoromethylphenylimino)ethyl]pyridine **2b** (100 mg, 0.22 mmol), $FeCl_2(thf)_2$ (60 mg, 0.22 mmol), THF 30 ml. Compound **7b** was obtained as a dark blue powder, yield 114 mg (0.2 mmol, 89%). FI^+-HR-MS: *m/z* 575.0053 (calcd.), found 574.9968 for $C_{23}H_{17}N_3F_6Cl_2Fe$, $\delta = 8.5$ mDa. $C_{23}H_{17}N_3F_6Cl_2Fe$: calcd. C 47.94, H 2.97, N 7.29, found C 47.64, H 2.72, N 6.98.

1-{*6*-[*N*-(*3-trifluoromethyl*)*ethanimidoyl*]*pyridin-2-yl*} *ethanone iron*(*II*) *chloride* (**8a**): 1-{6-[N-(3-trifluoromethyl) ethanlimidoyl]pyridin-2-yl}ethanone **3a** (150 mg, 0.49 mmol), $FeCl_2(thf)_2$ (133 mg, 0.49 mmol), THF 30 ml. Compound **8a** was obtained as a dark blue powder, yield 127 mg (0.29 mmol, 60%). ESI^+-MS: $m/z = 446$ ($M^+ + NH_4^+$). $C_{16}H_{13}N_2OF_3Cl_2Fe$: calcd. C 44.37, H 3.02, N 6.46, found C 44.67, H 3.28, N 6.11.

2.3. Oligomerization procedure

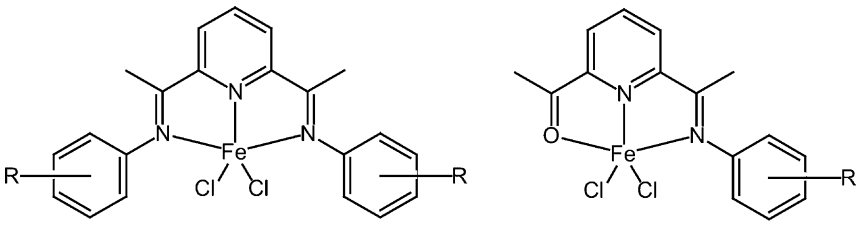
(a) *Low-pressure tests*: The precatalyst was dissolved in 30 ml of solvent in a Schlenk-flask under argon. A complete solution was obtained by leaving the flask in an ultrasonic bath for several minutes. A 150 ml glass reactor was evacuated and then filled with argon. The precatalyst solution was added under argon into the reactor vessel. Under stirring the co-catalyst MAO (0.6 ml, approximately 100 eq of a 10 mol% MAO solution in toluene) and *n*-tridecane standard solution were added under argon. For several minutes ethylene was introduced while streaming through the reactor to displace the argon. Then the reactor was closed and pressurized to 3 bar with ethylene. The reactor pressure maintained constant throughout the oligomerization run by manually controlled addition of ethylene. Runs were terminated by venting off volatiles and extracting the solution with dilute hydrochloric acid and water. Quantitative GC analysis of the organic layer was performed immediately after the extraction.

(b) *High-pressure tests*: Same procedure as described for low-pressure tests. Instead of a glass reactor was used a 150 ml stainless steel reactor with cooling mantle. After the reactor was closed it was pressurized to 30 bar with ethylene. The temperature of the reaction was controlled by cooling the reactor vessel with water.

3. Results and discussion

Iron-based bis(imino)pyridine complexes **6** and **7** and the acetyliminopyridine complex **8a** were prepared to investigate the influence of methoxy- and trifluoromethyl-substituted phenyl groups in the ligands (Fig. 1) [24].

It was previously reported that the length of the formed macromolecule and the selectivity to α-olefins depends on the steric bulk and on the electronic characteristics of the substituents on each aryl ring of the bis(imino)pyridine complexes [11,12]. We developed bis(imino)pyridine **1**, **2** and the acetyliminopyridine ligand **3a** with substituents which especially influence the electronic properties in the ferric precursor complexes **6**–**8a**. 2,6-Bis(acetyl)pyridine reacts with *m*,*p*-methoxy and *m*,*p*-trifluoromethyl substituted anilines under different reaction conditions to the corresponding bis(imino)pyridine ligands **1**, **2** and to the acetyliminopyridine **3a**. For the syntheses of **1a**, **2a**, and **3a** both reactants have to be stirred in benzene for many days whereas the reaction conditions are different for the syntheses of **1b** and **2b** [24]. The yields were not optimized and are fairly low for **2b** (8%) and higher up to 90% for **1b**. The ligands **1**–**3a** react with $FeCl_2(thf)_2$ [17] to the Fe(II) complexes **6**–**8a** (Fig. 2). It failed to prepare ligands with mixed methoxy- and trifluoromethyl- substituents because



5 R = H
6a R = *m*-OMe **6b** R = *p*-OMe
7a R = *m*-CF_3 **7b** R = *p*-CF_3
8a R = *m*-CF_3

Fig. 1. Structure of the precatalysts **5**-**8a**.

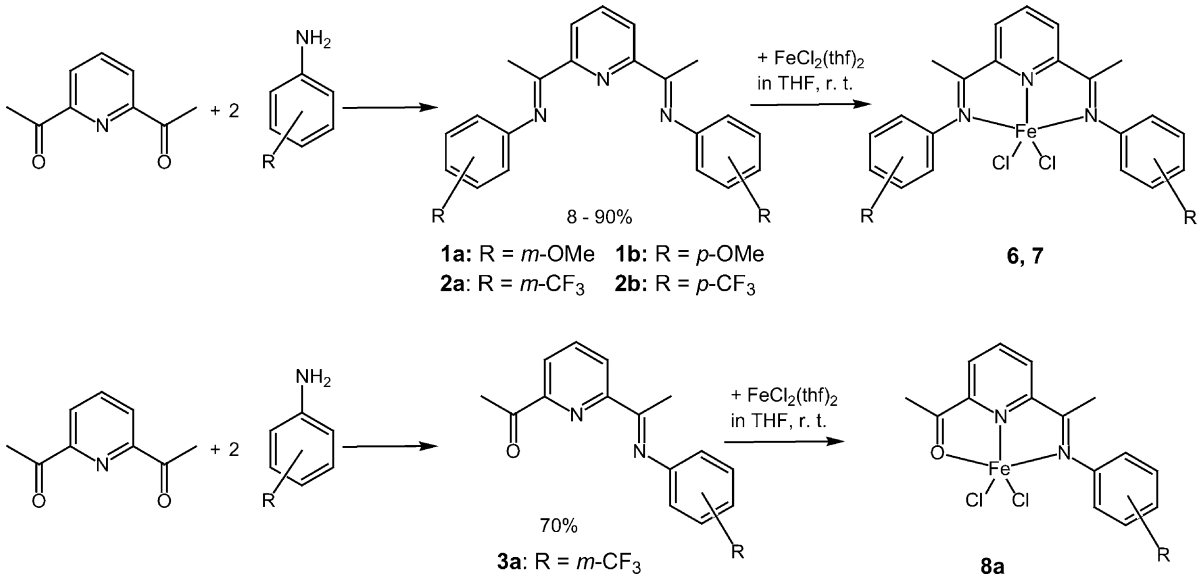


Fig. 2. Synthesis of the Fe(II) complexes **6**–**8a**.

of decomposition of the reactants and the formation of side-products.

The precatalysts **6**–**8a** are active compounds in combination with the co-catalyst MAO in the oligomerization of ethylene (Table 1). The turnover number for the unsubstituted precatalyst **5** is one of the highest among the tested catalysts but it lacks a good selectivity in the production of α-olefins. The *p*-methoxy substituted precatalyst **6b** produces α-olefins in up to 77% yield at 3 bar ethylene pressure, whereas when the pressure is increased to 30 bar it gives α-olefins in 88% yield with a loss of catalytic activity. A positive effect for the production of α-olefins is however only observed for the *p*-substituted derivative **6b**, not for the *m*-methoxy compound **6a**. This is in line with the results from catalytic experiments with electron withdrawing trifluoromethyl-substituted derivatives **7a** and **7b**: in fact in case of *p*-trifluoromethyl substituents in **7b** the selectivity is not improved. Only a low selectivity to α-olefins in 36 % yield is obtained with the *m*-trifluoromethyl derivative **7a**.

Table 2
Yield (%) of oligomers in the experiments 1–6

Fraction (%)	1	2	3	4	5	6
C_4	27.6	26.8	51.4	51.9	35.2	31.3
C_6	45.4	45.2	31.1	41.2	42.3	41.2
C_8	16.2	16.1	11.8	5.5	13.7	15.4
C_{10}	7.2	7.4	4.0	0.9	6.0	7.6
C_{12}	2.5	2.8	1.2	0.3	2.2	3.0
C_{14}	1.0	1.1	0.5	0.1	0.5	1.1
C_{16}	0.3	0.4	0.1	0.03	0.1	0.3
C_{18}	–	0.1	–	–	–	0.1

A different behavior of the precatalysts **5**–**8a** is also shown in the distribution of the formed oligomers (Tables 2 and 3 and Fig. 3). Mostly hexenes are formed with the bis(imino)pyridine precatalysts **5, 6a** and **7**, while butenes outweigh in case of the acetyliminopyridine precatalyst **8a**. On the other hand **6b** mostly gives butenes both at 3 bar and 30 bar ethylene pressure.

Table 1
Results of oligomerization of ethylene with catalysts **5**–**8a**

Number	Catalyst[a]	Loading (μmol)	Time (h)	*p* (bar)	*T* (°C)	Yield (g)[b]	TON	TOF ($\times 10^{-3}$/h)	Solvent	α	α-Olefins[b] (%)
1	**5**	10	2	3	22–75	11.4	40813	20.4	Toluene	0.36	28
2	**6a**	10	2.5	3	22–75	12.0	43032	17.2	Toluene	0.39	29
3	**6b**	10	2.5	3	22–60	1.0	3710	1.5	Toluene	0.39	77
4	**6b**	10	1	30	22–60	0.3	892	0.9	Toluene	0.30	88
5	**7a**	9.3	2.5	3	22–75	9.3	35750	14.3	Toluene	0.30	36
6	**7b**	10	2	3	22–75	7.8	27890	13.9	Toluene	0.36	27
7	**8a**	10	2.75	3	22–70	2.5	8989	3.3	Toluene	0.39	77
8	**8a**	10	1.5	30	22–70	10.5	37332	24.9	Toluene	0.36	82

[a] All precatalysts were first dissolved in 30 ml of solvent in an ultrasonic bath and then activated with approximately 100 eq MAO (0.6 ml of a 10 mol% MAO solution in toluene).

[b] The yield and the 1-olefin content C_4–C_{18} were determined by GC using calibration curves with standard solutions.

Table 3
Yield (%) of oligomers in the experiments 7–8

Fraction (%)	7	8
C_4	49.3	46.7
C_6	31.0	35.3
C_8	12.8	12.4
C_{10}	4.6	3.4
C_{12}	1.4	1.4
C_{14}	0.6	0.5
C_{16}	0.2	0.2
C_{18}	0.1	0.1

The reaction temperature rises in all catalytic experiments with **5**–**8a**. The catalytic activity decreases or completely stops when cooling the reaction vessel and keeping it at room temperature during the reaction. Higher ethylene pressure leads to an increased formation of α-olefins [11] in up to 82% yield (runs 4, 8, Table 1).

The distribution of oligomers obtained in the catalyzed ethylene oligomerization with **5**–**8a** follows Schulz–Flory rules for oligomers >C_4, which can be characterized by the constant α representing the probability of chain propagation (α = rate of propagation/[(rate of propagation) + (rate of chain transfer)] = (moles of C_{n+2})/(moles of C_n)) [25–28]. The α value can be determined in our case by the molar ratio of C_{12} and C_{14} fractions (Fig. 4); the obtained α values range between 0.30 and 0.39 for the catalytic oligomerization runs with **5**, **6**, **7**, and **8a**. Pressure shows nearly no effect on the α-values (runs 4, 8), which is consitent with previous observations in bis(iminopyridine) complexes [11,12]. All α numbers found in the catalytic runs 1–8 are much lower than those described in the ethylene oligomerization catalyzed by the monoalkyl-substituted iron complexes which reach α values of 0.70–0.85 [11,12]. In contrast α between 0.33 and 0.34 are found for the reported 2,4-difluoro-substituted bis(imino)pyridine complexes [16], which is in line with the results for the precatalysts **5**–**8a**.

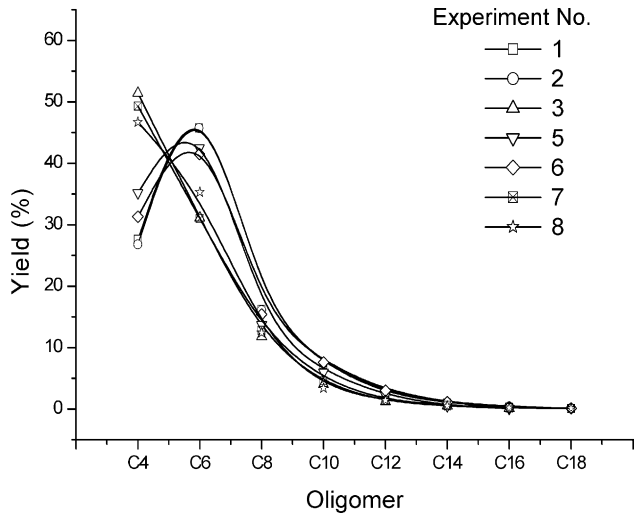


Fig. 3. Oligomer distribution: yield of each oligomer fraction vs. carbon number.

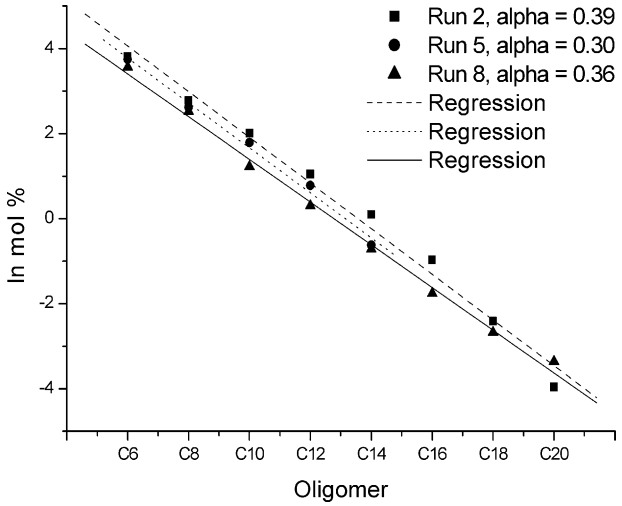


Fig. 4. Schulz–Flory distribution: ln mol% of each fraction vs. carbon number.

4. Conclusions

In summary, the described bis(imino)pyridine and the acetyliminopyridine complexes **5**–**8a** reveal differences in their behavior as precatalysts for the oligomerization of ethylene, which depend on the different electronic influence of the various substituents at the rings and on the reaction conditions in these experiments, too. Olefins ranging from C_4–C_{18} are produced in all experiments but the turnover numbers vary between 1000 and 43000. Additionally, variation of the catalyst ligand, temperature and pressure has a significant influence on α-olefin selectivity and on the formation of the main olefin species in the products. The complexes **5**–**8a** show small Schulz–Flory α values, which prove a low chain propagation.

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