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Bis(arylimino)pyridine iron(III) complexes as catalyst precursors for the oligomerization and polymerization of ethylene

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ABSTRACT

A series of 26 bis(arylimino)pyridine iron(III) complexes containing either electron withdrawing or electron donating substituents in their ligand frameworks was synthesized and characterized. After activation with methylaluminoxane (MAO), these catalysts oligomerize or polymerize ethylene to give both linear and branched products. In contrast to iron(II) complexes, the presence of at least one ortho-substituent at the iminophenyl rings is not obligative for catalytic activities of the iron(III) complexes. A couple of such iron(III) complexes containing meta- and para-substituted bis(arylimino)pyridine compounds were accessible and their oligomerization behaviour revealed interesting differences to the well known iron(II) analogues since both internal and branched olefins were found in the product mixtures beside the expected linear α -olefins. The widths of the resulting molecular weight distributions and the degrees of isomerization of the resulting oligomers strongly depend on the substitution pattern at the ligand frameworks.

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1. Introduction

Gibson [1-4] and Brookhart [5-7] independently reported the application of 2,6-bis(arylimino) pyridine iron complexes as effective catalysts for the polymerization and oligomerization of ethylene leading to highly linear products. Especially the substitution pattern of the iminophenyl rings has a great influence on the polymerization activities and the product compositions [1-17]. Iron complexes bearing small substituents (alkyl or halogene) at the 2-positions of the iminophenyl rings proved to be excellent catalyst precursors for the oligomerization of ethylene to give low molecular weight α -olefins. These α -olefins are industrially highly desired compounds which are useful, e.g., for copolymerization reactions with ethylene to give linear low density polyethylene (LLDPE). In this context, halogenated 2,6-bis(arylimino)pyridine compounds play an important role as valuable ligand precursors and some of their transition metal complexes are known in the literature [1,5,18-25]. In the past five years, 2,6-bis(arylimino)pyridine iron complexes with halogen substituted iminophenyl rings were reported by Qian et al. and Ionkin et al. [8,9,14]. While fluoro, chloro, and bromo substituted compounds are known for a longer time [8-10,26-28], the analogous iodo substituted compounds were described by our group in 2007 [29]. As demonstrated by Ionkin et al. [14], bromo substituents at the iminophenyl rings can be exchanged with aryl groups applying Suzuki coupling reactions. As an alternative method, Sonogashira coupling reactions of terminal alkynes with 2,6-bis(arylimino)pyridine compounds containing para-bromo and para-iodo substituted iminophenyl rings proved to be a successful pathway to give 2,6-bis(arylimino)pyridine compounds with extended ligand frameworks [29]. The vast majority of these literature known complexes rely on iron(II) compounds. One of the characteristics of 2,6-bis(arylimino)pyridine iron(II) complexes is the fact that the iminophenyl rings of the ligand frameworks must contain at least one substituent at the ortho-position to the iminophenyl nitrogen atoms to be stable against ligand transfer reactions. Although the synthesis of the iron(II) complex with the tridentate ligand precursor 2,6-bis(1-(phenylimino)ethyl)pyridine, a ligand without any substituents at the iminophenyl rings, was described by Abu-Surrah et al. [30], this complex does not exist in the common form (L)FeCl₂ (L=bis(arylimino)pyridine ligand) but can be isolated as an air stable ionic compound of the composition $[(L)_2Fe]^{2+}[FeCl_4]^{2-}$. Analogous ion-pair complexes were described for 2,6-bis(1-(2-fluorophenyl)ethyl)pyridine [28], 2,6-bis(1-(3,5-dibromo-4-methylphenyl)ethyl)pyridine [14], 2,6bis(1-(2,6-dibromophenyl)ethyl)pyridine [31], and 2,6-bis(1-(4nitrophenyl)ethyl)pyridine [13]. According to these results, methyl groups seem to be the smallest ortho-substituents that prevent this ligand transfer reaction. While a great deal of work has been spent on bis(arylimino)pyridine iron(II) complexes, only a few publications report about the corresponding iron(III) complexes despite their higher catalytic activities towards olefin

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oligomerization and polymerization [14,24,29,32-39]. Although both iron(II) and iron(III) complexes can be undoubtedly characterized, the oxidation state of the iron centers (Fe(II) or Fe(III)) after activation with aluminoxane cocatalysts and the nature of the active species still remains unclear [4,36,40]. Actual DFT calculations by Cruz et al. [41,42] and Raucoules et al. [43] give strong evidence for the enhanced oligomerization/polymerization ability of active iron(III) species compared with iron(II) species. However, iron centers in both oxidation states may be present in the same catalyst system ("multicentered catalysts") and lead, e.g., to polyethylenes with broad or even bimodal molecular weight distributions [41,44]. The increased activities of the bis(arylimino)pyridine iron(III) complexes can be explained with the stronger Lewis acidic character of iron(III) centers compared with iron(II) centers and, therefore, an enhanced affinity to coordinate electron rich olefin molecules. Lopez Reyes [24], Devore [35], Bryliakov [36], and Prades [37] describe some bis(arylimino)pyridine iron(III) complexes with ortho-disubstituted iminophenyl rings useful for ethylene polymerization reactions. As mentioned above, Ionkin et al. [14,19] explored the reactivity of halogen substituted bis(arylimino)pyridine compounds towards Suzuki coupling. During these studies, three iron(III) complexes were described along with a huge number of iron(II) complexes which were applied for ethylene oligomerization. The synthesis of ω-alkenyl substituted bis(arylimino)pyridine compounds and their corresponding iron(II) and iron(III) complexes was described by our group [33]. While their ethylene oligomerization and polymerization behaviour was superior compared with analogous alkyl substituted bis(arylimino)pyridine iron complexes, self-immobilization [45] as described for metallocene complexes was not observed during the oligomerization/polymerization runs. Due to the extreme preference of the iron centers to ethylene molecules compared with higher α -olefins, the incorporation rates of such higher olefins are very low [46-48]. While the early literature mainly emphasizes the influence of substituents at the ortho-positions of the iminophenyl rings, more actual publications laid the focus on the meta- and para-substituents [13,14,24,29]. The introduction of electron withdrawing substituents into the ligand backbones resulted in an enhanced temperature stability and, therefore, lead to higher activities. According to Gong [38], bis(arylimino)pyridine transition metal complexes without any substituents at the iminophenyl rings can be applied for the polymerization of 1,3-butadiene. These results engaged us to synthesize bis(arylimino)pyridine iron(III) complexes containing halogen or other electron withdrawing substituents on the iminophenyl rings and to investigate their abilities towards selective ethylene oligomerization/polymerization including the question if catalytic activities are also observed when the iminophenyl rings of the ligand frameworks do not contain substituents in ortho-positions to the former amino groups.

2. Experimental

2.1. General considerations

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. The solvents n-pentane, diethyl ether, toluene und tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride, toluene was additionally dried over phosphorus pentoxide. Methylene chloride was dried over phosphorus pentoxide and calcium hydride. Methanol and ethanol were dried over magnesium. 1-Butanol (p.a.) was purchased from Merck and used without prior distillation. Methylalumoxane was purchased from Crompton (Bergkamen; 30% in toluene) and Albemarle (Baton Rouge, USA/Louvain – La Neuve, Belgium; 10% in toluene). Ethylene (3.0) and argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All other starting materials were commercially available and were used without further purification.

NMR spectra were recorded at 25 °C on a Varian inova 400 spectrometer. The chemical shifts in the ¹H NMR spectra are referred to the residual proton signal of the solvent (δ = 7.24 ppm for CDCl₃) and in ¹³C NMR spectra to the solvent signal (δ = 77.0 ppm for CDCl₃). EI mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, E = 70 eV) and a VARIAN MAT 8500 spectrometer. MALDI-TOF MS measurements were performed on a Bruker Daltonic Reflex TOF using graphite as matrix. The laser intensity was set to 60-70%. GC/MS spectra were recorded with a Thermo Focus gas chromatograph in combination with a Thermo DSQ mass detector (EI, 70 eV) using a HP-5MS GC column (length: 30 m, film thickness: 0.25 µm, flow: 1.5 ml/min, split ratio: 1:50) and helium as the carrier gas. The routinely used temperature program contained a starting phase (2 min at 50 °C), a heating period (10 K/min for 24 min) and a plateau phase (15 min at 290 °C) resulting in a run length of 41 min. At the Zentrale Analytik of the University of Bayreuth, GC/MS spectra were routinely recorded with a HP5890 gas chromatograph in combination with a MAT 95 mass detector. For the analysis of oligomer mixtures, GC spectra were obtained with an Agilent 6890N gas chromatograph equipped with a HP-5 column (length: 30 m, film thickness: 1.5 µm, flow: 150 ml/min, split ratio: 1:50). The temperature program included a starting phase (6 min at 35 °C), two heating ramps (1 K/min up to 55 °C, then 20 K/min up to $250 \circ C$) and a plateau phase (20 min at $250 \circ C$) resulting in a run length of 55.75 min. This temperature program allowed the separation of most of the hexene isomers. GPC measurements were routinely performed by SABIC Company (Riyadh, Saudi Arabia). Elemental analyses were performed with a VarioEl III CHN instrument using acetanilide for calibration.

2.2. Synthesis of 2,6-bis(arylimino)pyridine compounds applying molecular sieves and a heterogeneous SiO₂/Al₂O₃ catalyst (Method A)

To a solution of 2.6-diacetylpyridine (0.49 g; 3 mmol) in toluene (20 ml) were added molecular sieves (4Å or 3Å; 15 g), the corresponding amine or aniline compound (7 mmol), and the silica/alumina catalyst (0.5 g). The reaction mixture was heated to 45-50 °C for 24 h. If the reactions were not completed (according to GC/MS analyses), the heating period was prolonged till completion. After cooling to room temperature, the mixture was filtered over sodium sulfate, and the residue was washed several times with toluene. After removal of the solvent, methanol was added for precipitation. After storage at -20 °C for 24 h, the precipitated bis(imino)pyridine compounds were isolated and dried in vacuo (yields: 40-90%). Their spectroscopical data are given in the Supporting Information (Tables A1 and A2).

2.3. Synthesis of 2,6-bis(arylimino)pyridine compounds applying a Dean-Stark trap (Method B)

To a solution of 2,6-diacetylpyridine (0.82 g; 5 mmol) in 150 ml of toluene were added a substituted aniline (12.5 mmol; 2.5 equivs.) and a few milligrams of para-toluenesulfonic acid. The reaction mixture was heated under reflux for 8–48 h applying a Dean-Stark-trap. After cooling to room temperature, a saturated sodium hydrogencarbonate solution (200 ml) was added. The organic phase was separated and filtered over sodium sulfate and silica. The solvent was removed and methanol (20 ml) was added. The imino compounds precipitated when stored at -20 °C for some days

(yields: 35–50%). Their spectroscopical data are given in the Supporting Information (Table A1).

2.4. Sonogashira coupling reaction of 13 with phenylacetylene

In 15 ml of triethylamine, the iodo substituted 2,6-bis (arylimino)pyridine compound **13** (0.35 mmol), phenylacetylene (0.70 mmol), bis(triphenylphosphino)palladium dichloride (7 μ mol) and copper(I) iodide (14 μ mol) were dissolved. The mixture was stirred for 20 h at room temperature. After removal of the solvent, water (50 ml), n-pentane (50 ml), and methylene chloride (15 ml) were added. The organic phase was separated, and the aqueous phase was extracted several times with a 3:1 (v/v) mixture of n-pentane/methylene chloride. The combined organic phases were dried over sodium sulfate. Removal of the solvent in vacuo and recrystallization from methanol furnished the coupling product **21** as a bright yellow powder (yield: 63%). The spectroscopical data of **21** are given in the Supporting Information (Table A1).

2.5. General synthesis of the 2,6-bis(arylimino)pyridine iron(III) complexes **28–54**

An amount of 1 mmol of the 2,6-bis(arylimino)pyridine compound was dissolved in 1-butanol (20 ml; alternatively, THF or a 1:1 mixture of THF and diethylether were used) and reacted with anhydrous iron(III)chloride (1 mmol) resulting in an immediate colour change to brown, orange, or red). The mixture was stirred for 3 h at room temperature (for **54** derived from benzy-lamine: t = 5 min), whereby the complexes precipitated. n-Pentane (20 ml) was added for complete precipitation, and the mixture was stirred for another 15 min. The iron complexes were filtered over a glass frit, washed three times with 15 ml n-pentane, and dried in vacuo (yields: 50–95%). The data of MS and elemental analyses of complexes **28–54** can be found in the Supporting Information (Table A3).

2.6. Polymerization of ethylene in the 1 l Büchi autoclave

The desired iron complex (0.2-2 mg) was suspended in toluene (5 ml). Methylaluminoxane (30% in toluene or 10% in toluene) was added to maintain a ratio Fe:Al = 1:2500 resulting in an immediate colour change. The mixture was added to a 11 Schlenk flask filled with 250 ml n-pentane. This mixture was transferred to a 11 Büchi laboratory autoclave under inert atmosphere and thermostated at 60 °C. An ethylene pressure of 10 bar was applied for 1 h. After cooling down to 15 °C, the ethylene pressure was carefully released. To the oligomer/polymer mixtures was added diluted hydrochloric acid resulting in biphasic systems. The polymers were filtered off using a glass frit, washed with water and acetone, and finally dried in vacuo.

The oligomer solutions were separated and dried over sodium sulfate. Most of the solvent n-pentane was distilled off using a Vigreux column. The resulting oligomer mixtures were characterized by gas chromatography.

3. Results and discussion

3.1. Preparation of substituted 2,6-bis(arylimino)pyridine compounds

Condensation reactions of 2,6-diacetylpyridine with anilines containing electron-withdrawing substituents yielded the 2,6-bis(arylimino)pyridine compounds (Scheme 1). Besides halogen substituted anilines, aromatic amines containing phenoxy, phenylthio, or nitro groups were applied. For comparison purposes, some ligand precursors were prepared using alkyl substituted anilines or cycloalkylamines. Condensation reactions using 2,4,6-triphenylaniline [11], 3-ethynylaniline, 4-ethynylaniline, 4ethynyl-2,6-dimethylaniline, and 1-aminoadamantane as amine compounds did not lead to imino compounds but gave condensation products of the corresponding anilines. However, a Sonogashira cross-coupling reaction of 2,6-bis[1-(4iodophenylimino)ethyl]pyridine [29] (13) with phenylacetylene provided the phenylethynyl substituted compound **21** in good yield (see Scheme 2). 2,6-Bis(arylimino)pyridine compounds containing electron withdrawing substituents on their iminophenyl rings were found to be much more sensitive towards air and moisture (easy hydrolysis of the imine groups!) compared with alkyl or aryl substituted analogues. Additionally, all iodo substituted ligand precursors appeared to be light sensitive. Former literature usually reported the use of para-toluenesulfonic acid as a catalyst for the condensation reactions of 2,6-diacetylpyridine with aniline derivatives (Method B) [2,5,49]. The great disadvantage of this method is the comparably high reaction temperature of about 130 °C due to azeotropic water removal using a Dean-Stark trap and the poor solubility of para-toluenesulfonic acid in toluene at lower temperatures. As a result, some temperature sensitive aniline and amine compounds decomposed under these quite harsh reaction conditions and did not provide the desired bis(arylimino)pyridine compounds. To overcome these problems, an elegant method introduced by Qian et al. [8,50] was applied using a heterogeneous silica/alumina catalyst (13% Al₂O₃/87% SiO₂) and molecular sieves 3 Å as the water absorbing agent (Method A). The heterogeneous catalyst acts as a Lewis acid and, additionally, as a scavenger for impurities in the aniline compounds. Due to the lower reaction temperatures (40–45 °C), no decomposition products were found in the reaction mixtures and the bis(imine) compounds could be readily isolated. However, nitro substituted aniline derivatives did not give the corresponding bis(imine) compounds (see compounds 19 and 20 in Table 1) under these mild reaction conditions. Applying Method B, compounds 19 and 20 could be isolated in moderate

yields and were found to be extremely sensitive towards hydrolysis (= back reaction). Table 1 gives an overview of the prepared 2,6bis(arylimino)pyridine compounds, while the ¹H NMR, ¹³C NMR, ¹⁹F NMR, and MS data for compounds **1–27** can be found in the Supporting Information (Tables A1 and A2).

3.2. Synthesis of the iron(III) complexes

The bis(arylimino)pyridine compounds 1-27 were reacted with iron(III)chloride either in n-butanol or a 1:1 (v/v) mixture of diethylether and THF to give the corresponding bis(arylimino)pyridine iron(III) complexes 28-54 (Scheme 3 and Table 1) which could be isolated as orange or brown solids. When 2,6-bis[1-(2-iodophenylimino)ethyl]pyridine (5) was reacted with iron(III)chloride, the complexation reaction failed and no product could be obtained. This result may be explained with the increased steric bulk caused by the iodo substituents at the ortho-positions to the imino nitrogen atoms compared with other halogen substituents. Except complex 28 which was described by Gong et al. [38] and used for the polymerization of 1,3-butadiene, complexes **29–54** are not known in the literature. Among these complexes, there are the first examples for bis(arylimino)pyridine iron(III) complexes whose ligands do not contain ortho-substituents at the aryl rings (33-40, 46, 48-50).

As described in the introduction chapter, bis(arylimino)pyridine compounds without or with small substituents at the orthopositions of the iminophenyl rings immediately form ion-pair complexes in reactions with iron(II)chloride. However, some examples for such iron(II) complexes were described as (L)FeCl₂ type complexes (e.g., see Ref. [30]), but after thoroughly reviewing



Scheme 1. General synthesis of 2,6-bis(arylimino)pyridine compounds.



Scheme 2. Synthesis of bis(arylimino)pyridine compound 21 via palladium catalyzed Sonogashira coupling reaction.

Table 1	
Synthesized 2,6-bis(arylimino)pyridine compounds and their corresponding iron(III) chloride complexes.	

bis(Imino) compound	\mathbb{R}^1	R ²	R ³	\mathbb{R}^4	R ⁵	Method of synthesis	Iron(III) complex
1	Н	Н	Н	Н	Н	Α	28
2	F	Н	Н	Н	Н	Α	29
3	Cl	Н	Н	Н	Н	A	30
4	Br	Н	Н	Н	Н	A	31
5	Ι	Н	Н	Н	Н	Α	[32]
6	Н	F	Н	Н	Н	A	33
7	Н	Cl	Н	Н	Н	A	34
8	Н	Br	Н	Н	Н	Α	35
9	Н	Ι	Н	Н	Н	Α	36
10	Н	Н	F	Н	Н	Α	37
11	Н	Н	Cl	Н	Н	Α	38
12	Н	Н	Br	Н	Н	Α	39
13	Н	Н	I	Н	Н	А	40
14	F	Н	F	Н	Н	Α	41
15	Cl	Н	Cl	Н	Н	А	42
16	Br	Н	Br	Н	Н	А	43
17	O-phenyl	Н	Н	Н	Н	А	44
18	S-phenyl	Н	Н	Н	Н	А	45
19	Н	Н	NO ₂	Н	Н	В	46
20	Me	Н	NO ₂	Н	Н	В	47
21	Н	Н	Phenylethynyl	Н	Н	Scheme 2	48
22	Н	t-Bu	Н	Н	Н	А	49
23	Н	t-Bu	Н	t-Bu	Н	А	50
24	Amine compound: cyclopentylamine					А	51
25	Amine compound: cyclohexylamine				Α	52	
26	Amine compound: 2-methylcyclohexylamine				Α	53	
27	Amine compoun	d: benzylamine	1			A	54



Scheme 3. Synthesis of the bis(arylimino)pyridine iron complexes 28-54.



Scheme 4. Literature known bis(arylimino)pyridine iron(II) complexes of the type (L)FeCl₂ lacking ortho-substituents at the iminophenyl groups.

these articles only three complexes seem to exist in the state (L)FeCl₂ [29,51,52] (see Scheme 4). All other compounds should be expressed as ion pairs $[L_2Fe]^{2+}$ [FeCl₄]²⁻ according to the given experimental data (a good indicator is the deep purple or violet colour of these ion pair complexes).

In contrast, reactions of such bis(arylimino)pyridine compounds with iron(III)chloride cleanly provided the desired mono-ligated complexes of the general formula (L)FeCl₃. However, the resulting complexes are not stable towards ligand transfer reactions when they are kept in polar solvents (like THF or alcohols, see Refs. [14] and [36]) for some hours. Additionally, at longer reaction times these iron(III) complexes can act as oxidation reagents towards the solvent THF resulting in the abstraction of hydrogen atoms, the loss of HCl, and the formation of the corresponding iron(II) complexes [53–55].

Therefore, the time limit for the complexation reactions and the subsequent isolation procedures was determined to about 3 h. The iron complex **54** (ligand derived from 2,6-diacetylpyridine and benzylamine) exhibited an extreme instability in the chosen reaction media (1-butanol or a 1:1 mixture of Et₂O and THF) and decomposed after about 15 min to give the ion-pair complex $[L_2Fe]^{3+}$ [FeCl₆]³⁻ (as indicated by MS analyses). Since the desired

mono-ligated complex immediately started to precipitate after the addition of iron trichloride to a solution of the bis(imine) compound **27**, the reaction was worked up after 5 min and complex **54** could be obtained in good yield (76%). All complexes were stored in the dark to prevent the iron(III) centers from reduction to iron(II), as light also seemed to have a detrimental influence on the complex stabilities.

The iron(III) complexes were characterized by mass spectrometry (EI-MS and MALDI-TOF MS) and elemental analyses. Compared with analogous iron(II) complexes, the iron(III) complexes are less stable to fragmentation in EI-MS, so in most cases the molecular ion was not detectable. In contrast, MALDI-TOF MS analyses gave more significant results and the molecular ions could be found for all complexes. As expected, mass distributions due to the presence of chloro atoms (and in some cases additionally bromo atoms) were obtained. Due to their paramagnetism, ¹H NMR analyses of these iron complexes appeared to be less significant, since no defined signals could be found in the range between –2000 and 2000 ppm (relative to Me₄Si). The MS and elemental analyses data of complexes **28–54** are given in the Supporting Information (Table A3).

Scheme 5 shows the MALDI-TOF mass spectrum of complex **36**. Around m/z = 728, the molecular ion mass distribution was

Table 2

Ethylene oligomerization and polymerization results for the iron complexes 28-54 (solvent: 250 ml n-pentane, activator: MAO, Fe:Al = 1:2500, 10 bar ethylene, 1 h). The oligomer share is defined as the content of liquid α -olefins in the product mixture.

Com-plex	Reaction temperature [°C]	Activity [kg prod./mol Fe·h]	Oligomer share [wt.%]	Schulz–Flory coefficient, α	C ₆ in the product mixture [%]	1-Hexene in the C ₆ fraction [%]
28	60	4150	100	0.27	52.1	49.3
29	40	21530	99	0.71	32.4	46.8
29	60	4260	100	0.39	37.0	65.7
29	80	1850	100	0.36	43.1	70.3
30	40	87420	91	0.91	16.2	>99
30	60	13770	95	0.71	23.7	97.9
30	80	13380	98	0.69	26.5	97.0
31	40	63540	61	0.97	9.3	> 99
31	60	19065	84	0.87	15.2	98.6
31	80	4410	93	0.72	28.9	98.1
33	60	7320	100	0.36	40.2	56.3
34	60	52050	100	0.34	26.4	68.6
35	60	22000	100	0.34	26.5	80.8
36	60	19070	100	0.36	42.9	55.4
37	60	4485	100	0.43	41.7	41.5
38	60	3250	100	0.29	54.0	49.3
39	60	4680	100	0.28	51.5	49.3
40	60	22825	100	0.38	46.0	45.9
41	60	25470	96	0.64	31.4	60.1
42	60	7760	90	0.83	14.2	95.7
43	60	9000	73	0.85	14.6	98.6
44	60	240	100	0.37	38.5	87.6
45	60	940	100	0.35	57.4	92.0
46	60	14510	100	0.47	39.1	57.6
47	60	14750	60	0.87	13.7	93.5
48	60	8370	100	0.55	34.6	57.5
49	60	7900	100	0.25	44.5	70.9
50	60	20400	100	0.20	47.1	73.0
51	60	0	-	-	-	-
52	60	0	-	-	-	-
53	60		Traces of hexene isomers		100 ^a	76.2
54	60	285	100	0.65	39.6	48.1

^a Only traces of hexenes were found in the product mixture.



Scheme 5. MALDI-TOF mass spectrum of complex **36** (ions with m/z < 500 were omitted for clarity).

observed. The base peak at m/z = 691/693 resulted from the loss of one chloro ligand, while the ion at m/z = 656/658 had its origin in the loss of two chloro ligands. At m/z = 566, an ion corresponding to the protonated ligand [M_{ligand} + 1] was detected. Similarly to complex **36**, MALDI-TOF mass spectra of most of the complexes revealed that the base peaks mainly result from the loss of either one or two chloro ligands (see Supporting Information, Table A3).

Slow diffusion of toluene into dichloromethane solutions of complexes **36** and **37** afforded thin orange brown colored needles. However, due to their geometry these crystals were found to be unsuitable for X-ray analyses. Similarly to the three literature known crystal structures of bis(arylimino)pyridine iron(III) complexes [14,32,38], the *R* values were too high (corresponding to an increased uncertainty for the geometry of the molecule), so, finally, the refinement procedures could not be finished successfully.

3.3. Results of the catalytic oligomerization and polymerization of ethylene

3.3.1. Oligomerization/polymerization activities and product molecular weight distributions

The iron complexes **28–54** were applied as catalyst precursors for the homogeneous polymerization and oligomerization of ethylene. The complexes were activated with methylaluminoxane (MAO) applying a ratio Fe:Al = 1:2500. Oligomerization/polymerization runs were routinely performed in a 11 Büchi steel reactor at a temperature of 60 °C over 1 h employing an ethylene pressure of 10 bar. As a solvent n-pentane was used. Due to the big differences in their activities, the complexes were used in appropriate molar amounts to keep the exothermic reaction under control. The oligomerization/polymerization results are given in Tables 2 and 3. The liquid fractions (noted as "oligomer share"

Table 3

GPC analyses of the polyethylenes obtained at a polymerization temperature of 40 $^\circ\text{C}.$

Complex	Polymerization	GPC data of th	GPC data of the PE fractions			
	temperature [°C]	Mn [g/mol]	Mw [g/mol]	PD		
29	40	410	2690	6.62		
30	40	535	41,150 ^a	76.93		
31	40	380	1680	4.41		
41	60	750	2460	3.28		
42	60	640	4010	6.22		
43	60	655	6950	10.61		
47	60	720	33,070	45.80		

^a Bimodal MWD.

in Table 2) consisted mainly of linear low molecular weight α olefins and, in some cases, branched olefins. These mixtures can, to some extent, dissolve higher molecular weight olefins (up to ~C₅₀), however, their detected amounts decreased dramatically with increasing carbon numbers. The obtained oligomer mixtures were characterized by gas chromatography (olefins with chain lengths of C₄-C₄₀ could be detected via GC or GC/MS analyses) while the polymers were characterized using GPC analyses (Table 3).

For nearly all oligomerization/polymerization runs, very high initial ethylene uptake rates could be observed (~101 of ethylene/min). Due to the gradual catalyst degradation, the ethylene flows drop distinctively during the experiments, and for the systems 28/MAO, 33/MAO and 54/MAO the ethylene flow had ceased completely at the end of the regular run time (1 h) corresponding to a complete deactivation of the active catalyst species. The "life time" of a catalyst could be determined by the period in which an ethylene flow was detectable. All 2,6-bis(arylimino)pyridine iron complexes bearing at least one non-hydrogen substituent at the ortho-positions of the iminophenyl rings in their ligand frameworks were found to be still catalytically active after 1 h. In contrast, the bis(cycloalkylimino)pyridine iron complexes 51 and 52 were completely inactive in ethylene oligomerization reactions, and complex 53 only afforded traces of hexenes. Since the sizes of cyclohexyl and phenyl rings are quite similar, this dramatic effect most likely originates from different electron densities around the iron centers. Cycloalkyl groups stabilize the cationic iron centers due to their electron donating nature (+I effect), so the coordination of ethylene molecules is not favored. Complex 54 bearing benzyl groups in the ligand framework exhibits a slightly higher electron deficit compared with the cycloalkyl derived complexes 51–53. The coordination of an ethylene molecule therefore becomes more facile, and a moderate oligomerization activity was observed (285 kg prod./mol Fe·h). Complexes 28-50 whose ligands are derived from substituted anilines showed distinctively higher activities due to their greater lack of electron density at the positively charged iron centers compared with the catalyst precursors 51-54. Depending on the size, the nature, and the position of a substituent at these aryl rings, a wide range of olefinic products could be obtained from the activated complexes 28-50 and 54. At 60°C (the routinely used reaction temperature for oligomerization/polymerization experiments), complexes 30-31 and 41-43 containing 2-halo- or 2,4-dihalo substituted iminophenyl rings gave mixtures of liquid olefins and low molecular weight polyethylenes (see Table 2). With increasing the size of the halogen substituent, the amount of polyethylene also increased while correspondingly the oligomer shares, i.e., the liquid mass



Fig. 1. GC spectrum of the oligomer mixture produced with **29**/MAO at 40 °C (C_4 - C_{10} region; signals for higher oligomers were omitted for clarity). Offset: enlarged view of the C_6 region (hexenes).

fractions of the product mixtures, became lower. The catalytic systems 30/MAO and 31/MAO gave mixtures with oligomer contents of 95%, and 84%, respectively, while the dihalo substituted complexes 41-43 lead to mixtures containing 96%, 90%, and 73% of liquid products. At 40°C, also 29/MAO produced a small amount of low molecular weight polyethylene. For both the 2-halo and the 2.4-dihalo substituted complexes, this result can be referred to the increased steric bulk of the bromo substituents compared with the much smaller fluoro and chloro atoms. The initial publications of Brookhart and Gibson [1–7] depicted the same effect for differently alkyl substituted 2,6-bis(arylimino)pyridine iron(II) complexes. While the trends of the product compositions of complexes 29-31 and **41–43** are guite similar, their oligomerization/polymerization activities exhibited dramatic differences. Within the series 29-31 (containing 2-halo substituted compounds), the 2-chloro derivative **30** showed an extremely high activity of 87,420 [kg prod./mol Fe-h] which is distinctively higher compared with the 2-bromo and the 2-fluoro derivatives 31 and 29. The "medium"-sized chloro atoms apparently leave enough space for the coordination of ethylene molecules and the growing chain, whereas the ortho-bromo atoms may partially interfere with incoming ethylene molecules leading to a somewhat lower activity (63,540 [kg prod./mol Fe·h]). The comparatively low activity of the 2-fluoro substituted complex 29 could be explained with a faster deactivation of the catalytically active centers due to the above described ligand transfer reaction. A visible proof of that assumption was the purple colour of the resulting oligomer mixture. The small size of the ortho-fluoro atoms and the polar structure of the activated catalyst molecules favors this ligand transfer reaction, so its rate constant becomes dominant over the rate constant of ethylene insertion. A completely different result was found for the 2,4-dihalo substituted complexes **41–43**, where the 2,4-difluoro substituted compound **41** showed a much higher activity compared with the heavier analogues 42 and 43. The introduction of halogen substituents in the para-positions of the iminophenyl rings proved to be beneficial in some cases [8,9,23,49,56,57], and the highest activities for this complex type were found for 2-methyl-4-halogen substituted bis(arylimino)pyridine iron complexes [29,58]. Only a few substitution patterns at the iminophenyl rings allowed such high activities, and the presence of more than one halogen substituent per iminophenyl ring makes explanations of reactivities more difficult, however, it can be stated that combinations of an electron donating group (at ortho or para position) and an electron withdrawing substituent (at para or ortho position) within one aryl ring gave the best activities. As described by Ionkin [32] and Zhang [59], ligand systems of oligomerization/polymerization catalyst precursors must be electronically flexible to accept a partial positive charge after activation with an aluminoxane co-catalyst. Since the heavier halogen atoms can be polarized easier compared with the small fluorine atoms, the complexes 42 and 43 containing four chloro, respectively, bromo substituents in their ligand backbones may be better stabilized and are, therefore, less prone to coordinate olefin molecules. Reduced catalytic activities of iron catalysts containing para-chloro and para-bromo substituted bis(arylimino)pyridine ligands compared with their fluoro or iodo analogues were also observed for the para-substituted complexes **37–40** (see below) and were already described in the literature [29,58].

The Schulz–Flory coefficient α was found to be a useful parameter for the description of the product compositions, i.e., the molecular weight distributions of the oligomer mixtures [60–65]. It can be calculated from both the reaction rate constants and the GC integrals of the oligomer fractions. Since the GC integrals are easily accessible and are related to the molar amounts of the oligomers, α can be defined as the quotient of the molar amounts of two subsequent oligomer fractions whose carbon numbers differ by a number of 2:

$$\alpha = \frac{k_{\text{propagation}}}{k_{\text{propagation}} + k_{\text{termination}}} = \frac{\text{mol}(C_{n+2})}{\text{mol}(C_n)}$$
(1)

A higher coefficient α directly corresponds to an increased propagation probability resulting in higher molecular weight products. The upper limit α = 1 is only reached when molecular weight distributions are obtained in which the maximum peak appears at



Fig. 2. GC spectrum (taken from GC/MS analyses) of the oligomer mixture produced with **30**/MAO at 40 $^{\circ}$ C (C₆-C₂₀ region). Offset: enlarged view of the C₆ region (hexenes). The peak for the solvent n-pentane was omitted.

higher carbon numbers (usually butenes or hexenes are the main products) but in these cases the mathematical requirements for a Schulz–Flory distribution are not fulfilled (an ideal Schulz–Flory distribution is obtained for $\alpha \sim 0.7$). Equation 1 shows that higher values for α are equivalent to increased amounts of higher olefins in the product mixtures. Since such mixtures can be hardly separated, it is desirable to design more selective catalysts. Many efforts have been made especially to prepare catalysts which produce, e.g., only 1-hexene or 1-octene with high selectivities, since these α -olefins are consumed in large amounts as comonomers in the synthesis of linear low density polyethylenes (LLDPE). At present, chromium catalysts based on [PNPN] ligands represent the upper limit for the selective trimerization of ethylene to give 1-hexene ([66] and references therein).

During our investigations of bis(arylimino)pyridine iron(II) and iron(III) catalysts, we found that iron(III) catalysts usually produced mixtures of shorter chain length olefins compared to their iron(II) analogues bearing the same bis(arylimino)pyridine ligand [33,67]. The surprising result that 2,6-bis(1-(4iodophenylimino)ethyl)pyridine iron(II) chloride was active in ethylene oligomerization [29] encouraged us to evaluate the oligomerization behaviour of analogous iron(III) complexes in more detail. As evident from Table 2, complexes 29-31 and 41-43 produced broad molecular weight distributions, and in all cases low molecular weight polyethylenes were obtained besides the desired α -olefins. The Schulz–Flory coefficients α increased with enlarging the sizes of the ortho-halogen substituents. Additional para-halogen substituents in complexes 41-43 lead to substantially lower α values indicating a reduced steric bulk around the catalytically active center. Probably, the para-substituents lead to a better separation of the cationic iron center and the anionic MAO cages.

The size of the ortho-substituent at the iminophenyl rings also effected the isomerization behaviour of the bis(arylimino)pyridine iron(III) catalysts. If these ortho-substituents were either hydrogen or fluorine atoms, the catalysts produced not only the expected $\alpha\text{-olefins}$ (**29** and **41**), but additionally gave internal olefins (see Fig. 1).

Similar product mixtures containing both α - and internal olefins were also obtained with bis(arylimino)pyridine vanadium(III) catalysts [23,67]. According to early publications of Brookhart and Gibson [5,56], iron complexes bearing one ortho-methyl group at the iminophenyl rings exclusively produced highly linear α -olefins indicating that these methyl groups are voluminous enough to suppress isomerization reactions of terminal into internal olefins. For the bulkier ortho-chloro and ortho-bromo substituted analogues (**30**, **31**, **42**, and **43**), mainly linear α -olefins (>95%) were detected by GC analyses (see Fig. 2 for example) confirming this assumption.

The temperature dependences of the oligomer shares and, correspondingly, the Schulz-Flory values were investigated for complexes 29-31. Therefore, complexes 29-31 were additionally tested for ethylene oligomerization at 40, 60, and 80°C. For all three catalysts, dramatically reduced activities were observed at elevated temperatures corresponding to a faster deactivation process. As could be expected, complex 29 was least stable among these three catalysts due to its small ortho-fluoro substituents. The oligomer shares increased at elevated temperatures, however, complexes 30 and 31 still produced small amounts of low molecular weight polyethylenes at 80 °C. For complexes 30 and 31, the resulting α values decreased at higher temperatures, and were found to fit a more ideal Schulz–Flory distribution (α = 0.69 for **30** at 80 °C, α = 0.72 for **31** at 80 °C), while a dramatic decrease of the α value was observed for complex 29 (see Table 2) which predominantly produced 1-butene, 1-hexene, and 1-octene at 80 °C along with some isomerization products (see Section 3.3.2).

Since the activated complex **29** appeared to be a good approach to a catalyst system that produces low molecular weight α -olefins more selectively, complexes with a further reduced steric bulk at the ortho-positions of the iminophenyl rings looked very promising to give narrower Schulz–Flory distributions. This was realized with complexes **28**, **33–40**, **46**, and **48–50** which only contain hydrogen atoms at the ortho-positions of the iminophenyl rings.



Fig. 3. C_4-C_8 region (content of oligomers with C>8 is lower than 2%) of the oligomer mixture produced with 50/MAO.

As **28** was described to be catalytically active in the polymerization of 1,3-butadiene [38], it seemed reasonable to test this complex also for the oligomerization of ethylene. Indeed, after activation with MAO, complex **28** exhibited a moderate activity in ethylene oligomerization (4150 kg prod./mol Fe·h), however, due to its lack of any substituents at the iminophenyl rings, complete deactivation had to be noted after a run time of only 10 min when no more ethylene was consumed. The Schulz–Flory coefficient was determined to α = 0.27 indicating a very narrow product distribution.

Regarding the fast deactivation of 28, complexes 33-40 bearing meta and para mono-halogen substituted iminophenyl rings were considered to exhibit an improved shield of the iron center. Similarly to 28, these complexes produced low molecular weight olefins, and the determined Schulz-Flory coefficients range from 0.28 (for 39/MAO) to 0.43 (for 37/MAO). Compared with the orthohalogen functionalized complexes 29-31, the activities of the metaand para-halogen substituted complexes 33-40 were lower, as partial deactivation by ligand transfer reactions occurred. While among the meta-halogen substituted complexes 33-36 the chloro compound **34** gave the highest activity, complex **40** bearing iodo substituents at the ligand backbones proved to be the most active candidate in the para-halogen substituted series 37-40. With an activity of 52,050 [kg prod./mol Fe·h], 34/MAO actually is the most active bis(arylimino)pyridine iron catalyst which does not contain any substituents at the ortho-positions to the former amino nitrogen atoms. Similarly to the ortho-substituted series 29-31, the chloro compound revealed to be the most active candidate in ethylene oligomerization reactions among the meta-series 33-36 what may be explained with the medium size of the chloro atoms and their high electronegativity. The latter leads to a strong decrease of the electron density in the iminophenyl rings favouring the coordination of ethylene molecules. However, if chloro substituents are introduced at the para-positions (complexes 38 and 42), the activities dropped. These results are in accordance to Pelascini et al. [11] who also described a negative effect of chloro substituents on the polymerization activities of a series of iron(II) and cobalt(II) catalysts. The beneficial effect of introducing iodo substituents at the para-positions of bis(arylimino)pyridine ligands was already

described by our group [29] which may be explained with the size and the good polarizability of the voluminous iodo atoms due to partial compensation of the positive charges at the iron centers during the oligomerization process. The high activity (22,825 kg prod./mol Fe-h) of **40**/MAO is therefore in accordance with our former results. In the presence of the smaller para-halogen substituents in complexes **37–39**, distinctively lower activities were noticed corresponding to less shielded active iron centers.

Differences in the Schulz-Flory coefficients were observed when considering ortho-, meta- and para-halogen substituted bis(arylimino)pyridine iron complexes. As expected, α increases in the 2-halogen substituted series **29–31** (**29**: $\alpha = 0.71 < 30$: $\alpha = 0.91 < 31$: $\alpha = 0.97$) with increasing size of the halogen substituent. The meta- and para-substituted derivatives 33-40 yielded substantially lower α values (0.28 < α < 0.43). For the meta-halogen series **33–36**, α remains nearly constant ($\alpha \sim 0.35$) with increasing size of the halogen substituent, but no general trend could be observed for the para-series 37-40. The narrowest molecular weight distribution among the mono-halogen substituted bis(arylimino)pyridine iron(III) complexes was found for the para-bromo substituted complex **39** (α = 0.28). The para-halogen substituted catalysts showed the highest tendencies towards isomerisation products, and remarkably low 1-hexene contents (<50%) among the C_6 fractions were found (see Table 2).

Besides halogen substituted bis(arylimino)pyridine compounds, complexes containing other electron withdrawing substituents at their bis(arylimino)pyridine ligand frameworks (**44–47**) also proved to be active in ethylene oligomerization reactions. Literature known nitro substituted bis(arylimino)pyridine iron(II) catalysts proved to be thermally more stable compared with alkyl functionalized analogues [13]. Complex **46** containing para-nitro groups at the iminophenyl rings showed a lower activity compared with the 4-iodo derivative **40** and, additionally, a broader molecular weight distribution ($\alpha = 0.47$ for the oligomer mixture obtained with **46**/MAO). Similarly to the *ortho*-halogen substituted complexes **29–31**, complex **47** produced a quite high amount of low molecular weight polyethylene, however, its productivity was much lower (14,750 kg prod./mol Fe·h). The strong electron withdrawing effect of the nitro groups leads to an



Fig. 4. Hexene fraction in the gas chromatogram of the oligomer mixture produced with **39**/MAO.

increased affinity of the cationic iron center towards electron rich ethylene molecules resulting in longer oligomer/polymer chains.

Very low activities were recorded for the phenoxy- and phenylthio substituted complexes **44** and **45** (see Table 2). The presence of oxygen and sulfur atoms in the ligand frameworks causes a special deactivation reaction, since these heteroatoms are assumed to coordinate irreversibly to the cationic iron centers. Despite their low activities, the resulting product molecular weight distributions were very narrow ($\alpha = 0.35-0.37$) and only α -olefins were obtained.

For comparison purposes, complexes **48–50** containing metaalkyl (**49** and **50**) or para-phenylethynyl (**48**) substituted bis(arylimino)pyridine ligands were tested for the oligomerization of ethylene. While the catalytic system **48**/MAO showed a moderate activity of 8370 kg prod./mol Fe·h which is similar to the 4-halogen substituted complexes **37–40**, the resulting product distribution (α = 0.55) is much broader compared with the distributions of the 4-halogen derivatives.

Since halogen substituents at the meta-positions of the iminophenyl rings lead to narrow product molecular weight distributions (33-36) and, therefore, low values for the Schulz-Flory coefficient α , complexes **49** and **50** revealed to be interesting candidates for ethylene oligomerization reactions. Indeed, both complexes produced mixtures with very narrow molecular weight distributions ($\alpha = 0.25$ for **49**/MAO and $\alpha = 0.20$ for **50**/MAO) indicating high selectivities towards low molecular weight olefins (Fig. 3). Additionally, their selectivities towards α -olefins are decisively higher compared with the above described halogen substituted catalysts. The presence of two bulky tert-butyl groups per iminophenyl ring in complex 50 protects the iron center moderately from deactivation by ligand transfer reactions leading to a good activity of 20,400 kg prod./mol Fe h. On the other hand, its lack of substituents at the ortho positions provides enough space for the coordination of ethylene molecules.

3.3.2. Isomerization and in situ copolymerization of α -olefins

Complexes **28**, **29**, **33–41**, **46**, and **48–50** are the first examples of bis(arylimino)pyridine iron complexes which, after activation with MAO, isomerize and most likely copolymerize small α -olefins to a greater extent indicating that the lack of ortho substituents at the iminophenyl rings is an essential requirement for this behaviour since all other complexes produced highly linear products with selectivities to α -olefins greater than 90% (see Table 2). Both the isomerization of α -olefins and the copolymerization of ethylene with small α -olefins (especially the gaseous 1-butene) can be verified

via GC analyses, since branched and internal alkenes are obtained along with the expected 1-alkenes. Isomerization of terminal into internal olefins probably proceeds through the coordination of an α -olefin and its insertion in a 2,1-mode into the postulated hydrido iron species with subsequent β -hydrogen elimination to yield an internal olefin. These results are in accordance with the calculations of Ramos [46] regarding the inability of bis(arylimino)pyridine iron catalysts bearing ortho-methyl substituents on the iminophenyl rings to copolymerize ethylene with higher α -olefins.

The degrees of isomerization of the produced α -olefins, especially 1-hexene, which were observed for 29 at three different temperatures, became interestingly lower at elevated temperature (40°C: 46.8%; 60°C: 65.7%; 80°C: 70.3%), and at 80°C the highest relative content of 1-hexene (among the C₆ fraction) could be detected (see Table 2). This result could again be explained with an accelerated deactivation process (ligand transfer) which does not allow the "recoordination" and subsequent isomerization of a produced α -olefin molecule to the active center to a greater extent. Less steric bulk around the iron centers most likely favors the coordination of 1-butene or higher α -olefins which may then further undergo 1,2- or 2,1-insertion either into a postulated cationic iron hydride species [7,33,68] or into an iron-alkyl species (= the growing chain). The different ways of coordination and subsequent chain termination reactions lead to a broad spectrum of linear and branched isomers. Fig. 1 shows the C_6 fraction of the oligomer mixture produced with 29/MAO at 40 °C along with an assignment of the detected isomers which was proven by GC analyses of the pure hydrocarbons. Obviously, both branched and internal olefins were produced, however, the overall selectivity towards linear C₆ alkenes (1-hexene, cis/trans-2-hexene) still exceeded 90%. Compared to the results for complex 29, the degree of isomerization of the hexene fraction for the catalytic system 28/MAO is very similar, and the relative amount of 1-hexene in the C_6 fraction was calculated to 49.3%. Besides the complexes 28 and 29, the para-halogen substituted complexes 37-40 exhibited the greatest tendencies towards isomerization reactions, since the contents of 1-hexene in the C₆ fractions of the product mixtures was always lower than 50% (see Table 2). Among this series, 37/MAO only gave 41% of 1-hexene. The C₆ region in the GC spectrum of the oligomer mixture obtained with 39/MAO is shown in Fig. 4. Beside the expected 1-hexene (retention time: 6.43 min), signals for cis- and trans-4-methyl-2-pentene, 2-methyl-1-pentene, cisand trans-2-hexene, 2-methyl-2-pentene, 2-ethyl-1-butene, and 2,3-dimethyl-2-butene could be assigned by comparison of the GC retention times of the pure compounds and further GC/MS correlation using the NIST mass spectral database.

According to the assignments in Fig. 4, the para-halogen substituted complexes 37-40 also afforded branched oligomers. While the occurrence of linear internal olefins can be explained with recoordination of the α -olefins to the iron center in a 2,1insertion mode and subsequent β -hydrogen elimination, branched products additionally require the incorporation of at least one ethylene or 1-butene molecule into the growing chain (see "chain running" mechanism known for bis(imine)nickel catalysts [69]) before β -hydrogen elimination takes place. Especially the exclusively para-substituted complexes produced remarkable amounts of branched oligomers indicating that the lack of substituents in both ortho and meta positions provided sufficient space for adequate coordination of "non-ethylene" olefins. In conclusion, the iron(III) complexes with ortho-unsubstituted iminophenyl rings display the first examples of this complex type which are able to isomerize and copolymerize small olefins (except an ω-alkenyl substituted complex described by our group [33] for which another chain propagation mechanism was proposed).

Compared with complexes **37–40**, complexes **33–36** bearing halogen substituents at the meta positions of the iminophenyl rings

afforded increased amounts of 1-hexene (55–80%) in the C₆ fractions (see Table 2) and, therefore, lower amounts of isomerized and branched hexenes were detected.

As indicated above, the meta-tert-butyl substituted complexes **49** and **50** featured lower tendencies towards isomerization compared with the complexes bearing electron withdrawing substituents (**33–36**). Due to the bulky tert-butyl groups, the coordination of higher α -olefins to the iron centers is hindered resulting in lower amounts of isomerized and branched olefins. The selectivities towards 1-hexene (among the C₆ fraction) were determined to 70.9% (49) and 73.0% (50), respectively, representing the highest selectivity values among the ortho-unsubstituted complexes.

4. Conclusion

Bis(arylimino)pyridine iron(III) complexes containing electron withdrawing substituents in their ligand frameworks were synthesized and characterized. After activation with methylaluminoxane (MAO), the resulting catalysts proved to be highly active in ethylene oligomerization reactions. Both the size and the electronegativity of the substituents as well as their positions at the iminophenyl rings strongly influence the product compositions. The major difference of the iron(III) complexes compared with analogous iron(II) complexes is the fact, that catalytic activities are also observed when the iminophenyl rings of the ligand frameworks do not contain substituents in ortho-positions to the former amino groups. These iron(III) complexes did not only produce α -olefins, but also internal and branched olefins. An explanation for this behaviour considers the coordination and insertion of small α -olefins like 1-butene into the growing chains. In other words, these complexes are the first examples for bis(arylimino)pyridine iron catalysts which seem to be able to copolymerize ethylene with higher α -olefins and to isomerize terminal into internal olefins.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.06.010.

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