

Iron complexes with ω -alkenyl substituted bis(arylimino)pyridine ligands as catalyst precursors for the oligomerization and polymerization of ethylene

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Abstract

A series of 15 iron complexes with ω -alkenyl functionalized bis(arylimino)pyridine ligands was synthesized and characterized. After activation with methylalumoxane (MAO), these catalysts oligomerize or polymerize ethylene to give highly linear products. Their potential for self-immobilization during the polymerization process was investigated. The product composition and the molecular weights of the polyethylenes were analyzed and compared with the values resulting from analogously alkyl substituted bis(arylimino)pyridine iron complexes.

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Keywords: Bis(arylimino)pyridine iron complexes; Ethylene polymerization; Oligomerization; Self-immobilization; Polyethylene

1. Introduction

In 1998, a new class of zirconocene complexes was presented containing ω -alkenyl or internal alkynyl substituents in their ligand framework [1]. Many of these complexes had a potential for self-immobilization during the homogeneous polymerization of ethylene. The incorporation of the terminal double bond of the catalyst into the growing polymer chain made the initially homogeneous system heterogeneous, whereby the activated catalysts acted as comonomers. The avoidance of an additional support and their lack of “fouling” made this class of complexes interesting for industrial applications. Gibson [2,3] and Brookhart [4,5] independently reported the synthesis of 2,6-bis(arylimino)pyridine iron complexes which are effective catalysts for the polymerization and oligomerization of ethylene leading to highly linear products. While a couple of complexes containing alkyl or halogen substituted 2,6-bis(arylimino)pyridine ligands are known [2–10], only a few ω -alkenyl functionalized complexes were published by Jin [11] and Herrmann [12]. In this paper, the synthesis of a series of ω -alkenyl functionalized bis(arylimino)pyridine iron complexes is

described. Their tendencies for self-immobilization were investigated. The differences in the product compositions and the molecular weights of the resulting polyethylenes compared with the values for analogous complexes containing alkyl substituted ligands are presented.

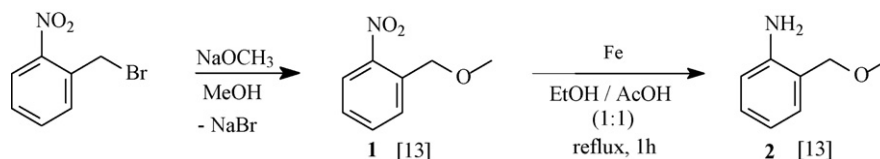
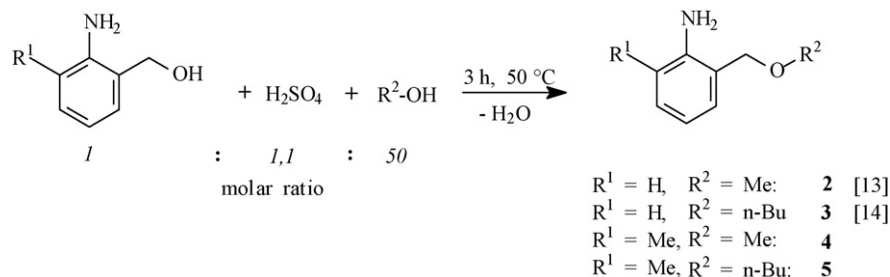
2. Results and discussion

2.1. Synthesis of ω -alkenyl substituted anilines

The reaction of 2-alkoxymethyl anilines with unsaturated Grignard reagents proved to be a common way for the synthesis of ortho substituted ω -alkenyl anilines. 2-Methoxymethyl aniline (2) was prepared starting from 2-nitrobenzyl bromide. The nucleophilic substitution reaction of 2-nitrobenzyl bromide with sodium methylate lead to 2-nitrobenzyl methyl ether (1) which was reduced with iron powder in a 1:1 mixture of ethanol and glacial acetic acid to give 2-methoxymethyl aniline (2) (Scheme 1).

Alkoxyethyl anilines could also be prepared under acidic conditions: the reaction of 2-aminobenzyl alcohol or 2-amino-6-methylbenzyl alcohol with a large excess of methanol or *n*-butanol and an equimolar amount of sulfuric acid yielded the methoxy-methyl and butoxymethyl derivatives 2–5 (Scheme 2).

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Scheme 1. Synthesis of 2-methoxymethyl aniline (**2**) [13].Scheme 2. Synthesis of the 2-alkoxymethyl anilines **2–5** [13,14].

The alkoxymethyl anilines **2–5** were then reacted with ω -alkenyl Grignard reagents furnishing the ω -alkenyl anilines **6–9** in yields up to 65% (Scheme 3).

The reaction mechanism was investigated by Mann and Stewart [20,21] in 1954. In the first step one equivalent of the Grignard reagent deprotonates the alkoxymethyl aniline. Elimination of the magnesium salt leads to the highly reactive *o*-chinomonemethane imine that also exists in a more stable 1,4-dipolar tautomeric form. Nucleophilic attack of a second Grignard molecule at the methylene carbon atom and subsequent hydrolysis yields the ω -alkenyl anilines (see Scheme 4).

Starting from 2-nitrobenzaldehyde, 2-vinyl aniline (**11**) was synthesized [22–24]. Wittig reaction of 2-nitrobenzaldehyde with methylene triphenylphosphorane lead to 2-nitrostyrene (**10**) which was then reduced to 2-vinyl aniline (**11**) (Scheme 5).

2.2. Synthesis of 2,6-bis(arylimino)pyridine compounds

Condensation reactions of 2,6-diacetylpyridine with the ω -alkenyl substituted anilines **6–9** and **11** yielded the 2,6-bis(arylimino)pyridine compounds **12–16** (see Scheme 6). The reaction time varied between 15 h and 1 week depending on the

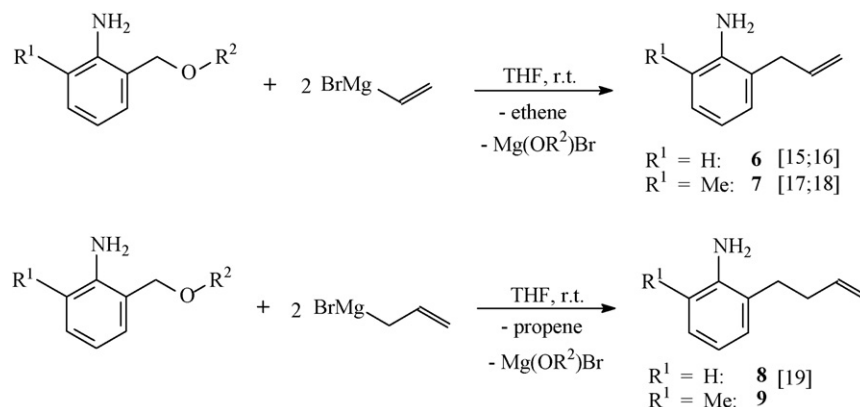
substitution pattern of the applied aniline. The yield of compound **15** was very low preventing further reactions.

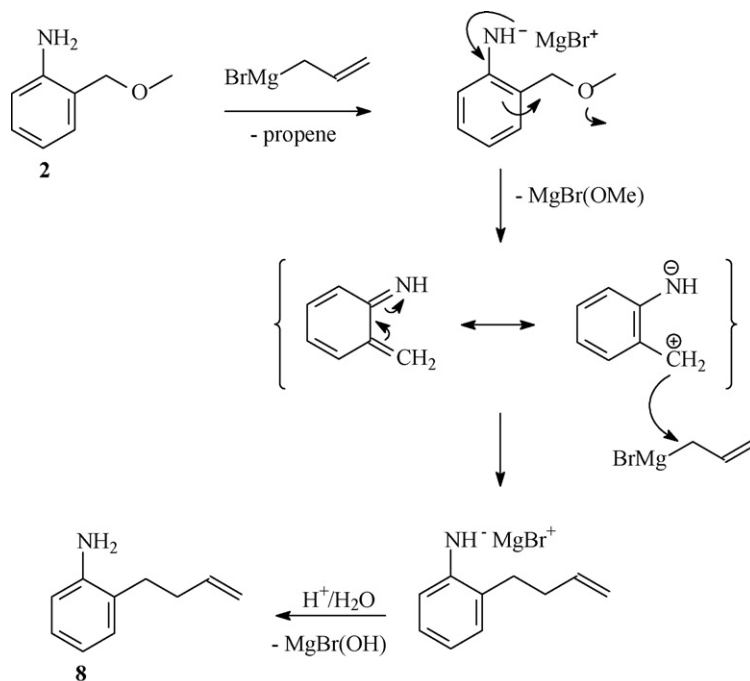
For comparison purposes, the 2,6-bis(arylimino)pyridine compounds **17–19** with alkyl substituents were synthesized (Scheme 7).

Another way to introduce ω -alkenyl groups into 2,6-bis(arylimino)pyridines was described by McTavish [27] and Herrmann [12]. Deprotonation of one of the iminomethyl groups with strong, not nucleophilic bases like sodium bis(trimethylsilyl)amide and subsequent alkylation with ω -alkenyl bromides resulted in the formation of unsymmetrically substituted 2,6-bis(arylimino)pyridine compounds. Starting from the literature known compounds **20–26**, seven unsymmetrical ligand precursors (**27–33**) were prepared (see Scheme 8).

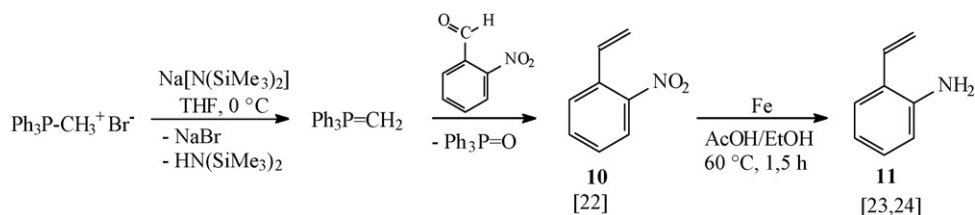
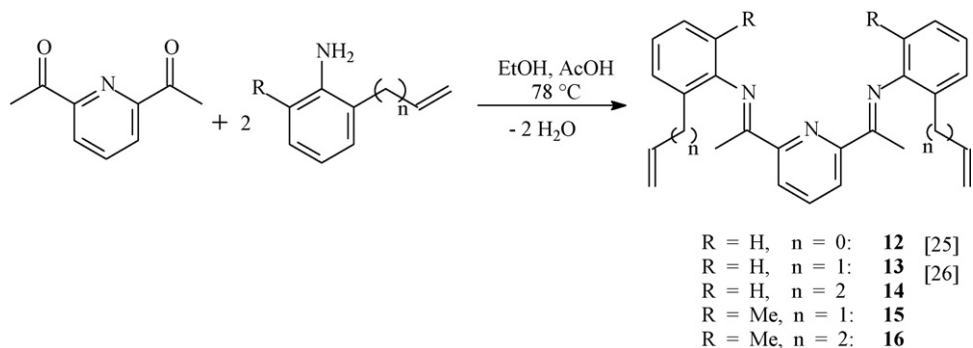
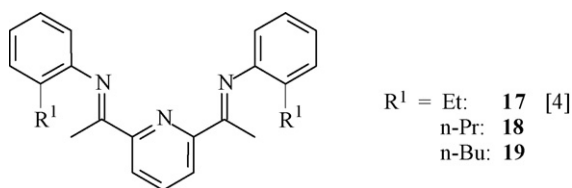
2.3. Synthesis of 2,6-bis(arylimino)pyridine iron complexes

The iron complexes **34–58** were prepared according to Britovsek et al. [3]. After dissolving the 2,6-bis(arylimino)pyridine compound in 1-butanol, water free iron(II) chloride or iron(III) chloride was added resulting in an immediate color change from yellow (dissolved ligand) to blue (iron(II) com-

Scheme 3. Synthesis of the ω -alkenyl anilines **6–9** [15–19].

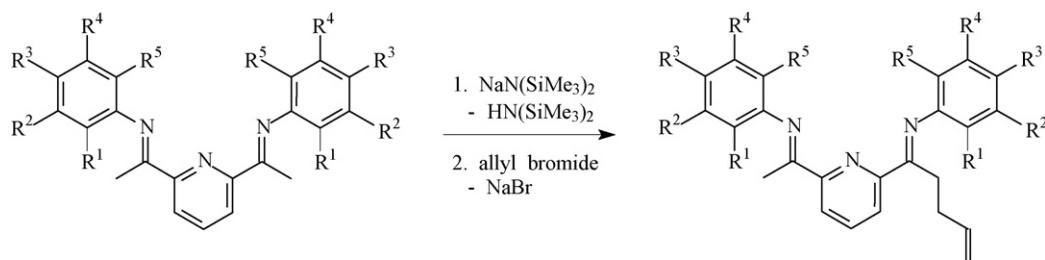


Scheme 4. Mechanism of the reaction of 2-methoxymethyl anilines with Grignard reagents.

Scheme 5. Synthesis of 2-vinyl aniline (**11**) [22–24].Scheme 6. Synthesis of the ω-alkenyl substituted 2,6-bis(arylimino)pyridine compounds **12–16** [25,26].Scheme 7. Synthesized complexes **17–19** [4].

plexes) or orange brown (in case of iron(III) complexes). The complexes could be isolated in very high yields (80–95%).

All iron complexes were characterized by mass spectrometry and elemental analysis. In some cases ¹H NMR spectroscopy was also useful [3]. Due to the paramagnetism of these complexes, the signals appear as broad singlets over a wide ppm range (–50 ppm to +100 ppm). No couplings were observed. Complexes with highly symmetrical ligand frameworks show sharper signals in ¹H NMR spectra than complexes containing long alkyl or alkenyl chains (Scheme 9).



starting compound	R ¹	R ²	R ³	R ⁴	R ⁵	product
20 [28]	Me	H	H	Me	H	27
21 [29]	Me	H	H	H	Me	28
22 [3]	Me	H	Me	H	Me	29
23 [30]	Me	H	H	H	i-Pr	30
24 [31]	i-Pr	H	H	H	i-Pr	31 [12]
25 [30]	Et	H	H	H	Et	32
26 [3]	t-Bu	H	H	H	H	33

Scheme 8.

Scheme 10 shows the mass spectrum of complex **38**. The molecular ion appears at $m/z = 547$. The loss of FeCl_2 results in the formation of the base peak at $m/z = 421$ corresponding to the bis(arylimino)pyridine ligand. The peaks at $m/z = 406$ and 380 arise from the loss of either one iminomethyl group or one allyl group from the ligand framework.

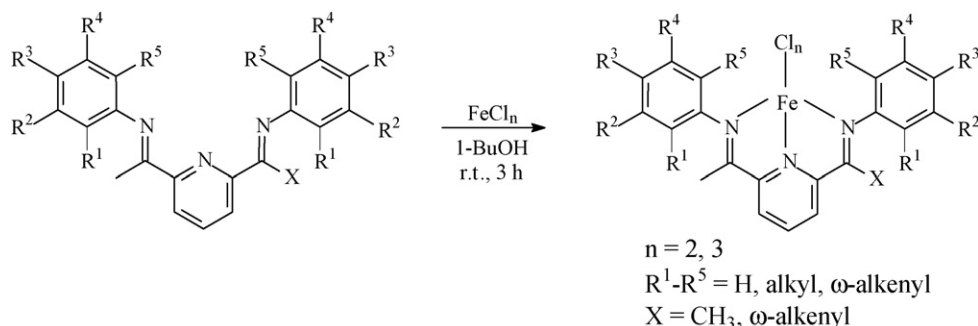
2.4. Results of the homogeneous ethylene polymerization and oligomerization

The iron complexes **34–58** were used as catalyst precursors for the homogeneous polymerization and oligomerization of ethylene. The complexes were activated with methylalumoxane (MAO) applying a ratio $\text{Fe}:\text{Al} = 1:2500$. The polymerization runs were routinely performed at a temperature of 60°C over 1 h employing an ethylene pressure of 10 bar. As a solvent *n*-pentane was used. The polymerization results are given in Table 1. Some

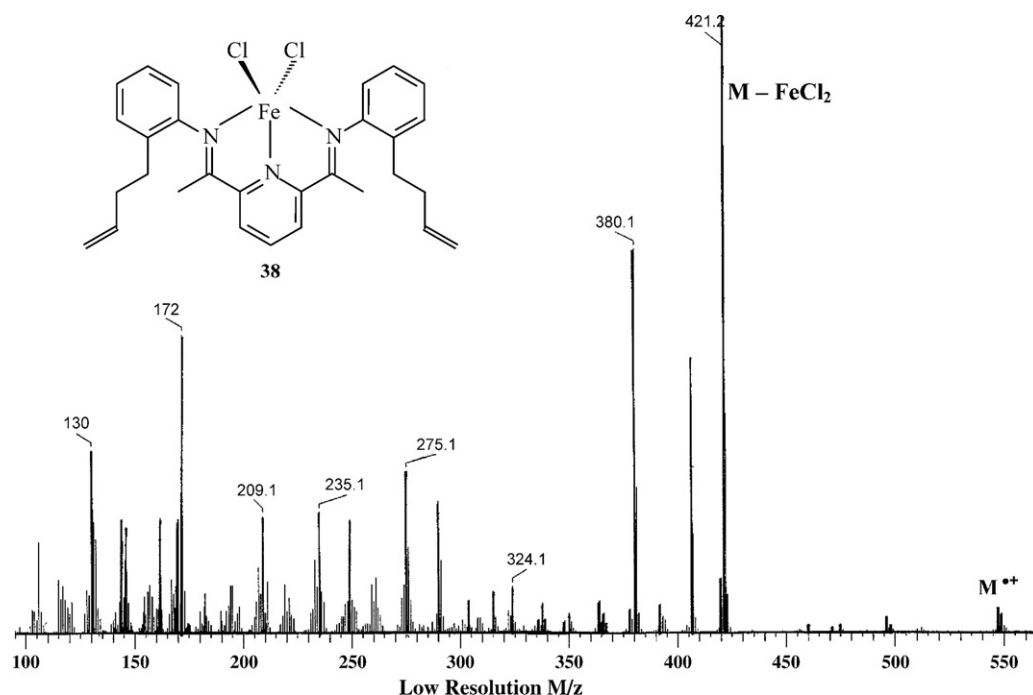
complexes produced mixtures of polyethylene and oligomeric products. The liquid fractions (noted as “oligomer share” in Table 2) contain α -olefins (chain lengths $\text{C}_6\text{--C}_{40}$) with purities higher than 95%. These oligomer mixtures were characterized by gas chromatography while the polymers were characterized using GPC.

2,6-Bis(arylimino)pyridine iron complexes bearing substituents both at positions 2 and 6 of the iminophenyl rings only produced polyethylene. If only one of the ortho positions of the imino nitrogens was substituted, these complexes produced oligomer/polymer mixtures or pure oligomer mixtures depending on the size of the substituent and the reaction conditions [4]. Scheme 11 shows the gas chromatogram of an oligomer mixture produced with **34**/MAO revealing the high selectivity of the catalyst towards linear α -olefins.

While iron(III) complexes with alkyl substituted iminophenyl rings usually show higher polymerization activities than their



Scheme 9. Synthesis of 2,6-bis(arylimino)pyridine iron complexes.

Scheme 10. Mass spectrum of **38** (peaks with $m/z < 100$ are left out).

iron(II) analogues [10], the ω -alkenyl substituted iron(III) complexes **35**, **37**, **39** and **41** exhibited similar activities compared with their iron(II) analogues **34**, **36**, **38**, and **40** (see Scheme 12).

The electron acceptor effect of the terminal vinyl groups resulted in comparably low polymerization activities for com-

plexes **34** and **35**. By introduction of spacer methylene groups between the vinyl groups and the phenyl rings (complexes **36–41**) the electron withdrawing effect is reduced and the activities increase. Longer ω -alkenyl substituents seem to stabilize the cationic metal center resulting in similar activities for analogously substituted iron(II) and iron(III) complexes.

Table 1

Ethylene polymerization results for the iron complexes **34–58** (solvent: 250 ml *n*-pentane, activator: MAO, Fe:Al = 1:2500, 10 bar ethylene, 60 °C, 1 h)

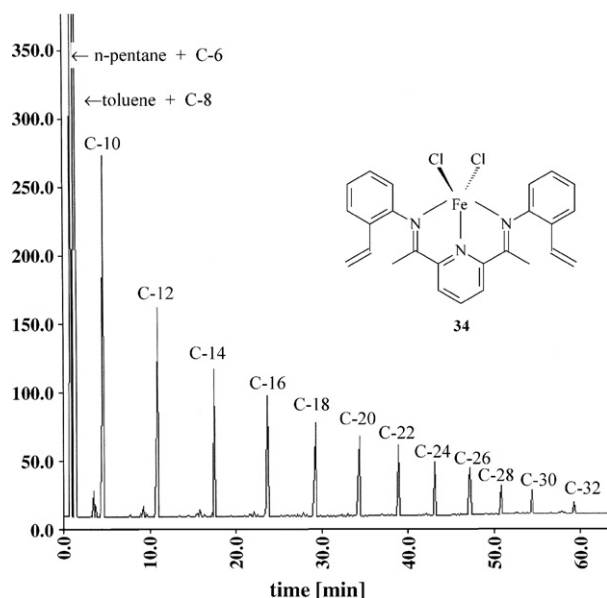
Compound	Activity (kg/mol Fe h)	M_n (g/mol)	M_w (g/mol)	PD	Oligomer share (wt.%)
34	5890	5120	395,700	75.8	61.9
35	5610	3370	336,000	99.7	42.7
36	18,600	1027	60,910	59.3	29.5
37	16,025	984	34,000	34.5	31.4
38	39,780	800	49,560	62.1	–
39	25,600	1260	115,500	91.5	–
40	32,970	10,800	119,700	11.1	–
41	32,320	23,160	171,700	7.40	–
42	60,200	–	–	–	89.2
43	36,630	1138	12,315	10.82	67.9
44	8880	–	–	–	61.0
45	118,610	725	9140	12.6	87.2
46	27,900	6670	90,950	13.6	–
47	51,900	14,000	148,000	10.7	–
48	66,960	–	–	–	–
49	16,020	53,800	281,800	5.3	–
50	69,180	–	–	–	–
51	7500	3100	313,000	78.1	–
52	91,970	794	2172	2.74	64.0
53	30,940	13,700	114,200	8.30	–
54	19,830	8210	55,400	6.74	–
55	41,860	43,600	594,100	13.6	–
56	9250	33,380	317,600	9.50	–
57	4980	36,600	248,500	6.78	–
58	8580	47,810	352,400	7.37	–

Table 2
Synthesized 2,6-bis(arylimino)pyridine iron complexes

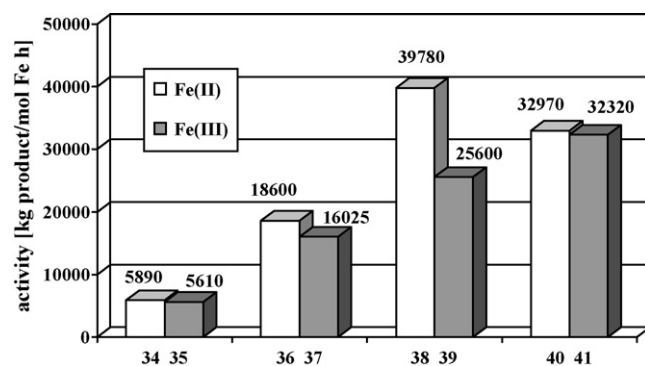
Compound	R ¹	R ²	R ³	R ⁴	R ⁵	X	n
34 [25]	Vinyl	H	H	H	H	Me	2
35	Vinyl	H	H	H	H	Me	3
36 [26]	Allyl	H	H	H	H	Me	2
37	Allyl	H	H	H	H	Me	3
38	3-Butenyl	H	H	H	H	Me	2
39	3-Butenyl	H	H	H	H	Me	3
40	3-Butenyl	H	H	H	Me	Me	2
41	3-Butenyl	H	H	H	Me	Me	3
42 [4]	Et	H	H	H	H	Me	2
43	<i>n</i> -Propyl	H	H	H	H	Me	2
44	<i>n</i> -Butyl	H	H	H	H	Me	2
45 [28]	Me	H	H	Me	H	Me	2
46 [29]	Me	H	H	H	Me	Me	2
47 [3]	Me	H	Me	H	Me	Me	2
48 [30]	<i>i</i> -Propyl	H	H	H	Me	Me	2
49 [31]	<i>i</i> -Propyl	H	H	H	<i>i</i> -Propyl	Me	2
50 [30]	Et	H	H	H	Et	Me	2
51 [3]	<i>tert</i> -Butyl	H	H	H	H	Me	2
52	Me	H	H	Me	H	3-Butenyl	2
53	Me	H	H	H	Me	3-Butenyl	2
54	Me	H	Me	H	Me	3-Butenyl	2
55	Me	H	H	H	<i>i</i> -Propyl	3-Butenyl	2
56 [12]	<i>i</i> -Propyl	H	H	H	<i>i</i> -Propyl	3-Butenyl	2
57	Et	H	H	H	Et	3-Butenyl	2
58	<i>tert</i> -Butyl	H	H	H	H	3-Butenyl	2

The polyethylenes produced with the catalyst precursors **34–39** show very broad molecular weight distributions. The polydispersity values range from 35 to 100, while complexes **40** and **41** produced polyethylenes with PD values of 11.1, respectively 7.4.

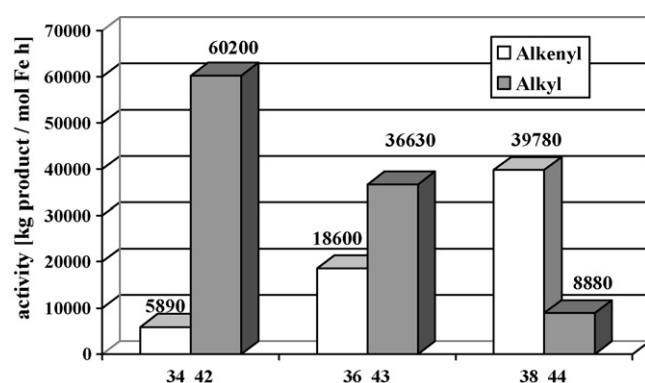
Comparisons of the polymerization activities of complexes **34**, **36**, and **38** with their saturated analogues **42**, **43** and **44** show the positive effect of longer ω -alkenyl chains, while



Scheme 11. Gas chromatogram of the oligomer mixture produced with **34**/MAO (10 bar ethylene, 60 °C, 250 ml *n*-pentane, Fe:Al = 1:2500, 1 h).



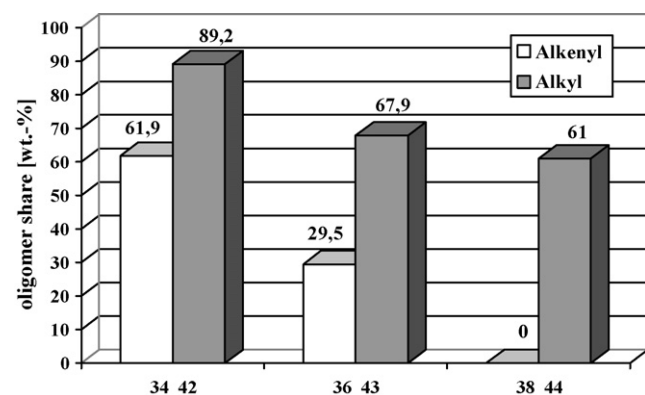
Scheme 12. Comparison of the polymerization activities of various Fe(II) and Fe(III) 2,6-bis(arylimino)pyridine complexes with ω -alkenyl substituted iminophenyl rings.



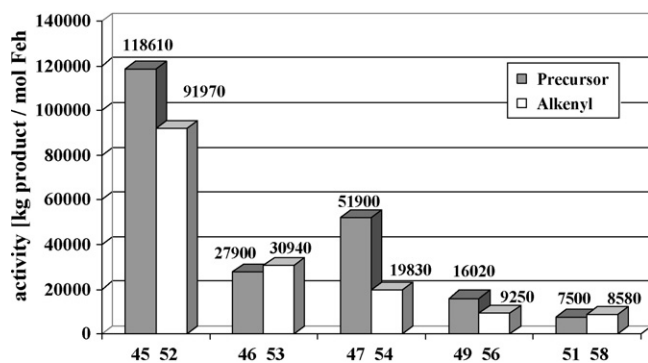
Scheme 13. Comparison of the activities of various alkenyl and alkyl substituted bis(arylimino)pyridine iron complexes.

longer alkyl chains contrarily lead to a decrease in activity (see Scheme 13).

The stabilizing influence of the alkenyl substituents can obviously be seen by analyzing the product compositions. The polymer shares are substantially higher in case of complexes containing ω -alkenyl substituted ligands (see Scheme 14) corresponding to a lower rate of β -hydrogen elimination. While the butenyl substituted complex **38** only produced polymer, the oligomer share resulting from the butyl derivative **44** was still higher than 60 wt.%.



Scheme 14. Comparison of the oligomer shares of mixtures produced with either ω -alkenyl or alkyl substituted catalyst precursors.



Scheme 15. Comparison of the polymerization activities of complexes allylated at the iminomethyl moiety with their “precursor” complexes.

While the change from ω -alkenyl substituted to alkyl substituted iminophenyl rings has a great impact on polymerization activity and product composition, the influence of an additional allyl group at the iminomethyl moiety is significantly lower.

According to Scheme 15, the polymerization activity decreases when sterically more demanding substituents are introduced into the iminophenyl rings, while the average molecular weights of the resulting polyethylenes increase from methyl over *iso*-propyl to *tert*-butyl substituents. The complexes with allylated ligand frameworks usually yield polyethylenes with slightly higher molecular weights compared with their allyl free analogues (see Table 3). Due to the additional alkenyl groups, the tendency of the growing polymer chain towards β -hydride elimination is reduced leading to about 15% higher average molecular weights.

The additional allyl group in **52** leads to an increase of the polymer share to 36% (13% for the allyl free complex **45**).

2.5. Experiments investigating the ability of ω -alkenyl substituted 2,6-bis(arylimino)pyridine iron complexes towards self-immobilization

Polymerization and oligomerization reactions at low ethylene pressure (0.2 bar) were performed to investigate the ability of alkenyl substituted 2,6-bis(arylimino)pyridine iron complexes towards self-immobilization. In case of alkenyl substituted zirconocene complexes prepolymerization for 30 min at low ethylene pressure lead to self-immobilized complexes used as heterogeneous catalysts for ethylene polymerization [1]. When the activated iron complexes were incorporated into the polymer, the orange brown color of the solution would completely disappear while the polymer became colored. In contrast to the

Table 3
Molecular weights M_w of polyethylenes produced with allyl substituted, respectively allyl free 2,6-bis(arylimino)pyridine iron complexes

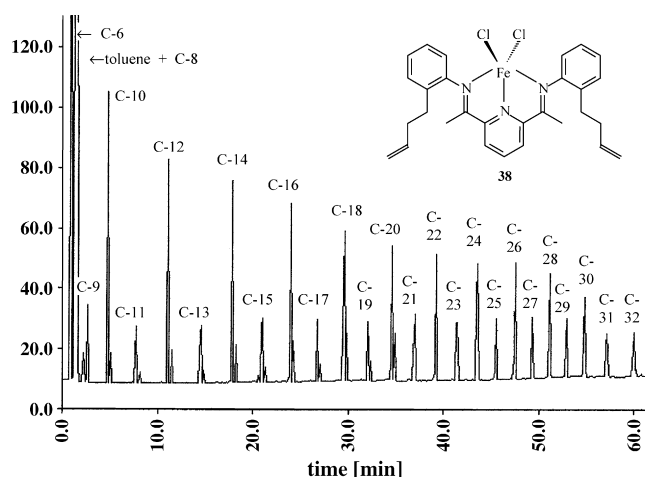
Complex	M_w (g/mol)	Allyl complex	M_w (g/mol)
45	9140	52	2170
46	90,950	53	114,200
47	148,000	54	55,400
49	281,800	56	317,600
51	313,000	58	352,400

results of Herrmann [12], prepolymerization of ethylene with the iron complexes **34–41** and **52–58** neither lead to changes in color intensity nor to color transfer from the reaction solution to the produced polymers indicating that the incorporation of the iron complexes into the polymer chain failed. The polymers were filtered from the solutions, washed with toluene and *n*-pentane and they were vacuum dried. When used as heterogeneous catalysts for the polymerization of ethylene in a 1 l Büchi laboratory autoclave, no polymerization activity could be observed. Therefore the tendency of 2,6-bis(arylimino)pyridine iron complexes towards copolymerization seems to be negligible. DFT calculations performed by Ramos et al. [32] confirmed the presented experimental data.

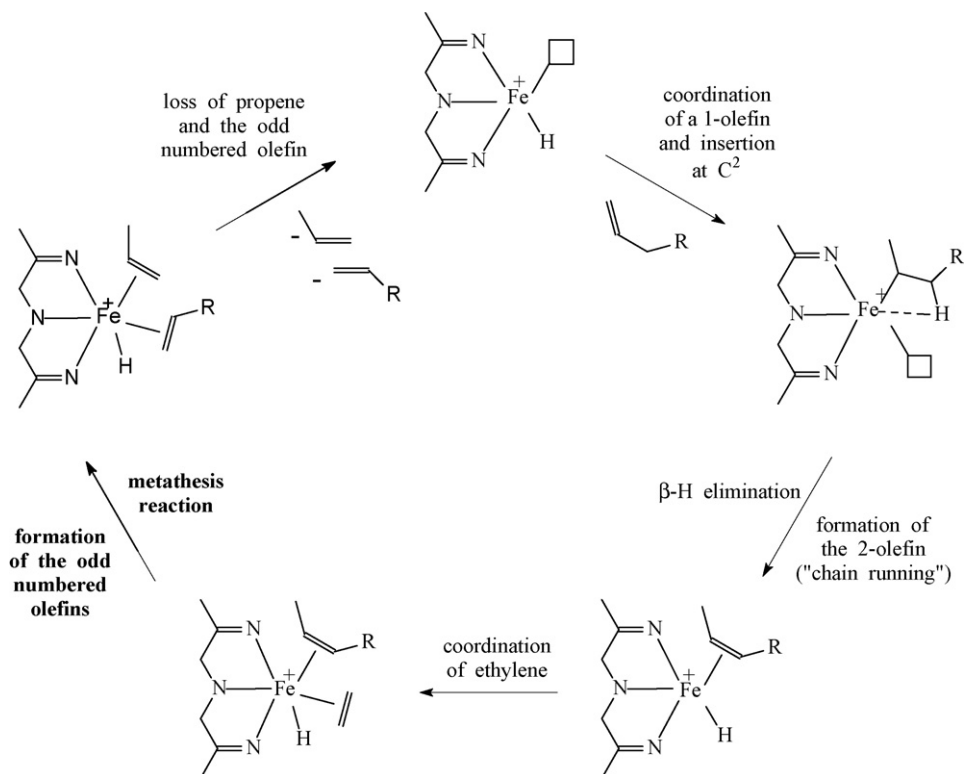
Despite of “no self-immobilization” of ω -alkenyl substituted 2,6-bis(arylimino)pyridine iron complexes, the analysis of the residual toluene solution from the reaction of **38**/MAO yielded a surprising result.

While **38**, when activated with MAO, produced only polyethylene at an ethylene pressure of 10 bar (see Table 1), the reaction solution of the prepolymerization run at 0.2 bar ethylene pressure also contained some oligomers. This kind of pressure dependence of the product composition was already described by Gibson [2] and Brookhart [4,5,33]. However, in case of complex **38**, odd numbered α -olefins were found in the gas chromatogram besides the expected even numbered 1-alkenes (see Scheme 16). The same phenomenon was described by Seitz [10] and Kestel-Jakob [34] for similar catalyst systems. GC/MS analyses were performed proving that the additional peaks in the gas chromatogram could be assigned to olefins with odd numbers of carbon atoms and do not belong to isomers of the even numbered olefins. The comparison of the mass spectra of the odd numbered olefins with reference spectra revealed the best consistency for the 1-olefins, since characteristic fission reactions were missing in the spectra. Nevertheless, the position of the double bond could not be determined undoubtedly.

While the concentrations of the even numbered α -olefins approximately obey to a poisson distribution ($\alpha = 0.96$), the con-



Scheme 16. Gas chromatogram of the oligomer fraction produced with **38**/MAO at an ethylene pressure of 0.2 bar.



Scheme 17. Proposed mechanism for the catalytic formation of odd numbered olefins.

centrations of the odd numbered compounds remained nearly constant. The overall percentage of odd numbered olefins in the solution was determined to 29%. Compared with complex **38**, the other ω -alkenyl substituted 2,6-bis(arylimino)pyridine iron complexes produced significantly lower amounts of odd numbered olefins (max. 5% of the overall yield) when applying the same reaction conditions.

Since β -hydrogen elimination as predominating chain termination reaction generally leads to 1-olefins (except the very first catalytic cycle when starting with an iron-methyl species), the formation of odd numbered olefins must follow another reaction pathway. A possible reaction scheme includes the “chain running” mechanism proposed by Brookhart [35] starting with an isomerization reaction of 1-olefins to give the corresponding 2-olefins. After β -hydrogen elimination, the 2-olefin remains in the coordination sphere of the metal center. Further coordination of an ethylene molecule may be followed by a metathesis reaction yielding propene and an odd numbered 1-olefin (see Scheme 17). This kind of metathesis reaction has already been established in our research group [10].

Complex **38** is the only iron(II) complex showing a dark violet color when activated with MAO indicating an intramolecular coordination of one of the terminal double bonds of the alkenyl groups to the cationic metal center, while all other synthesized iron(II) complexes changed their colors from blue to orange brown during activation. Therefore, intramolecular coordination of a terminal double bond seems to demand a spacer length of at least four carbon atoms.

3. Experimental

All experimental work was routinely carried out using Schlenk technique. Dried and purified argon was used as inert gas. *n*-Pentane, diethyl ether, toluene und tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride. Methylene chloride was dried with phosphorus pentoxide and calcium hydride. Methanol and ethanol were dried over molecular sieves. 1-Butanol (p.a.) was purchased from Merck and used without prior distillation. Deuterated solvents (CDCl_3 , CD_2Cl_2) for NMR spectroscopy were stored over molecular sieves (3 Å).

Methylalumoxane (30% in toluene) was purchased from Crompton (Bergkamen) and Albemarle (Baton Rouge, USA/Louvain, La Neuve, Belgium). Ethylene (3.0) und argon (4.8/5.0) were supplied by Rießner Company (Lichtenfels). All other starting materials were commercially available and were used without further purification.

3.1. NMR spectroscopy

The spectrometer Bruker ARX 250 was available for the recording of the NMR spectra. The samples were prepared under inert atmosphere (argon) and routinely recorded at 25 °C. The chemical shifts in the ^1H NMR spectra are referred to the residual proton signal of the solvent ($\delta = 7.24$ ppm for CDCl_3 , $\delta = 5.32$ ppm for CD_2Cl_2) and in ^{13}C NMR spectra to the solvent signal ($\delta = 77.0$ ppm for CDCl_3 , $\delta = 53.5$ ppm for CD_2Cl_2).

3.2. Mass spectrometry

Mass spectra were routinely recorded at the Zentrale Analytik of the University of Bayreuth with a VARIAN MAT CH-7 instrument (direct inlet, EI, $E=70$ eV) and a VARIAN MAT 8500 spectrometer.

3.3. GC/MS

GC/MS spectra were recorded with a HP 5890 gas chromatograph in combination with a HP 5971A mass detector. A 12 m J&W Scientific fused silica column (DB1, diameter 0.25 mm, film 0.33 μm , flow 1 ml/min), respectively 25 m J&W Scientific fused silica column (DB5ms, diameter 0.25 mm, film 0.33 μm , flow 1 ml/min) were used, helium (4.6) was applied as carrier gas. Using a 12 m column, the routinely performed temperature program started at 70 °C (2 min). After a heating phase of eleven minutes (20 K/min, final temperature 290 °C) the end temperature was held for a variable time (plateau phase).

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.

3.4. Gas chromatography

For the analysis of organic compounds, especially oligomer mixtures, a Perkin-Elmer Auto System gas chromatograph (column: HP1, 28 m, diameter 0.32 mm/carrier gas helium, flow 5.7 ml/min, split 3.5 ml/min) was used. The standard temperature program contained a starting phase at 50 °C (3 min), a heating phase of 50 min (heating rate 4 K/min, final temperature 250 °C) and a plateau phase at 250 °C (37 min).

3.5. Gel permeation chromatography (GPC)

GPC measurements were routinely performed by SABIC Company (Riyadh, Saudi Arabia).

3.6. Elemental analysis

Some of the analyses were performed by the Mikroanalytisches Labor Pascher, Remagen.

The residual analyses were performed with a VarioEl III CHN instrument. Therefore, 4–6 mg of the complex was weighed into a standard tin pan. The tin pan was carefully closed and introduced into the auto sampler of the instrument. The raw values of the carbon, hydrogen, and nitrogen contents were multiplied with calibration factors (calibration compound: acetamide).

3.7. Synthesis of 2-nitrobenzyl methylether (1) and 2-methoxymethyl aniline (2)

To a solution of 2-nitrobenzyl bromide (5.18 g/24 mmol) in 25 ml of methanol 9 ml (48 mmol) of a sodium methylate solution (30% in methanol) was added slowly at room

temperature. After 1 h 200 ml of a saturated sodium hydrogen-carbonate solution was added and the mixture was extracted with methylene chloride. The organic phase was washed again with saturated sodium hydrogencarbonate solution and brine and then dried over sodium sulfate. Removing the solvent yielded 2-nitrobenzyl methylether (3.3 g/83%) as a light brown solid.

For the reduction reaction 3.3 g (20 mmol) 2-nitrobenzyl methylether and 4.4 g (79 mmol/4 equiv.) iron powder were heated under reflux for 5 h in a 1:1 mixture of ethanol and glacial acetic acid (20 ml/20 ml). Then 150 ml of a sodium carbonate solution was added. Extraction with methylene chloride, drying the organic phase over sodium sulfate and final vacuum distillation gave 2-methoxymethyl aniline in a 77% yield (2.1 g) as colorless liquid.

3.8. Synthesis of the 2-alkoxymethyl anilines 3–5

2-Aminobenzyl alcohol (15 mmol) or 2-amino-6-methylbenzyl alcohol (15 mmol) were dissolved in 100 ml of methanol or *n*-butanol. Then 1.44 g (16 mmol) of concentrated sulfuric acid was slowly added and the mixture was stirred at 50 °C for 3 h. For neutralization, 100 ml of a sodium carbonate solution was added. Subsequent extraction with methylene chloride, drying of the organic phase over sodium sulfate and vacuum distillation furnished the alkoxymethyl anilines as viscous oils (55–75%).

3.9. Synthesis of the ω -alkenyl substituted anilines 6–9

To 17.5 ml (35 mmol) of a 2-M solution of the corresponding Grignard reagent in THF, 15 mmol of the desired 2-alkoxymethyl aniline in 200 ml THF were slowly added, whereby gas evolution could be observed. The mixture was stirred over night and afterwards hydrolyzed with 0.05-M hydrochloric acid. Extraction with methylene chloride, drying the organic phase over sodium sulfate and final vacuum distillation yielded the ω -alkenyl anilines as colorless liquids (yields: 32–65%).

3.10. Synthesis of 2-nitrostyrene (10) and 2-vinyl aniline (11)

An amount of 25 g (70 mmol) methyltriphenylphosphonium bromide was reacted with 35 ml (70 mmol) of a 2-M solution of sodium bis(trimethylsilyl)amide in THF. The mixture was stirred at 50 °C for 2 h. After cooling to room temperature 10.00 g (66 mmol) of 2-nitrobenzaldehyde were added to the bright yellow phosphorane solution and the mixture was stirred over night. Filtration over sodium sulfate and silica, removing the solvent with a rotary evaporator and subsequent vacuum distillation yielded 2-nitrostyrene as a bright yellow liquid (m.p. -12 °C, b.p. 66 °C_[0.1 Torr], yield 26%).

The reduction of 2-nitrostyrene was performed according to the method described in Section 3.7 yielding 2-vinyl aniline as a colorless liquid (yield: 64%, b.p. 46 °C_[0.1 Torr]).

Table 4
NMR and MS data for compounds 1–33

Compound	¹ H NMR	¹³ C NMR	MS (<i>m/z</i>)
1	8.08 dd (1H, Ar–H), 7.88 dd (1H, Ar–H), 7.67 ψ -td (1H, Ar–H), 7.45 ψ -td (1H, Ar–H), 4.86 s (2H, CH ₂), 3.51 s (3H, CH ₃)	147.0, 135.2 (C _q), 133.7, 128.4, 127.9, 124.6 (Ar–CH), 71.1 (CH ₂), 58.9 (CH ₃)	167 M ^{o+} (1), 135 M – MeOH (28), 121 M – NO ₂ (11), 79 (100)
2	7.06–7.18 m (2H, Ar–H), 6.71–6.79 m (2H, Ar–H), 4.47 s (2H, CH ₂), 3.48 s (3H, CH ₃), 2.26 s (b, 2H, NH ₂)	146.2, 122.0 (C _q), 130.0, 129.2, 118.0, 115.9 (Ar–CH), 73.7 (CH ₂), 57.4 (CH ₃)	137 M ^{o+} (100), 122 M – Me (35), 106 M – OMe (90), 105 M – MeOH (87)
3	7.08–7.16 m (2H, Ar–H), 6.75–6.81 m (2H, Ar–H), 4.55 s (2H, CH ₂), 4.52 s (b, 2H, NH ₂), 3.62 t (2H, O–CH ₂), 1.55 m (2H, CH ₂), 1.38 m (2H, CH ₂), 0.93 t (3H, CH ₃)	145.0, 123.2 (C _q), 129.8, 129.5, 118.7, 116.4 (Ar–CH), 71.9, 69.7, 31.2, 19.4 (CH ₂), 13.9 (CH ₃)	179 M ^{o+} (35), 122 M – <i>n</i> -Bu (29), 106 M – OBU (100)
4	6.86–6.81 m (1H, Ar–H), 6.71–6.74 m (2H, Ar–H), 4.41 s (2H, CH ₂), 4.22 s (b, 2H, NH ₂), 3.49 s (3H, CH ₃), 2.93 s (3H, CH ₃)	147.6, 127.4, 124.5 (C _q), 128.9, 125.1, 118.6 (Ar–CH), 73.6 (CH ₂), 58.0, 17.3 (CH ₃)	151 M ^{o+} (90), 136 M – Me (21), 120 M – OMe (72), 119 M – MeOH (100)
5	7.12–7.19 m (1H, Ar–H), 6.76–7.01 m (2H, Ar–H), 4.67 s (2H, CH ₂), 4.35 s (b, 2H, NH ₂), 3.59 t (2H, O–CH ₂), 2.99 s (3H, CH ₃), 1.75 m (2H, CH ₂), 1.52 m (2H, CH ₂), 0.80 t (3H, CH ₃)	144.7, 125.6, 122.2 (C _q), 130.6, 127.9, 117.4 (Ar–CH), 72.4, 69.4, 32.0, 19.6 (CH ₂), 17.4, 14.1 (CH ₃)	193 M ^{o+} (59), 136 M – <i>n</i> -Bu (30), 120 M – OBU (90), 119 M – BuOH (100)
6	7.06–7.14 m (2H, Ar–H), 6.75–6.84 m (2H, Ar–H), 5.92–6.10 m (1H, =CH), 5.09–5.17 m (2H, =CH ₂), 3.69 s (b, 2H, NH ₂), 3.34 m (2H, CH ₂)	144.8, 123.9 (C _q), 135.9 (=CH) 130.1, 127.5, 118.8, 115.8 (Ar–CH), 116.0 (=CH ₂), 36.5 (CH ₂)	133 M ^{o+} (100), 132 M – H (56), 118 M – Me (63), 106 M – Vinyl (48)
7	6.96–7.04 m (2H, Ar–H), 6.72 ψ -t (1H, Ar–H), 5.94–6.12 m (1H, =CH), 5.12–5.20 m (2H, =CH ₂), 3.68 s (b, 2H, NH ₂), 3.34–3.38 m (2H, CH ₂) 2.22 s (3H, CH ₃)	143.0, 123.3, 122.3 (C _q) 136.1 (=CH), 128.8, 128.0, 118.1 (Ar–CH), 116.1 (=CH ₂), 36.8 (CH ₂), 17.6 (CH ₃)	147 M ^{o+} (100), 132 M – Me (92), 120 M – Vinyl (26)
8	7.13–7.19 m (2H, Ar–H), 6.75–6.87 m (2H, Ar–H), 5.94–6.13 m (1H, =CH), 5.12–5.26 m (2H, =CH ₂), 3.70 s (b, 2H, NH ₂), 2.66–2.73 m (2H, CH ₂), 2.48–2.54 m (2H, CH ₂)	144.2, 126.0 (C _q), 138.2 (=CH) 129.5, 127.1, 118.8, 115.7 (Ar–CH), 115.2 (=CH ₂), 32.9, 30.8 (CH ₂)	147 M ^{o+} (18), 106 M – Allyl (100)
9	6.97 d (2H, Ar–H), 6.69 t (1H, Ar–H) 5.89–6.00 m (1H, =CH), 5.01–5.16 m (2H, =CH ₂), 3.63 s (b, 2H, NH ₂), 2.59–2.65 m (2H, CH ₂) 2.36–2.45 m (2H, CH ₂), 2.21 s (3H, CH ₃)	142.7, 125.5, 122.8 (C _q) 138.2 (=CH), 128.4, 127.1, 118.0 (Ar–CH), 115.0 (=CH ₂), 32.8, 31.0 (CH ₂) 17.8 (CH ₃)	161 M ^{o+} (16), 120 M – Allyl (100)
10	7.91–7.95 m (1H, Ar–H), 7.59–7.65 m (2H, Ar–H), 7.38–7.45 m (1H, Ar–H) 7.18 dd (1H, =CH), 5.75 dd (1H, =CH ₂) 5.48 dd (1H, =CH ₂)	147.8, 133.3 (C _q), 132.4 (=CH), 134.0, 128.5, 128.3, 124.4 (Ar–CH), 118.9 (=CH ₂)	149 M ^{o+} (2), 132 M – OH (54), 120 (63), 77 (100)
11	7.31–7.36 m (1H, Ar–H), 7.08–7.16 m (1H, Ar–H), 6.80–6.85 m (2H, Ar–H), 6.71 dd (1H, =CH), 5.68 dd (1H, =CH ₂), 5.36 dd (1H, =CH ₂), 3.97 s (b, 2H, NH ₂)	143.6, 124.1 (C _q), 132.7 (=CH), 128.7, 127.3, 119.0, 116.1 (Ar–CH), 115.7 (=CH ₂)	119 M ^{o+} (100), 118 M – H (82), 91 M – ethene (53)
12	8.44 d (2H, PyH ₃), 7.84 t (1H, PyH ₄), 7.25–7.35 m (4H, Ar–H), 7.06–7.18 m (4H, Ar–H), 6.73 dd (2H, =CH), 5.71 dd (2H, =CH ₂), 5.21 dd (2H, =CH ₂), 2.35 s (6H, CH ₃)	167.8, 162.1, 154.0, 127.3 (C _q) 132.9 (=CH), 137.2, 128.3, 127.8, 125.9, 123.8, 122.4 (Ar–CH), 114.4 (=CH ₂), 16.6 (CH ₃)	365 M ^{o+} (66), 350 M – Me (33), 337 M – ethene (100)
13	8.46 d (2H, PyH ₃), 7.96 t (1H, PyH ₄), 7.09–7.34 m (4H, Ar–H), 6.66–6.80 m (4H, Ar–H), 5.90–6.09 m (2H, =CH), 5.06–5.37 m (4H, =CH ₂), 3.81 dd (2H, CH ₂), 3.35 dd (2H, CH ₂), 2.43 s (6H, CH ₃)	166.5, 155.8, 149.4, 130.1 (C _q), 138.0 (=CH), 135.4, 129.2, 127.5, 124.8, 122.6, 122.3 (Ar–CH), 113.1 (=CH ₂), 36.2 (CH ₂), 16.4 (CH ₃)	393 M ^{o+} (100), 378 M – Me (86)
14	8.41 d (2H, PyH ₃), 7.92 t (1H, PyH ₄), 7.21–7.28 m (4H, Ar–H), 7.09–7.13 m (2H, Ar–H), 6.68–6.72 m (2H, Ar–H), 5.76–5.93 m (2H, =CH), 4.92–5.04 m (4H, =CH ₂), 2.59–2.66 m (2H, CH ₂), 2.40 s (6H, CH ₃), 2.32–2.39 m (2H, CH ₂)	166.7, 155.4, 149.5, 131.4 (C _q) 138.3 (=CH), 136.9, 129.7, 126.7, 123.9, 122.3, 118.6 (Ar–CH), 114.9 (=CH ₂), 33.9, 31.6 (CH ₂), 16.6 (CH ₃)	421 M ^{o+} (100), 406 M – Me (40), 380 M – Allyl (71)
15	8.28 d (2H, PyH ₃), 7.80 t (1H, PyH ₄), 6.86 d (4H, Ar–H), 6.53 t (2H, Ar–H), 5.77–5.88 m (2H, =CH), 4.84–4.98 m (4H, =CH ₂), 2.38–2.44 m (4H, CH ₂), 2.04 s (6H, CH ₃), 1.98 s (6H, CH ₃)	163.2, 160.4, 149.4, 132.1, 128.2 (C _q), 142.0 (=CH), 133.8, 128.7, 128.0, 126.9, 124.5 (Ar–CH), 114.7 (=CH ₂), 34.8 (CH ₂), 17.8, 16.4 (CH ₃)	421 M ^{o+} (100), 406 M – Me (63)
16	8.25 d (2H, PyH ₃), 7.70 t (1H, PyH ₄), 6.88 d (4H, Ar–H), 6.75 t (2H, Ar–H), 5.50–5.77 m (2H, =CH), 4.67–4.83 m (4H, =CH ₂), 2.38–2.44 m (4H, CH ₂), 2.09–2.30 m (4H, CH ₂), 2.04 s (6H, CH ₃), 1.83 s (6H, CH ₃)	167.2, 155.1, 148.4, 126.0 (C _q) 138.5 (=CH), 136.9, 128.2, 126.9, 123.3, 122.2 (Ar–CH), 115.0 (=CH ₂), 33.4, 31.5 (CH ₂), 17.9, 16.4 (CH ₃)	449 M ^{o+} (89), 434 M – Me (95), 408 M – Allyl (100)

Table 4 (Continued)

Compound	¹ H NMR	¹³ C NMR	MS (<i>m/z</i>)
17	8.50 d (2H, Py _{H3}), 7.91 t (1H, Py _{H4}), 7.24–7.34 m (4H, Ar–H), 7.11–7.17 m (2H, Ar–H), 6.73–6.76 m (2H, Ar–H), 2.61 q (4H, CH ₂), 2.47 s (6H, CH ₃), 1.24 t (6H, CH ₃)	166.6, 155.5, 149.4, 133.5 (C _q) 136.9, 128.7, 126.4, 123.9, 122.3, 118.3 (Ar–CH), 24.9 (CH ₂), 16.4, 14.2 (CH ₃)	369 M ^{o+} (52), 354 M – Me (100)
18	8.40 d (2H, Py _{H3}), 7.90 t (1H, Py _{H4}), 7.20–7.25 m (4H, Ar–H), 7.06–7.10 m (2H, Ar–H), 6.65–6.69 m (2H, Ar–H), 2.45 t (4H, CH ₂), 2.37 s (6H, CH ₃), 1.50–1.64 m (4H, CH ₂), 0.90 t (6H, CH ₃)	166.5, 155.4, 149.4, 132.1 (C _q) 136.8, 129.6, 126.3, 123.7, 122.1, 118.3 (Ar–CH), 33.8, 22.9 (CH ₂), 16.4, 14.1 (CH ₃)	397 M ^{o+} (81), 382 M – Me (78), 368 M – Et (100)
19	8.41 d (2H, Py _{H3}), 7.91 t (1H, Py _{H4}), 7.19–7.28 m (4H, Ar–H), 7.06–7.11 m (2H, Ar–H), 6.67–6.70 m (2H, Ar–H), 2.52 t (4H, CH ₂), 2.39 s (6H, CH ₃), 1.52–1.61 m (4H, CH ₂), 1.32–1.41 m (4H, CH ₂), 0.89 t (6H, CH ₃)	166.5, 155.5, 149.4, 132.3 (C _q) 136.8, 129.5, 126.3, 123.7, 122.1, 118.3 (Ar–CH), 31.9, 31.3, 22.5 (CH ₂), 16.3, 13.9 (CH ₃)	425 M ^{o+} (69), 410 M – Me (54), 382 M – <i>n</i> -Pr (100)
20	8.38 d (2H, Py _{H3}), 7.88 t (1H, Py _{H4}), 7.12 d (2H, Ar–H), 6.86 d (2H, Ar–H), 6.52 s (2H, Ar–H), 2.33 s (6H, CH ₃), 2.31 s (6H, CH ₃), 2.05 s (6H, CH ₃)	167.7, 155.2, 148.6, 132.0, 125.7 (C _q), 137.1, 131.5, 128.9, 124.8, 123.4 (Ar–CH), 25.9, 18.2, 16.5 (CH ₃)	369 M ^{o+} (68), 354 M – Me (100)
21	8.56 d (2H, Py _{H3}), 7.94 t (1H, Py _{H4}), 6.97–7.15 m (6H, Ar–H), 2.25 s (6H, CH ₃) 2.12 s (12H, CH ₃)	167.2 155.1, 148.8, 125.4 (C _q) 136.9, 128.0, 123.1, 122.3 (Ar–CH), 18.0, 16.5 (CH ₃)	369 M ^{o+} (37), 354 M – Me (100)
22	8.53 d (2H, Py _{H3}), 7.92 t (1H, Py _{H4}), 6.95 s (4H, Ar–H), 2.35 s (6H, CH ₃), 2.30 s (6H, CH ₃), 2.08 s (12H, CH ₃)	167.4, 155.2, 146.3, 132.2, 125.3 (C _q), 136.8, 128.6, 122.2 (Ar–CH) 20.8, 17.9, 16.4 (CH ₃)	397 M ^{o+} (41), 382 M – Me (100)
23	8.53 d (2H, Py _{H3}), 7.94 t (1H, Py _{H4}), 7.20–7.24 m (2H, Ar–H), 7.03–7.13 m (4H, Ar–H), 2.88 sept (2H, CH), 2.31 s (6H, CH ₃), 2.08 s (6H, CH ₃), 1.25 d (6H, CH ₃), 1.19 d (6H, CH ₃)	167.2, 155.1, 147.5, 136.3, 125.1 (C _q), 136.9, 127.8, 123.4, 123.2, 122.3 (Ar–CH), 28.4 (CH ₂), 23.2, 22.9, 18.2, 16.8 (CH ₃)	425 M ^{o+} (100), 410 M – Me (50)
24	8.50 d (2H, Py _{H3}), 7.93 t (1H, Py _{H4}), 7.07–7.20 m (6H, Ar–H), 2.77 sept (2H, CH), 2.28 s (6H, CH ₃) 1.16 d (12H, CH ₃)	167.4, 155.0, 146.0, 135.8 (C _q) 136.9, 123.6, 123.0, 122.3 (Ar–CH), 28.3 (CH), 23.2, 17.1 (CH ₃)	481 M ^{o+} (58), 466 M – Me (100)
25	8.57 d (2H, Py _{H3}), 7.96 t (1H, Py _{H4}) 7.08–7.22 m (6H, Ar–H), 2.39–2.60 m (8H, CH ₂), 2.35 s (6H, CH ₃), 1.23 t (12H, CH ₃)	167.0, 155.2, 147.8, 131.2 (C _q) 137.0, 126.0, 123.4, 122.3 (Ar–CH), 24.7 (CH ₂), 16.9, 13.8 (CH ₃)	425 M ^{o+} (28), 410 M – Me (100)
26	8.42 d (2H, Py _{H3}), 7.93 t (1H, Py _{H4}), 7.43–7.46 m (2H, Ar–H), 7.07–7.24 m (4H, Ar–H), 6.55–6.58 m (2H, Ar–H), 2.43 s (6H, CH ₃), 1.39 s (18H, CH ₃)	165.3, 155.6, 149.7, 139.7 (C _q) 136.9, 126.4, 126.3, 123.8, 122.3, 119.8 (Ar–CH), 35.2 (CH), 29.6, 16.9 (CH ₃)	425 M ^{o+} (100), 410 M – Me (68)
27	8.10 d (1H, Py _{H3}), 7.97 d (1H, Py _{H3}), 7.87 ψ-t (1H, Py _{H4}), 7.02–7.26 m (2H, Ar–H), 7.00 s (2H, Ar–H), 6.52–6.83 m (2H, Ar–H), 5.32–5.50 m (1H, =CH) 4.56–4.85 m (2H, =CH ₂) 2.67–3.12 m (2H, CH ₂) 2.28–2.49 m (2H, CH ₂) 2.08, 2.05, 2.03, 1.98 s (12H, Ar–CH ₃) 1.82 s (3H, N=C–CH ₃)	165.7, 164.9 (C _q , C=N), 156.2, 155.8 (C _q , PyC ₂), 147.5, 147.3 (C _q , C=N), 138.1 (=CH), 135.3 (CH, PyC ₄), 134.9 (C _q , ArylC ₅), 131.5 (CH, ArylC ₃), 128.6, 128.2 (CH, ArylC ₆), 129.0, 128.7 (C _q , ArylC ₂), 124.5 (CH, PyC ₃), 123.5 (CH, ArylC ₄), 111.9 (=CH ₂), 33.3, 24.6 (CH ₂), 25.9, 25.3, 18.2, 17.9 (Ar–CH ₃), 16.4 (N=C–CH ₃)	409 M ^{o+} (37), 394 M – Me (17), 368 M – Allyl (100), 354 M – Butenyl (38)
28	8.33–8.49 m (2H, Py _{H3}), 7.68–7.78 m (1H, Py _{H4}), 6.74–7.00 m (6H, Ar–H), 5.32–5.55 m (1H, =CH), 4.59–4.80 m (2H, =CH ₂), 2.51–2.61 m (2H, CH ₂), 2.23–2.43 m (2H, CH ₂), 2.06, 2.03, 2.01, 2.00 s (12H, Ar–CH ₃) 1.86 s (3H, N=C–CH ₃)	164.0, 163.2 (C _q , C=N), 155.5, 155.0 (C _q , PyC ₂), 150.4, 150.3 (C _q , C=N), 137.6 (=CH), 135.3 (CH, PyC ₄), 128.1 (CH, ArylC _{3/5}), 127.9, 127.6 (C _q , ArylC _{2/6}), 124.5, 124.4 (CH, PyC ₃), 124.3 (CH, ArylC ₄), 114.0 (=CH ₂), 33.3, 24.7 (CH ₂), 18.2, 18.0, 17.9, 17.8 (Ar–CH ₃), 16.5 (N=C–CH ₃)	409 M ^{o+} (82), 394 M – Me (63), 368 M – Allyl (22), 354 M – Butenyl (100)
29	8.60–8.69 m (2H, Py _{H3}), 7.93–8.00 m (1H, Py _{H4}), 6.89–6.90 m (4H, Ar–H), 5.60–5.65 m (1H, =CH), 4.83–4.87 m (2H, =CH ₂), 2.81–2.75 m (2H, CH ₂), 2.15–2.32 m (2H, CH ₂), 2.32, 2.28, 2.28, 2.27, 2.20, 2.06, 2.05 s (21H, CH ₃)	164.0, 163.2 (C _q , C=N), 155.5, 155.0 (C _q , PyC ₂), 150.6, 150.5 (C _q , C=N), 138.1 (=CH), 135.3 (CH, PyC ₄), 133.4, 133.1 (C _q , ArylC _{2/6}), 128.6 (CH, ArylC _{3/5}), 127.4 (C _q , ArylC ₄), 124.5, 124.4 (CH, PyC ₃), 113.9 (=CH ₂), 33.3, 24.6 (CH ₂), 20.4 (2 signals), 18.9 (4 signals) (Ar–CH ₃), 16.4 (N=C–CH ₃)	437 M ^{o+} (69), 422 M – Me (57), 396 M – Allyl (23), 382 M – Butenyl (100)

Table 4 (Continued)

Compound	¹ H NMR	¹³ C NMR	MS (<i>m/z</i>)
30	8.40–8.52 m (2H, Py _{H3}), 7.93 t (1H, Py _{H4}), 6.99–7.23 m (6H, Ar–H), 5.57–5.76 m (1H, =CH), 4.81–4.90 m (2H, =CH ₂), 2.85–2.73 m (4H, CH ₂ /2 ⁱ Pr–CH), 2.15–2.33 m (2H, CH ₂), 2.24 s (3H, N=C–CH ₃), 2.06, 2.04 s (6H, Ar–CH ₃), 1.12–1.24 m (12H, ⁱ Pr–CH ₃)	166.0, 165.1 (C _q , C=N), 155.1, 154.6 (C _q , PyC ₂), 145.6, 145.5 (C _q , C–N), 139.0, 138.7 (C _q , ArylC _{2/6}), 138.1 (=CH), 135.8 (CH, PyC ₄), 129.0 (2 signals; CH, ArylC ₅), 127.8, 127.4 (C _q , ArylC ₆), 124.7 (2 signals; CH, PyC ₃), 122.9 (2 signals; CH, ArylC ₃), 122.6 (2 signals; CH, ArylC ₄), 115.1 (=CH ₂), 31.5, 26.3 (CH ₂), 28.2 (2 signals; ⁱ Pr–CH), 23.5, 22.1 (ⁱ Pr–CH ₃), 18.8, 18.6 (Ar–CH ₃), 16.4 (N=C–CH ₃)	465 M ^{o+} (76), 450 M – Me (30), 424 M – Allyl (11), 410 M – Butenyl (100)
31	8.35–8.44 m (2H, Py _{H3}), 7.93 t (1H, Py _{H4}), 7.07–7.18 m (6H, Ar–H), 5.58–5.79 m (1H, =CH), 4.81–4.90 m (2H, =CH ₂), 2.72–2.85 m (4H, CH ₂ /2 ⁱ Pr–CH), 2.20–2.29 m (2H, CH ₂), 2.24 s (3H, N=C–CH ₃), 1.12 1.26 m (24H, ⁱ Pr–CH ₃)	167.9, 167.1 (C _q , C=N), 154.7, 154.2 (C _q , PyC ₂), 146.1, 146.0 (C _q , C–N), 138.9, 138.6 (C _q , ArylC _{2/6}), 136.9 (=CH), 135.3 (CH, PyC ₄), 123.9, 123.8 (CH, PyC ₃), 123.1, 123.0 (CH, ArylC _{3/5}), 122.5, 122.3 (CH, ArylC ₄), 114.7 (=CH ₂), 31.5, 26.3 (CH ₂), 28.2 (2 signals; ⁱ Pr–CH), 23.3, 22.1 (ⁱ Pr–CH ₃), 18.8, 18.6 (Ar–CH ₃), 16.4 (N=C–CH ₃)	521 M ^{o+} (30), 506 M – Me (8), 478 M – C ₃ H ₇ (13), 466 M – Butenyl (32), 242 Ar–N=C ₅ H ₇ (100)
32	8.42–8.53 m (2H, Py _{H3}), 7.94 t (1H, Py _{H4}), 7.01–7.14 m (6H, Ar–H), 5.57–5.73 m (1H, =CH), 4.81–4.90 m (2H, =CH ₂), 2.74–2.77 m (2H, CH ₂), 2.20–2.57 m (10H, CH ₂), 2.34 s (3H, N=C–CH ₃), 1.17 t (6H, CH ₃), 1.15 t (6H, CH ₃)	168.0, 167.6 (C _q , C=N), 155.4, 155.3 (C _q , PyC ₂), 147.8, 147.6 (C _q , C–N), 138.3 (=CH), 137.5 (CH, PyC ₄), 130.7, 130.2 (C _q , ArylC _{2/6}), 126.0, 125.8 (CH, ArylC _{3/5}), 123.6, 123.4 (CH, PyC ₃), 122.5, 122.3 (CH, ArylC ₄), 114.5 (=CH ₂), 31.6, 30.3 (CH ₂), 17.2 (N=C–CH ₃), 13.7, 13.4 (CH ₃)	465 M ^{o+} (58), 450 M – Me (79), 436 M – Et (25), 410 M – Butenyl (100)
33	8.33–8.50 m (2H, Py _{H3}), 7.87–7.93 m (1H, Py _{H4}), 7.40–7.43 m (2H, Ar–H), 7.07–7.23 m (4H, Ar–H), 6.51–6.59 m (2H, Ar–H), 5.70–5.97 m (1H, =CH), 4.80–5.06 m (2H, =CH ₂), 2.87–2.93 m (2H, CH ₂), 2.37–2.54 m (2H, CH ₂), 2.38 s (3H, N=C–CH ₃), 1.54 (9H, ^t Bu), 1.35, 1.33, 1.32 s (9H, ^t Bu)	171.3, 170.5 (C _q , C=N), 155.6, 155.5 (C _q , PyC ₂), 149.7, 149.5 (C _q , C–N), 139.4, 139.1 (C _q , ArylC _{2/6}), 137.6 (=CH), 136.5 (CH, PyC ₄), 127.9, 127.8 (CH, ArylC ₃), 126.4, 126.3 (CH, ArylC ₅), 124.0, 123.8 (CH, PyC ₃), 123.2, 122.9 (CH, ArylC ₄), 119.8, 119.6 (CH, ArylC ₂), 115.0 (=CH ₂), 33.8, 33.6 (C _q , ^t Bu) 31.0 (CH ₃ , ^t Bu), 29.7, 29.6, 29.5 (CH ₃ , ^t Bu), 31.8, 27.3 (CH ₂), 16.6 (N=C–CH ₃)	465 M ^{o+} (58), 450 M – Me (11), 424 M – Allyl (100), 410 M – Butenyl (28)

3.11. Synthesis of the 2,6-bis(arylimino)pyridine compounds 12–16

To a solution of 0.33 g (2 mmol) 2,6-diacetylpyridine in 20 ml of ethanol 5 mmol of the appropriate aniline and a few drops of glacial acetic acid were added. The mixture was heated under reflux for 1–4 days depending on the aniline. Some of the imine compounds already precipitated when cooling down the solution to room temperature and the products could be filtered. If the compound did not precipitate from the reaction solution, the mixture was filtered over sodium sulfate and silica and the solvent was removed in vacuo. After addition of 10 ml of ethanol and storage at –20 °C for some days these compounds also precipitated (yields: 38–75%).

3.12. Synthesis of the 2,6-bis(arylimino)pyridine compounds 17–26

To a solution of 0.82 g (5 mmol) 2,6-diacetylpyridine in 150 ml of toluene were added 12.5 mmol (2.5 equiv.) of an alkyl

substituted aniline and a few milligrams of para-toluenesulfonic acid. The reaction mixture was heated under reflux for 8–24 h applying a Dean-Stark-trap. After cooling down to room temperature, 200 ml of a saturated sodium hydrogencarbonate solution were added, the organic phase was separated, filtered over sodium sulfate and silica. The solvent was removed and 10 ml ethanol were added. The imino compounds precipitated when stored at –20 °C for some days (yields: 50–80%).

3.13. Synthesis of the allylated 2,6-bis(arylimino)pyridines 27–33

An amount of 1.0 mmol of the bis(arylimino)pyridine precursor was dissolved in 20 ml of THF. At room temperature, 0.5 ml (1.0 mmol) of a 2-M solution of sodium bis(trimethylsilyl)amide in THF were added resulting in a color change from yellow to dark violet. After 2 h, the mixture was treated with 1.0 mmol (0.09 ml) allyl bromide and then stirred at room temperature for 20 h. The solvent and bis(trimethylsilyl)amine were removed in vacuo, the residue was extracted with *n*-pentane and filtered

Table 5
MS, ^1H NMR, and elemental analysis data of the iron complexes **34–58**

Complex	MS (m/z)	^1H NMR	C_{exp} (%)	C_{theor} (%)	H_{exp} (%)	H_{theor} (%)	N_{exp} (%)	N_{theor} (%)
34	491 $\text{M}^{\text{O}+}$ (2), 425 $\text{M} - 2$ ethene (11), 336 $\text{M} - \text{FeCl}_2 - \text{ethane} - \text{H}$ (45), 144 $\text{Me} - \text{C}=\text{N}(\text{C}_8\text{H}_7)$ (62)	82.61, 81.79 (2H, $\text{Py}_{\text{H}3/5}$), 38.43 (1H, $\text{Py}_{\text{H}4}$), 18.60, 11.12, -15.73 , -18.93 (8H, Ar-H), 13.90, -12.17 , -12.92 (6H, $=\text{CH}=\text{CH}_2$), -24.57 (6H, $\text{N}=\text{C}-\text{CH}_3$)	59.8	61.0	4.87	4.71	8.61	8.54
35	526 $\text{M}^{\text{O}+}$ (2), 365 $\text{M} - \text{FeCl}_2$ (5), 350 $\text{M} - \text{FeCl}_2 - \text{Me}$ (7), 144 $\text{Me} - \text{C}=\text{N}(\text{C}_8\text{H}_7)$ (15)	–	56.5	56.9	4.59	4.39	7.90	7.96
36	519 $\text{M}^{\text{O}+}$ (15), 484 $\text{M} - \text{Cl}$ (10), 393 $\text{M} - \text{FeCl}_2$ (62), 378 $\text{M} - \text{FeCl}_2 - \text{Me}$ (58)	–	61.7	62.3	5.32	5.23	7.97	8.08
37	555 $\text{M}^{\text{O}+}$ (2), 458 $\text{M} - 3$ Cl (1), 393 $\text{M} - \text{FeCl}_3$ (48), 378 $\text{M} - \text{FeCl}_2 - \text{Me}$ (45)	–	57.8	58.4	4.87	4.90	7.35	7.56
38	547 $\text{M}^{\text{O}+}$ (13), 512 $\text{M} - \text{Cl}$ (4), 421 $\text{M} - \text{FeCl}_2$ (100), 406 $\text{M} - \text{FeCl}_2 - \text{Me}$ (45), 380 $\text{M} - \text{FeCl}_2 - \text{Allyl}$ (63)	81.16, 79.35 (2H, $\text{Py}_{\text{H}3/5}$), 34.54 (1H, $\text{Py}_{\text{H}4}$), 2.11, 2.06, -14.20 , -21.61 (8H, Ar-H), -30.24 (6H, $\text{N}=\text{C}-\text{CH}_3$) (signals for alkenyl groups could not be assigned)	63.1	63.5	5.62	5.70	7.63	7.66
39	582 $\text{M}^{\text{O}+}$ (1), 547 $\text{M} - \text{Cl}$ (2), 421 $\text{M} - \text{FeCl}_3$ (41), 406 $\text{M} - \text{FeCl}_2 - \text{Me}$ (34)	–	59.0	59.7	5.34	5.35	7.19	7.20
40	575 $\text{M}^{\text{O}+}$ (20), 540 $\text{M} - \text{Cl}$ (7), 449 $\text{M} - \text{FeCl}_2$ (100), 434 $\text{M} - \text{FeCl}_2 - \text{Me}$ (84), 408 $\text{M} - \text{FeCl}_2 - \text{Allyl}$ (89)	–	64.3	64.6	6.03	6.12	7.34	7.29
41	611 $\text{M}^{\text{O}+}$ (2), 449 $\text{M} - \text{FeCl}_3$ (5), 434 $\text{M} - \text{FeCl}_3 - \text{Me}$ (6), 185 $\text{Me} - \text{C}=\text{N}(\text{C}_{11}\text{H}_{13})$ (100)	–	60.0	60.9	5.66	5.77	6.75	6.87
42	495 $\text{M}^{\text{O}+}$ (5), 369 $\text{M} - \text{FeCl}_2$ (61), 354 $\text{M} - \text{FeCl}_2 - \text{Me}$ (100)	81.33 (1H, $\text{Py}_{\text{H}4}$), 79.73 (2H, $\text{Py}_{\text{H}3/5}$), 15.68 (4H, CH_2), 9.32 (6H, CH_3), 2.87, -1.57 , -14.31 , -20.60 (8H, Ar-H), -28.90 (6H, $\text{N}=\text{C}-\text{CH}_3$)	60.8	60.5	5.38	5.48	8.37	8.47
43	523 $\text{M}^{\text{O}+}$ (1), 397 $\text{M} - \text{FeCl}_2$ (47), 382 $\text{M} - \text{FeCl}_2 - \text{Me}$ (66), 368 $\text{M} - \text{FeCl}_2 - \text{Et}$ (100)	80.74, 79.05 (2H, $\text{Py}_{\text{H}3/5}$), 34.64 (1H, $\text{Py}_{\text{H}4}$), 9.41, 1.29, -13.52 , -20.36 (8H, Ar-H), -29.27 (6H, $\text{N}=\text{C}-\text{CH}_3$) (signals for propyl groups could not be assigned)	61.4	61.8	6.04	5.96	8.05	8.01
44	551 $\text{M}^{\text{O}+}$ (14), 516 $\text{M} - \text{Cl}$ (5), 501 $\text{M} - \text{Me} - \text{Cl}$ (11), 425 $\text{M} - \text{FeCl}_2$ (51), 410 $\text{M} - \text{FeCl}_2 - \text{Me}$ (54), 396 $\text{M} - \text{FeCl}_2 - \text{Et}$ (28), 382 $\text{M} - \text{FeCl}_2 - \text{Propyl}$ (100)	81.50, 79.77 (2H, $\text{Py}_{\text{H}3/5}$), 40.06 (1H, $\text{Py}_{\text{H}4}$), 17.73, 8.69, -14.50 , -22.48 (8H, Ar-H), -31.61 (6H, $\text{N}=\text{C}-\text{CH}_3$) (signals for butyl groups could not be assigned)	62.3	63.1	6.32	6.39	7.63	7.61
45	495 $\text{M}^{\text{O}+}$ (26), 460 $\text{M} - \text{Cl}$ (10), 369 $\text{M} - \text{FeCl}_2$ (61), 354 $\text{M} - \text{FeCl}_2 - \text{Me}$ (100)	80.57, 79.00 (2H, $\text{Py}_{\text{H}3/5}$), 37.46 (1H, $\text{Py}_{\text{H}4}$), 19.21, 15.43 (6H, 6H, Ar- CH_3), -4.31 , -9.70 , -17.85 (6H, Ar-H), -23.26 (6H, $\text{N}=\text{C}-\text{CH}_3$)	60.2	60.5	5.43	5.48	8.38	8.47
46	495 $\text{M}^{\text{O}+}$ (24), 460 $\text{M} - \text{Cl}$ (15), 444 $\text{M} - \text{Cl} - \text{H} - \text{Me}$ (26), 369 $\text{M} - \text{FeCl}_2$ (37), 354 $\text{M} - \text{FeCl}_2 - \text{Me}$ (100)	86.19 (2H, $\text{Py}_{\text{H}3/5}$), 39.60 (1H, $\text{Py}_{\text{H}4}$), 16.28 (4H, $\text{Aryl}_{\text{H}3/5}$), -11.31 (2H, $\text{Aryl}_{\text{H}4}$), 13.40 (12H, Ar- CH_3), -17.02 (6H, $\text{N}=\text{C}-\text{CH}_3$)	60.1	60.5	5.33	5.44	8.42	8.47
47	523 $\text{M}^{\text{O}+}$ (24), 488 $\text{M} - \text{Cl}$ (5), 397 $\text{M} - \text{FeCl}_2$ (41), 382 $\text{M} - \text{FeCl}_2 - \text{Me}$ (100)	–	61.2	60.8	6.04	5.96	7.95	8.01

Table 5 (Continued)

Complex	MS (<i>m/z</i>)	¹ H NMR	C _{exp} (%)	C _{theor} (%)	H _{exp} (%)	H _{theor} (%)	N _{exp} (%)	N _{theor} (%)
48	551 M ^{o+} (26), 425 M – FeCl ₂ (100), 410 M – FeCl ₂ – Me (50)	–	–	–	–	–	–	–
49	607 M ^{o+} (35), 582 M – Cl (10), 481 M – FeCl ₂ (80), 466 M – FeCl ₂ – Me (100)	82.26 (2H, Py _{H3/5}), 81.97 (1H, Py _{H4}), 14.98 (4H, Aryl _{H3/5}), –5.31, –6.34 (12H, 12H, <i>i</i> -Pr-CH ₃), –10.93 (2H, Aryl _{H4}), –22.48 (2H, <i>i</i> -Pr-H), –37.52 (6H, N=C-CH ₃)	64.7	65.1	7.11	7.12	6.92	6.91
50	551 M ^{o+} (10), 425 M – FeCl ₂ (28), 410 M – FeCl ₂ – Me (100)	–	–	–	–	–	–	–
51	551 M ^{o+} (14), 425 M – FeCl ₂ (100), 410 M – FeCl ₂ – Me (68)	78.71 (2H, Py _{H3/5}), 68.15 (1H, Py _{H4}), 17.02, 1.70, –14.33, –45.21 (8H, Ar-H), –2.32 (18H, <i>tert</i> -Bu-CH ₃) –24.10 (6H, N=C-CH ₃)	60.0	59.3	6.31	6.39	7.58	7.61
52	535 M ^{o+} (6), 500 M – Cl (2), 409 M – FeCl ₂ (46), 394 M – FeCl ₂ – Me (22), 368 M – FeCl ₂ – Allyl (100)	–	61.9	62.7	5.78	5.83	7.77	7.83
53	535 M ^{o+} (5), 500 M – Cl (2), 409 M – FeCl ₂ (54), 394 M – FeCl ₂ – Me (43)	–	62.2	62.7	5.77	5.83	7.86	7.83
54	563 M ^{o+} (16), 568 M – Cl (2), 437 M – FeCl ₂ (8), 422 M – FeCl ₂ – Me (7)	–	63.6	63.8	6.11	6.25	7.41	7.45
55	591 M ^{o+} (3), 556 M – Cl (2), 465 M – FeCl ₂ (30), 450 M – FeCl ₂ – Me (12), 410 M – FeCl ₂ – Butenyl (48)	–	64.0	64.9	6.57	6.63	7.03	7.09
56	647 M ^{o+} (2), 521 M – FeCl ₂ (19), 242 (Me-C=N-Aryl) (100)	–	66.2	66.7	7.23	7.31	6.29	6.48
57	591 M ^{o+} (5), 465 M – FeCl ₂ (38), 450 M – FeCl ₂ – Me (56), 410 M – FeCl ₂ – Butenyl (100)	–	64.4	64.9	6.56	6.63	6.93	7.09
58	591 M ^{o+} (2), 556 M – Cl (3), 465 M – FeCl ₂ (27), 424 M – FeCl ₂ – Allyl (100), 410 M – FeCl ₂ – Butenyl (28)	–	64.7	64.9	6.65	6.63	6.96	7.09

over sodium sulfate and silica. Removal of the solvent yielded the allylated bis(arylimino)pyridine compounds as yellow solids (75–85%) (Table 4).

3.14. General synthesis of the 2,6-bis(arylimino)pyridine iron(II) and iron(III) complexes 34–58

An amount of 1.0 mmol of the 2,6-bis(arylimino)pyridine compound was dissolved in 20 ml 1-butanol and reacted with 1.0 mmol of water free iron(II) chloride or iron(III) chloride resulting in an immediate color change. The mixture was stirred for 3 h at room temperature, whereby the complexes precipitated. *n*-Pentane (10 ml) was added for complete precipitation. The iron complexes were filtered over a frit, washed three times with 15 ml *n*-pentane, and dried in vacuo. Yields: 65–98% (Table 5).

3.15. Prepolymerization and oligomerization of ethylene at low pressure

An amount of 1–2 mg of the appropriate iron complex was placed in a Schlenk tube and suspended in 100 ml of toluene. After activation with methyl alumoxane (30% in toluene, Fe:Al = 1:2500) an ethylene pressure of 0.2 bar was applied and the mixture was stirred for 1 h at room temperature. The mixture was then filtered over a glass frit to separate the polymer. The reaction mixture was carefully poured into 100 ml of diluted hydrochloric acid. The organic phase was then washed twice with 50 ml of water and dried over sodium sulfate. The toluene solution was analyzed by gas chromatography. The separated polymers were washed with toluene, vacuum dried, and used as heterogeneous catalysts for the polymerization of ethylene

in a 1 l Büchi reactor (10 bar ethylene, $T=60^{\circ}\text{C}$, 1 h). These catalysts did not show any polymerization activities.

3.16. Polymerization of ethylene in the 1 l Büchi autoclave

An amount of 0.2–2 mg of the desired iron complex was suspended in 5 ml of toluene. Methylalumoxane (30% in toluene, Fe:Al=1:2500) was added resulting in an immediate color change. The mixture was added to a 1 l Schlenk flask filled with 250 ml *n*-pentane. This mixture was transferred to a 1 l Büchi laboratory autoclave under inert atmosphere and thermostated at 60°C . An ethylene pressure of 10 bar was applied for 1 h. The polymer was filtered over a frit, washed with diluted hydrochloric acid, water, and acetone, and finally dried in vacuo.

To the oligomer solutions, diluted hydrochloric acid was added. The organic phase was separated and dried over sodium sulfate. *n*-Pentane was distilled off using a Vigreux column. The resulting oligomer mixtures were characterized using gas chromatography.

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