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ORIGINAL PAPER

Halogen substituted iron(III) di(imino)pyridine complexes as catalysts for 1-pentene/1-hexene co-oligomerization reactions

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Dedicated to Professor Uwe Rosenthal on the occasion of his 70th birthday

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ABSTRACT

Nine different bis(arylimino)pyridine complexes of Fe(III) with different halide substituents (F, Cl, Br, I) at different positions of the iminophenyl group of the ligand have been synthesized, characterized and applied for homogeneous 1-pentene and 1-hexene oligomerization and co-oligomerization reactions after activation with methylaluminoxane (MAO). The best activity in 1-hexene oligomerization (152 kg/mol.h) was observed for **4**/MAO with an iodine substituent in para position of the iminophenyl group. Fluorine substituents in the meta position of the iminophenyl group proved as disadvantageous (1 kg/mol.h) in homo-oligomerization reactions but advantageous in co-oligomerization reactions of 1-pentene and 1-hexene. Obviously, tiny electronic or steric differences at the active sites of the corresponding catalysts are responsible for this result (structure-property relationship). The product distributions of the co-dimerization reactions of 1-pentene and 1-hexene reflected a binominal behaviour with dominating co-products. The ratio of dimers is 1:2:1 (C10:C11:C12) while the trimers (pentadecenes up to octadecenes) show proportions of 1:3:3:1. **Polyolefins J (2020) 7: 79-89**

Keywords: Iron(III) di(imino)pyridine complexes; halide substituents; characterization of complexes; co-oligomerization of olefins; structure-property-relationships.

INTRODUCTION

In catalytic olefin polymerization reactions, the kinetics determine the length of the produced polymer chain. In the case of ethylene, the number of olefin insertions into a metal carbon bond can vary from 1 to 100000 depending on the parameters of the insertion and termination steps [1-3]. Di(imino)pyridine complexes can be excellent catalysts for ethylene polymerization [4-12]. Especially complexes with late transition metals like iron, nickel and cobalt, are attractive because they are more tolerant against hydrolysis than early transition metal complexes of titanium, zirconium and hafnium. In an earlier study, we have shown that such complexes can also oligomerize higher olefins like 1-pentene, 1-hexene, 1-heptene and 1-octene [13, 14]. This is an important feature for catalysts that is used for ethylene/olefin co-polymerization reactions because of the

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potential to transform low boiling olefins into higher boiling species useful as gasoline and diesel components. Another advantage of this class of catalysts is the fact that tiny changes in the molecular structure of the molecule can have a strong effect on the performance of these catalysts (structure-property relationship). Because of this situation, we prepared nine different halogen substituted di(imino)pyridine compounds, synthesized their 1:1 Fe(III) complexes, and investigated and compared their catalytic potential in homogeneous 1-pentene and 1-hexene oligomerization reactions.

EXPERIMENTAL

Materials

All reactions were carried out under an inert gas atmosphere of pure oxygen free argon using standard Schlenk techniques. n-Pentane, n-hexane, diethyl ether, toluene, and tetrahydrofuran were purified by distillation over Na/K alloy. Diethyl ether was additionally distilled over lithium aluminum hydride and toluene over phosphorus pentoxide. Methylene chloride and carbon tetrachloride were distilled over phosphorus pentoxide. Deuterated organic solvents ($CDCl_3$, CD_2Cl_2, and C_6D_6) for NMR spectroscopy were purchased from Euriso-Top and stored over molecular sieves (3 Å). Argon (5.0) and ethylene (3.5) were purchased from Rieβner Company. Methylaluminoxane (10% in toluene) was purchased from Chemtura Europe Limited (Bergkamen). All other starting materials were commercially available and used without further purification.

NMR spectroscopy

NMR spectra were recorded with Bruker ARX (250 MHz), Varian Inova (300 MHz) or Varian Inova (400 MHz) spectrometers. All spectra were recorded at 298 K. In the ^{1}H-NMR spectra, the chemical shift of the residual proton signal of the solvent was used as a reference ($\delta = 7.24$ ppm for chloroform, $\delta = 5.32$ ppm for methylene chloride and $\delta = 7.16$ ppm for benzene). In the ^{13}C-NMR spectra, the chemical shift of the solvent was used as a reference ($\delta = 77.0$ ppm for chloroform-d1, $\delta = 54.0$ ppm for methylene chloride-d_2 and $\delta = 128.0$ ppm for benzene-d_6).

GC/MS

GC/MS spectra were recorded with a Thermo FOCUS gas chromatograph combined with a DSQ mass detector. A 30 m HP-5 fused silica column (internal diameter 0.32 mm, film 0.25 µm and flow 1 mL/min) was used and helium (4.6) was applied as carrier gas. The measurements were recorded using the following temperature program:
Starting temperature: 50°C, duration: 2 min;
Heating rate: 20 K/min., duration: 12 min;
Final temperature: 290°C, duration: 27 min.

Mass spectrometry

Mass spectra were recorded with a VARIAN MAT CH-7 instrument (direct inlet, EI, E = 70 EV) and a VARIAN MAT 8500 spectrometer at the Zentrale Analytik of the University of Bayreuth. Matrix Assisted Laser Desorption Ionization Time-of-Flight Mass Spectrometry (MALDI-TOF-MS) measurements were performed on a Bruker Daltonic Reflex TOF using graphite as the matrix. The laser intensity was set to 60-65%. The sample solutions were prepared in toluene or methylene chloride at a concentration of 1 mg/mL.

Preparation of the di(imino)pyridine compounds 1-9

General procedure

A solution of 0.5 g (3 mmol) of 2,6-diacetylpyridine in 25 mL of toluene was treated with 0.5 g of an Al_2O_3/SiO_2 catalyst ($SiO_2 : Al_2O_3 = 87 : 13$) and ca 10 g molecular sieves (4 A°). Then 7 mmol of the corresponding amine was added and the suspension was stirred for 24 h at 50°C. Then the cold mixture was filtered over a frit loaded with sodium sulfate. The solvent was removed in vacuo and the remaining solid was recrystallized from methanol. The yields are given in Table 1, the ^{1}H and ^{13}C-NMR spectra in Table 2.

Table 1. Yields of the prepared di(imino)pyridine compounds **1-9**.

Compound	Yield [%]	Compound	Yield [%]
A	85	**5**	56
1	78	**6**	54
2	60	**7**	72
3	71	**8**	79
4	73	**9**	50

A = unsubstituted compound

Table 2. ^{1}H- and ^{13}C-NMR spectra of the ligand precursors **1-9**.

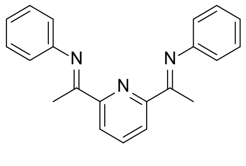
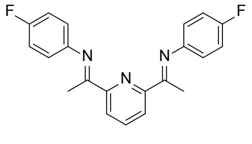
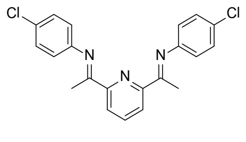
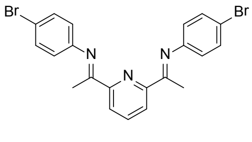
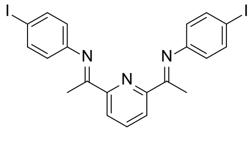
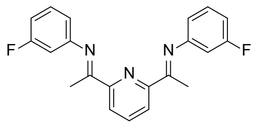
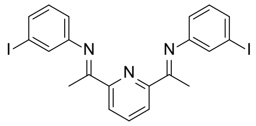
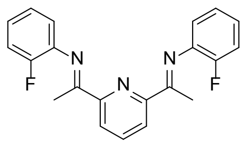
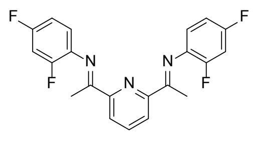
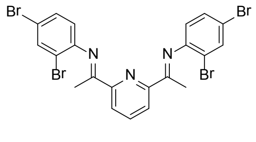
Nr.	^{1}H-NMR	^{13}C-NMR	Fragment [m/z] (%)	Formula
A	8.36 d (2H, Ar-H) 7.88 t (1H, Ar-H) 7.39 t (4H, Ar-H) 7.13 t (2H, Ar-H) 6.86 d (4H, Ar-H) 2.41 s (6H, CH_3)	167.3, 155.5, 151.3 (Cq) 136.8, 129.0, 123.6, 122.3, 119.2 (Ar-CH) 16.2 (CH_3)	313 $M^{\cdot+}$ (100) 298 M – and Me (12) 220 M - Me- Benzene (45) 118 Ph-N≡C-CH_3 (87) 77 Phenyl (58)	
1	8.34 d (2H, Ar-H) 7.87 t (1H, Ar-H) 7.08 t (4H, Ar-H) 6.82 dd (4H, Ar-H) 2.42 s (6H, CH_3)	168.0, 161.4, 155.3,147,1 (Cq) 136.8, 122.3, 120.7, 115.6 (Ar-CH), 162 (CH_3)	349 $M^{\cdot+}$ (100) 334 M - Me (14) 238 M - $[FC_6H_4N]$ (16) 136 FC_6H_4N≡C-CH_3 (100)	
2	8.23 d (2H, Ar-H) 7.85 t (1H, Ar-H) 7.28 - 7.36 m (4H, Ar-H), 6.75 - 6.81 m (4H, Ar-H) 2.40 s (6H, CH_3)	168.4, 155.6, 150.1, 129.4 (Cq) 137.4, 129.4, 122.1, 116.6 (Ar-CH), 16.7 (CH_3)	381 $M^{\cdot+}$ (62) 380 M - H (35) 254 M - $[ClC_6H_4N]$ (45) 152 ClC_6H_4N≡C-CH_3 (100)	
3	8.31 d (2H, Ar-H) 7.86 t (1H, Ar-H) 7.48 d (4H, Ar-H) 6.72 d (4H, Ar-H) 2.38 s (6H, CH_3)	168.3, 155.6, 150.6, 117.1 (Cq) 137.4, 132.5, 123.0, 121.5 (Ar-CH), 16.7 (CH_3)	471 $M^{\cdot+}$ (100) 300 M - $[BrC_6H_4N]$ (41) 198 BrC_6H_4N≡C-CH_3 (73)	
4	8.31 d (2H, Ar-H) 7.85 t (1H, Ar-H) 7.66 d (4H, Ar-H) 6.60 d (4H, Ar-H) 2.30 s (6H, CH_3)	168.2, 155.6, 151.3, 87.7 (Cq) 138.4, 137.4, 122.5, 117.7 (Ar-CH), 16.7 (CH_3)	565 $M^{\cdot+}$ (100) 564 M - H (19) 346 M - $[IC_6H_4N]$ (22) 244 IC_6H_4N≡C-CH_3 (36)	
5	8.33 d (2H, Ar-H) 7.85 t (1H, Ar-H) 7.31 dd (2H, Ar-H) 6.83 - 6.55 m (6H, Ar-H) 2.41 s (6H, CH_3)	168.4, 162.3, 155.6, 153.5 (Cq) 137.4, 130.7, 123.0, 115.3, 110.7, 107.0 (Ar-CH), 16.7 (CH_3)	349 $M^{\cdot+}$ (100) 239 M - $[FC_6H_4N]$ (17) 136 $[FC_6H_4N$≡C-$CH_3]$ (100)	
6	8.30 d (2H, Ar-H) 7.85 t (1H, Ar-H) 7.45 d (2H, Ar-H) 7.01 - 7.23 m (4H, Ar-H) 6.81 d (2H, Ar-H) 2.39 s (6H, CH_3)	168.4, 155.5, 153.0, 94.9 (Cq) 137.4, 133.0, 130.2, 128.5, 123.0, 119.1 (Ar-CH), 16.9 (CH_3)	565 $M^{\cdot+}$ (100) 438 M - I (9) 346 M - $[IC_6H_4N]$ (38) 244 $[IC_6H_4N$≡C-$CH_3]$ (61)	
7	8.38 d (2H, Ar-H) 7.90 t (1H, Ar-H) 7.07-7.15 m (6H, Ar-H) 6.92 t (2H, Ar-H) 2.41 s (6H, CH_3)	170.5, 154.5, 150.2, 139.0 (Cq) 137.4, 125.0, 123.3, 122.5, 116.5 (Ar-CH) 17.3 (CH_3)	349 $M^{\cdot+}$ (76) 240 M - $[FC_6H_4N]$ (18) 136 FC_6H_4N≡C-CH_3 (100)	
8	8.33 d (2H, Ar-H) 7.88 t (1H, Ar-H) 6.96 - 6.79 m (6H, Ar-H) 2.40 s (6H, CH_3)	171.2, 159.7, 155.3, 151.8, 135.1 (Cq) 137.4, 123.4, 122.9, 111.7, 104.8 (Ar-CH) 17.3 (CH_3)	385 $M^{\cdot+}$ (62) 266 M - F (8) 258 M - $[FC_6H_4N]$ (21) 154 $F_2C_6H_3N$≡C-CH_3 (100)	
9	8.41 d (2H, Ar-H) 7.90 t (1H, Ar-H) 7.76 d (2H, Ar-H) 7.42 dd (2H, Ar-H) 6.69 d (2H, Ar-H) 2.35 s (6H, CH_3)	169.9, 155.1, 149.2, 116.9, 114.8 (Cq) 137.6, 135.2, 131.5, 123.6, 121.6 (Ar-CH) 17.4 (CH_3)	629 $M^{\cdot+}$ (36) 548 M - Br (91) 276 $Br_2C_6H_3N$≡C-CH_3 (100)	

Table 3. Yields of the prepared di(imino)pyridine iron compounds **1a-9a**.

Compound	Yield [%]
1a	97
2a	99
3a	97
4a	99
5a	95
6a	65
7a	61
8a	97
9a	43

Preparation of the di(imino)pyridine iron complexes 1a-9a

General procedure

An amount of 0.1-0.3 g of the corresponding di(imino)pyridine compound **1-9** was dissolved in butanol and an equimolar amount of $FeCl_3$ was added. The corresponding mixture was stirred for 2 h at room temperature. Then the solvent was removed in vacuo and the residue was recrystallized from pentane. At the end, the product was dried in a high vacuum. The yields are given in Table 3, the elemental analyses in Table 4 and the mass spectra (MALDI-TOF) in Table 5.

Homogeneous oligomerization reactions of 1-pentene and 1-hexene and their 1:1 mixtures with 1a-9a/MAO

General procedure

An amount of 5 mg of the corresponding catalyst precursor was dissolved in 5 mL of toluene and activated with an MAO solution in toluene (Fe : Al = 1:500). Then 10 mL of 1-pentene or 1-hexene or a mixture of these two (1:1) was added to the reaction vessel. After a reaction time of 2 h, the reaction was quenched with a few drops of diluted HCl. The reaction mixture was filtered over a frit loaded with silica and sodium sulfate. The products were characterized with GC/MS.

RESULTS AND DISCUSSION

Preparation of halide substituted di(imino)pyridine compounds

Compounds **1-9** were prepared via condensation reactions of 2,6-diacetylpyridine and differently substituted anilines (Figure 1):

Table 6 gives an overview.

Characterization of compounds 1-9

Compounds **1-9** were characterized by ^{1}H- and ^{13}C-NMR and mass spectroscopy. The complete data are given in Table 2 (Experimental). As an example, the NMR spectra of compound **6** are discussed (Figures 2 and 3). The hydrogen atoms at the pyridine ring give a doublet for H2 at δ = 8,39 and a triplet for H1 at δ = 7,94 ppm ($^3J_{HH}$ = 8,0 Hz). The hydrogen atoms at the phenyl ring show a virtual triplet for H6 at δ = 7,18 ppm deriving from coupling with H5 at δ = 7.53 (d, $^3J_{HH}$ = 7,9 Hz) and H7, δ = 6,89 ppm, (d, $^3J_{HH}$ = 7,9 Hz)

The ^{13}C-NMR spectrum is indicative for the differently shielded carbon atoms. The assignments are given in Figure 3. The fluorine containing compounds **1**, **5**, **7** and **8** were also characterized by ^{19}F-NMR spectroscopy (Table 7).

The mass spectrum of **6** (Figure 4) shows the molecular ion at m/z = 565. The loss of the iodo substituent gives the fragment at m/z = 438, the loss of the iminophenyl ring results in m/z = 346. The fragment at m/z = 244 is the consequence of the complete loss of the ethyl(iminophenyl) rest.

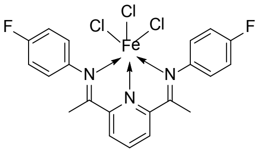
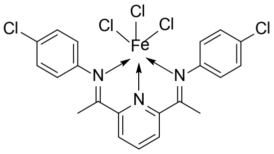
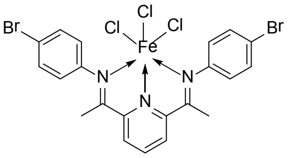
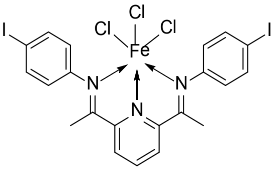
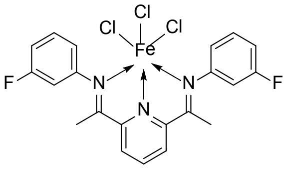
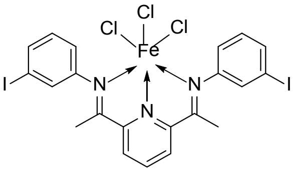
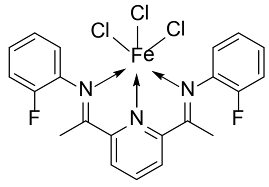
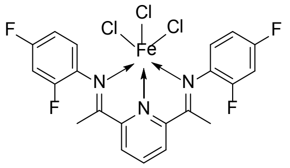
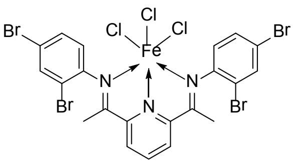
Synthesis and characterization of the iron complexes 1a - 9a

Complexes **1a - 9a** were prepared according to Figure 5. The corresponding di(imino)pyridine compound

Table 4. Elemental analyses of complexes **1a-9a**.

Nr.	Calculated [%]			Found [%]		
	C	H	N	C	H	N
1a	49.30	3.35	8.21	49.79	3.18	7.98
2a	46.32	3.15	7.72	46.28	3.19	7.55
3a	39.82	2.71	7.34	40.08	2.78	7.21
4a	34.68	2.36	5.78	34.86	2.36	5.66
5a	49.30	3.35	8.21	49.54	3.53	8.02
6a	34.68	2.36	5.78	34.71	2.42	5.60
7a	49.30	3.35	8.21	49.76	3.36	8.06
8a	46.06	2.76	7.67	46.30	2.85	7.49
9a	31.88	1.91	5.31	32.31	2.08	5.27

Table 5. Mass spectra (MALDI-TOF) of complexes **1a-9a**.

Nr.	EI-MS [m/z] (relative Intensity [%])	MALDI-TOF [m/z] (relative Intensity [%])	Structure
1a	510/512 $M^{\cdot+}$ (4) 417 M-Fe-Cl (7) 384 M-Fe-2Cl (22) 349 M-Fe-3Cl (100)	510/512/514 $M^{\cdot+}$ (4) 475/477 M-Cl (100) 440 M-2Cl (55) 350 [M+1]-Fe-3Cl (23)	
2a	542/544/546 $M^{\cdot+}$ (-) 507 M-Cl (5) 472 M-2Cl (7) 416 M-Fe-2Cl (15) 381 M-Fe-3Cl (78)	544/546/548 $M^{\cdot+}$ (11) 509/511/513 M-Cl (100) 472/474 M-2Cl (75) 404 M-3HCl-2Me (88)	
3a	632/634 $M^{\cdot+}$ (-) 553 M-Br (4) 518 M-Br-Cl (2) 484 M-Br-2Cl (9) 471 M-Fe-3Cl (88)	632/634/636/638 $M^{\cdot+}$ (11) 597/599/601 M-Cl (100) 560/562/564 M-2Cl (67) 492/494 M-3HCl-2Me (52) 471 M-Fe-3Cl (23)	
4a	726/728 $M^{\cdot+}$ (-) 691 M-Cl (6) 656 M-2Cl (5) 565 M-Fe-3Cl (17)	726/728/730 $M^{\cdot+}$ (6) 691/693 M-Cl (100) 656 M-2Cl (62) 588 M-3HCl-2Me (70)	
5a	510/512 $M^{\cdot+}$ (-) 475 M-Cl (6) 440 M-2Cl (14) 383 M-Fe-2Cl (8) 349 M-Fe-3Cl (100)	512/514 $M^{\cdot+}$ (20) 475/477 M-Cl (80) 440 M-2Cl (100) 405 M-3Cl (44) 350 [M+H]-Fe-3Cl (72)	
6a	726/728 $M^{\cdot+}$ (-) 692 M-Cl (3) 600 M-I (5) 598 M-Fe-2Cl (6) 565 M-Fe-3Cl (28)	727/729/731 [$M^{\cdot+}$+1](16) 691/693 M-Cl (100) 656/658 M-2Cl (89) 566 [M+1]-Fe-3Cl (29)	
7a	510/512 $M^{\cdot+}$ (-) 419 M-Fe-Cl (2) 384 M-Fe-2Cl (8) 349 M-Fe-3Cl (81)	510/512 $M^{\cdot+}$ (2) 475 M-Cl (100) 440 M-2Cl (31) 404 M-2Cl-HCl (34) 350 [M+H]-Fe-3Cl (15)	
8a	546/548 $M^{\times+}$ (1) 511 M-Cl (1) 476 M-2Cl (2) 385 M-Fe-3Cl (62)	546/548 $M^{\times+}$ (13) 511/513 M-Cl (100) 476/478 M-2Cl (52) 408 M-3HCl-2Me (11)	
9a	790/792/794 $M^{\times+}$ (1) 753 M-Cl (2) 737 M-Me-HCl(4) 714 M-Br (2) 629 M-Fe-3Cl (22) 549 M-Fe-3Cl-HBr (69)	790/792/794 $M^{\times+}$ (4) 753/755/757 M-Cl (73) 720/722 M-2Cl (100) 668 M-Br-Cl (26) 652 M-3HCl-2Me (68)	

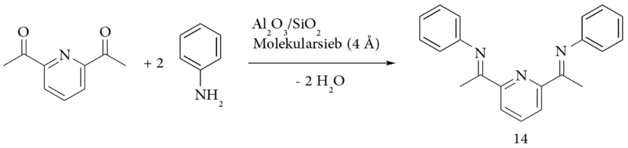


Figure 1. Preparation of di(imino)pyridine compounds.

was dissolved in butanol and reacted with $FeCl_3$. After two hours, the reaction was finished. The product is a precipitate. It was washed with pentane and dried in vacuum. Yields: around 90%.

Table 8 gives an overview of the synthesized complexes **1a-9a**. Since the iron(III) complexes are all paramagnetic, NMR spectra are not very informative. Elemental analyses and mass spectra were used for characterization (Tables 4 and 5, Experimental). In the following, the MALDI-TOF mass spectrum of **6a** is discussed (Figure 6).

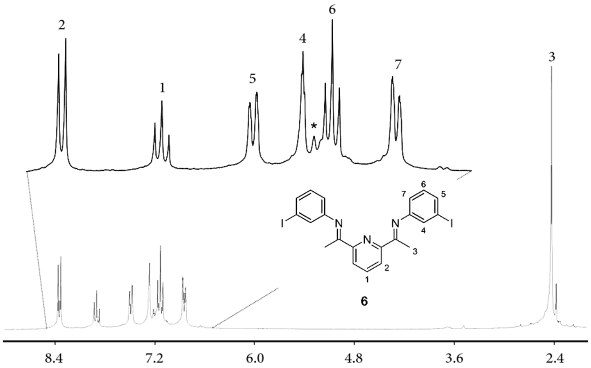
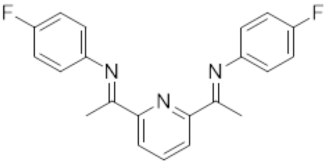
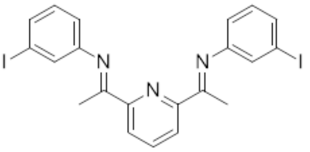
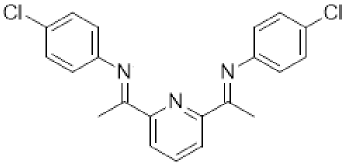
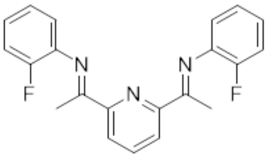
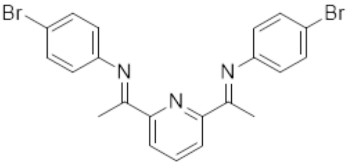
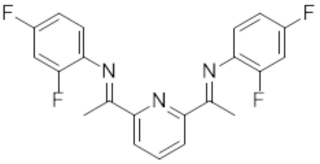
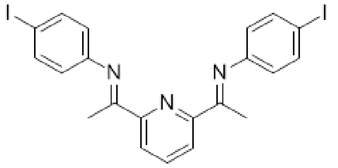
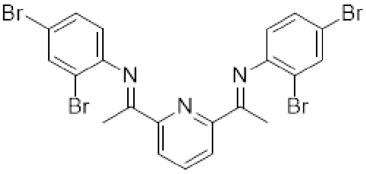
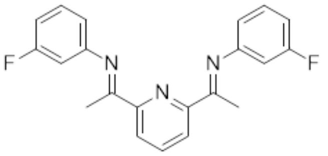


Figure 2. ^{1}H-NMR spectrum of **6** in $CDCl_3$.

The protonated molecular ion can be detected at m/e = 727. Elimination of HCl gives the fragment m/z = 656/658. Figure 7 shows the experimental and the calculated isotope distribution pattern.

Table 6. Synthesized di(imino)pyridine compounds **1-9**.

Nr.	Complex	Nr.	Complex
1		6	
2		7	
3		8	
4		9	
5			

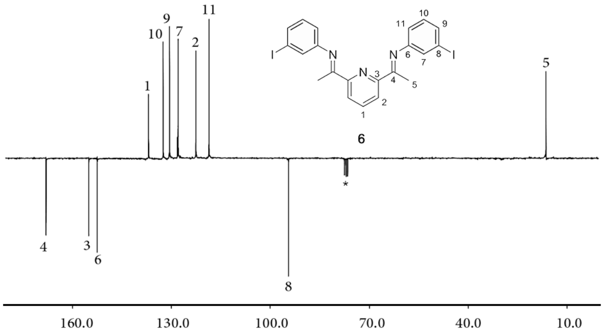


Figure 3. ^{13}C-NMR spectrum of **6** in $CDCl_3$.

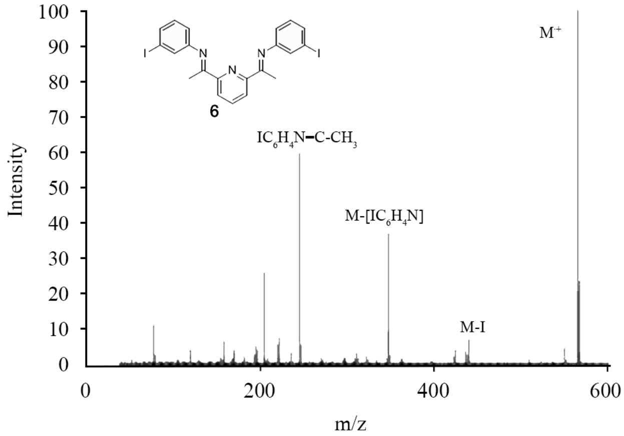


Figure 4. EI-mass spectrum of compound **6**.

Table 7. ^{19}F-NMR data for compounds **1**, **5**, **7** and **8**.

Compound	^{19}F-NMR δ [ppm]	Position of the F-atoms at the phenyl ring
1	- 126,8 s (2F)	2
5	- 112,9 3 (2F)	3
7	- 122,0 s (2F)	4
8	-119,5 d (2F); -127,7 d (2F)	2 and 4

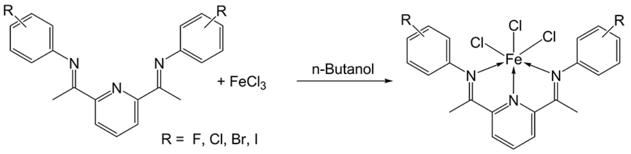
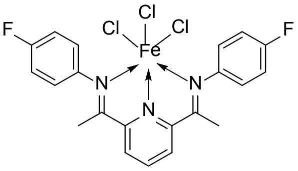
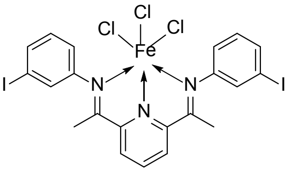
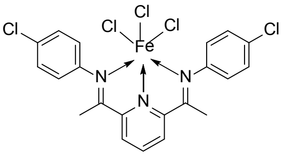
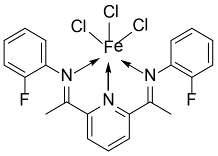
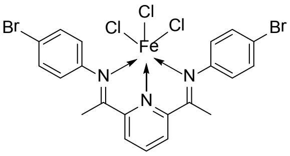
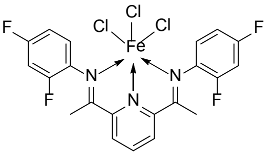
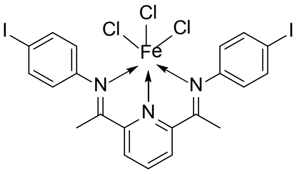
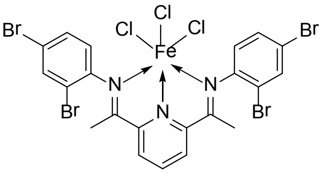
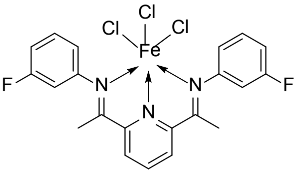


Figure 5. Synthesis of complexes **1a -9a**.

Table 8. gives an overview of the synthesized complexes **1a – 9a**.

Nr.	Complex	Nr.	Complex
1a		**6a**	
2a		**7a**	
3a		**8a**	
4a		**9a**	
5a			

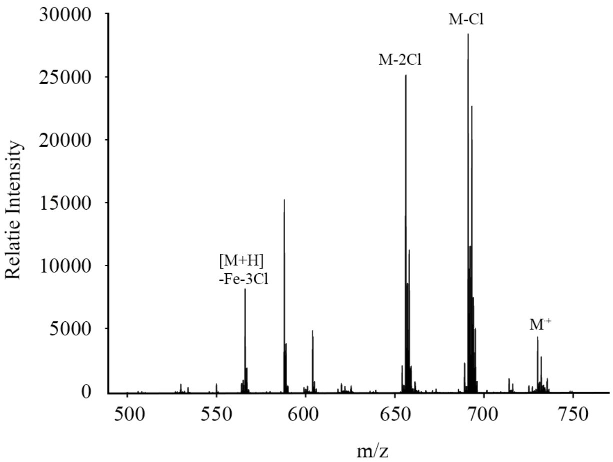


Figure 6. Mass spectrum of **6a**.

Homogeneous oligomerization reactions of 1-hexene with 1a - 9a /MAO catalysts

Complexes **1a-9a** were activated with MAO (Fe: Al = 1:500) in toluene solution and then added to 1-hexene at room temperature. Table 9 summarizes the results. A comparison of catalyst activities shows a decrease in the series **1a-4a** obviously resulting from the halide substituents in the para position of the iminophenyl ring: I>F>Br>Cl. The reason seems to be an electronic effect as it was detected in other cases [11-13]. The meta substituted complexes **5a** and **6a** show a similar behavior: the fluorine derivative gives low activity (1 kg/mol.h), the iodine derivative a good one (46 kg/mol.h) but substituents in the para position are still superior. Ortho substituents on the phenyl ring have mainly a steric influence. A comparison of **8a** and **9a** shows that the bromo derivative **9a** (4 kg/mol.h) has a much lower activity than the isostructural fluoro derivative **8a** (38 kg/mol.h). Similar results are known in the literature [15, 19]. A comparison of the fluorine containing complexes **1a**, **8a**, **7a** and **5a** demonstrates the strong influence of the position of the substituent on the catalyst performance (Table 10). Also in the case of disubstitution, the positions play an important role [15].

The product distribution (Figure 8) obtained from the oligomerization reactions of 1-hexene with the catalysts **1a-9a**/MAO shows the domination of dimers in all cases.

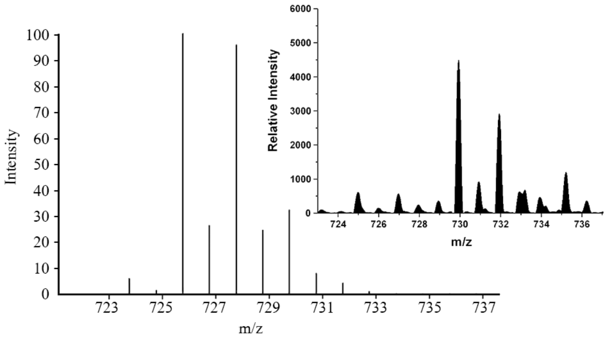


Figure 7. Experimental (right) and calculated (left) isotope distribution pattern of **6a**.

The fluorine-containing complex **5a** produced only the dimer dodecene but with low activity (1 kg/mol.h). The other candidates produced a trimer share of 5-11% and very little tetramers (0,3 – 2,7%). The iodine substituted complex **4a** had the best activity and the highest dimer selectivity (95%). The advantageous role of iodine could also derive from interactions with the cocatalyst MAO leading to elimination of the halogen. The dimer produced from the reaction of 1-hexene with **4a** is a mixture of isomers as assigned in Figure 9.

Table 11 describes the isomer distribution.

Linear dodecene is the main fraction (72%), with 67% of the cis-isomer, 4- and 5- dodecenes are products from ß-hydrogen elimination reactions after 1,2 and 2,1 insertion reactions of 1-hexene. Figure 10 describes the mechanism that is already known in the literature [20, 21].

5-Methyl-5-undecene can be obtained either by a double 1,2 insertion or by a double 2,1 insertion, followed by an isomerisation step like shown in Figure 11.

Since no 5,6-dimethyl-5-decene was detected, afford ing a primary 2,1 insertion, the 1,2 insertion must be favored.

Homogeneous co-oligomerization of 1-pentene and 1-hexene with catalysts 1a-4a/MAO and 6a-9a/MAO

The co-oligomerization reactions of 1-pentene and 1-hexene were performed in an analogous manner as

Table 9. Oligomerization reactions of 1-hexene with **1a-9a**/MAO catalysts.

Complex	1a	2a	3a	4a	5a	6a	7a	8a	9a
Yield [%]	63	73	61	76	1	27	50	73	4
Activity [kg/mol·h]	43	23	24	152	1	46	28	38	4

Table 10. Influence of the substituent position on the activity of fluorine containing catalysts.

Complex	1a	8a	7a	5a
Substituted position	para	para + ortho	ortho	meta
Activity [kg/mol·h]	43	38	28	1

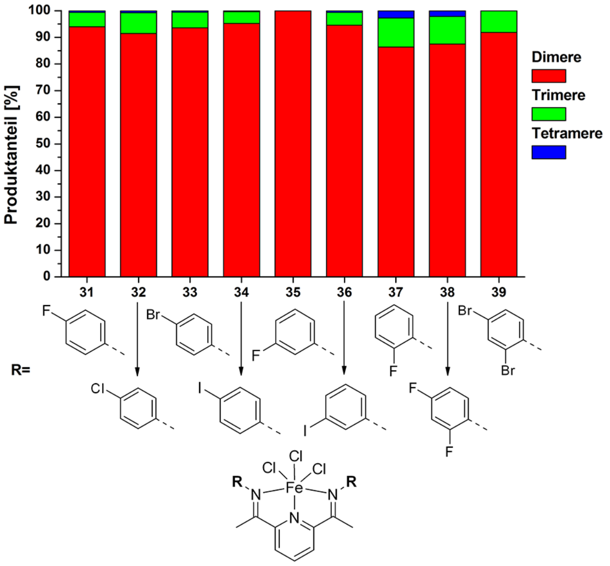


Figure 8. Product distribution of the oligomerization reactions of 1-hexene with catalysts **1a**-**9a**/MAO.

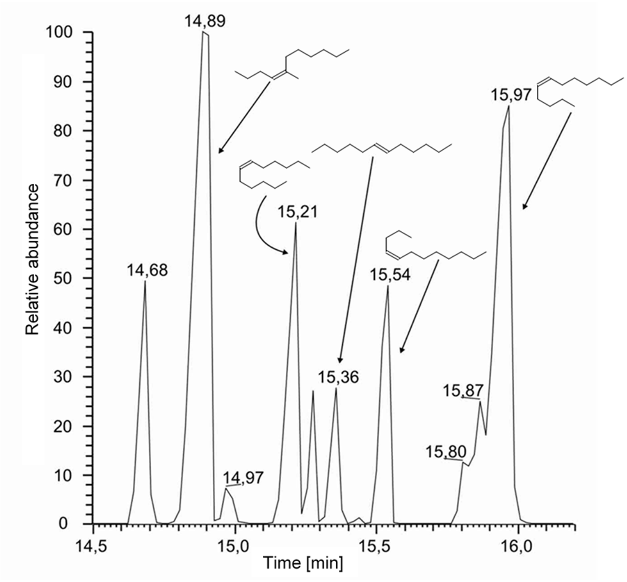


Figure 9. GC of the dimers generated from the reaction of 1-hexene with **4a**/MAO.

Table 11. Dodecene isomers from the oligomerization reaction of 1-hexene and **4a**/MAO.

Retention time [min]	Product	Product Share [%]
14,7-15,0	cis-5-Methyl-5-undecene	27,8
15,2-15,3	cis-6-Dodecene	18,2
15,36	trans-6-Dodecene	5,2
15,54	cis-4-Dodecene	10,5
15,97	cis-5-Dodecene	38,3

the homo-oligomerization reactions of 1-hexene. The results are given in Table 12.

Figure 12 shows the product distribution of co-oligomerization reaction depending on the corresponding catalyst. The share of dimers is dominating in all cases (Figure 13). Trimers are detected in a range of 5-11%. Tetramers were only formed from **8a**/MAO. In nearly all cases the catalyst activities were higher than in the case of the homo-oligomerization reactions of 1-hexene. This speaks for an easier insertion of the smaller monomer 1-pentene. Complex **1a** showed a surprisingly high activity of 144 kg/mol.h, better than the iodine derivative **4a** (31 kg/mol.h) that was superior in the homo-oligomerization reaction of 1-hexene. The lowest activity (15 kg/mol.h) was observed in the case of **9a**. The bromo substituents in the ortho position of the phenyl ring block the coordination of the monomers as observed in the case of the homo-oligomerization of 1-hexene.

In all dimerization products the biggest share was undecene (about 45%), indicating that the 1-pentene/1-hexene coupling reactions were favored compared with 1-pentene and 1-hexene homo coupling reactions. When the formation of decenes and dodecenes is compared, the C**12** species are favored indicating that homo 1-hexene coupling reactions are faster than homo 1-pentene coupling reactions. A similar situation is observed at the trimer compositions. It is interesting to note that the halide substituted di(imino) pyridine

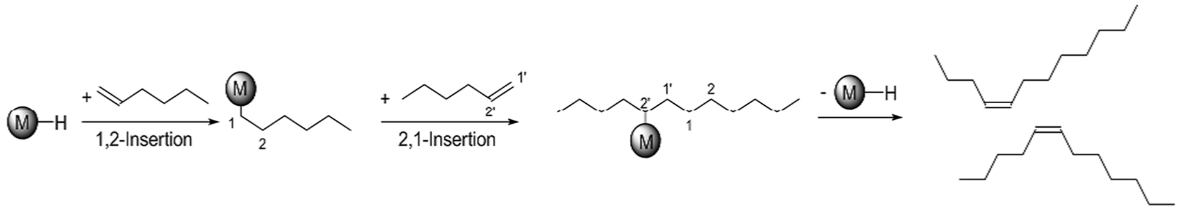


Figure 10: Mechanism for the formation of cis-4 and cis-5 dodecene in the 1-hexene dimerization reaction.

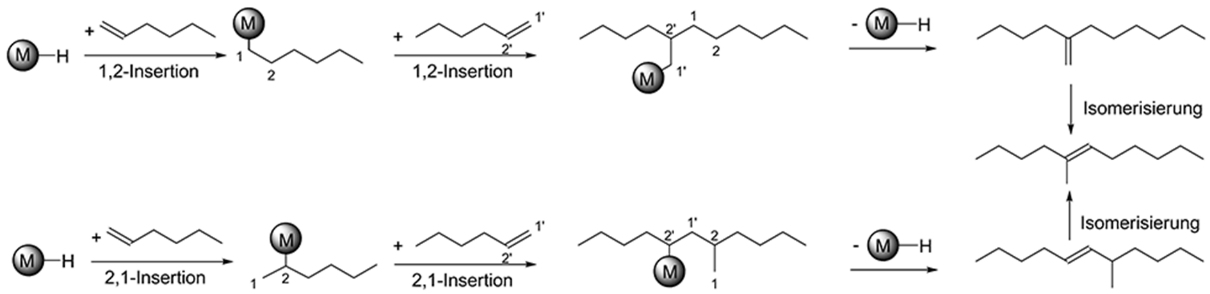


Figure 11. Mechanism for the formation of 5-methyl-5-undecene in the 1-hexene dimerization reaction.

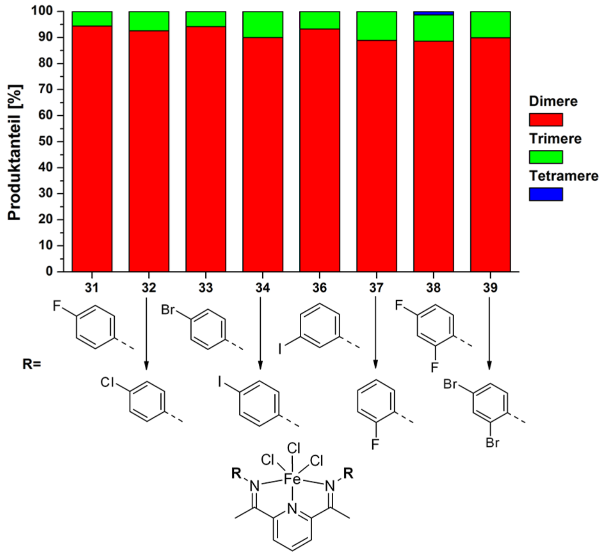


Figure 12. Product distribution of co-oligomerization reactions of 1-pentene/1-hexene with various catalysts.

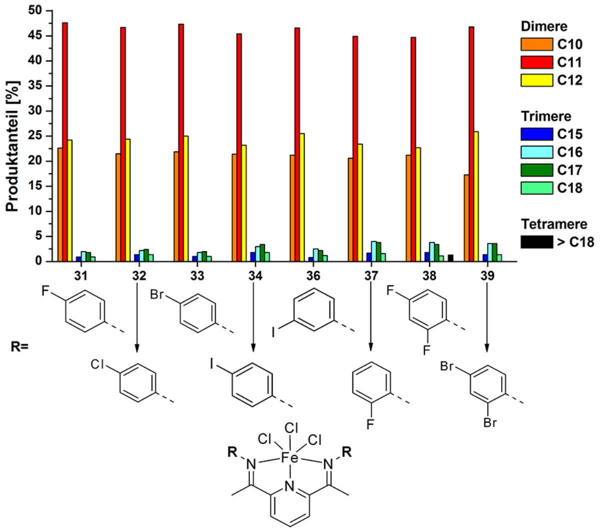


Figure 13. Product compositions from the co-oligomerization reactions of 1-pentene and 1-hexene.

Table 12. Products from the co-oligomerization reactions of 1-pentene and 1-hexene.

Complex	1a	2a	3a	4a	6a	7a	8a	9a
Yield [%]	81	79	77	84	73	82	84	14
Activity [kg/mol·h]	144	39	70	31	25	83	55	15
Selectivity for co-dimers [%]	48	47	47	45	47	45	45	47

iron complexes in combination with MAO showed a much better catalytic performance than the unsubstituted derivatives. As an explanation, the –I effect of the substituents can be discussed to improve the cationic features of the catalyst cations but also an interaction of the halide with the MAO counter anion leading to a better access of the monomers to the active center.

CONCLUSIONS

The iron di(imino)pyridine complexes **1a-9a** are a good example how halide substituents at certain positions at the ligand can have a very strong influence on the performance of such catalysts. Since kinetics in olefin oligomerization and polymerization reactions react very sensitive to subtle changes in a catalyst molecule and since MAO is still a "black box" in this respect, the best way is the experimental approach to study these catalysts.

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