Iron(II)-Based Catalysts for Ethene Oligomerization

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ABSTRACT: The synthesis of iron(II) complexes with various tridentate di(imino)pyridine ligands and their potential as ethene oligomerization catalysts are described. The ligands are characterized by ^{1}H- and ^{13}C-NMR spectroscopy and the complexes only by mass spectrometry due to their paramagnetism. After activation either with methylalumoxane (MAO) or with a heterogeneous cocatalyst consisting of partially hydrolyzed trimethylaluminum and silica gel, the prepared complexes proved to be good catalysts for the oligomerization of ethene. 1-Octene, 1-hexene, and 1-decene were the major products, formed in very high isomeric purity (99.9 %). © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 476–482, 2003

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INTRODUCTION

In 1998, Brookhart et al. and Gibson et al.[1–3] independently discovered that a well-known class of coordination compounds[4] consisting of iron or cobalt in the oxidation state +2 and tridentate N-containing ligands can be activated with methylaluminoxane (MAO)[5–8] to give highly active catalysts for the polymerization and oligomerization of ethene. Depending on the substitution pattern of the used aniline, either no products or oligomerization or polymerization products were found (Fig. 1).

In this context, it should be mentioned that the reaction of $FeCl_2$ and terpyridine (terpy) can give $[Fe(terpy)_2][FeCl_4]$ in the solid state.[9–11] It is likely that the unsubstituted di(imino)pyridine complex in combination with MAO is inactive in ethylene polymerization because of an analogous composition.

Recently, naphthyl-substituted derivatives of such complexes have been described that can be used as ethylene polymerization catalysts in a homogeneous solution.[12] In this study, we concentrated on catalysts which produce oligomers from ethene. The synthesis of the ligands and the corresponding iron(II) complexes are described.

The complexes were used under homogeneous and heterogeneous reaction conditions. For the homogeneous process, the complexes were activated with an excess of MAO. In contrast, the complexes in the heterogeneous process were immobilized and activated with partially hydrolyzed trimethylaluminum (PHT).[13,14] Products of low molecular weights were separated and the liquid oligomers were analyzed.

EXPERIMENTAL

All procedures were performed under an inert gas using a standard Schlenk technique to prevent traces of air or moisture. Purified and dried argon was used (BTS catalyst, molecular sieves) as an inert gas. All other preparations were carried out in air.

All solvents were purchased in technical grade and purified by distillation over a Na/K alloy under an argon atmosphere. All other chemicals were commercially available or were synthesized according to literature procedures.

NMR spectra were recorded in $CDCl_3$ at 25°C on a Bruker ARX 250 instrument. The chemical shifts of ^{1}H-NMR spectra were referenced to the residual proton signal of the solvent ($\delta = 7.24$ ppm for $CHCl_3$); the carbon resonances in the ^{13}C-NMR spectra were also referenced to the solvent signal ($\delta = 77.0$ ppm for $CDCl_3$).

Mass spectra were recorded on a Varian MAT CH7 instrument (direct inlet system, electron impact ionization of 70 eV). Oligomerizations were conducted in n-pentane at 60°C and 10 bar ethene pressure for 1 h.

General procedure for the reduction of nitroarenes

Ten grams (66.15 mmol) of a nitroarene was dissolved in 150 mL of a 1:1 mixture of ethanol/H_2O. Subsequently, 7.5 g of NaOH was added. While stirring, 50 g of $Na_2S_2O_4$ was added.[15] After stirring for an
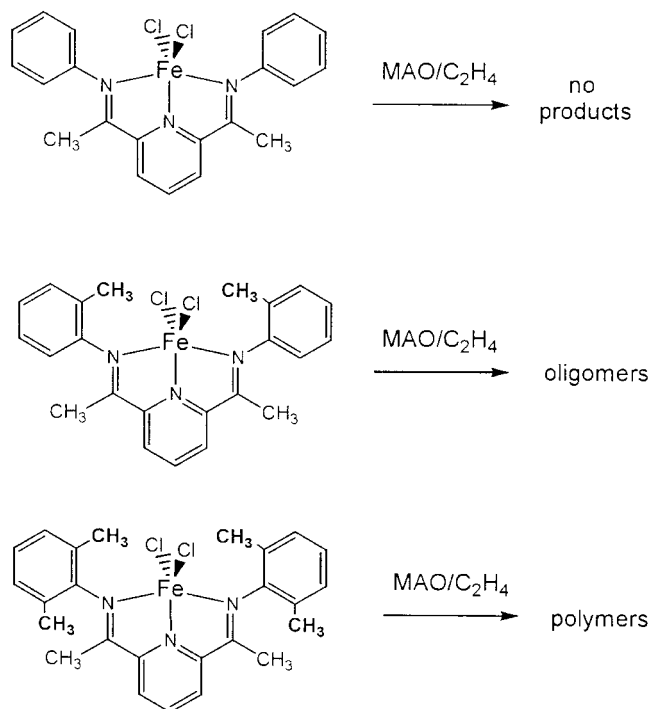
Figure 1 Product dependence on the substitution pattern (bold) of the used complex.

TABLE I
MS Data of the Synthesized Complexes

No.	Complex	MS M$^+$ [m/e]
7		495
8		495
9		537
10		537

additional 90 min at room temperature, the solution was heated to reflux for 2 h. The mixture was hydrolyzed with diluted H_2SO_4. The ethanol was removed *in vacuo*. NaOH was added in portions to the aqueous mixture until the solution was neutral. Then, the mixture was extracted three times with diethyl ether. The combined organic phases were washed with water and dried over Na_2SO_4. The solvent was removed *in vacuo*. Yields of the obtained anilines were about 55% of yellow oils.

General procedure for the preparation of a di(imino)pyridine ligand (condensation reactions)

p-Toluene sulfonic acid (0.05 g) was added to a stirred solution of the corresponding diketopyridine in toluene. The aniline compound was added in excess. The mixture was refluxed and the formed water was separated via a Dean–Stark trap. Refluxing was continued for at least 3 h up to 25 h (depending on the added aniline and/or the substituent at the diketopyridine). The reaction was monitored via GC/MS.

After cooling to room temperature, the mixture was washed twice with a diluted solution of Na_2CO_3 in water and twice with water. The organic layer was separated and the water phase was extracted twice with diethyl ether. The combined organic layers were dried over Na_2SO_4 and evaporated to dryness.

Ethyl alcohol was added to the dried residue. If crystallization did not start immediately, the solution was stored at −20°C overnight.

The crystals were filtered off, washed with ethyl alcohol, and dried in air. The liquid residue was reduced in volume to about 30–40%. A second crop of crystals could be obtained after storing at −20°C overnight. Overall yield: 90–95%

General procedure for the preparation of the iron complexes

A stoichiometric amount of iron dichloride was added to a stirred solution of diacetylpyridine in a mixture of diethyl ether and tetrahydrofuran at room temperature. Stirring was continued overnight. Filtration of the formed solids, washing with diethyl ether, and drying the solids in air gave an overall yield of 50–85%.
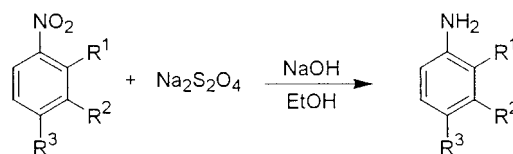
1 (R^1 = Me, R^2 = Me, R^3 = H)
2 (R^1 = Me, R^2 = H, R^3 = Me)

Figure 2 Preparation of substituted anilines.

Figure 3 Synthesis of ligands **3–6**.

3 (R^1 = Me, R^2 = Me, R^3 = H, X = H)
4 (R^1 = Me, R^2 = H, R^3 = Me, X = H)
5 (R^1 = Me, R^2 = Cl, R^3 = H, X = H)
6 (R^1 = Me, R^2 = H, R^3 = H, X = Cl)
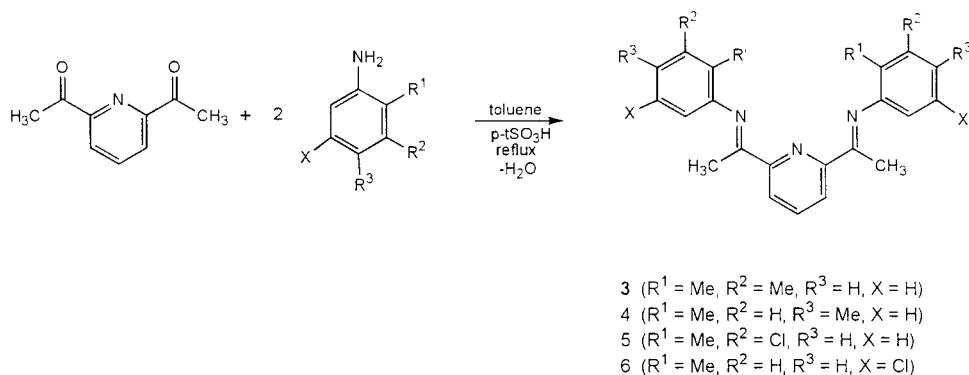
Characterization of the catalyst precursors 7–10

Due to the paramagnetism of the synthesized iron(II) complexes, the prepared catalyst precursors were characterized by mass spectrometry (Table I).

General procedure for the preparation of a supported catalyst

One hundred milliliters of toluene and 28.7 mL of a 1.764*M* solution of trimethylaluminum (TMA) in tol-

uene were added to 1 g of dried Davison silica (XPO 2410) in a 500-mL Schlenk flask. The mixture was vigorously stirred for 30 min. Another flask containing 0.70–1.5 mL of water was connected via a Teflon tube to the mixture and heated to 180°C. The Teflon tube ended at the bottom of the reaction flask. Dry nitrogen was purged through the water-containing flasks and a wet nitrogen stream was formed. This wet nitrogen stream transferred the vaporized water through the TMA/silica/toluene slurry. Purging continued until

TABLE II
NMR Spectroscopic and Mass Spectrometric Data of the Synthesized Ligands

No.	Ligands	^{1}H-NMR^a	^{13}C-NMR^b
3		8.40 (d, 1H), 7.87 (t, 2H), 7.12–6.52 (m, 6H), 2.32 (s, 6H), 2.30 (s, 6H), 2.04 (s, 6H)	(C$_q$): 164.9, 156.1, 149.4, 133.7, 121.1 (CH): 138.4, 131.0, 124.5, 124.0, 120.0 (CH$_3$): 20.0, 16.0, 13.8
4 [14]		8.38 (d, 1H), 7.86 (t, 2H), 7.04–6.56 (m, 6H), 2.33 (s, 6H), 2.31 (s, 6H) 2.09 (s, 6H)	(C$_q$): 166.9, 155.1, 147.4, 132.9, 127.1 (CH): 136.7, 131.1, 126.9, 122.1, 118.1 (CH$_3$): 20.8, 17.7, 16.2
5		8.39 (d, 1H), 7.90 (t, 2H), 7.16–7.09 (m, 2H), 6.92–6.81 (dt, 2H), 6.62–6.55(m, 2H), 2.34 (s, 6H), 2.17 (s, 6H),	(C$_q$): 167.7, 155.1, 151.0, 131.6, 125.7 (CH): 137.1, 131.7, 131.4, 123.5, 122.6118.4, 118.2, 114.6 (CH$_3$): 17.4, 16.6
6		8.38 (d, 1H), 7.89 (t, 2H), 7.25–6.64 (m, 6H), 2.34 (s, 6H), 2.12 (d, 6H)	(C$_q$): 167.6, 155.1, 151.2, 135.2, 125.4, (CH): 137.0, 127.0, 124.3, 122.5, 119.4116.7, 113.3 (CH$_3$): 16.5, 14.7

^{a} 25°C, in chloroform-d_1; δ [ppm] relative chloroform (7.24).
^{b} 25°C, in chloroform-d_1; δ [ppm] relative chloroform-d_1 (77.0).
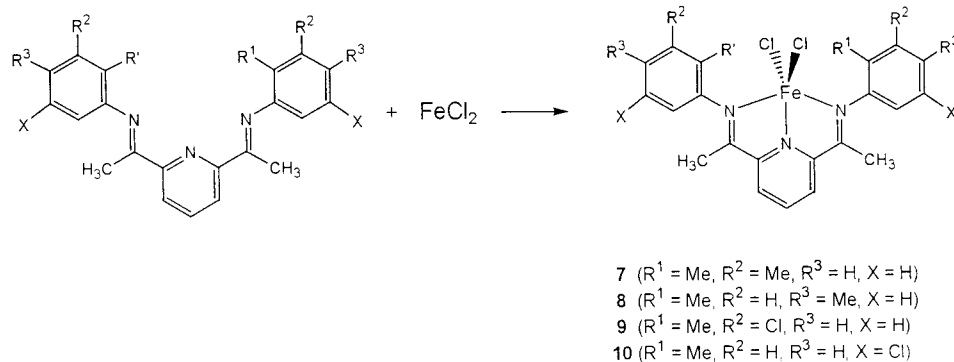
Figure 4 Synthesis of the catalyst precursors **7–10**.

7 (R^1 = Me, R^2 = Me, R^3 = H, X = H)
8 (R^1 = Me, R^2 = H, R^3 = Me, X = H)
9 (R^1 = Me, R^2 = Cl, R^3 = H, X = H)
10 (R^1 = Me, R^2 = H, R^3 = H, X = Cl)

all water had vaporized and was transferred to the mixture. The slurry became highly viscous and the temperature increased to about 60°C. Some toluene (ca. 50 mL) was added and the stirring continued until the reaction flask had cooled to room temperature.

The iron-containing catalyst precursor (0.2 mmol) was added to the mixture and stirring continued for at least 1 h. The mixture was filtered over a frit. After removing the toluene, the residue was washed with hexane and dried *in vacuo* to give a white solid. Overall yield: >95%.

TABLE III
Productivities of the Prepared Catalysts Under Different Process Conditions

No.	Complex	Productivity (homogeneous reaction) in g (product)/g (Fe) h^{-1}	Productivity (heterogeneous reaction) in g (product)/g (Fe) h^{-1}
7[a]		1,620,000	130,000
8[a]		1,370,000	110,000
9		2,030,000	160,000
10		3,660,000	310,000

Polymerization conditions: 10-bar ethene pressure, 500 mL *n*-pentane, 1.0 mL TIBA (1.6*M* in *n*-hexane), 60°C; homogeneous (MAO): Al/Fe = 2.000/1; heterogeneous (PHT): Al/Fe = 253: 1; 1 h.
[a] Independent of this work, **7** and **8** have recently been published.[21]
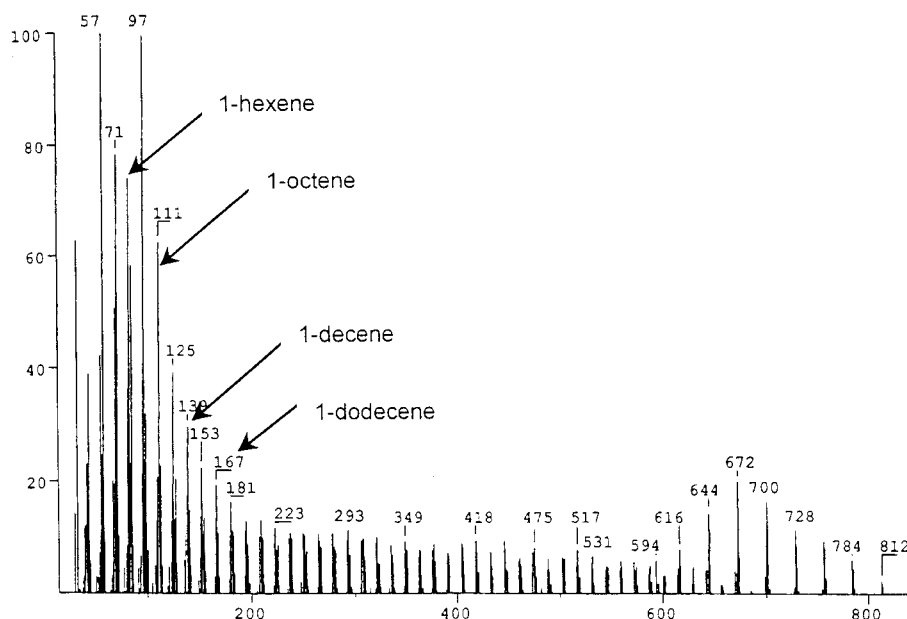
Figure 5 GC/MS of oligomers produced with catalyst **10**/PHT. Numbers above the peaks show the corresponding masses.

Oligomerization reactions

For homogeneous oligomerization reactions, an amount of 2–3 mg of the corresponding catalyst precursor was suspended in 500 mL of pentane and activated with MAO (Al:Fe = 2000:1). Then, 1.0 mL of TIBA (1.6M in n-hexane) was added to the mixture. For heterogeneous oligomerization reactions, PHT (silica as a support) was used for activation (Al:Fe = 253:1) as a suspension in 500 mL pentane.

In all cases, the oligomerization reactions were performed in a 1-L Büchi steel autoclave, at 60 ± 2°C, with an ethylene pressure of 10 bar, for 1 h. After the reaction period, the reactor was cooled to room temperature and the liquid products were analyzed by GC.

RESULTS AND DISCUSSION

Synthesis of suitable anilines

Suitable substituted anilines were synthesized by reduction of their corresponding nitro-derivatives (Fig. 2)[16] or were commercially available.

TABLE IV
Ratios of the Oligomers in the Liquid Products

Oligomers	**10/PHT** (heterogeneous) mass % of oligomers	**10** (homogeneous) mass % of oligomers
Butenes	13.62	5.01
Hexenes	22.81	17.68
Octenes	15.98	16.95
Decenes	12.36	14.33
Dodecenes	9.33	11.47
Tetradecenes and higher oligomers	25.90	34.56
Total	100	100

Solvents are not listed.

Synthesis of ligands 3–7

The corresponding diketone can be reacted with a suitable aniline in a condensation reaction (Schiff's base reaction[4]) to give the ligands **3–6** (Fig. 3).

Characterization of ligands 3–6

The ligands **3–6** were prepared according to the described procedure and analyzed via ^{1}H-NMR and ^{13}C-NMR spectroscopy and mass spectrometry (Table II).

Preparation of the catalyst precursors 7–10

Complexes **7–10** can be synthesized by an addition reaction of the corresponding ligands **3–6** and iron(II) chloride in either a tetrahydrofuran or diethyl ether solution (Fig. 4).

Preparation of the activated catalysts

The synthesized catalyst precursors were tested as oligomerization catalysts after activation with either MAO (homogeneous process conditions) or after immobilization and activation with PHT. PHT was developed in our research group. It is a universal heterogeneous cocatalyst that can be prepared from PHT in the presence of silica as a support material. In the subsequent activation step, the added homogeneous catalyst precursor is fixed automatically on the prepared heterogenized cocatalyst (see Experimental part). Thus, PHT is a substitute for other heterogeneous MAOs.[17–20]

Oligomerization results

The homogeneous and heterogeneous oligomerization reactions were performed at 60°C in *n*-pentane with 10.0-bar ethene pressure. In Table III, the productivities under homogeneous and heterogeneous conditions are presented.

Table III shows the activities of the catalyst precursors **7–10** under the chosen conditions. All catalysts showed high activities under homogeneous conditions. The corresponding heterogenized catalysts showed activities of about 1/10 compared with the homogeneous catalysts. The reaction mixture consisted of 18% insoluble polymer and 82% oligomers.

The oligomers were analyzed via GC/MS. The spectrum (Fig. 5) shows the oligomers obtained from **10**/PHT as a heterogeneous catalyst. A detailed analysis of the oligomers is summarized in Tables IV and V.

TABLE V
Purities of the Found 1-Olefins in the Corresponding Fractions

1-Olefins	10/PHT purity in %	10 (homogeneous) purity in %
1-Hexene	99.78	98.57
1-Octene	99.86	98.77
1-Decene	99.91	99.70
1-Dodecene	99.89	99.73
1-Tetradecene	99.10	99.78
1-Hexadecene	99.69	99.39

Discussion of the results

The investigated iron complexes proved to be good catalysts for the oligomerization of ethene. The formation of the higher oligomers in very high purity (99.8–99.9%) is a strong indication that β-H-elimination reactions[22,23] terminate the growth of the alkyl chains. The formation of saturated hydrocarbons can also be explained with this reaction pathway.

The oligomer distribution shown in Figure 5 indicates a Schulz–Flory behavior. The ratios of oligomers (Table IV) in the liquid phase can only speak for a trend but they are not very accurate because part of the volatile olefins, butene and hexene, are lost because of the reactor venting at the end of the reaction.

A further surprise of the iron catalysts is the fact that the generated 1-alkenes are not copolymerized with ethene under the reaction conditions. Various nickel[24] and chromium catalysts[25] are known for this behavior. Further experiments are planned to determine the reaction parameters that are responsible for the various reaction products.

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